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Characterisation of Model Three-Way Catalysts

II. Infrared Study of the Surface Composition of Platinum–Rhodium Alumina Catalysts

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In order to determine the surface composition of platinum-rhodium/alumina catalysts, successive CO and NO adsorptions were studied by FTIR spectroscopy. The objective was to develop an experimental procedure in order to reach the number of surface rhodium and platinum atoms. Thus, it was observed on Rh/Al_2O_3 that adsorption of NO at 473 K for one night leads to a unique νNO band near 1910 cm^{-1} corresponding to Rh^{I}-NO^{+} species. After the same treatment under NO, the irreversible adsorption of CO at 298 K on Pt/Al_2O_3 produces a unique νCO band near 2085 cm^{-1}. By using monometallic solids of known dispersion, a correlation was established between the absorbance (optical density) of each of these bands and the number of surface rhodium or platinum atoms. This experimental protocol, based upon the successive adsorption of NO at 473 K and CO at 298 K, was applied to four bimetallic PtRh/alumina catalysts having a ca 3 wt% metal loading and an atomic Pt/Rh ratio between 0.4 and 3. The total numbers of surface atoms measured by this method were in rather good agreement with those obtained by hydrogen adsorption, which supports the validity of the method. Moreover, the surface composition determined from the FTIR measurements corresponded to a surface enrichment in rhodium for all the bimetallic catalysts. This point is discussed in relation to the characterisation protocol which could induce a migration of the rhodium atoms during heating under NO. The discussion includes also the possible inaccuracies involved in the method, particularly the influence of the alloying on the calibration coefficients. © 1998 Academic Press

1. INTRODUCTION

The surface composition of bimetallic solids is one of the parameters which control their catalytic properties. This is particularly true for Pt-Rh three-way catalysts (1–2), where each metal behaves specifically and orientates the reaction towards CO and hydrocarbon oxidation (Pt), or NO reduction (Rh). Therefore, numerous theoretical as well as experimental studies have been devoted to the measurement of the surface composition of bimetallic catalysts (3–7). There are several models which are used to predict, in bimetallic solids, a superficial enrichment in one element. The model of Sachtler and Van Santen (4), called "ionic binding model," anticipates that the particles surface will be enriched in the element which has the lowest sublimation energy, i.e. rhodium in the Pt-Rh catalysts case. If the two components have heats of sublimation close together, the surface will tend to be enriched in the minority element. A second model by Wynblatt and Ku (5), or "regular solutions model," predicts that the surface will be enriched in the element having the lowest surface tension, platinum in the case of a three-way catalyst. In order to explain a significant enrichment of Pt in the surface observed for clean Pt-Rh alloys, a model was elaborated by taking into account the difference in vibrational entropy of bulk and surface atoms of Rh and Pt (9). Calculations based on the electronic structure of the alloy using the tight binding Ising model have also predicted a Pt surface enrichment whatever the bulk concentration and temperature (10). However, for real catalysts, there exists two fundamental restrictions about the use of these models: (i) they were established for clean Pt-Rh alloy, i.e. constituted by two unsupported metals, and (ii) all the experiments should be performed using ultraclean samples, the surface segregation in Pt-Rh alloys being very sensitive to traces of impurities. Now, in three-way catalysis, the metals are always supported. Consequently the elements of the support can interact with each of the metallic components and result in the formation of new stabilised entities. Effectively, different species were observed when such metals deposited upon Al_2O_3 and/or CeO_2 are heated at high temperature under reducing or oxidative atmosphere, for example Rh-Al or Rh-Ce (8, 11–14) and Pt-Al or Pt-Ce (8, 14–15). Therefore, measuring the surface composition of a bimetallic system constitutes often a

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challenge but is essential to gain information on the active sites and follow their evolution during the ageing processes.

In a general characterisation study of model three way-catalysts, we previously reported on possible methods for measuring the extent of the ceria surface area in the ceria-alumina supported catalysts (16–19). Concerning the metallic phase, a first paper was devoted to the determination of the accessible metallic area (20). The measurement was global and no distinction was made between the surface platinum and rhodium atoms. The present work is concerned with the determination of the metal surface composition. Rather than physical methods (XPS, AES, ISS), we have chosen chemical methods to determine the surface composition, since they appear more able to give quantitative data. For example, Duprez and Kacimi (6–7) developed on such catalysts a neat method using $^{18}O/^{16}O$ or D_2/H_2 isotopic exchange. This is based upon the different isotopic exchange rates for platinum and rhodium. The use of this method is limited by the presence of impurities like chlorine which behaves as a strong inhibitor for the isotopic exchange (7). Consequently, this method cannot be easily applied when chlorinated precursors are used for the preparation of metallic catalysts, as in the case for our model three-way catalysts. Therefore, we have used a method based upon the successive chemisorption of NO and CO followed by infrared spectroscopy. The principle is based upon the differentiation and the quantification of infrared bands corresponding specifically to one metallic site, following the adsorption of a probe molecule. This method is particularly convenient for catalysts with a low accessible metallic area because the contribution of the support to the total adsorption can be ruled out. Primet *et al.* have developed such a method for the determination of the dispersion of platinum supported catalysts by using CO as a probe molecule (21). For bimetallic catalysts, CO has also often been utilised, for example in the case of Pt-Ru and Pt-Pd (22–23). There are also studies on the adsorption of CO on Pt-Rh systems (24–26), but the surface composition could not be determined. In the present paper, we study the successive adsorption of NO and CO by FTIR in order to quantify the surface rhodium Rh_s with NO as a probe molecule and the surface platinum Pt_s by CO adsorption. The work was carried out first on $PtRh/Al_2O_3$ catalysts. The results are discussed in relation to the measurement of the total accessible metallic area.

