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An Infrared Study of the Interaction of CO and NO with a Silica Supported Pt–Rh Alloy Catalyst

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A comparative study of the infrared spectra of CO, NO, and a CO–NO mixture on Pt/SiO_2, Rh/SiO_2, and a $Pt_{0.5}$–$Rh_{0.5}$ alloy/SiO_2 catalyst has been made at five different temperatures: 300, 350, 425, 525, and 625 K. Evidence is found for both Pt and Rh sites on the surface of the alloy catalyst. The CO molecules have the tendency to coordinate to Pt sites, whereas the NO molecules coordinate primarily to Rh sites. A mixed Pt–Rh dual site is proposed to explain the position of ν(CO) for the multiply coordinated CO species. © 1990 Academic Press, Inc.

INTRODUCTION

There is great interest in Pt–Rh catalysts, especially because of their application as a three-way catalyst (TWC) to control emissions from automobile exhaust. There are indications that Pt–Rh alloy particles are formed in the TWC (*1*). It is known that the selectivity and activity of an alloy may be quite different as compared to the constituent metals (*2*). For these reasons, it is interesting to acquire more detailed knowledge of the behavior of Pt–Rh alloy catalysts.

In earlier papers from our laboratory the surface composition and chemical properties of some selected Pt–Rh alloy single-crystal surfaces have been described (*3*). Recently, the performance of silica-supported Pt–Rh alloy catalysts in the CO–O_2 and CO–NO reactions have been studied and compared with those of pure Pt and pure Rh catalysts (*4*).

To gain a complete understanding of the behavior of Pt–Rh alloy catalysts, a large number of questions must still be answered. To understand the processes at an atomic scale, knowledge is required of the distributions of Pt and Rh atoms over the surface, the influence of the gas-phase composition on the topography, the possible preference of the relevant gases to adsorb on one of the component atoms, and the sites involved in the various processes. For example, it is not known whether CO and NO have a preference for Pt, Rh, or, perhaps, mixed Pt–Rh sites on a Pt–Rh alloy catalyst. Possibly, IR spectroscopy might provide some of the desired information.

In the present paper an IR study is described concerning the interaction of CO, NO, and CO–NO mixtures with a $Pt_{0.5}$–$Rh_{0.5}$ alloy catalyst. The purpose of this study was to obtain information concerning the adsorption sites and adsorption intermediates of both CO and NO on the Pt–Rh alloy catalyst. For comparison, similar studies were carried out with Pt/SiO_2 and Rh/SiO_2 catalysts.

EXPERIMENTAL

Apparatus. The infrared spectrometer used for this study was a Perkin–Elmer 580B double-beam grating IR spectrometer (resolution 5 cm^{-1}) equipped with a stainless-steel cell in which the sample disk is placed. The cell has silicon windows and is part of a vacuum chamber (base pressure, 1×10^{-4} mbar) with a gas introduction system. An oven placed around the cell allows catalyst temperature of up to 625 K. A mi-

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crocomputer was used to control the infrared spectrometer and to collect and process the data. Because of the temperature dependence of the IR spectra of the catalyst and the silica support, background spectra were taken at five selected temperatures from 625 to 300 K. After dosing the gases to the catalyst, spectra were recorded at these selected temperatures: 300, 350, 425, 525, and 625 K. The proper background spectrum was subtracted and the resulting spectrum smoothed using a 25-point smoothing function.

Gases were dosed to the catalyst until a stable pressure of 2 mbar was reached. The CO–NO mixture was prepared by mixing the gases before dosing to the catalyst. All the IR spectra were obtained in the presence of a gas atmosphere of 2 mbar to simulate conditions similar to the working conditions of a catalyst. A more detailed description of the IR system and of the data handling system can be found in Ref. (*5*).

