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An Infrared Study of the Adsorption of CO and NO on Silica-Supported Ru–Pt Bimetallic Clusters

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The infrared spectra of CO and NO adsorbed on a supported bimetallic Ru–Pt sample (62 at% Ru) have been recorded. In addition, the stability of adsorbed CO to NO (g) and the stability of adsorbed NO to CO (g) have been determined using infrared spectroscopy. These studies reveal that there are both Ru and Pt surface sites present on the bimetallic Ru–Pt sample. The following band assignments have been made: for CO adsorbed on the Ru–Pt sample a broad asymmetric band at 2055 cm^{-1} and a weak high frequency bank at 2145 cm^{-1} are observed. The broad asymmetric bank at 2055 cm^{-1} was found to have two components, a sharp band at 2055 cm^{-1} assigned to $\nu_{(CO)}$ for Pt–Co and a broad band on the low frequency side of this band assigned to $\nu_{(CO)}$ for Ru–CO. The band at 2145 cm^{-1} was assigned to $\nu_{(CO)}$ for CO adsorbed on a RuO surface site. For NO adsorbed on a bimetallic Ru–Pt sample two bands are observed in the infrared spectra, a strong band at 1805 cm^{-1} assigned to $\nu_{(NO)}$ for $Ru^{\delta-}$–$NO^{\delta+}$ and a band of medium intensity at 1590 cm^{-1} assigned to $\nu_{(NO)}$ for $Ru^{\delta+}$–$NO^{\delta-}$. The results of this infrared study of the adsorption of CO and NO on a bimetallic Ru–Pt sample are compared with earlier studies of the adsorption of CO and NO on supported monometallic Ru and Pt samples.

INTRODUCTION

There has been recent interest in the effect of alloying on the catalytic activity of supported metals. [These supported alloys have been defined as bimetallic clusters (*1*).] It has been observed that the surface composition of an alloy may be markedly different than the bulk composition; furthermore, the catalytic activity of the alloy was found to depend on the surface composition. An example of this effect is found in the classic work of Sinfelt *et al.* (*2*). These authors studied the hydrogenolysis of C_2H_6 to CH_4 over Cu–Ni alloys. It is known that Ni is an effective catalyst for this hydrogenolysis, whereas Cu is inactive. The catalytic activity of Ni for this reaction decreased markedly when a Cu–Ni alloy with only 5 at% Cu was used; the surface composition of the 5 at% Cu alloy was estimated to be 40–60 at% Cu. The strong adsorption of H_2 on the Ni surface is known to be an index of the concentration of Ni on the surface of Cu–Ni alloys.

Recently, Somo-Noto and Sachtler (*3*) have shown that infrared spectroscopy can be used to elucidate the surface composition of a bimetallic catalyst. These authors studied the adsorption of CO on a series of Pd–Ag bimetallic samples. Since it is known that Pd adsorbs CO strongly, whereas CO is not adsorbed on Ag, these authors studied the effect of alloying Pd with Ag by following changes in the intensities of the various CO bands observed when CO is adsorbed on Pd–Ag alloys of varying composition.

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In previous infrared studies we have characterized the adsorption of CO and NO and the relative stability of adsorbed CO and adsorbed NO on silica-supported Ru and silica-supported Pt (*4-6*). When CO was adsorbed on a reduced 6% Ru-silica sample, we observed a strong band at 2030 cm^{-1} and two weak bands at 2150 and 2080 cm^{-1}. The strong band at 2030 cm^{-1} was completely and rapidly displaced from the Ru surface when excess NO was added, whereas the two high frequency CO bands were stable to excess NO (g). When NO was adsorbed on a reduced 6% Ru-silica sample, we observed bands at 1860, 1820, and 1630 cm^{-1} and we found that all three NO bands were stable to excess CO (g). For CO adsorbed on a Pt-silica sample only one strong band at 2070 cm^{-1} was observed. When a Pt sample with full CO surface coverage was exposed to excess NO (g), the NO (g) slowly reacts with adsorbed CO to form CO_2 (g) and N_2O (g). For NO adsorbed on a 6% Pt-silica sample we observed a band at 1760 cm^{-1} and we found that this adsorbed NO was completely and rapidly displaced from the Pt surface when excess CO (g) was added.

From these previous infrared studies we conclude that NO is strongly adsorbed on the Ru surface, whereas CO is strongly adsorbed on the Pt surface. Thus, an infrared study of the adsorption of CO and NO on a bimetallic Ru-Pt sample and the relative stability of CO and NO adsorbed on this surface should provide valuable insight into the surface composition of the bimetallic Ru-Pt sample.