2. EXPERIMENTAL

2.1. *Materials*

The alumina support was obtained from Rhône-Poulenc (SCM129X). It was impregnated with aqueous solutions of H_2PtCl_6 or/and $RhCl_3$ in order to prepare mono and bimetallic catalysts, with metal content between 2 and 3 wt%. These relatively high loading were chosen in order to improve the accuracy of the calibration procedure. For the bimetallic catalysts, the atomic Pt/Rh ratio was varied between 0.4 and 3.

TABLE 1

Chemical Analysis of the Catalysts (wt%)

Catalyst	Pt wt%	Rh wt%	Pt/Rh (atomic ratio)
Pt/Al	2.02		
Rh/Al		1.94	
C1	2.02	0.35	3.04
C2	2.11	0.86	1.29
C3	2.11	1.01	1.1
C4	1.23	1.63	0.4

The impregnated supports were dried during one night under vacuum at 383 K and then treated for 2 h at 773 K under flowing nitrogen, with a 5 K min^{-1} heating ramp. They were reduced for 5 h at 773 K after a 2 K min^{-1} heating ramp. The obtained catalysts are presented in Table 1 with the corresponding chemical analysis of the metal content.

2.2. *Characterisation Methods*

The infrared measurements were obtained with a Fourier transform spectrometer BRUKER IFS 110 on self supported wafers samples (0.01 to 0.03 g/cm^2). The spectral domain was between 4000 and 1000 cm^{-1} with a 4 cm^{-1} resolution. CO and NO adsorption were carried out for specific detection of the quantity of platinum and rhodium present at the surface. Specific protocols were used as detailed below. The sample pretreatment consisted in a 1-h evacuation at 773 K followed by an *in situ* reduction under hydrogen (27 kPa) for one night at 773 K and a 2-h desorption under vacuum at the same temperature. Then, the wafer was cooled to room temperature before adsorption. The infrared spectra were recorded at room temperature.

Metallic accessible areas (or dispersions) were measured by classical volumetric H_2 irreversible adsorption at room temperature, followed by successive titration by oxygen and hydrogen (20, 27). They were performed upon the samples reduced at 773 K and evacuated at the same temperature. The successive steps were as follows: hydrogen chemisorption (H_c), titration by oxygen (O_{T1}), titration by hydrogen (H_{T1}) and titration by oxygen (O_{T2}).

3. RESULTS

3.1. *Measurement of the Global Metallic Area Accessible by Hydrogen Chemisorption and Titration*

The measurement of the metallic accessible area was carried out on the monometallic and bimetallic solids. Table 2 gives the dispersion values obtained from each adsorption and expressed as H/M, assuming a stoichiometry

TABLE 2

Exposed Metallic Fractions (%) of the Pt or/and Rh/Al_2O_3 Catalysts Obtained by Hydrogen Chemisorption and H_2/O_2 Titration

Catalyst	H_C	O_{T1}	H_{T1}	O_{T2}
Pt/Al	51.5	44.3	48.8	46.4
Rh/Al	36.3	52.9	50.6	38
C1	43.5	47.8	48.8	46.4
C2	—	54.5	48.7	39.7
C3	49.9	—	49	—
C4	40.4	62.4	55.2	39

of 1 hydrogen per metal atom. There is a good agreement in the case of Pt/Al_2O_3. For Rh/Al_2O_3, the dispersion decreases with the number of titrations, and there exists a difference between H_c and the titration values. In the case of bimetallic catalysts, this gap between the different values seems to increase with the rhodium content. However, the values of each series are in a reasonable agreement. For the following, the dispersion values (H/M) for each solid will be those deduced from the first titration by hydrogen H_{T1}. They are nearly constant and range between 49 and 55%.

3.2. Infrared Spectroscopy Study of CO and NO Adsorption on Pt or/and Rh/Al_2O_3

The objective is to define the experimental conditions for which a well-defined band specific of one metal can be obtained. Although the results are already well known, we summarise first the spectra obtained at room temperature by using CO and NO as probe molecules. Since these adsorptions give νCO or νNO bands too close to allow a clear identification of the two metals in a bimetallic system, tentative runs were carried out by reacting first NO at 473 K before adsorbing CO at room temperature. From the results, a method was deduced and the experimental protocol was applied to the case of bimetallic catalysts so that the surface composition could be estimated.

3.2.1. CO adsorption on Pt or/and Rh/Al_2O_3 at 298 K. The adsorption of CO at room temperature on platinum or rhodium supported on alumina is already known. As shown on Fig. 1, CO is irreversibly adsorbed at 298 K on platinum and gives two bands νCO near 2075 cm^{-1} (linear CO) and 1850 cm^{-1} (bridged CO) (28–30). The contribution of this second band to the total absorption is lower than 5%. A relationship between the optical density (OD) or absorbance of the 2070–2075 cm^{-1} band, expressed per gram of Pt, characteristic of the Pt°-CO species and the platinum accessible area was established by Primet *et al.* for catalysts of different dispersion and supported on Al_2O_3, SiO_2, CeO_2, or MgO (21). If S_{Pt} is expressed in m^2g^{-1} Pt, the relation obtained in their conditions was given by $S_{Pt} = 0.23$. OD. In an equivalent manner, an optical density of 1 (per gram of platinum) corresponded to 4.77 μmol Pt_s.

