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Characterization of Model Three-Way Catalysts

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

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The surface composition of model and commercial bimetallic PtRh catalysts supported on ceria–alumina was tentatively determined by FTIR spectroscopy using the successive adsorption of NO at 473 K and CO at 298 K method which was previously applied to the case of PtRh/Al_2O_3 catalysts. The study of monometallic model catalysts shows that the adsorption of NO at 473 K on rhodium gives an intense band at 1912 cm^{-1} which is not modified by the presence of ceria and therefore can be used to quantify the number of surface rhodium atoms. However, the chemisorption properties of platinum toward the subsequent adsorption of CO at 298 K are strongly modified and the quantification of the surface platinum atoms could not be directly measured. However, their number could be indirectly obtained by combining the NO adsorption for rhodium and hydrogen volumetric adsorption for the total number of surface metal atoms, assuming that NO adsorption does not induce an important segregation of rhodium for bimetallic particles. Thus, for the fresh bimetallic model catalyst, the same composition was obtained at the surface and in the bulk. After aging at 1273 K, no rhodium was detected at the surface. This absence of surface rhodium atoms was confirmed by the data obtained from the direct adsorption of CO on platinum at room temperature, which gave the same number of surface atoms as hydrogen chemisorption. Similar results have been obtained with two commercial three-way catalysts. In particular, after aging at 1273 K, rhodium was practically not detected on the surface. © **1999 Academic Press**

Key Words: **platinum–rhodium catalyst; platinum catalyst; rhodium catalyst; three-way catalyst; ceria–alumina; NO adsorption; CO adsorption; surface composition by FTIR.**

1. INTRODUCTION

In a preceding paper, we developed a methodology for measuring the surface composition of bimetallic Pt–Rh catalysts supported on alumina (1). The principle of the method was based on the quantification of the optical densities of infrared bands, specific of a metallic site after adsorption of a probe molecule. Thus, it was found that the successive adsorption of NO at 473 K and CO at 298 K followed by FTIR spectroscopy made it possible to quantify the surface rhodium atoms Rh_s with NO (1910 cm^{-1} band corresponding to Rh^I–NO^+ species) and the surface platinum atoms Pt_s by CO (band at 2065–2085 cm^{-1} depending on the state of platinum, alloyed or not). This method was applied to four bimetallic catalysts, always supported on alumina and highly metal loaded (≈3 wt%), assuming that the successive treatments under NO and CO do not segregate rhodium or platinum to the surface in the case where alloyed particles have been formed. The validity of the method has been supported by the fact that the total numbers of metallic sites obtained by infrared were found in good agreement with those deduced from hydrogen adsorption volumetric measurements. The formation of bimetallic particles in these highly metal loaded catalysts was also deduced from the shift in the position of the νCO band bound to platinum. However, a slight rhodium enrichment was also observed compared to the nominal composition of the fresh bimetallic catalyst, but it was not possible to conclude if this property was inherent to the catalyst or resulted from the characterization method itself.

With the objective of characterization of three-way catalysts, this type of study was extended to Pt and/or Rh/CeO_2–Al_2O_3 systems prepared as models for three-way catalysts. It must be noticed that the experimental protocol determined for PtRh/alumina catalysts does not require that the

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two metals are alloyed or not. The purpose of the measurements is to determine the total number of surface metal atoms and the specific number of each metal component. Thus, the only requirement is the initial reduction of platinum or rhodium to the metallic state. However, starting with the results obtained with the PtRh/Al_2O_3 catalysts, it was necessary to ascertain that the presence of ceria in the support did not modify the chemisorption properties of platinum and rhodium. For this reason, this study was started with monometallic Pt or Rh/CeO_2–Al_2O_3 solids in order to calibrate the intensity of the infrared bands with the accessible metallic area values. After measuring the surface composition on a model bimetallic catalyst, the method was applied to two commercial catalysts deposited on a monolith. The results are presented both for fresh state and aged samples (aging at 1273 K) in order to verify the validity of the method and to study the effects of the aging process.

2. EXPERIMENTAL

2.1. Materials

The model Pt and/or Rh/CeO_2–Al_2O_3 catalysts are those used in previous studies (2, 3). The ceria–alumina support was prepared by grafting Ce(acac)$_3$ on an alumina support (Rhodia SCM129) and calcination at 673 K (3, 4). The final cerium content was around 19 wt%, value representative of the cerium content in the industrial three-way catalysts. This support was impregnated with aqueous solutions of H_2PtCl_6 or/and $RhCl_3$ in order to prepare mono- and bimetallic catalysts with a global metal content between 0.5 and 2.0 wt%.

