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Surface Characterization of Supported Pt–Ru Bimetallic Clusters Using Infrared Spectroscopy

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The feasibility of determining the surface composition of a series of supported Pt–Ru bimetallic cluster catalysts using infrared spectroscopy has been explored. The nominal bulk compositions of Ru in these samples were 10, 22, 38, 62, and 80 atom%; total metal content of each sample was 6% by weight. The infrared absorption bands of CO(g) selectively adsorbed on Pt sites and those of NO(g) selectively adsorbed on Ru sites were stable *in vacuo* at room temperature. As the concentration of Ru was increased, there was a gradual shift in the frequencies of these bands indicating the weakening of the CO bond and strengthening of the NO bond. Prolonged exposure of each bimetallic catalyst (fully covered by both CO and NO) to NO(g) resulted in reaction between NO(g) and CO(ads) yielding CO_2(g) and N_2O(g). As the content of Ru was increased, there was a corresponding increase in the NO-band intensity and a decrease in the CO-band intensity. If both extinction coefficients and stoichiometric coefficients are taken to be independent of surface composition, a simple linear correlation between the absorbance ratio and the bulk metal composition was obtained, suggesting that the composition of the surface changed in the same way as that of the bulk. Such a plot provides a quick and inexpensive method of determining surface compositions of supported Pt–Ru cluster catalysts.

INTRODUCTION

The effect of alloying on the catalytic activity of metals offers exciting possibilities. It has been observed that the surface composition of an alloy may be markedly different from that of the bulk; furthermore, the catalytic activity of a bimetallic cluster has been found to depend on the surface composition. A very good example of this effect is found in the classic work of Sinfelt *et al.* (*1*) who studied the hydrogenolysis of C_2H_6 to CH_4 over Cu–Ni alloys. It is well known that Ni is an effective hydrogenolysis catalyst, whereas Cu is inactive. The catalytic activity of Ni for this reaction decreased markedly when a Cu–Ni alloy with only 5 atom% Cu was used; the surface composition of the 5-atom% Cu alloy was estimated to be 40–60 atom% Cu. In this case, the strong adsorption of H_2 on the Ni surface was used to estimate the surface composition of the Cu–Ni alloy.

In the case of supported Ru–Cu and Os–Cu bimetallic clusters, Sinfelt (*2*) has shown that the resulting metal particles contain both metallic components even though the metals are totally immiscible in the bulk. He also noted that the catalytic activity of these supported bimetallic cluster catalysts were dependent on their surface composition.

In view of the possible preferential surface enrichment by one of the metallic components in either an alloy or a sup-

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ported bimetallic cluster, the experimental characterization of surface composition has drawn a great deal of attention over the last few years. With the development of modern sophisticated instrumentation, progress in this area has been very impressive. Techniques such as ESCA, SIMS, ISS, EXAFS, and AES have certainly enabled investigators to obtain reasonably good estimates of surface compositions (*3*). Most of these instruments have two limitations: (1) They are enormously expensive, and (2) they do not sample the uppermost surface layer. In view of these drawbacks, and also taking into consideration that very precise measurements of surface composition are often not necessary, the search for alternate experimental techniques useful in the characterization of surface structures should be a worthwhile task.

If one excludes these electron spectroscopic techniques, one is inevitably left with chemisorption and infrared spectroscopy as potentially useful tools. Generally speaking, chemisorption is useful in the characterization of bimetallic clusters formed between group VIII and group IB metals (*1*, *2*). It can generally be assumed that hydrogen is not chemisorbed on group IB metals but adsorbs strongly and dissociatively on most group VIII metals. In view of this, hydrogen chemisorption can be used to estimate the group VIII metal surface area.

When selective adsorption is applied to group VIII bimetallic clusters, the problem is not as straightforward. Selective chemisorption techniques have not yet been successfully applied to supported bimetallic clusters of group VIII metals. However, the use of infrared spectroscopy appears to be a potentially very useful tool which, for some reason, has not received much attention in this application.