On rhodium, under the same conditions, four bands are observed at 2105, 2040, 2060, and 1890 cm^{-1} (Fig. 1). They correspond respectively to the symmetric and anti-symmetric νCO vibrations of the Rh^I-$(CO)_2$ gem-dicarbonyl, the linear CO (Rh°-CO), and the bridged CO ($(Rh)_2$-CO) (32–37). The proportion of the created Rh^I-$(CO)_2$ species is not constant and decreases when the rhodium particle size increases. For highly dispersed Rh/Al_2O_3 catalysts, the gem-dicarbonyl species prevails. Observations have been made that these entities can be formed during CO adsorption by the oxidation of the Rh° sites by the protons of the hydroxyls groups on the surface of the support (38–41). Therefore, the study of the νCO, characteristic of the linear species Rh°-CO, does not yield the rhodium metallic area, and effectively no linear relationship could be clearly established, in contrast to the case for platinum.

For the bimetallic solids, the adsorption of CO leads to the superimposition of the specific bands for Pt and Rh. The spectra look like that reported for platinum, with a shift of the wave number of the main band and more or less marked shoulders corresponding to rhodium. The selective identification of each metal by deconvolution is questionable, and it seems impossible to obtain a precise quantification of the superficial composition.

3.2.2. NO adsorption on Pt or Rh/Al_2O_3 at 298 K. The adsorption of NO on platinum at 298 K gives three νNO bands at 1800, 1775, and 1710 cm^{-1}. On evacuation, the irreversible adsorption is characterised mainly by the 1775 cm^{-1} band (Fig. 2a) corresponding to linearly bonded NO chemisorbed on reduced platinum Pt°-NO (42–44) with

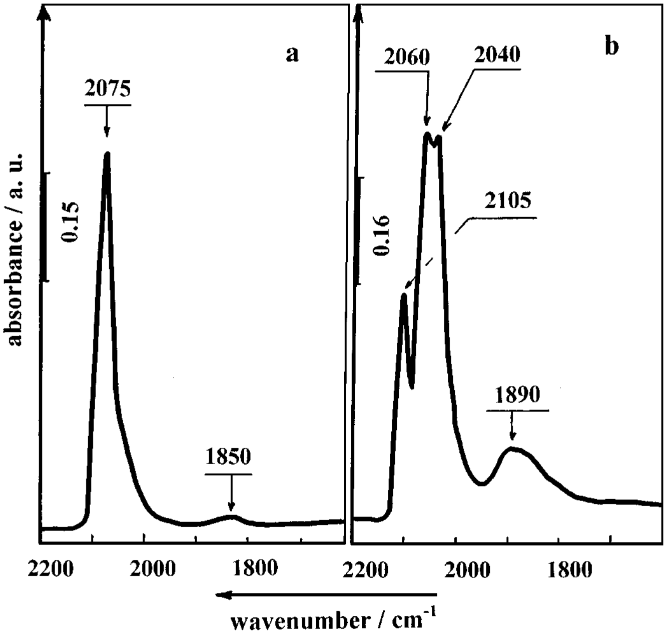

FIG. 1. Infrared spectra of CO irreversibly adsorbed at 298 K on monometallic catalysts: (a) Pt/Al_2O_3; (b) Rh/Al_2O_3.

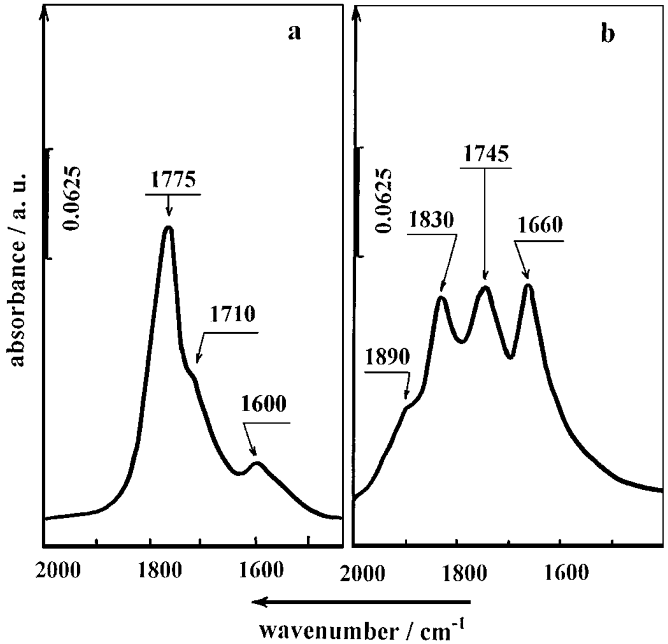

FIG. 2. Infrared spectra of NO irreversibly adsorbed at 298 K on monometallic catalysts: (a) Pt/Al_2O_3; (b) Rh/Al_2O_3.

a position depending upon the platinum particle size (42). The two other weaker bands at around 1710 and 1600 cm^{-1} are attributed, depending on the authors, to nonlinear or bent Pt-NO species (24). The band at 1600 cm^{-1} could be also assigned to nitrate species bounded to the support (43). That could originate from NO disproportionation, hypothesis which is supported by the presence of a small band at ca 2225 cm^{-1}, eliminated under vacuum, which is characteristic of gaseous N_2O (45–46).