EXPERIMENTAL METHODS

Materials

The gases used in this study were subjected to the following purification prior to use: CO (Matheson Research Grade) was purified by passing it through a liquid N_2 trap. NO (Matheson Technical Grade) was first purified by a standard vacuum distillation; dissolved N_2 was removed by the freeze-thaw technique. In the freeze-thaw technique, the NO sample is first frozen at liquid N_2 temperatures (−196°C) and evacuated for 5 min. The liquid N_2 trap is removed, the first portion is pumped off and the remainder is stored for use in a 1-liter glass bulb. CO_2 (g) was obtained from the vaporization of a dry ice [CO_2 (s)] pellet. This pellet was formed by the high pressure condensation of liquified CO_2. Commercial H_2 was used in the reduction of the catalyst and in adsorption experiments. It was purified before use by first passing it through a Deoxo unit to convert O_2 impurities to H_2O, which was then removed by a molecular sieve and a liquid N_2 trap. The purity of all gases was periodically checked on a Dupont Model 104 mass spectrometer.

In certain experiments a mixture of equal amounts of CO and NO were slowly co-adsorbed onto the Ru-Pt sample. This gaseous mixture was prepared in the following manner: first, 5 Torr NO was expanded into a 1-liter glass flask with a Teflon stopcock and frozen at liquid N_2 temperatures (−196°C); 5 Torr CO was then expanded into the same flask and the stopcock was closed. The liquid N_2 trap was then removed and the gases were allowed to mix 12 hr. Prior to use, the purity of the CO/NO mixture was checked by a mass spectral analysis.

The silica-supported bimetallic Ru-Pt sample (3% Ru-3% Pt, by weight; 62 at% Ru) used in this study was prepared by the coprecipitation of $H_2PtCl_6 \cdot 6H_2O$ (Engelhard Industries) and $RuCl_3 \cdot 3H_2O$ (Engelhard Industries) onto the silica support. Initially the appropriate weight of $H_2PtCl_6 \cdot 6H_2O$ was dissolved in a minimum amount of deionized H_2O. The appropriate weight of $RuCl_3 \cdot 3H_2O$ was then added to this solution and deionized H_2O was added to completely dissolve the Ru salt. This solution was mixed with Cab-O-Sil, Grade M-5, (Cabot Corp., Boston, Mass.) and

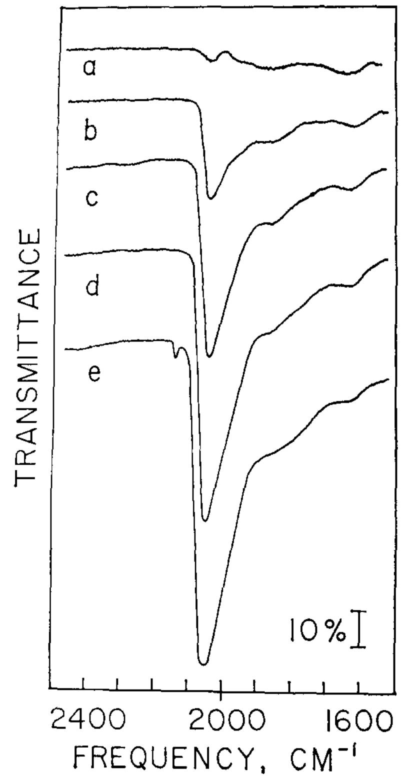

FIG. 1. Infrared spectra of CO adsorbed on a silica-supported Ru–Pt bimetallic sample: (a) background; (b) first exposure to CO; (c) second exposure to CO; (d) third exposure to CO; (e) full CO surface coverage.

deionized H_2O was slowly added until the sample had the consistency of a thick paste. The slurry was then air dried at room temperature for 1 week and stirred regularly during the drying process to retain uniformity. The dried catalyst was ground to a fine powder, less than 45 μm, and pressed into self supporting discs 2.5 cm in diameter and less than 0.05 cm thick.

Alloy formation of the silica-supported Ru–Pt sample prepared in this manner was verified by the appearance of a broad peak at 62.2° in the X-ray diffraction pattern. This peak is found between the Pt(111) line and the Ru(002) line and it is indicative of the formation of a Ru–Pt solid solution. Previous investigators have reported conflicting data on the formation of a Ru–Pt solid solution in this concentration range, i.e., 62 at% Ru (*7–10*). In the most recent report, Bowman and Sachtler (*10*) suggested a miscibility gap in the range between 50–70 at% Ru; however, these authors formed their Ru–Pt alloys by annealing thin films of Ru and Pt at elevated temperatures (~600°C). Sinfelt (*1*) has observed that highly dispersed supported metal samples do form bimetallic clusters, even when it is known that the two metals are immiscible in the bulk. For example, Sinfelt observed formation of supported Ru–Cu bimetallic clusters; in the bulk, Ru and Cu are virtually totally immiscible. Considering the results of the X-ray diffraction analysis, the supported Ru–Pt sample used in this study is known to be a true solid solution.