A recent study by Soma-Noto and Sachtler (*4*) on the adsorption of CO on silica-supported Pd–Ag clusters has been useful in the elucidation of the surface structure of these clusters. It is generally accepted that CO can adsorb on a single Pd site or can be multiply associated with several surface sites (*5*, *6*). Infrared absorption bands above 2000 cm^{-1} are supposedly responsible for linearly adsorbed CO, whereas bands occurring below 2000 cm^{-1} have been assigned to multiply adsorbed CO. As CO is not significantly adsorbed on Ag, dilution of the surface Pd atoms with Ag should then reduce the number of multiple sites to which CO can adsorb resulting in a decrease in the intensity of CO absorption bands below 2000 cm^{-1}. The results reported by Soma-Noto and Sachtler show this to be true. Very little in the way of quantitative information can be obtained from such a study, however. A more promising approach would be to find two different gases which would be adsorbed selectively on the different metallic components of a bimetallic cluster.

In previous infrared measurements (*7*–*9*), the adsorption of CO and NO and the relative stability of adsorbed CO and adsorbed NO on silica-supported Ru and silica-supported Pt have been studied. When CO was adsorbed on a reduced 6% Ru–silica sample, a strong band at 2030 cm^{-1} was observed. This band was completely and rapidly displaced from the Ru surface by excess NO(g). When NO was adsorbed on a 6% Ru–silica sample, bands at 1860, 1820, and 1630 cm^{-1} were observed (*9*). All three bands were stable to excess CO(g). When a 6% Pt–silica sample was exposed to CO, one strong band at 2070 cm^{-1} was observed (*8*). When this sample was exposed to excess NO(g), it was found that there was a slow reaction between NO(g) and adsorbed CO to form CO_2(g) and N_2O(g). For NO adsorbed on a 6% Pt–silica sample a single band at 1760 cm^{-1} was observed. This band was completely displaced from the Pt surface sites by CO(g). When a gaseous mixture consisting of CO and NO was adsorbed on a 6% bimetallic Ru–Pt sample (62 atom% Ru), it was found that CO was selectively adsorbed on the Pt component of the bimetallic cluster and NO was equally selectively adsorbed on the Ru surface (*10*).

In view of these infrared results, we felt that it would be constructive to extend these studies to include supported Pt–Ru clusters having a wide range of compositions with the idea of quantifying the results by measuring relative absorbances of CO adsorbed on the Pt component and NO adsorbed on the Ru component.

EXPERIMENTAL METHODS

Materials. The gases used in this study were subjected to the following purification treatment: 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 procedure in which only the middle cut was retained; dissolved N_2 was removed by the freeze–thaw technique. In this technique, NO is first frozen at 77°K and evacuated for 5 min. The NO is then thawed by removing the liquid N_2 trap and the process is repeated until a mass spectral analysis shows that the N_2 has been reduced to an acceptable level. Commercial $H_2(g)$ (Cranston Welding Supplies) was used in the reduction of the catalyst. 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 backed up by a liquid N_2 trap. The purity of all gases were periodically checked at high resolution on a Dupont Model 104 mass spectrometer.

The silica-supported bimetallic Ru–Pt samples used in this study, were prepared by the coprecipitation of $H_2PtCl_6 \cdot 6H_2O$ and $RuCl_3 \cdot 3H_2O$ (Strem Chemical) 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 sufficient deionized H_2O was then added to completely dissolve the Ru salt. This solution was mixed with Cab-O-Sil, Grade M-5 (Cabot Corp., Boston, Mass.) until a slurry having the consistency of a thick paste was formed. The slurry was then air dried at room temperature for 1 or 2 days and stirred regularly during the drying process to retain uniformity. The dried catalyst was ground into a fine powder, less than 45 μm, and pressed into self-supporting disks 25 mm in diameter and less than 0.5 mm thick.

Bimetallic cluster formation was checked by observing the X-ray diffraction pattern of the catalysts prepared in this manner. The appearance of a broad peak at 62.2° between the Pt(111) and Ru(002) lines was interpreted as evidence for bimetallic clustering.