As shown on Fig. 2b, the NO adsorption on rhodium is characterised by four bands. Those at 1890, 1830, and 1745 cm^{-1} are attributed to Rh^I-NO^+ species (44, 47–51) and to symmetric and antisymmetric νNO stretching vibrations of Rh-$(NO)_2$ dinitrosyl complex, respectively (48). In addition, the band observed at 1660 cm^{-1} is probably due to a bent rhodium-mononitrosyl species. Thus, the adsorption at 298 K results in multiples bands, making impossible a clear estimate of the quantity of surface rhodium. Also, as for platinum, a slight decomposition in N_2O is observed, with the characteristic wave number at 2225 cm^{-1}.

3.2.3. NO adsorption on Pt or Rh/Al_2O_3 after one night under NO at 473 K. The results above show that the presence of rhodium complicates singularly the spectra both for CO or NO adsorption. To overcome this difficulty, different conditions were tested in order to better differentiate the two metals by well-separated bands : desorption of adsorbed CO at different temperatures, reaction of adsorbed CO with oxygen, selective displacement of adsorbed CO by NO, and the reverse, influence of a pretreatment under oxygen at room temperature. These different experiments do not allow discrimination between Rh_s and Pt_s species.

However, Anderson *et al.* (48) have observed that the adsorption of NO at 473 K on a 1% Rh/Al_2O_3 leads to the development of a band at 1910 cm^{-1} (Rh^I-NO^+) at the expense of the two bands of the Rh-$(NO)_2$ dinitrosyl complex and the formation of new bands attributed to nitrates (1650, 1550, 1320, and 1230 cm^{-1}). The later result from the reaction of adsorbed oxygen with NO or from NO_2 adsorption.

Consequently, we have performed similar experiments in order to determine the best conditions to obtain the oxidation of all the surface rhodium atoms and consequently a unique adsorption band near 1910 cm^{-1} for (Rh^I-NO^+). Thus the reduced sample was heated overnight at 473 K under 1.5 kPa NO, cooled to room temperature and evacuated at the same temperature. The spectra are represented in Fig. 3. The initial spectra is strongly modified. An intense band νNO is obtained at 1915 cm^{-1} (Rh^I-NO^+ species),

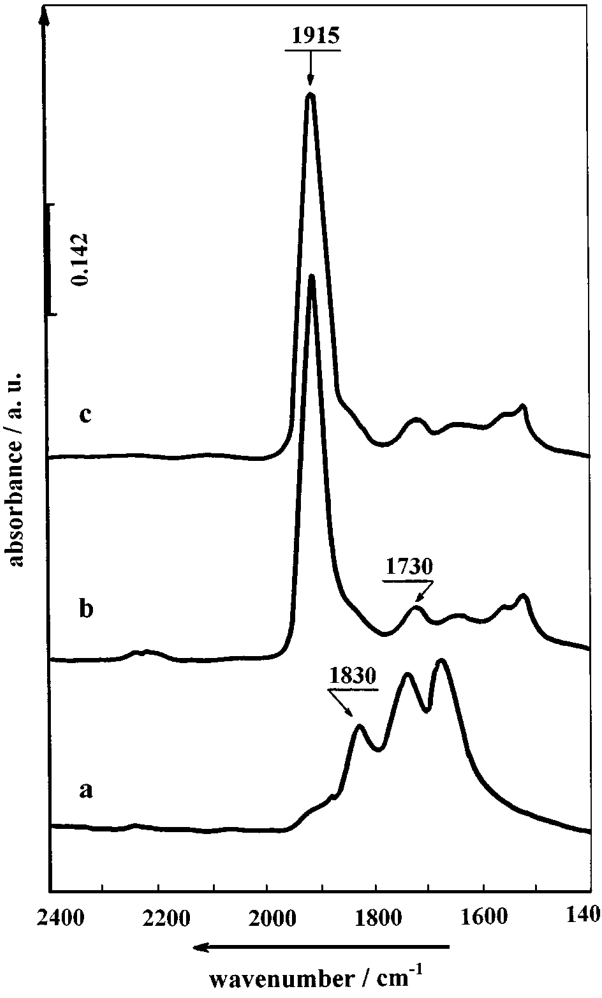

FIG. 3. Infrared spectra of adsorbed NO on Rh/Al_2O_3 treated at 298 and 473 K under 1.5 kPa NO: (a) NO at 298 K (P = 1.5 kPa); (b) after one night at 473 K under NO, NO at 298 K (P = 1.5 kPa); (c) vacuum, 298 K.