Techniques

Prior to the adsorption experiments, the bimetallic Ru–Pt samples were subjected to the following pretreatment: evacuated at 325°C for 1 hr, reduced in flowing H_2 (150 ml/min) for 2 hr at 325°C, and evacuated for 2 hr at 325°C. If the sample pellet is heated to temperatures greater than 350°C, it suffers an irreversible loss in the transmittance of the infrared radiation.

The infrared cell and the adsorption apparatus have been described in an earlier report (*4*).

All infrared spectra were recorded at room temperature on a Perkin-Elmer Model 521 infrared spectrometer using the double beam method. In the double beam mode of operation identical bimetallic Ru–Pt pellets are placed in both the sample and reference beams of the infrared spectrometer. The absorption bands due to the silica support in the sample beam are cancelled by the same absorption bands in the reference beam. In this way a relatively flat baseline is obtained from 4000 to 1300 cm^{-1}. Below 1300 cm^{-1} the silica support completely absorbs the infrared radiation.

RESULTS AND DISCUSSION

The infrared spectra of the stepwise adsorption of CO on the bimetallic Ru–Pt sample are illustrated in Fig. 1. With the first addition of CO we observe a band at 2040 cm^{-1}, which is highly asymmetric to the low frequency side. With increasing CO surface coverage the intensity of this band increases and the frequency shifts to 2055 cm^{-1}. At high CO surface coverage we observe development of only one weak high frequency CO band at 2145 cm^{-1}.

When excess NO (g) is added to a bimetallic Ru–Pt sample with full CO surface coverage (excess CO (g) was previously removed by a 5 min evacuation, NO (g) was not evacuated), we observe a decrease in the intensity of the CO band at 2055 cm^{-1} and note a change in the band contour, as shown in Fig. 2. After the addition of NO, the CO band at 2055 cm^{-1} becomes sharp and symmetric; we also observe two NO bands, a strong sharp band at 1805 cm^{-1} and a broad band of medium intensity at 1590 cm^{-1} (Fig. 2b and c). This sample was then evacuated for 15 min and we find that all the bands in the infrared spectrum are stable to evacuation at 25°C.

The infrared spectra of the adsorption of NO on a bimetallic Ru–Pt sample as a function of surface coverage are shown in Fig. 3. After the first addition of NO a sharp band at 1780 cm^{-1} and a weak broad band at 1560 cm^{-1} appear. With increasing NO surface coverage we observe an increase in the intensities of both bands; however, we do not observe development of a high frequency NO band in the 1850 cm^{-1} region. At full NO surface coverage the frequency of the band first observed at 1780 cm^{-1} shifts to 1805 cm^{-1} and the low frequency NO band shifts to 1590 cm^{-1}.

When a trace amount of CO (g) is added to a bimetallic Ru–Pt sample with full NO surface coverage [excess NO (g) was previously removed by a 5 min evacuation, whereas CO (g) was not evacuated], we observe no change in the intensities or the band shapes of the NO bands at 1805 and 1590 cm^{-1}; however, we do observe a sharp CO band at 2040 cm^{-1}. These spectra are illustrated in Fig. 4. When increasing amounts of CO are added to the cell, the CO band intensifies and the frequency of this band shifts to 2055 cm^{-1} (Fig. 4c–e). No band is observed in the 2180 cm^{-1} region of these infrared spectra. From an inspection of these spectra we conclude that NO is not adsorbed on certain sites on the bimetallic Ru–Pt surface.

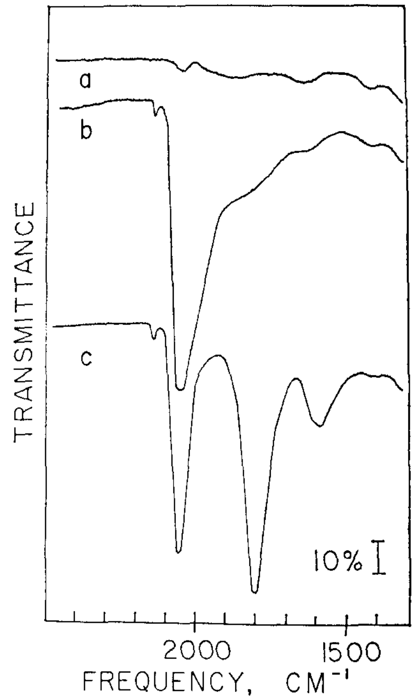

FIG. 2. Infrared spectra of a silica-supported Ru–Pt sample with full CO surface coverage exposed to excess NO: (a) background; (b) full CO surface coverage and evacuated 15 min; (c) 5 Torr NO (g) added.