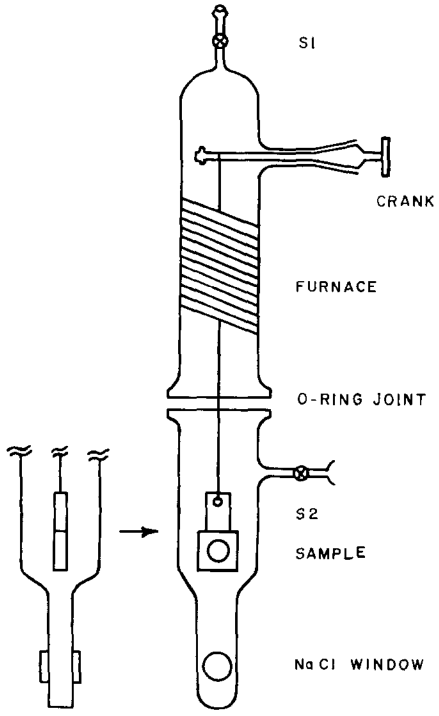

FIG. 1. Infrared cell.

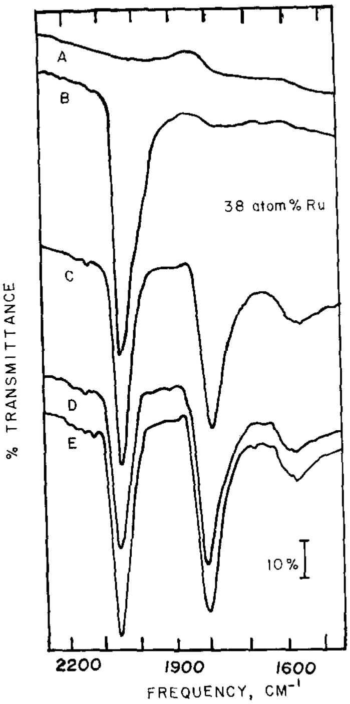

FIG. 2. Infrared spectra of CO and NO coadsorbed on a 38-atom% Ru, Pt–Ru bimetallic sample at 25°C: (A) background; (B) full CO coverage; (C) NO added to monolayer coverage; (D) excess NO added; (E) cell evacuated for 5 min, followed by the addition of 50 Torr CO at 25°C.

Apparatus and procedure. A new improved infrared cell, shown in Fig. 1, was used in this study to obviate some limitations of cells used in previous investigations (*7–10*). The cell was made from a 50-mm O-ring joint without a cooling water jacket. By the use of rectangular tubing the path length inside the cell was reduced to a minimum and the cell could be easily positioned within the sample compartment of the instrument. Polished NaCl windows were secured in place to the rectangular tubing using Glyptal cement. Further details on the design of this cell will appear elsewhere.

Prior to an adsorption experiment, the supported bimetallic pellet was treated as follows: heated at 325°C in vacuum for 1–2 hr, reduced in flowing H_2 (250 ml/min) for 4–5 hr at 325°C, evacuated for 1 hr at 325°C, and cooled slowly to room temperature under vacuum. In one experiment, the surface was purposely oxidized by exposing the sample to 50 Torr (1 Torr = 133.3 N m^{-2}) of O_2(g) for 30 sec at 325°C. Following the evacuation of O_2 at 325°C for 1 hr, the sample was cooled to room temperature thereby leaving a layer of chemisorbed O_2 at the surface.

All infrared spectra were recorded at room temperature on a Perkin–Elmer Model 521 infrared spectrometer using the double-beam technique. In the double-beam mode of operation, two reduced catalyst pellets of identical infrared transmittance are placed in the sample and reference beams of the instrument. In this way, the absorption bands due to the silica-support will be cancelled in both beams and a relatively flat baseline is obtained from 2700 to 1300 cm^{-1}. Below 1300 cm^{-1} the silica absorbs the infrared radiation completely.

The adsorption experiments were performed *in situ* with the infrared cell placed in the sample compartment of the instrument. CO(g) was admitted through a liquid N_2 trap, whereas NO(g) was admitted through a dry ice–acetone bath. The measurements of the spectra were repeated several times before the final spectra were recorded. The adsorption of each gas was carried out sequentially in several small steps, and for each step the spectra were recorded.