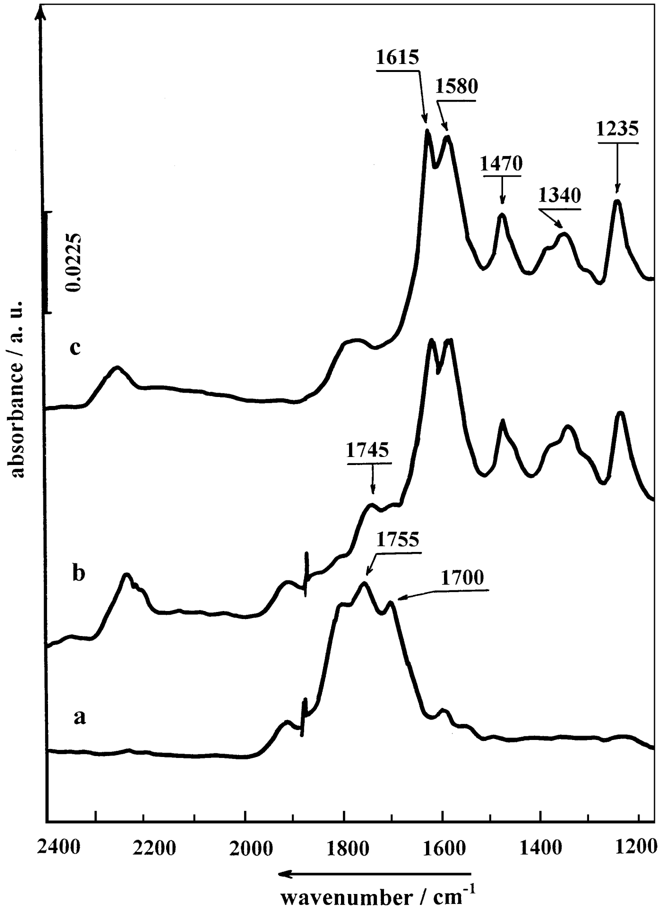

FIG. 4. Infrared spectra of adsorbed NO on Pt/Al_2O_3 treated at 298 and 473 K under 1.5 kPa NO: (a) NO at 298 K (P = 1.5 kPa); (b) after one night at 473 K under NO, NO at 298 K (P = 1.5 kPa); (c) vacuum, 298 K.

whereas the bands at 1830 and 1730 cm^{-1} remain as shoulders. Heating for 1 h under NO at 573 K gives a comparable result, which means that no more surface rhodium atoms can be oxidised in Rh^I-NO^+ species.

The same treatment at 473 K under NO for one night was carried out on the platinum-alumina catalyst. The spectra is deeply modified (Fig. 4). After evacuation at room temperature, it remains a broad band of limited intensity at around 1795–1760 cm^{-1}. Simultaneously, more intense bands are developed at 1615, 1580, 1470, 1340, 1235, and 1050 cm^{-1}. They can be ascribed to nitrate species bounded both to platinum and support surfaces (43). A band at ca 2255 cm^{-1} is also observed. This component was not evidenced in the case of the rhodium alumina sample after the same treatment under NO at 473 K. Being "blue-shifted" compared to gaseous nitrous oxide, it could be tentatively attributed to weakly adsorbed N_2O. This hypothesis is supported by the observation of the same wavenumber for N_2O irreversibly adsorbed at 298 K on alumina dehydrated at $T > 573$ K (46). However, the specific influence of platinum on the formation of this band remains unclear.

From the comparison between Figs. 3 and 4, it is clear that platinum does not give bands of adsorbed NO in the frequency domain of the Rh^I-NO^+ species at 1915 cm^{-1}. Consequently, these observations suggest the possibility of measuring selectively the rhodium metallic area, provided that the band at 1910 cm^{-1} corresponds exactly to the surface rhodium atoms and that a linear relationship exists between the optical density (or absorbance) of the 1910 cm^{-1} band and the rhodium dispersion. The calibration coefficient was established with the monometallic Rh/Al_2O_3 catalyst treated one night at 473 K under 1.5 kPa NO using the dispersion measured by hydrogen chemisorption. An optical density of 1 per gram of rhodium was found to be equivalent to 6.5 μmol Rh_s.

3.3. Method of Successive NO and CO Adsorption on Pt or Rh/Al_2O_3

In complement to the measurement of the number of surface rhodium atoms, we have considered the possibility of measuring selectively the area of metallic platinum in a bimetallic Pt-Rh catalyst. In this respect, the adsorption of CO (2.7 kPa) was performed at 298 K after the previous treatment under 1 kPa NO at 473 K.

The Pt/Al_2O_3 solid under these conditions gives a unique, sharp, and intense band at 2085 cm^{-1} (Fig. 5). The other

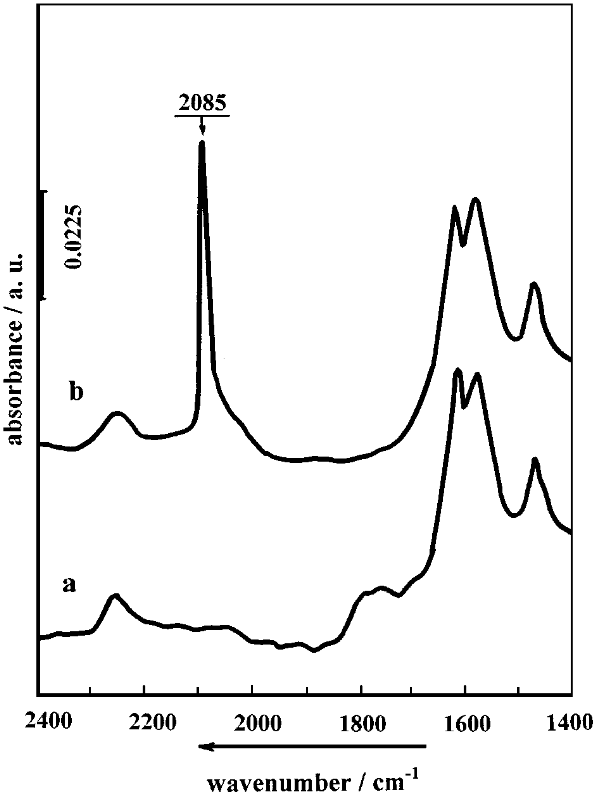

FIG. 5. Irreversible adsorption of CO at 298 K on Pt/Al_2O_3 following the treatment at 473 K under 1.5 kPa NO: (a) before CO adsorption; (b) introduction of 2.7 kPa CO at 298 K and evacuation at 298 K.