Excess CO (g) was then removed by a 5 min evacuation with a mechanical pump and 50 Torr H_2 (g) was added to the cell. The effect of the addition of H_2 to adsorbed CO and NO is shown in Fig. 5. As this sample is exposed to excess H_2 (g) for an extended period of time (24 hr), we observe

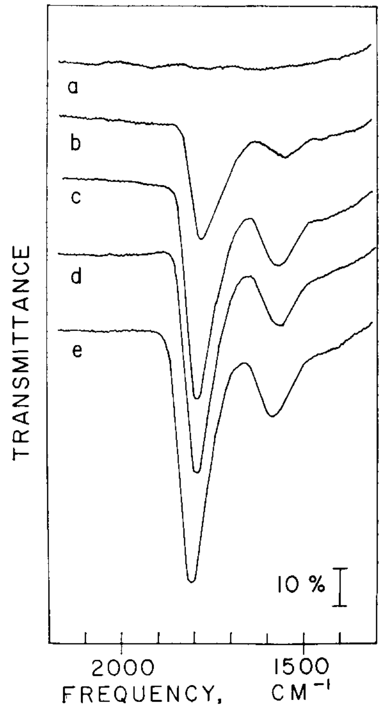

FIG. 3. Infrared spectra of NO adsorbed on a silica-supported Ru–Pt bimetallic sample: (a) background; (b) first exposure to NO; (c) second exposure to NO; (d) third exposure to NO; (e) full NO surface coverage.

a gradual decrease in the intensity of the NO bands at 1805 and 1590 cm^{-1}. We also note that as the intensity of the CO band at 2055 cm^{-1} increases, this band again becomes asymmetric to the low frequency side (Fig. 5c–e). Thus, we conclude that adsorbed NO is reacting in the presence of excess H_2 (g) and thereby creating vacant sites on the Ru–Pt surface. Traces of CO (g), which were not removed by a 5 min evacuation, can then adsorb on these vacant surface sites. After a 24 hr exposure to excess H_2 (g) the structure of the CO band is similar to that observed when excess CO (g) is added to a reduced bimetallic Ru–Pt sample. After exposure to excess H_2 for 24 hr, two new bands are observed in the infrared spectrum, a weak broad band at 2180 cm^{-1} and a broad band of medium intensity at 1425 cm^{-1} (Fig. 5c).

To better understand the effect of adsorbed NO on the adsorption of CO on the bimetallic Ru–Pt sample, we recorded the spectra of the stepwise adsorption of a CO/NO gaseous mixture on the Ru–Pt sample (the ratio of CO to NO was approximately 50:50). These spectra are shown in Fig. 6. After the first addition of the CO/NO mixture, we observe a CO band at 2055 cm^{-1} that is slightly asymmetric to the low frequency side and two NO bands, a band of medium intensity at 1780 cm^{-1} and a weak broad band at 1560 cm^{-1} (Fig. 6b). With increasing surface coverage we note that as the intensity of the CO band at 2055 cm^{-1} increases, this band becomes sharp and symmetric; the NO bands first observed at 1780 and 1560 cm^{-1} intensify and the frequencies of these bands shift to 1805 and 1590 cm^{-1}, respec-

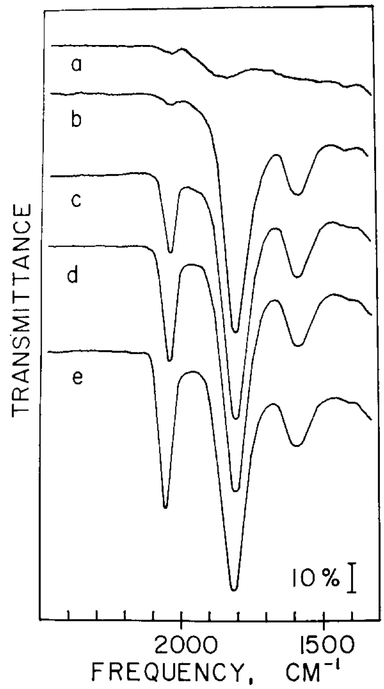

FIG. 4. Infrared spectra of a silica-supported Ru–Pt sample with full NO surface coverage exposed to CO: (a) background; (b) full NO surface coverage and evacuated 15 min; (c) first exposure to CO; (d) second exposure to CO; (e) excess CO added.