Materials. Pt and Rh catalysts were prepared by homogeneous precipitation (*6*) of Aerosil 200 (200 m^2/g) with aqueous solutions of $Rh(NO_3)_2$ or $H_2Pt(OH)_6$ (*4*). The Pt–Rh alloy catalyst was prepared by homogeneous precipitation of Aerosil 200 with aqueous solutions of both $Rh(NO_3)_2$ and $H_2Pt(OH)_6$. The metal loading of all three catalysts was 5 wt%, while for the alloy the Pt/Rh atomic ratio was unity. The resulting catalyst was dried overnight in an oven at 383 K and, subsequently, reduced in flowing H_2 at 673 K for 16 h, ground, and pressed into a disk. The final step was an *in situ* reduction at 623 K for 16 h. All three catalysts were examined using X-ray diffraction to determine the average particle size and, in the case of the alloy catalyst, to ensure that alloy particles had been formed. The average particle size for the alloy catalyst was 16 nm, while the rhodium and the platinum catalysts had average particle sizes of approximately 6 nm. Only one peak corresponding to the (111) reflection was present in the XRD spectrum of the bimetallic Pt–Rh sample at the correct position between those of Pt and Rh, indicating that alloy particles were formed. Finally, metal surface areas were determined by CO adsorption assuming a 1 : 1 stoichiometry between noble metal atoms and adsorbed CO molecules. These measurements showed that the difference in specific surface areas of the three catalysts was less than 25%.

RESULTS AND DISCUSSION

Much attention has already been given in the literature to the adsorption of CO and NO and the interaction of NO with CO on Pt/SiO_2 and Rh/SiO_2 catalysts. In many of these studies infrared spectroscopy was used to characterize surface species. For Rh catalysts three CO species have been identified: gem-dicarbonyl species, $Rh(CO)_2$, linear species, and bridged coordinated species (*7–10*). For Pt catalysts several CO species have been reported: linearly coordinated CO (*11–13*), twofold-coordinated CO, and even threefold-coordinated CO (*14, 15*). In the case of NO adsorption three species have been reported for both Pt (*16*) and Rh (*17–20*) catalysts and attributed to $NO^{\delta-}$, NO, and $NO^{\delta+}$. There is also evidence for other NO species like dinytrosil (*21*) species and bridged coordinated species (*22*).

Our results obtained for pure Pt and Rh catalysts are, generally, consistent with those reported in the literature.

Pt/SiO₂

In Table 1 the locations and assignments of the bands found in the infrared spectra obtained for the Pt/SiO_2 catalyst are shown. After exposing the catalyst to CO an intense band at 2080 cm^{-1} is observed, which is assigned to linear CO coordinated to a single Pt atom. A very weak band at 1870 cm^{-1} is attributed to CO multiply coordinated to Pt atoms. When the temperature is raised from 300 to 625 K a shift is observed for the linear CO from 2080 to 2050 cm^{-1} while the intensity decreases. This shift can be attributed to decreasing dipole–dipole

TABLE 1

Locations (in cm^{-1}) and Assignments of the IR Bands Found after Exposure of the Pt Catalyst to Various Gases

Adsorbate	T (K)					Assignment	
	300	350	425	525	625		
CO	2080	2075	2075	2065	2045	PtCO	(vs)[a]
	1870	1870	1870	1865	—	Pt_2CO	(vw)
NO	1760	1740	—	—	—	$PtNO^{\delta+}$	(vw)
	1690	1655	—	—	—	PtNO	(vw)
	1605	1580	—	—	—	PtNO (bent)	(vw)
CO/NO	2075	2075	2070	2060	2045	PtCO	(vs)
	1855	1865	1870	1855	1850	Pt_2CO	(vw)

[a] vs, very sharp; vw, very weak.

coupling as the surface coverage decreases with increasing T due to desorption (*23*).

The exposure of Pt/SiO_2 to NO shows three very weak bands at 1760, 1690, and 1605 cm^{-1}. These bands disappear above 350 K, and the resulting spectra are similar to the background spectra within experimental accuracy. The major band at 1760 cm^{-1} is ascribed to NO linearly bonded to a single Pt atom, and the band at 1605 cm^{-1} to a negatively charged (bent) NO species (*24*). It is not clear to what kind of NO species the band at 1690 cm^{-1} can be assigned.