The impregnated supports were dried overnight under vacuum at 383 K and then treated 2 h at 773 K under flowing nitrogen. The obtained catalysts are presented in Table 1 with the corresponding chemical analysis of the metals (3).

Two commercial catalysts referenced as COM1 and COM2 were also investigated. The precious metal loading was 32 and 40 g foot^{-3}, respectively (1 cubic foot = 28.317 × 10^{-3} m^3), and the washcoat percentage was ca. 31% for both systems. The content of the precious metals in the washcoat (Table 1) gives a corresponding Pt/Rh wt% ratio of 5/1 and 10/1. The commercial catalysts were ground before characterization.

The aged catalysts were prepared by treating the solids during 5 h at 1273 K under flowing nitrogen (6 L h^{-1}) containing 10 vol% water vapor. The model catalyst 1Pt0.2Rh/CeO_2–Al_2O_3 was reduced during 5 h at 773 K before aging.

TABLE 1

Metal Content of the Catalysts Expressed in wt% and Number of Metal Atoms

Catalyst	Pt (wt%)	Rh (wt%)	Pt_t (μmol g^{-1})	Rh_t (μmol g^{-1})	$Pt_t + Rh_t$ (μmol g^{-1})
0.5Pt/CeAl	0.59		30.2		
2Pt/CeAl	2.09		107.1		
0.5Rh/CeAl		0.45		43.7	
1Pt–0.2Rh/CeAl	1.13	0.19	57.9	18.5	76.3
COM1[a]	0.49	0.10	25.3	9.8	35.1
COM2[a]	0.68	0.068	35.0	6.6	41.6

[a] The amount of noble metals were calculated by considering only the washcoat.

2.2. Characterization Methods

Most of the data on the accessible metallic area (or dispersion) of the monometallic solids were obtained previously (2). They were deduced from volumetric hydrogen chemisorption measurements performed in static conditions according to the procedure previously described (2). The reduction temperature was 573 K. The accessible metallic area or dispersion values are expressed as H/M.

The infrared measurements were carried out with a Fourier transform spectrometer BRUKER IFS 110. The experimental procedure was that described for the alumina supported catalysts (1). However, taking into account results on the accessibility of metals in the presence of ceria and the possibility of strong metal support interaction (SMSI) effects (2), the experimental protocol was modified compared to the case of alumina as support, by lowering the reduction temperature from 773 to 573 K. Thus, the samples were first pretreated at 723 K under high vacuum. Then 27 k*Pa* of hydrogen was introduced on the wafer at 573 K during 1 h before desorption under vacuum at the same temperature. This treatment was repeated two times in order to eliminate the water produced by the reduction. After a final evacuation at 573 K for 3 h, the wafer was cooled to room temperature and put in contact with 1.5 kPa NO. Then the catalyst was heated at 473 K for one night under NO, cooled to 298 K and evacuated. The last treatment consisted of the adsorption of 2.7 k*Pa* CO and final evacuation, always at room temperature. For each probe molecule, the infrared spectra were recorded at room temperature after a 30-min vacuum treatment.

3. RESULTS AND DISCUSSION

3.1. Sequential NO and CO Adsorption on Pt or Rh/CeO_2–Al_2O_3

In order to apply the sequential adsorption method to the case of PtRh/CeO_2–Al_2O_3 model systems, it is necessary to study first the behavior of the support alone and that of the monometallic catalysts. Indeed, cerium oxide is well known for its redox properties and its presence in the support is likely to bring strong modifications to the adsorption properties of the surfaces, on both the metal and the oxide phases.

3.1.1. Support CeO_2–Al_2O_3. The adsorption of NO was studied on the support reduced at 573 or 773 K. After reduction and evacuation at 573 K and before any adsorption, a small band at 2120–2130 cm^{-1} is obtained. It is more intense after reduction at 773 K and must be associated to the formation of Ce^{3+} ions. This band, which had been previously attributed in the case of ceria to occluded CO resulting from the partial reduction of carbonates species, results in fact from an electronic transition from a donating level localized near the conduction band (5, 6).