tively (Fig. 6c and d). At higher surface coverage a weak broad band at 2180 cm^{-1} is also observed. When an excess of the CO/NO gaseous mixture is added to the cell, no further spectral changes are observed. Thus, the sharp CO band at 2055 cm^{-1} is stable to excess NO (g) and the NO bands at 1805 and 1590 cm^{-1} are stable to excess CO (g) at 25°C.

A comparison of these spectra with those observed when CO is adsorbed on a reduced 6% Ru–silica and a 6% Pt–silica sample provides insight into possible band assignments. These band assignments are summarized in Table 1. For CO adsorbed on a Pt–silica sample, only a strong sharp band at 2070 cm^{-1} was observed; furthermore, we found that this adsorbed CO slowly reacted with excess NO (g) to form CO_2 (g) and N_2O (g) (*5*). This band at 2070 cm^{-1} has been assigned to $\nu_{(CO)}$ for CO linearly adsorbed on a Pt surface site, Pt–CO (*11*). When CO was adsorbed on a reduced 6% Ru–silica sample, we observed a strong band at 2030 cm^{-1} which was highly asymmetric to the low frequency side. At high CO surface coverage two weak bands at 2150 and 2080 cm^{-1} were also observed. When a Ru-silica sample with full CO surface coverage was exposed to excess NO (g), we observed a sharp decrease in the intensity of the CO band at 2030 cm^{-1}, whereas there was no change in the intensities of the CO bands at 2150 and 2080 cm^{-1}. The following band assignments have been made: the band at 2030 cm^{-1} was assigned to $\nu_{(CO)}$ for CO linearly

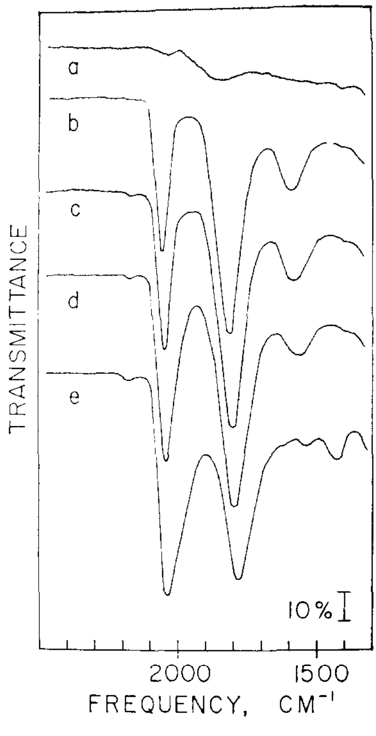

FIG. 5. Infrared spectra illustrating the effect of the addition of excess H_2 to a silica-supported Ru–Pt sample with NO and the CO adsorbed on the surface: (a) background; (b) full NO surface coverage; excess CO (g) added and cell evacuated 5 min; (c) 50 Torr H_2 added, time = 15 min; (d) exposed to 50 Torr H_2 for 1 hr; (e) exposed to 50 Torr H_2 for 24 hr.

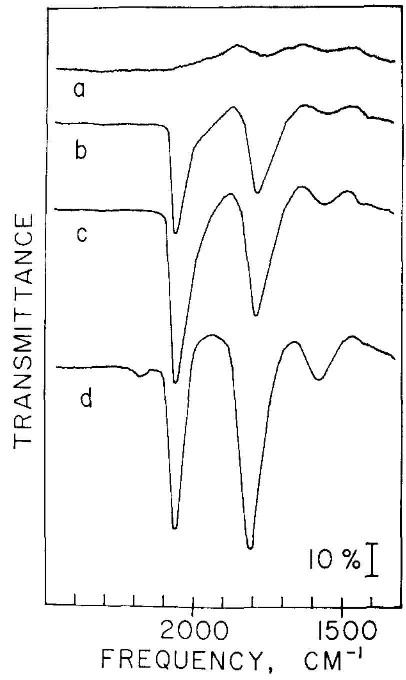

FIG. 6. Infrared spectra of a CO/NO gaseous mixture adsorbed on a silica-supported Ru–Pt sample: (a) background; (b) first exposure to CO/NO mixture; (c) second exposure to CO/NO mixture; (d) excess CO/NO mixture added and cell evacuated 5 min.