The absence of intense NO absorption bands on the Pt/SiO_2 catalyst is surprising. The intensity of the observed bands is very weak (a factor of 30) when compared to the intensity of the CO band. A study of Solymosi *et al.* (*25*) showed that the intensity of the linear CO absorption band compared to that of linear NO is only three to four times greater when adsorbed on Pt/SiO_2. There are a number of possible reasons for the low intensity of the NO absorption bands. First, it is possible that the NO molecules are not bonded perpendicular to the surface, but at an angle resulting in a smaller net dipole moment perpendicular to the surface, and hence in a lower intensity of the NO bands. In the literature tilted NO was first tentatively postulated by Pirug *et al.* (*26*), while Arai and Tominaga (*17*) compared the position of the NO adsorption bands with metal–NO complexes and expected an angle between the NO molecule and the Rh atom of 120°.

Another explanation might be dissociation of NO on Pt at low temperatures on the Pt catalyst. De Jong *et al.* (*22*) found some dissociation at room temperature for NO interacting with a Pt/SiO_2 catalyst, but stated that molecular adsorption dominates over dissociation. Therefore, it seems unlikely that the low intensity of the absorption bands is caused only by dissociation of NO. As a last model insufficient reduction of the Pt catalyst should be considered, although great care was taken to preclude oxidation of the catalyst. It is known that oxidation of the catalyst causes a weakening of the Pt–NO bond (*22, 27*). This would result in a lower surface concentration of the NO species and, consequently, in a low intensity of the absorption band. However, the CO spectra do not support this model. At present, the low intensity of the NO absorption bands is not well understood.

When the Pt/SiO_2 catalyst is exposed to a 1 : 1 mixture of CO and NO, only one intense band is observed at 2075 cm^{-1}. In addition to this major band, a very weak band is observed at 1855 cm^{-1}. The main band at 2075 cm^{-1} is due to linearly coordinated CO, and its intensity decreases with increasing temperature. This result is in line with experiments done by Brown and Gonzalez (*13*). These authors found that at room temperature NO is displaced by CO when adsorbed on a Pt/SiO_2 catalyst. However, preadsorbed CO is not displaced by NO but reacts with NO to form CO_2 and N_2O. The intensity of the band due to linear CO and its position (2075 cm^{-1} compared to 2080 cm^{-1} in the presence of mere CO) suggests that the NO surface concentration must be very low and too small to be detected by IR.

Formation of surface isocyanate species, characterized by an absorption band around 2175 cm^{-1} (*28*), was not observed. The absence of isocyanate absorption bands on Pt/SiO_2 can be ascribed to the rel-

TABLE 2

Locations (in cm^{-1}) and Assignments of the IR Bands Found after Exposure of the Rh Catalyst to Various Gases

Adsorbate	T (K)					Assignment	
	300	350	425	525	625		
CO	2095	2090	n.m.[a]	—	—	$Rh(CO)_2$	(s)[b]
	2070	2065	n.m.	2030	2015	RhCO	(vs)
	2025	2020	n.m.	—	—	$Rh(CO)_2$	(s)
	1845	1835	n.m.	(1785)	(1735)	Rh_2CO	(s)
NO	—	1920	1910	—	—	$RhNO^{\delta+}$	(vw)
	1800	1795	1795	—	—	RhNO	(w)
	1680	1680	1660	—	—	RhNO (bent)	(s)
CO/NO	2185	2185	2090	2090	—	RhNCO	(s)
	2095	2095	2095	2090	—	$Rh(CO)_2$	(s)
	2065	2055	—	—	—	RhCO	(s)
	2030	2025	2025	2020	—	$Rh(CO)_2$	(s)
	1785	1795	—	—	—	RhNO	(w)
	1680	1665	—	—	—	RhNO (bent)	(s)
	1555	1550	1540	1535	—	$RhCO_3^-$	(w)

[a] Not measured.

[b] vs, very sharp; s, sharp; w, weak; vw, very weak.

atively strong Pt–CO bond compared with the Pt–NO bond combined with the low NO surface concentration. Because the decrease in intensity of the linear CO band with increasing temperature is not very great and because no isocyanate species were observed, no evidence is found for a reaction between CO and NO on the Pt/SiO_2 catalyst. This is in line with results from our group (*4*) which show that under flow conditions almost no reaction takes place between CO and NO below 575 K.