RESULTS AND DISCUSSION

The infrared spectra of the adsorption of CO and NO on a bimetallic Ru–Pt sample having a nominal 38 atom% Ru are shown in Fig. 2. With the addition of excess CO(g) a strong sharp band centered at 2068 cm^{-1} which was asymmetric to the low frequency side was observed. A very weak band at 2135 cm^{-1} was also observed in the infrared spectrum. These bands were found to be stable to evacuation at

25°C for 15 min. When NO(g) was added to this bimetallic Ru–Pt sample with full CO surface coverage [excess CO(g) and NO(g) had previously been removed by evacuation], a decrease in the intensity of the CO band at 2068 cm^{-1} was observed. After the addition of NO, the CO band at 2068 cm^{-1} became sharp and symmetric; two NO bands were also observed, a strong sharp band at 1800 cm^{-1} and a broad band of medium intensity centered at 1580 cm^{-1}. All bands were stable to evacuation, and no further spectral changes occurred on standing for a period of 30 min. When excess NO(g) was added to this sample, a gradual decrease in the intensity of the CO band at 2068 cm^{-1} was observed. A small increase in the intensity of the NO band at 1800 cm^{-1}, followed by a slight change in the band contour such that it became broader and asymmetric to the low frequency, was also observed. At this point, the gas phase was sampled and analyzed using high resolution mass spectroscopy. Both CO_2 and N_2O were found to be present in the gaseous mixture thus clearly showing that a reaction between NO(g) and CO(ads) had occurred. The infrared cell was then evacuated for 15 min and 50 Torr CO(g) was added to the cell. The resulting spectrum shown in Fig. 2, spectrum E, essentially reproduces that in Fig. 2, spectrum C. No further spectral changes were observed when the sample was exposed to 50 Torr CO(g) for 45 min.

The results are interpreted as follows. Initial adsorption of CO occurs on both Pt and Ru surface sites. A comparison of these spectra with those observed when CO is adsorbed on a reduced 6% Ru–silica and a 6% Pt–silica sample gives considerable insight into the possible band assignments. For CO adsorbed on a Pt–silica sample, only one strong sharp band at 2070 cm^{-1} was observed (*8*); furthermore, it was found that this adsorbed CO slowly reacted with excess NO(g) to form CO_2(g) and N_2O(g) (*8*). This band at 2070 cm^{-1} has been assigned to ν(CO) for CO linearly adsorbed on a Pt surface site, Pt–CO (*8*). When CO was adsorbed on a reduced 6% Ru–silica sample, a strong band centered at 2030 cm^{-1} was observed. This band was asymmetric to the low-frequency side. At high surface coverage, weak bands were observed at 2150 and 2080 cm^{-1}. The band at 2030 cm^{-1} was assigned to ν(CO) for CO linearly adsorbed on a Ru surface site, Ru–CO, the band at 2080 cm^{-1} was assigned to ν(CO) for CO adsorbed on an oxygen perturbed Ru surface site, and the band at 2150 cm^{-1} was assigned to ν(CO) for CO adsorbed on a RuO surface site (*7*).

As NO(g) is added to the bimetallic Ru–Pt sample with full CO surface coverage, CO is immediately displaced from the Ru surface sites but not from the Pt surface sites where it is more strongly adsorbed. The resultant spectrum shows a sharp and symmetric band at 2068 cm^{-1} in addition to a strong sharp Ru–NO band at 1800 cm^{-1} and another Ru–NO band of medium intensity at 1580 cm^{-1}. As long as NO(g) was not present in the gas phase, all three bands were stable indicating the absence of a surface reaction between CO adsorbed on Pt surface sites and NO adsorbed on Ru surface sites. When NO(g) was present in excess in the infrared cell, there was a gradual decrease in the intensity of the Pt–CO band at 2068 cm^{-1} indicating the occurrence of a reaction between NO(g) and CO(ads). As the reaction progressed, Pt surface sites became available for NO adsorption as evidenced by an increase in the intensity of the band at 1800 cm^{-1} which also broadened due to the appearance of a new component at 1760 cm^{-1}, indicative of NO adsorption on Pt. This band at 1760 cm^{-1} was readily displaced by CO(g) on a 6% Pt–silica sample.