TABLE 1

Infrared Bands Observed for CO and NO Adsorbed on Supported Bimetallic Ru–Pt

Gas adsorbed	Frequency (cm^{-1})	Assignment	Comment
CO	2145 (w)	RuO–CO	The CO band at 2055 cm^{-1} is broad and asymmetric to the low frequency side.
	2055 (s, asy)	Pt–CO Ru–CO	The sharp band at 2055 cm^{-1} is $\nu_{(CO)}$ for Pt–CO; the broad low frequency component is $\nu_{(CO)}$ for Ru–CO.
NO	1805 (s)	$Ru^{\delta-}$–$NO^{\delta+}$	
	1590 (m)	$Ru^{\delta+}$–$NO^{\delta-}$	
CO_2	2055 (m, sharp)	Pt–CO	
NO + CO	1805 (s)	$Ru^{\delta-}$–$NO^{\delta+}$	The intensities and the band shapes of the NO bands at 1805 and 1590 cm^{-1} do not change when the sharp CO band at 2055 cm^{-1} appears. Thus, certain surface sites will not adsorb NO.
	1590 (m)	$Ru^{\delta+}$–$NO^{\delta-}$	
	2055 (m, sharp)	Pt–CO	
CO + NO	2145 (w)	RuO–CO	When NO is added, the band at 2055 cm^{-1} becomes sharp and symmetric. A sharp weak band at 2180 cm^{-1} develops when both CO and NO are on the surface. The band at 1760 cm^{-1} develops in the presence of excess NO.
	2055 (s, asy)	Pt–CO Ru–CO	
	1805 (s)	$Ru^{\delta-}$–$NO^{\delta+}$	
	1590 (m)	$Ru^{\delta+}$–$NO^{\delta-}$	
	2180 (w, sharp)	$Ru^{\delta+}$–$NCO^{\delta-}$	
	1760 (m)	Ru:NO	

adsorbed on a Ru surface site, Ru–CO, the band at 2080 cm^{-1} was assigned to $\nu_{(CO)}$ for CO adsorbed on an oxygen perturbed Ru surface site, and the band at 2150 cm^{-1} was assigned to $\nu_{(CO)}$ for CO adsorbed on a RuO surface site (*4*).

When CO is adsorbed on a bimetallic Ru–Pt sample, we observe a broad asymmetric band at 2055 cm^{-1} and a weak band at 2145 cm^{-1}. The broad asymmetric band at 2055 cm^{-1} appears to have two components, a sharp band at 2055 cm^{-1} and a broad band on the low frequency side of this band. The sharp band at 2055 cm^{-1} is stable to excess NO (g), whereas the low frequency component of this band is displaced by excess NO (g). Thus, we conclude that the sharp band at 2055 cm^{-1} is $\nu_{(CO)}$ for CO adsorbed on a Pt surface site, Pt–CO; the unusual band contour results from $\nu_{(CO)}$ for CO adsorbed on a Ru surface site, Ru–CO. The weak band at 2145 cm^{-1} is assigned to $\nu_{(CO)}$ for CO adsorbed on a RuO surface site. It is interesting to note that we do not observe a CO band in the 2080 cm^{-1} region for CO adsorbed on this bimetallic sample.

The assignment of the sharp CO band at 2055 cm^{-1} to $\nu_{(CO)}$ for Pt–CO can be verified by a study of the adsorption of CO_2 on a bimetallic Ru–Pt sample. When excess CO_2 (g) is exposed to a 6% Ru–silica sample, we observe no change in the infrared spectrum, i.e., normally CO_2 is not adsorbed on the Ru surface (*5*). However, it is known that CO_2 dissociates to CO over supported Pt, i.e., a CO band at 2070 cm^{-1} is observed (*12*). When CO_2 (g) is slowly adsorbed on a bimetallic Ru–Pt sample, we observe a sharp CO band that first appears at 2040 cm^{-1} and shifts to 2055 cm^{-1} with increasing surface coverage. These spectra are illustrated in Fig. 7. This adsorbed CO is stable to room temperature evacuation, as shown in Fig. 7e. Thus, we conclude that this sharp band at 2055 cm^{-1} is $\nu_{(CO)}$ for CO adsorbed on a Pt surface site, Pt–CO. [In these spectra we note changes in the contour of the atmospheric CO_2 absorption band in the 2349 cm^{-1} region. These changes are due to the addition of CO_2 (g) to the sample cell.]