Rh/SiO₂

In contrast with the platinum catalyst, the infrared spectra obtained for the rhodium catalyst are much more complex. The location and assignments of the IR absorption bands are given in Table 2. At 300 K two major CO absorption bands are observed, one at 2070 cm^{-1} and the other at 1845 cm^{-1}. In addition, two small bands appear at 2095 and 2025 cm^{-1}. The band at 2070 cm^{-1} is attributed to linearly coordinated CO, while the band at 1845 cm^{-1} is ascribed to a multiply coordinated CO species. The two small bands at each side of the linear CO band are attributed to the symmetric and asymmetric stretching vibrations of a gem-dicarbonyl species. This gem-dicarbonyl becomes more pronounced at 350 K and disappears at 525 K. With increasing temperature the linear CO band decreases in intensity, while at the same time the CO band of low wavenumber increases in intensity. This low-wavenumber CO band, ascribed to multiply bonded CO, shows a remarkably large shift of 110 cm^{-1}. This shift is much larger than can be expected from the diminishing dipole–dipole interaction alone. The most likely cause is a change in the nature of the adsorbed CO, for example, by deposition of carbon due to some CO dissociation or by an increase of its coordination with Rh atoms.

The absorption bands of CO adsorbed on Rh/SiO_2 show good agreement with previous studies (*29*).

In the spectra obtained after exposing Rh/SiO_2 to NO, one intense band at 1680

cm^{-1} is observed. This band is assigned to a negatively charged nitrosyl species. At 1800 cm^{-1} a less intense band can be ascribed to neutral nitrosyl species, Rh–NO. At 350 K a new minor band is formed at 1920 cm^{-1} that has been assigned in previous studies to the presence of positively charged nitrosyl species, Rh–$NO^{\delta+}$. With increasing temperature all bands disappear; at 525 K no bands can be distinguished from the background spectra.

After exposure of the Rh/SiO_2 catalyst to the CO/NO (1 : 1) mixture, bands are observed at 2185, 2095, 2065, 2030, 1785, 1680, and 1555 cm^{-1}. The three bands at 2095, 2065, and 2030 cm^{-1} belong to adsorbed CO; the band at 2065 cm^{-1} can be ascribed to linearly coordinated CO and the bands at 2095 and 2030 cm^{-1} to a gem-dicarbonyl species. As reported previously by Unland (*30*) an isocyanate species coordinated to the metal has an absorption band in the region between 2180 and 2200 cm^{-1}, while isocyanate coordinated to the carrier (for example, Al_2O_3 or SiO_2) has an absorption band between 2260 and 2270 cm^{-1} (*31*). Bearing this in mind, the band at 2185 cm^{-1} can be assigned to an isocyanate species directly coordinated to a rhodium atom. This band does not shift with increasing temperature, indicating that the most likely binding sites for these species are isolated or edge rhodium atoms. The bands at 1785 and 1680 cm^{-1} can be assigned in accordance with the bands found for NO adsorption to neutral nitrosyl species and negatively charged nitrosyl, respectively. Finally, the band at 1555 cm^{-1} can be assigned to a carbonate species, which usually shows a broad band.

The reaction of CO with NO shows some interesting features. The 300 K spectra are in good agreement with previous work by Zhong (*29*), except for the multiply coordinated CO band which is almost completely absent in our work. When we compare CO + NO adsorption with NO adsorption it is evident that the temperature at which the NO band disappears changes from 350 to 425 K in the presence of CO. At the same temperature the linear CO band also disappears, which can be due to a decreased CO surface concentration. A high concentration of nitrogen atoms on the Rh surface may be expected due to NO dissociation. These nitrogen atoms will prevent CO adsorption. At the same temperature the reaction between CO and O_{ads} also lowers the CO surface concentration. It is also likely that reaction between CO and NO takes place between 350 and 425 K. The fact that the gem-dicarbonyl bands remain uninfluenced points to a lower reactivity as compared to linear CO. Again this is in good agreement with literature data (*30, 32*). The low reactivity of the gem-dicarbonyl species can be understood on the basis of their adsorption sites. Because the gem-dicarbonyl bands do not shift with decreasing coverage, Yang and Garland (*7*) proposed that the most likely binding site should be an isolated Rh^I atom or a rhodium edge atom. In that case, the gem-dicarbonyl species are almost isolated from the other adsorbed species, resulting in a decreased reactivity. The importance of these gem-dicarbonyl species in relation to the stability of the catalyst has been discussed by Dictor and Roberts (*33*), who related the sintering of the Rh particles to the gem-dicarbonyl species.