After the evacuation of the gases in the cell, followed by the addition of excess

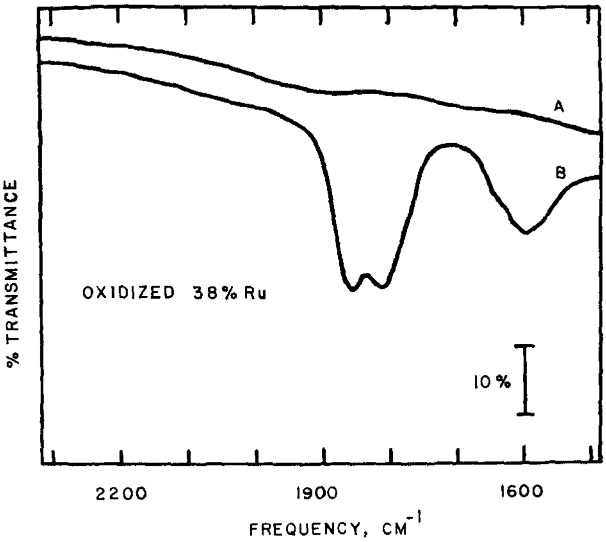

FIG. 3. Infrared spectra showing the effect of adsorbing NO onto a 38-atom% Ru, Pt–Ru bimetallic sample exposed to 50 Torr of O_2 for 30 sec at 325°C and then cooled to 25°C: (A) background; (B) partial NO coverage at 25°C.

CO(g), the CO band at 2068 cm^{-1} is fully restored and the NO band at 1800 cm^{-1} again becomes sharp and symmetric and is reduced to its original intensity. The stability of all bands to 50 Torr of CO(g) shows that there is no reaction between CO(g) and adsorbed NO. We are quite confident that under these conditions CO is selectively adsorbed on Pt surface sites and NO is also selectively adsorbed on Ru surface sites.

There are significant differences in the adsorption of both CO and NO on the silica-supported Ru–Pt bimetallic sample and silica-supported Ru. When NO was adsorbed on a well-reduced 6% Ru–silica sample, bands at 1860, 1820, and 1630 cm^{-1} were observed (*9*). The strong band at 1860 cm^{-1} appeared at high surface coverage and was assigned to NO adsorbed on an oxygen-perturbed Ru surface site. This suggested that NO decomposed on the Ru sites at high surface coverages followed by a partial oxidation of the surface. Subsequent NO adsorption then occurred on oxygen-perturbed Ru surface sites giving rise to the high-frequency band at 1860 cm^{-1}. In the case of CO adsorption on a 6% Ru–silica sample, similar observations were made; however, the effects were not nearly as pronounced as in the adsorption of NO (*7*). It is now believed that at high surface coverages, a small amount of CO is dissociatively adsorbed resulting in a partial oxidation of the Ru surface. The high-frequency CO bands are therefore caused by the adsorption of CO on these oxygen-perturbed Ru sites. The assignment of the high-frequency bands in both cases was made after comparing the foregoing results with those obtained on a bimetallic cluster pretreated with oxygen prior to the adsorption experiments. The NO adsorption spectra of such a bimetallic sample are shown in Fig. 3. These high-frequency bands did not appear when NO was adsorbed on a well-reduced silica-supported bimetallic Pt–Ru sample. In the case of CO adsorption, only one very weak high-frequency band at 2135 cm^{-1} was observed. This result indicates that unlike the case for the 6% Ru–silica sample, NO is nondissociatively adsorbed on the supported bimetallic Pt–Ru sample. The supported

38-atom% Ru bimetallic sample was purposely oxidized by exposing it to oxygen at 50 Torr for 30 sec at 573°K. When NO was adsorbed on this oxidized sample, a high-frequency band was observed at 1860 cm^{-1}. This result is shown in Fig. 3. It is concluded from these results that both CO and NO are linearly and mostly nondissociatively adsorbed on a supported Ru–Pt bimetallic sample. This conclusion encouraged us to pursue the coadsorption of CO and NO on supported Pt–Ru bimetallic cluster catalysts having a wide range of compositions with the hope of characterizing the disposition of surface metal atoms.