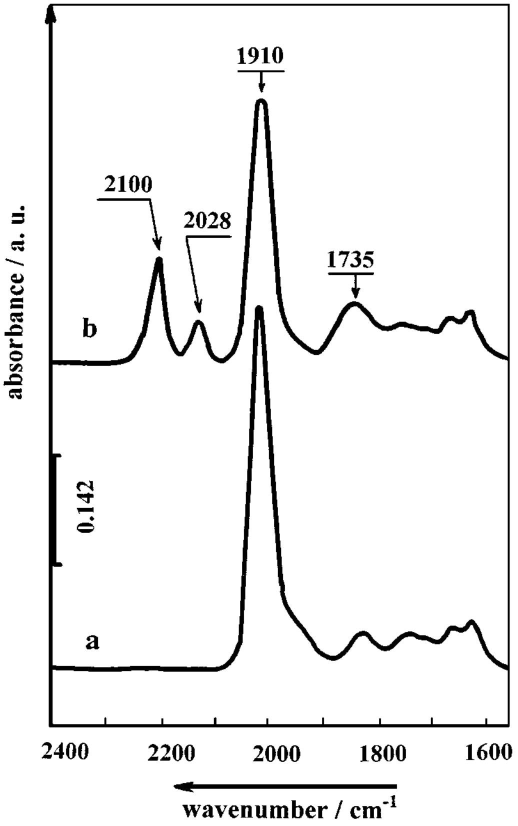

FIG. 6. Irreversible adsorption of CO at 298 K on Rh/Al_2O_3 following the treatment at 473 K under 1.5 kPa NO: (a) before CO adsorption; (b) introduction of 2.7 kPa CO at 298 K and evacuation at 298 K.

bands in the nitrate domain remain practically unchanged. The slight increase of the wavenumber from 2075 cm^{-1} for a freshly reduced sample to 2085 cm^{-1} can be considered as typical of a CO bounded to partially oxidised platinum (30, 52). This is in agreement with the absence of residual Pt°-NO band at 1785 cm^{-1}, indicating that the metallic platinum has been oxidised. By calculating the absorbance of the 2085 cm^{-1} band, it was found that an optical density of 1 per gram of catalyst corresponded to 18 μmol of Pt_s per gram of catalyst.

In the case of Rh/Al_2O_3, following the treatment under NO at 473 K, the CO adsorption at 298 K results in a decrease of the intensity of the 1910 cm^{-1} band (Fig. 6). Two new bands are observed at 2100 and 2028 cm^{-1}, which can be attributed to the Rh(I) gem-dicarbonyl complex. However, the relative intensities of these bands are different. The relative increase in the intensity of the 2100 cm^{-1} band could be explained by the contribution of a Rh(CO)(NO) species, the corresponding NO stretching frequency being located at 1910 cm^{-1}. By evacuation at 298 K, the intensities of the 2100 and 2028 cm^{-1} bands are readjusted and the intensity of the band corresponding to Rh^I-NO^+ is increased. In summary, the monometallic Rh/Al_2O_3 system produces the two bands of the gem-dicarbonyl species, but no band of CO adsorbed on metallic rhodium, which is normally expected after the oxidising treatment under NO.

Since there is no residual metallic rhodium under these conditions (νCO close to 2060 cm^{-1}), it results that for a bimetallic Pt-Rh/Al_2O_3 catalyst it will be possible to discriminate platinum from rhodium only by isolating and deconvoluting the νCO band at 2085 cm^{-1} ascribed to Pt from those at 2100 and 2028 cm^{-1} (Rh^I-$(CO)_2$ gem-dicarbonyl). There is no interference arising from the 1915 cm^{-1} band.

3.4. *Application of the Method to $PtRh/Al_2O_3$ Catalysts*

To test the validity of this method, the four different bimetallic Pt-Rh/Al_2O_3 catalysts were studied. As mentioned before, the protocol consisted of a reduction under H_2 at 773 K, followed by an evacuation at the same temperature. Then the samples were submitted to the following sequence: at 473 K, treatment for at least 12 h under 1.5 kPa NO, cooling to 298 K under NO, evacuation, introduction of 2.7 kPa CO and a final evacuation, always at room temperature. The quantification for rhodium was obtained using the spectra recorded before the CO introduction. We have used the calibration coefficients determined from monometallic catalysts with the Rh^I-NO^+ 1915 cm^{-1} band for Rh and the $Pt^{\delta+}$-CO 2085 cm^{-1} band after the treatment at 473 K under NO for Pt. As mentioned above, they were found equal to 6.5 μmol Rh_s and 18 μmol Pt_s, respectively, for an optical density (or absorbance) of 1 per gram of metal. The carbonyl band of CO adsorbed on platinum was deconvoluted using spectra adjustment software. The curve adjustments are given in Fig. 7 for the four catalysts.

The results obtained from the exploitation of the spectra are summarised in Table 3. For rhodium, the frequency of the NO band remains between 1910 and 1918 cm^{-1}, and after the CO adsorption those of the gem-dicarbonyl are the same as for the monometallic rhodium solid. For CO adsorbed on platinum, the spectra of the C1 catalyst, which is platinum rich, can be deconvoluted in two bands at 2082 and 2067 cm^{-1}. The first one is close to that

TABLE 3

νNO and νCO Wavenumbers Obtained for the Bimetallic $PtRh/Al_2O_3$ Catalysts by the Sequential Adsorption Method (NO at 473 K, then CO at 298 K) and the Corresponding Surface Metal Atoms (Subscript s)

Catalyst	C1	C2	C3	C4
νNO (cm^{-1}) (Rh)	1918	1918	1912	1910
Rh_s (μmol g^{-1})	25.3	55	45.4	99.6
νCO (cm^{-1}) (Rh^I $(CO)_2$)	2105	2100	2098	2098
	2023	2027	2023	2026
νCO (cm^{-1}) (Pt)	2082			
	2067	2066	2064	2060
Pt_s (μmol g^{-1})	37.6	40.5	28.6	14.9