The results show that both CO and NO are adsorbed at 300 K on the Rh catalyst in the presence of a CO–NO mixture, whereas on the Pt catalyst no indication was found of adsorbed NO. Furthermore, no evidence has been found for reaction between CO and NO on the Pt/SiO_2 catalyst, while the reaction on the Rh/SiO_2 catalyst takes place at low temperatures.

Pt–Rh alloy

Figure 1 shows the infrared spectra of Pt–Rh/SiO_2 exposed to CO at five different temperatures. At 300 K two bands are observed, the major one at 2070 cm^{-1} and a broad one at 1875 cm^{-1}. The band at 2070 cm^{-1} can be assigned to linear CO and

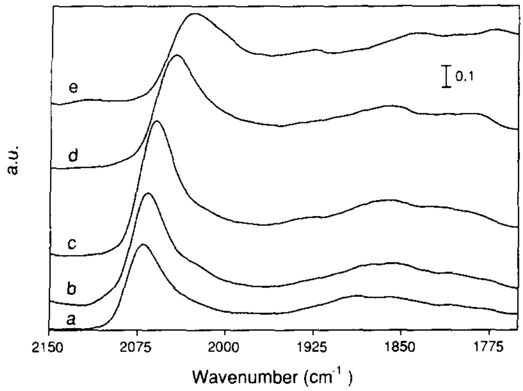

FIG. 1. Infrared spectra of 2-mbar CO adsorbed on the $Pt_{0.5}$–$Rh_{0.5}$ alloy catalyst: (a) 300 K, (b) 350 K, (c) 425 K, (d) 525 K, (e) 625 K.

ν(CO) shifts to 2030 cm^{-1} with increasing temperature while its intensity decreases (Table 3). This shift is due to a weakening of the dipole–dipole interaction, as a result of a decreasing CO coverage due to desorption. This band can be assigned to CO coordinated to a Pt or a Rh atom. It is not clear from the shift of the band with increasing temperature and, hence, decreasing coverage, whether CO has any preference for one of the two metal atoms at low coverage. For Pt the linear CO band shifts to 2045 cm^{-1}, while for Rh it shifts to 2015 cm^{-1} at high temperature. On the alloy catalyst it shifts to 2030 cm^{-1}. The band, at high temperature, can be ascribed to a CO species coordinated to Pt, in which case the wavenumber has decreased 15 cm^{-1}, or to CO coordinated to Rh, in which case the wavenumber has increased 15 cm^{-1}. The results suggest that the formation of the alloy has no large effect on the linearly bonded CO, because CO is adsorbed to both Pt and Rh atoms in the linear fashion.

When the spectra of CO on Pt and Rh are compared it is evident that the main difference is the absence of gem-dicarbonyl bands on the Pt catalyst. On the Pt–Rh alloy no gem-dicarbonyl bands are observed. It has been suggested that these species exist mainly on Rh^{I} atoms (*34*). Because Pt enhances Rh reducibility (*35*) and, thus, reduces the number of oxidized Rh atoms, the absence of a gem-dicarbonyl absorption band can be understood. Several authors found evidence that the dicarbonyl species are formed on isolated Rh^{I} atoms (*36, 37*). In this light, it is likely that our Pt–Rh alloy catalyst does not contain isolated Rh atoms and, hence, that the Rh atoms are present in alloy particles.

TABLE 3

Locations (in cm^{-1}) and Assignments of the IR Bands Found after Exposure of the $Pt_{0.5}$–$Rh_{0.5}$ Alloy Catalyst to Various Gases

Adsorbate	*T* (K)					Assignment	
	300	350	425	525	625		
CO	2070	2065	2060	2040	2030	PtCO	(s)[a]
	1870	1860	1855	1845	1830	(Rh–Pt)CO	(w)
NO	—	1860	1870	—	—	$RhNO^{\delta+}$	(vw)
	1790	1795	1790	—	—	RhNO	(w)
	1645	1645	1665	—	—	RhNO (bent)	(s)
	—	—	1600	—	—	?	(w)
	—	—	1520	—	—	?	(w)
	—	1440	1440	—	—	?	(w)
CO/NO	2180	2180	2195	—	—	RhNCO	(w)
	2075	2070	2055	2045	2040	PtCO	(vs)
	1875	1860	1850	1845	—	(Rh–Pt)CO	(w)
	1645	1645	1645	—	1635	RhNO (bent)	(vw)

[a] vs, very sharp; s, sharp; w, weak; vw, very weak.