Based on the results obtained on a 38-atom% Ru bimetallic sample, the following experimental technique was adopted in the characterization of the bimetallic samples: (1) adsorption of CO(g) to monolayer coverage, followed by a 15-min evacuation at room temperature; (2) adsorption of NO(g) to monolayer coverage, followed by a 15-min evacuation at room temperature; and (3) exposure to CO(g) at 50 Torr for 30 min. The absorbances of the CO band (around 2070 cm^{-1})

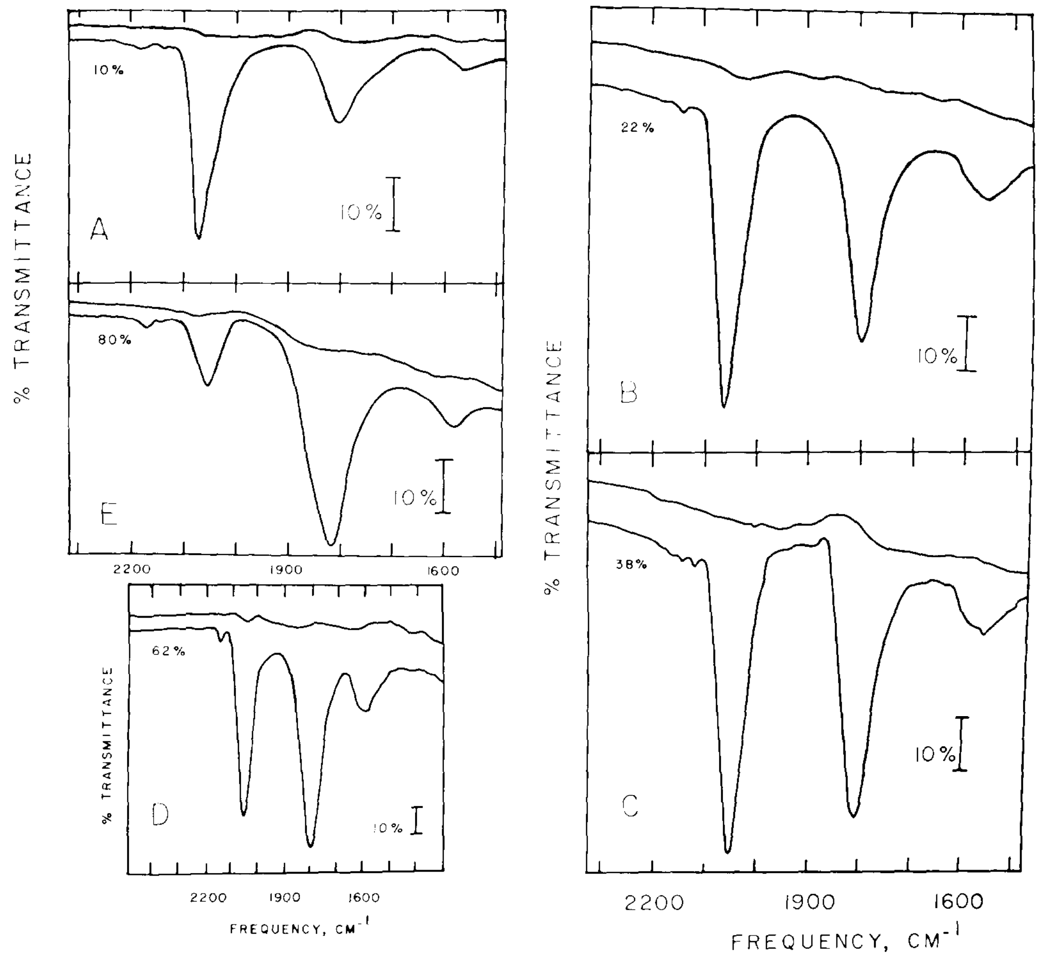

FIG. 4. Infrared spectra showing monolayer coverage on Pt–Ru bimetallic samples having different nominal bulk compositions: (A) 10%; (B) 22%; (C) 38%; (D) 62%; (E) 80%.