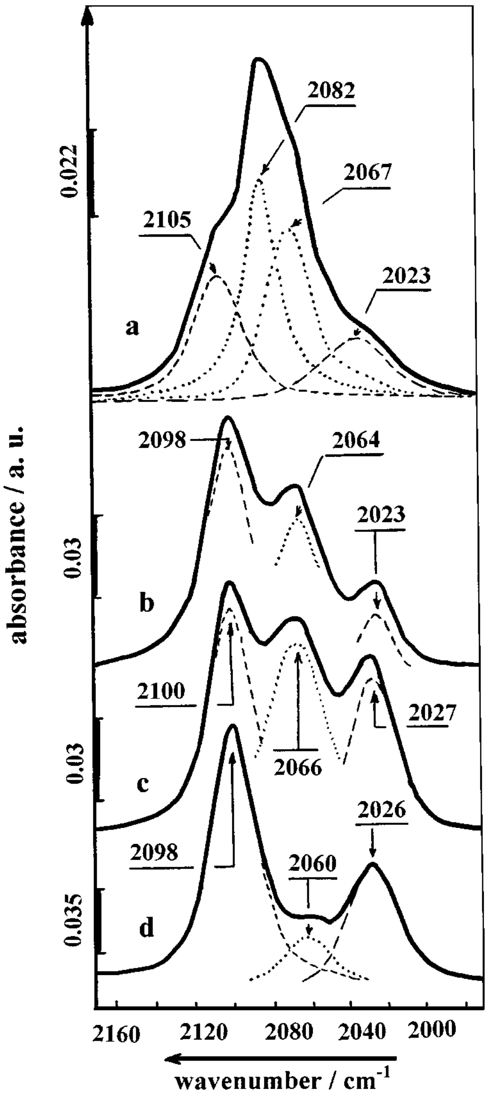

FIG. 7. Curve adjustment of the νCO band observed on the PtRh/Al_2O_3 catalysts, corresponding to the irreversible adsorption of CO at 298 K after one night at 473 K under 1.5 kPa NO: (a) C1, Pt/Rh = 3.04; (b) C3, Pt/Rh = 1.1; (c) C2, Pt/Rh = 1.29; (d) C4, Pt/Rh = 0.4.

observed for the monometallic Pt/Al_2O_3 treated under the same conditions and could be ascribed to nonalloyed platinum. The second one at 2067 cm^{-1} is observed also for the other bimetallic catalysts which are more loaded in rhodium (2066–2060 cm^{-1}) and could be attributed to platinum alloyed with rhodium.

Using the calibration coefficient determined above for each metal, we have calculated the number of Rh_s and Pt_s per gram of catalyst from the 1910–1918 cm^{-1} and 2082–2060 cm^{-1} bands. The values are given also in Table 3. For the solid C1, considering the proximity of the two bands at 2082 and 2067 cm^{-1}, the number of Pt_s was calculated using the optical density of the 2082 cm^{-1} after subtraction of the contribution of the rhodium gem-dicarbonyl at this wavenumber.

4. DISCUSSION

Table 4 gives a summary of the main data obtained in this study. The total number of platinum and rhodium atoms per gram of catalyst has been calculated from the chemical analysis. Volumetric adsorption leads to the total number of surface atoms without discriminating Pt or Rh, whereas the infrared method allows the specific determination of surface rhodium or platinum atoms and, therefore, the specific dispersion corresponding to platinum and rhodium.

The total dispersion (H/M) is nearly constant for the studied catalysts, between 49 and 55%. For the same platinum loading, it does not change when the rhodium content increases (C1 to C3 catalysts). For the C4 catalyst which contains the highest number of metal atoms, the small increase observed in the dispersion value for the C4 solid can be related to a lower platinum content. However, these variations are practically insignificant, and we have already noticed that the differences between direct hydrogen chemisorption values and those obtained by titration can be more important.

From the results of the FTIR method, it is possible to calculate the number of rhodium and platinum surface atoms. Knowing the real content of each metal, we have calculated a relative dispersion for each metal. It appears from Table 4 that, generally speaking, it is lower for platinum (24–37%) than for rhodium (46–74%). The global dispersion calculated with the infrared data is close to 50%, that for the C3 catalyst being lower at 36%. These dispersion values, or the number of Pt + Rh surface atoms as well, are very

TABLE 4

Comparison between the Number of Surface Metal Atoms and "Dispersion" Values Obtained on the PtRh/Al_2O_3 Catalysts by Volumetry and by FTIR Using the Method of Sequential Adsorption of NO and CO

Catalyst	C1	C2	C3	C4
Chemical analysis				
Pt_t (μmol g^{-1})	103.5	108.2	108.2	63
Rh_t (μmol g^{-1})	34	83.6	98.2	158.4
$Pt_t + Rh_t$ (μmol g^{-1})	137.5	191.8	206.4	221.4
Volumetric adsorption				
H/M (%)	48.8	48.7	49	55.2
$(Pt + Rh)_s$ (μmol g^{-1})	67.1	93.4	101.1	122.2
FTIR spectroscopy				
$(Pt + Rh)_s$ (μmol g^{-1})	62.9	95.5	74	114.5
Pt_s/Pt_t	36	37	26	24
Rh_s/Rh_t	74	66	46	63
$(Pt + Rh)_s/(Pt + Rh)_t$	46	50	36	52
Pt/Rh atomic ratio				
Theoretical	3.04	1.29	1.1	0.40
From FTIR spectroscopy	1.49	0.74	0.63	0.15

Note. The subscripts s and t refer to the surface and total number of metal atoms.

close to the corresponding numbers determined by hydrogen titration. This agreement supports the validity of the FTIR approach.