The infrared spectra of NO adsorbed on a bimetallic Ru–Pt sample can also be clarified by a comparison with the spectra obtained when NO was adsorbed on silica-supported Pt and silica-supported Ru. When NO was adsorbed on a 6% Pt–silica sample, we observed a broad band at 1760 cm^{-1} that was completely and rapidly displaced by the addition of CO (g). This band at 1760 cm^{-1} was assigned to $\nu_{(NO)}$ for NO adsorbed on a Pt surface site, Pt–NO (*5*). The spectra obtained of NO adsorbed on a reduced 6% Ru–silica sample is complex. At low NO surface coverage we observed bands at 1820 and 1630 cm^{-1}, whereas at high NO surface coverage we found development of a high frequency band at 1860 cm^{-1}. The band at 1630 cm^{-1} was assigned to $\nu_{(NO)}$ for NO^- adsorbed on a Ru surface site, $Ru^{\delta+}$–$NO^{\delta-}$, whereas the band at 1820 cm^{-1} was assigned to $\nu_{(NO)}$ for NO^+ adsorbed on a Ru surface site, $Ru^{\delta-}$–$NO^{\delta+}$. The high frequency NO band at 1860 cm^{-1} was assigned to $\nu_{(NO)}$ for NO adsorbed on an oxygen perturbed Ru surface site (*6*).

For NO adsorbed on a bimetallic Ru–Pt sample we observed a strong sharp band at 1805 cm^{-1} and a broad band at 1590 cm^{-1}. These adsorbed NO surface species are stable to CO (g); however, in the presence of excess CO (g) we do observe formation of a sharp CO band at 2055 cm^{-1}. The stability of the NO bands at 1805 and 1590 cm^{-1} to excess CO (g) indicates that the NO surface species are bound to Ru surface sites. From analogous assignments made for the adsorption of NO on a 6% Ru–silica sample, the band at 1805 cm^{-1} is assigned to $\nu_{(NO)}$ for NO^+ adsorbed on a Ru surface site, $Ru^{\delta-}$–$NO^{\delta+}$, whereas the band at 1590 cm^{-1} is assigned to $\nu_{(NO)}$ for NO^- adsorbed on a Ru surface site, $Ru^{\delta+}$–$NO^{\delta-}$. It is interesting to note that the strong adsorption of NO on Ru surface sites hinders the adsorption of NO on Pt surface sites. The appearance of the CO band at 2055 cm^{-1} when CO (g) is added to a sample with full NO surface coverage confirms the fact that there are exposed Pt surface sites that will not adsorb NO. A similar effect was observed when a CO/NO gaseous mixture was co-adsorbed on a 6% Pt–silica sample, i.e., in the presence of the

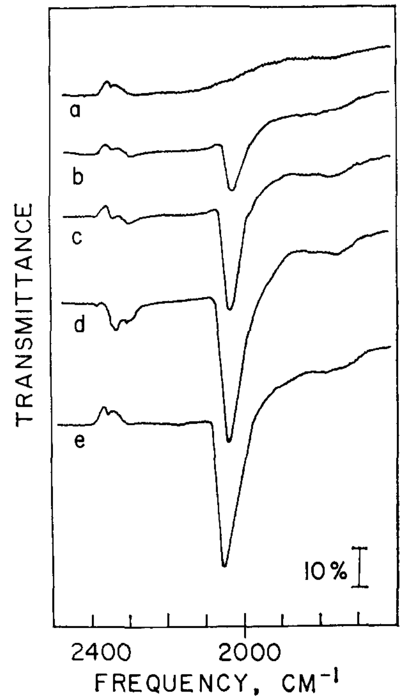

FIG. 7. Infrared spectra of CO_2 adsorbed on a silica-supported Ru–Pt sample: (a) background; (b) first exposure to CO_2; (c) second exposure to CO_2; (d) 10 Torr CO_2 added; (e) cell evacuated 5 min.

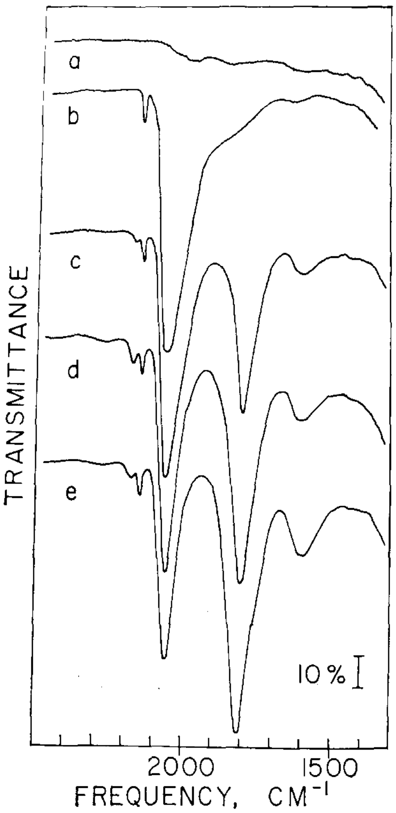

FIG. 8. Infrared spectra of the stepwise displacement of CO adsorbed on a silica-supported Ru–Pt sample by NO: (a) background; (b) full CO surface coverage and evacuated 15 min; (c) first addition of NO, t = 30 min; (d) second addition of NO, t = 30 min; (e) 5 Torr NO added.