TABLE 1

Summary of Data for the Adsorption of CO and NO over Supported Pt–Ru Bimetallic Clusters

	Atom% Ru						
	100	80	62	38	22	10	0
(Pt)/(Ru) bulk	0	0.250	0.615	1.63	3.56	9.00	∞
A_{CO}	—	0.0517	0.617	0.482	0.417	0.215	—
A_{NO}	—	0.204	0.914	0.381	0.267	0.072	—
$A_{\mathrm{CO}}/A_{\mathrm{NO}}$	0	0.253	0.675	1.27	1.56	2.98	∞
ν_{CO} (cm^{-1})	2030	2050	2055	2068	2065	2074	2070
ν_{NO} (cm^{-1})	1820	1817	1805	1800	1801	1804	1760

and the NO band (around 1810 cm^{-1}) were taken as measures of the surface concentration of Pt and Ru atoms, respectively. The final infrared spectra of the adsorption of CO and NO on silica-supported Pt–Ru bimetallic clusters of five nominal compositions are shown in Fig. 4, and the data are presented in tabular form in Table 1.

As the concentration of Ru in the sample increases, the intensity of the NO band around 1800 cm^{-1} increases relative to that of the CO band around 2070 cm^{-1}. In addition to the changes in band intensities, there is a gradual shift in the frequencies of these bands to lower wavenumbers indicating a progressive weakening of the CO bond. The decrease in the wavenumber of the CO stretching frequency is associated with a small increase in wavenumber corresponding to the NO band, indicating a slight strengthening of the NO bond. These changes in the spectral frequencies are consistent with an increase in the degree of backbonding between Pt and C brought about by the transfer of electrons from Ru to Pt. As the Pt–C bond is strengthened through backbonding, the C–O bond is weakened. This transfer of electrons from Ru to Pt is probably caused by an increased tendency for the adsorbed NO to transfer its antibonding electron to Ru as the Ru concentration is gradually increased. This propensity of NO to become more electropositive as the Ru concentration is increased results in a gradual strengthening of the NO bond. This strengthening of the NO bond is consistent with the apparent inhibition of the NO decomposition on the bimetallic samples.

If it is assumed that the extinction coefficients and the adsorption stoichiometric coefficients are independent of surface composition, one can write,

$$A_{\mathrm{CO}} = k_{\mathrm{CO}} S_{\mathrm{CO}} (\mathrm{Pt})_s \qquad (1)$$

$$A_{\mathrm{NO}} = k_{\mathrm{NO}} S_{\mathrm{NO}} (\mathrm{Ru})_s, \qquad (2)$$