However, for the C3 catalyst, there is a poor correlation between the total dispersions measured by the two methods, 49% by volumetry and 36% by the infrared method. In fact, considering the variations of the metal loading for the series of catalysts, the value given by volumetry (49%) is in the continuity of the values obtained for the others. This is not the case for the dispersion value obtained from FTIR which is much lower than the expected value. This is particularly evident for rhodium for which the dispersion value (46%) is well below the values of the other bimetallic catalysts (74–63%). The explanation for this peculiar behaviour is difficult. There is no peculiarity in the FTIR spectrum and the band at 1912 cm^{-1} is well defined. In fact, this difference in the obtained dispersion values can be considered as an illustration of the limitations of the infrared method, as is discussed below.

In Table 4, the Rh/Pt atomic ratios obtained from the infrared method are compared also to the theoretical ratios determined by chemical analysis. The infrared results suggest an enrichment of the surface in rhodium at the expense of platinum. In the four bimetallic catalysts, there are nearly twice as many rhodium atoms at the surface of the solid as expected for a homogeneous composition. Since the dispersion of the monometallic Pt or Rh catalysts are very similar, it seems difficult to attribute this enrichment of the surface in rhodium to different sizes in the metal particles. This surface enrichment can be inherent in the catalysts themselves, in agreement with the Van Santen “ionic binding model.” It supposes that bimetallic particles were formed initially, although there was no peculiar procedure intended to form them. However, the relatively high metal loading (2.4 to 3.1%) could explain the easiness to form such bimetallic particles. It can be recalled that the presence of two CO bands for the C1 catalyst was interpreted for one of them as due to an alloy between Rh and Pt. The shift of the νCO band bounded to platinum from 2067 to 2060 cm^{-1} when the Rh/Pt ratio increases supports also the idea of bimetallic particles in which platinum and rhodium interact.

The characterisation method must be discussed since it is able to modify the surface composition. Indeed, for applying the method, it must be supposed that the treatment by NO at 473 K does not selectively extract rhodium in a bimetallic particle. Moreover, the oxidative disruption of rhodium particles under NO may modify the apparent rhodium particle size. Effectively, in the present study, the adsorption of NO at high temperature appears to oxidise preferentially the rhodium atoms, the platinum being less easily oxidised, since after this reaction at 473 K, CO is able to be adsorbed on platinum atoms, whereas no metallic rhodium is observed. However, considering the variation of the Rh/Pt ratio by a factor of eight between C1 and C4 solids, which leads to bimetallic particles having probably very different composition, one would expect large changes in the relative dispersion for rhodium and platinum. Indeed, the proportion of rhodium atoms migrating towards the surface should decrease when the rhodium concentration increases. In other words, the more the catalyst is rich in rhodium, the less the surface will tend to be enriched in rhodium atoms. Therefore, the fact that the relative dispersions are not deeply modified by changing the bulk Rh/Pt ratio is not in favour of the hypothesis of a selective extraction of rhodium at the surface of the bimetallic particle. Other specific characterisation on model catalysts would be necessary to confirm this conclusion. However, whatever the nature of this enrichment, the proposed method has the advantage of studying the system under conditions comparable to those of the CO + NO reaction.

Another limitation of the method has to be stressed to be aware of possible inaccuracies in the discussion of the results. The point is that the method is based on calibrations performed on a monometallic catalyst, whereas it is applied to bimetallic catalysts. If bimetallic particles are formed, as has been deduced in this study from the position of the wavenumbers for CO adsorbed on platinum, it is quite probable that this alloying effect modifies the infrared calibration coefficients, insofar as the variations in the CO stretching frequency variations go with force-constant modifications. In addition, if there is a proximity of alloyed and nonalloyed surface metal atoms, platinum, for example, in the C1 catalyst with the coexistence of two Pt CO bands at 2082 and 2067 cm^{-1}, the coupling between the two adsorbed CO creates some interferences which are not accounted for in the direct measure of the intensity of the band used to obtain the dispersion. The relative good agreement between the infrared and volumetric results seem to indicate that the inaccuracies resulting from these phenomena are limited in the present study, but these limitations must be kept in mind before applying this method to other catalysts presenting somewhat different characteristics (loading, dispersion).

5. CONCLUSION

If the classical measurement of the dispersion of bimetallic catalysts by hydrogen chemisorption and subsequent titration by oxygen and hydrogen give an estimation of the total number of surface metal atoms, it is essential to develop other methods to reach the specific number of each of the metal components. The results presented here show that it is possible to find probe molecules and adsorption conditions such as how each surface metal behaves specifically and is transformed into characteristic species well quantified by FTIR spectroscopy. Thus, by applying an experimental protocol based upon the successive adsorption of NO at 473 K and CO at room temperature, the surface composition of PtRh/alumina catalysts has been determined. The total numbers of surface atoms measured by this method are in rather good agreement with those obtained by hydrogen adsorption. Moreover, the measurements show a surface enrichment in rhodium, perhaps inherent in the catalysts or resulting from the characterisation protocol itself through the migration of rhodium towards the surface induced by the heating under NO. However, examination of the results in relation to the bulk Rh/Pt ratio seems to invalidate this last hypothesis.

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