strongly adsorbed CO surface species NO was not adsorbed on the Pt surface (*13*). This effect was observed at low surface coverage; thus, Pt surface sites were available for the adsorption of NO.

In the spectrum of NO adsorbed on the bimetallic Ru–Pt sample we do not observe an NO band at 1860 cm^{-1}; furthermore, we do not observe a CO band at 2080 cm^{-1} for CO adsorbed on the bimetallic sample. Previously, we assigned the CO band at 2080 cm^{-1} to $\nu_{(CO)}$ for CO adsorbed on an oxygen perturbed Ru surface site and the NO band at 1860 cm^{-1} to $\nu_{(NO)}$ for NO adsorbed on similar oxygen perturbed Ru surface sites. The failure to observe both the CO band at 2080 cm^{-1} and the NO band at 1860 cm^{-1} substantiates our assignment that these bands are due to the adsorption of CO or NO on the same type of surface site. Furthermore, it suggests that these oxygen perturbed Ru surface sites are not present on the bimetallic sample.

In studies made with a 6% Ru–silica sample we observed the formation of a surface isocyanate at 25°C when CO (ads) is slowly displaced from the Ru surface by NO (g); however, we did not observe isocyanate formation on a 6% Pt–silica sample (*5*). This surface isocyanate was identified by the appearance of a strong sharp band at 2180 cm^{-1} in the infrared spectrum. To determine if it is possible to form a surface isocyanate on a bimetallic Ru–Pt sample, we recorded the infrared spectra of the stepwise displacement of adsorbed CO by NO. These spectra are illustrated in Fig. 8. With the first addition of NO we observe both a decrease in the intensity of the CO band and a sharpening of the band contour; furthermore, we note the appearance of two NO bands at 1805 and 1590 cm^{-1}. A sharp weak band at 2180 cm^{-1} is also observed (Fig. 8b and c). After the second addition of NO we again note an increase in the intensity of the isocyanate band at 2180 cm^{-1} (Fig. 8d). In the presence of excess NO we observe a slight decrease in the intensity of the band at 2180 cm^{-1} and we note the appearance of a new band at 1760 cm^{-1}. This band at 1760 cm^{-1} was also observed when a Ru surface isocyanate, $Ru^{\delta+}$–$NCO^{\delta-}$, was exposed to excess NO (g) and it has been assigned to $\nu_{(NO)}$ for NO covalently bound to a Ru surface site, Ru:NO. A similar assignment is reasonable for the NO band observed at 1760 cm^{-1} on the bimetallic Ru–Pt sample, i.e., this band is $\nu_{(NO)}$ for Ru:NO.

From these spectra we conclude that the surface isocyanate is formed on the bimetallic Ru–Pt sample; however, this isocyanate band is not as strong as that observed on a 6% Ru–silica sample. Previously, we proposed a mechanism for isocyanate formation that involves the interaction of CO and NO that are adsorbed on adjacent Ru surface sites. When a Ru sample is alloyed with Pt, it would decrease the number of these nearest neighbor Ru surface sites; therefore, a less intense isocyanate band would be expected on the Ru–Pt sample. Furthermore, we suggest that the failure to observe isocyanate formation on a Pt–silica sample at 25°C was due to the stability of CO adsorbed on the Pt surface, i.e., a strong Pt–C bond. For a bimetallic Ru–Pt sample we do not observe isocyanate formation when CO is added to a Ru–Pt sample with full NO surface coverage (the sharp Pt–CO band at 2055 cm^{-1} was observed in this spectrum, Fig. 4). Thus, the presence of a weakly adsorbed CO surface species is an important criterion for isocyanate formation at 25°C.

This infrared study of the adsorption of CO and NO on a silica-supported bimetallic Ru–Pt sample has had twofold results: first, we observe that there are both Pt and Ru sites on the surface of the bimetallic sample. Secondly, these infrared data are consistent with our previous band assignments and our proposed mechanism for isocyanate formation on the Ru–silica surface.

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