where A is the absorbance, k_{CO} and k_{NO} are extinction coefficients, $(\mathrm{Pt})_s$ and $(\mathrm{Ru})_s$ represent the surface concentrations of Pt and Ru atoms, respectively, and S_{CO} and S_{NO} are stoichiometric coefficients which take into account the fact that the number of NO or CO molecules bound to surface Ru or Pt atoms need not necessarily be unity. The assumption that the extinction coefficients are independent of surface composition may be somewhat tenuous, but is justified in view of the relatively small shifts in absorption band frequencies observed over the range of compositions studied. If changes in surface composition parallel composition changes in the bulk, a plot of $A_{\mathrm{CO}}/A_{\mathrm{NO}}$ vs $(\mathrm{Pt})_b/(\mathrm{Ru})_b$ should be approximately S shaped going to zero for $(\mathrm{Pt})_b = 0$ and ∞ for $(\mathrm{Ru})_b = 0$, with a long linear portion at intermediate concentrations (the subscript b refers to bulk concentrations). This plot is shown in Fig. 5, and the correlation is excellent over the range of Ru compositions studied. On the basis of surface free energy data, it is expected that a slight surface enrichment in Pt should occur. Our data do not substantiate this surface enrichment in Pt, however, we should emphasize that small surface enrichments in one of the metallic components would be difficult to detect using this technique. Any substantial surface enrichment in one of the metallic components would be easily detected as a plot similar to that shown in Fig. 5, would be decidedly nonlinear and may show a maximum. The results reported here are in agreement with studies on Pt–Ru alloy films prepared by sequential evaporation followed by sintering at 770°K (*11*). At 30 atom% Pt, a hexagonal lattice structure is retained (cf. Pt.) These authors observed a miscibility gap in the 30- to 50-atom% region but found that in both single phase regions the composition of the surface appeared to change continuously with that of the bulk. It should be pointed out, however, that bimetallic cluster formation is possible even though the metals are entirely immiscible in the bulk (*2*); i.e., a miscibility gap in the 30- to 50-atom% region in the alloy does not guarantee such a miscibility gap in the bimetallic cluster. In this work, we saw no evidence of bimetallic segregation in the 30- to 50-atom% Ru range.

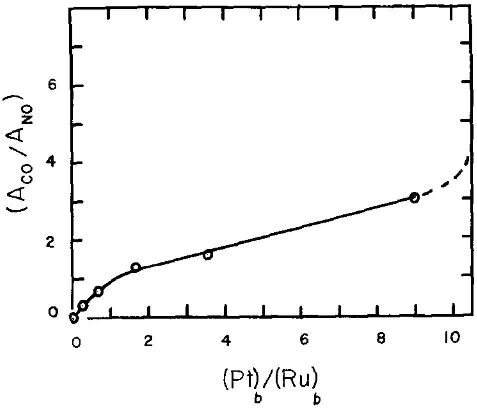

FIG. 5. Proposed correlation between A_{CO}/A_{NO} and $(Pt)_b/(Ru)_b$, where $(Pt)_b$ and $(Ru)_b$ represent bulk compositions in atom percents.

It is appropriate to speculate at this point whether the surface consists of bimetallic clusters or whether separate Ru and Pt metal particles are present. The experimental evidence, based on the following observations, strongly suggest the presence of bimetallic clusters.

(i) The appearance of a broad peak at 62.2° in the X-ray diffraction pattern. This peak is found between the Pt(111) and the Ru(002) line and is indicative of the formation of a Ru–Pt cluster.

(ii) As the bulk composition is varied, there is a gradual shift in the position of both the CO and the NO infrared absorption bands indicating the presence of Pt and Ru atoms at adjacent surface sites. The shift in absorption frequencies is attributed to electronic effects which transfer the antibonding electron in NO to the Ru atom. This is accompanied by a proportional increase in the electron density around Pt thereby increasing the degree to which Pt is backbonded to CO.

(iii) The apparent stability of NO relative to dissociation over bimetallic clusters must be attributed to the presence of Pt. If separate Ru and Pt particles were present, one would expect dissociation to occur over Ru particles in agreement with published data on the adsorption of NO on silica-supported Ru (*9*).

(iv) The presence of isocyanate formation which requires a large number of adjacent Ru sites (*8*) is only observed at high Ru concentrations.

CONCLUSIONS

It was shown that it is possible to characterize, both qualitatively and quantitatively, the disposition of surface atoms on supported Ru–Pt bimetallic samples using infrared spectroscopy. This can be done rapidly and inexpensively without the use of specialized and costly instrumentation that is scarce in most surface chemistry laboratories. We realize that the accuracy of our experiments is not as good as that which can be obtained using other electron spectroscopic techniques. On the other hand, a very accurate characterization of the surface composition is not always necessary in many applications of catalysis by clusters. The infrared technique described here does have two very important advantages over the spectroscopic techniques in that only the surface layer is sampled and the surface is not destroyed during the sampling process. We are hopeful and confident that in the future we can extend this study to include other supported group VIII bimetallic cluster catalysts.

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