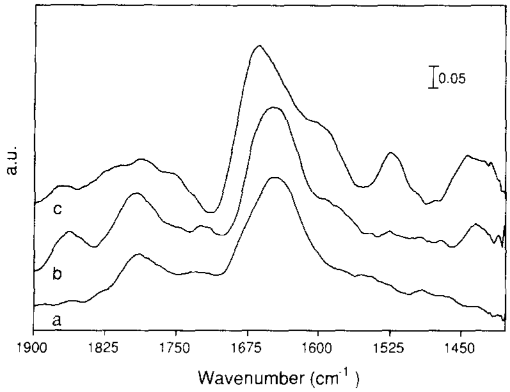

FIG. 2. Infrared spectra of 2-mbar NO adsorbed on the $Pt_{0.5}$–$Rh_{0.5}$ alloy catalyst: (a) 300 K, (b) 350 K, (c) 425 K, (d) 525 K, (e) 625 K.

An interesting feature is the band at 1875 cm^{-1} which is ascribed to multiply coordinated CO. With increasing temperature the multiply coordinated CO band shifts to 1845 cm^{-1} at high temperature and, hence, low coverage. The absorption band of multiply coordinated CO is very weak on the Pt catalyst and is observed at 1870 cm^{-1}, while on the Rh catalyst these species show a strong band at 1845 cm^{-1}. Recently, multiply coordinated CO species on supported Pt catalysts have been observed at 1840 cm^{-1}, and on Pt(111) Hayden and Bradshaw (*38*) found multiply coordinated CO at 1870 cm^{-1}. It is known that upon alloying, frequency shifts of IR absorption bands can occur. For weakly exothermic alloys these effects are caused largely by changes in dipole–dipole coupling effects (*39*), while ligand or electronic effects should be small for alloys like Pt–Rh. However, the difference in the frequency of multiply coordinated CO on Rh and Pt–Rh cannot be attributed to changes in dipole–dipole coupling effects of CO multiply bonded on Rh, because that should imply a higher concentration of CO multiply bonded on Rh for the alloy than for pure Rh. It is also very unlikely that the presence of Rh would result in a higher concentration of CO multiply bonded to Pt.

A more likely explanation for the multiply bonded CO is that the CO molecule is coordinated to both a Pt and a Rh atom (mixed Pt–Rh sites); this kind of species would have a band at a higher wavenumber than on the Rh catalyst. In a study by Ramamoorthy and Gonzalez (*40*) concerning the decomposition of CO on a Pt–Ru alloy catalyst, a Pt–Ru dual site was used to explain the enhanced CO dissociation.

In Fig. 2 the infrared spectra of NO exposure to Pt–Rh/SiO_2 are shown. Above 425 K no adsorption of NO is observed. At lower temperatures two bands can be seen, one at 1790 cm^{-1} and the other at 1645 cm^{-1}. In accordance with the literature (*10*) the band at 1645 cm^{-1} can be assigned to a negatively charged nitrosyl species, while the band at 1790 cm^{-1} is ascribed to a neutral nitrosyl species, NO. With increasing temperature the band at 1790 cm^{-1} remains at the same place, but the one at 1645 cm^{-1} shifts to higher frequency. At 350 K a band at 1860 cm^{-1} is seen which could be assigned to a positively charged nitrosyl species, $NO^{\delta+}$. The formation of these species could be caused by oxidation of Rh atoms with oxygen from the dissociation of NO. At the same temperature a small shoulder starts to form at 1620 cm^{-1} but it it not clear to what kind of species this shoulder can be ascribed.

The spectra of NO adsorbed on the Pt–Rh alloy catalyst are similar to those of NO adsorbed on the Rh catalyst. Both the location of the bands and their intensities are almost the same. Although we observed no bands indicating the adsorption of NO to Pt atoms, one should bear in mind that the intensity of NO adsorbed on the Pt catalyst was smaller than on the Rh catalyst.

The spectra in Fig. 3 are those of a CO/NO 1/1 mixture dosed to the Pt–Rh/SiO_2 catalyst at 5 different temperatures. There are a couple of distinct bands in the spectra, especially the band at 2075 cm^{-1} which can be readily ascribed to linear CO. The small band at 2180 cm^{-1} is in the region in which metal-isocyanate species are most likely to

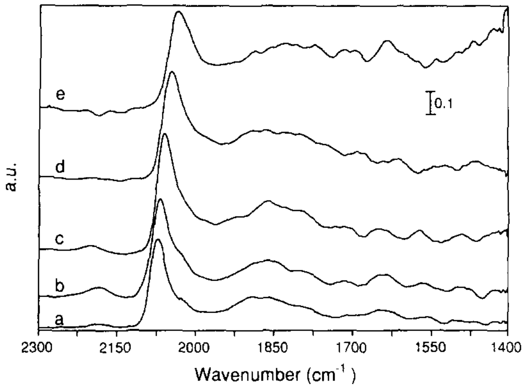

FIG. 3. Infrared spectra of 2-mbar CO/NO (1/1) mixture adsorbed on the $Pt_{0.5}$–$Rh_{0.5}$ alloy catalyst: (a) 300 K, (b) 350 K, (c) 425 K, (d) 525 K, (e) 625 K.

absorb. This is confirmed by Hecker and Bell (*41*), who found a band at 2170–2190 cm^{-1} upon adsorption of both CO and NO on a Rh/SiO_2 catalyst. Two other bands are observed in the spectra: a broad band at 1875 cm^{-1} which is most likely caused by the absorption of a twofold bridged coordinated CO, and a band at 1645 cm^{-1} which is ascribed to a negatively charged nitrosyl species coordinated to a Rh atom. No indication was found of NO coordinated to a Pt atom.

With increasing temperature the isocyanate band goes through a maximum at 350 K and disappears at 525 K. The effect of the temperature increase on the CO bands was as expected: the linearly coordinated CO band at 2075 cm^{-1} shifts to lower frequency until it reaches 2040 cm^{-1}, while the band at 1875 cm^{-1} shifts to 1845 cm^{-1}. However, the band at 1645 cm^{-1} remains at the same place; only the intensity varies with increasing temperature. As the temperature rises the intensity of the linear CO band goes through a maximum at 425 K, while the intensity of the bridged coordinated CO band seems to vary less.

The absorption band at 2075 cm^{-1} is also observed when CO is solely adsorbed to the Pt–Rh alloy catalyst. The band is stable with increasing temperature, similar to the band on Pt catalyst. On the Rh catalyst the linear CO absorption band disappears at 425 K in the presence of the CO–NO mixture. Furthermore, the shift of the absorption band reaches 2040 cm^{-1} at 625 K on the Pt–Rh alloy catalyst and 2045 cm^{-1} on the Pt catalyst compared with 2015 cm^{-1} on the Rh catalyst. These two facts combined make it likely that the absorption band at 2075 cm^{-1} is due mainly to CO linearly coordinated to a Pt atom. In accordance with the assignment used above with the CO adsorption, the band at 1875 cm^{-1} is ascribed to CO multiply coordinated to a mixed Pt–Rh site. The band at 2180 cm^{-1} is ascribed to isocyanate coordinated to a rhodium atom, because the interaction of CO and NO on the Pt catalyst showed no evidence for these species and, hence, isocyanate may be expected to be more stable on Rh sites than on Pt sites. The intensity of the isocyanate band is less than that on the Rh catalyst, indicating that fewer sites were available for the formation of these species or that the reaction is faster.

In conclusion, we have found evidence that both Pt and Rh sites are present on the surface of the $Pt_{0.5}$–$Rh_{0.5}$ alloy catalyst. The CO molecules have the tendency to coordinate to Pt sites, while the NO molecules coordinate primarily to Rh sites. A mixed Pt–Rh dual site is proposed to explain the position of ν(CO) of the multiply coordinated CO species.

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