After NO adsorption at 298 K, the 2120 cm^{-1} band disappears and a broad band centered at 2224 cm^{-1} is observed. Its intensity is nearly the same after heating one night at 473 K under NO, whereas a slight band at 2350 cm^{-1} is formed, specially after reduction at 773 K. These bands disappear under vacuum. The 2224 cm^{-1} band can be ascribed to gaseous N_2O and that at 2350 cm^{-1} after heating at 473 K corresponds to gaseous CO_2 (7, 9). Thus the reduced ceria–alumina decomposes NO into N_2O. Moreover, upon heating at 473 K under NO, there are deep modifications of the spectrum in the 1100–1700 cm^{-1} frequency domain, with the main bands observed at 1550, 1360, and 1175 cm^{-1}. They correspond to the formation of nitrate or nitrite species, the decomposition of some carbonate species explaining the presence of CO_2. Consequently, it can be concluded that the treatment by NO at 473 K deeply modifies the surface of the reduced ceria–alumina support.

Formation of surface isocyanate species was not observed. Characterized by absorption bands in the range 2270–2140 cm^{-1} (10), they could eventually explain or contribute to the 2224 cm^{-1} band as resulting from the reaction between NO and CO possibly present in the reduced support. However, this hypothesis is not supported in the present study, because no carbonyl band could be observed and the formation of isocyanate species is usually associated with a strong band at 2260–2270 cm^{-1} (10).

3.1.2. Determination of the relation between the optical density of the 1912 cm^{-1} band and the number of surface rhodium atoms in Rh/CeO_2–Al_2O_3 catalysts. At 294 K, the adsorption of NO on the reduced 0.5Rh/CeO_2–Al_2O_3 catalyst gives three bands of relatively low intensity, at 1905, 1820, and 1725 cm^{-1} (Fig. 1). Their relative intensities differ from those observed on the alumina supported system (1). After the treatment at 473 K under NO, the first band is shifted to 1912 cm^{-1} and its intensity strongly increases, whereas the two others practically disappear. It must be noted that, on CeO_2–Al_2O_3, the bands at 1820 and 1725 cm^{-1} are eliminated after the treatment at 473 K, whereas on alumina the small bands at 1830 and 1730 cm^{-1} were still observed (1). That would indicate a more complete oxidation of the surface rhodium atoms in Rh^I in presence of ceria which is a well known redox support. Besides, before evacuation at room temperature, the presence of the characteristic band of N_2O at 2224 cm^{-1} is noted, which again originates from the NO decomposition on the reduced ceria–alumina.

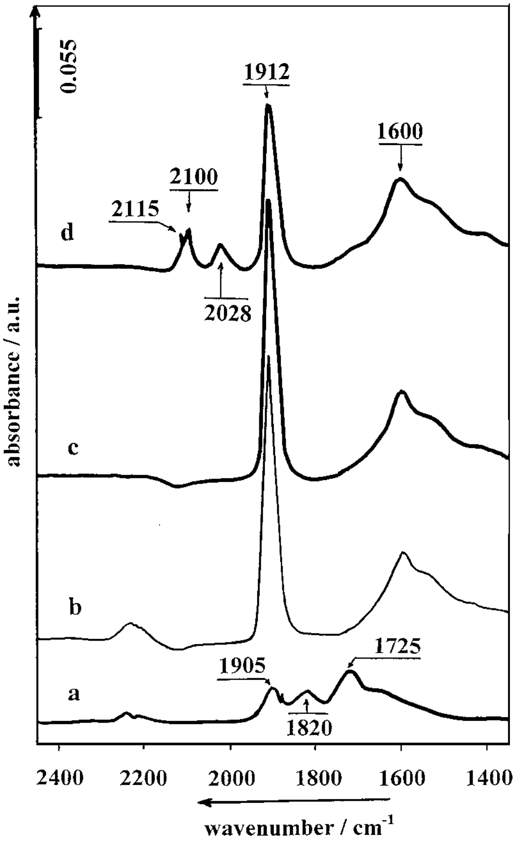

FIG. 1. Adsorption of NO at 298 and 473 K on the 0.5Rh/CeO_2–Al_2O_3 catalyst. (a) NO at 298 K ($P = 1.5$ k*Pa*); (b) after one night under NO at 473 K, NO at 298 K ($P = 1.5$ k*Pa*); (c) vacuum, 298 K; (d) after adsorption of 2.7 kPa CO at 298 K; vacuum, 298 K.

Knowing the rhodium dispersion determined by hydrogen chemisorption (38%), it is possible to calculate from the spectrum after evacuation that an optical density of 1 per gram of catalyst for the 1912 cm^{-1} band corresponds to 2.0 μmol Rh_s per gram of catalyst.

The same calibration procedure was applied to the 0.5Rh/CeO_2–Al_2O_3 catalyst after aging at 1273 K. Its dispersion was found to be equal to 1.7 or 2.7% when determined by hydrogen chemisorption or cyclohexane aromatization activity measurement, respectively (3). The obtained calibration value was 1.1–1.7 μmol Rh_s per gram of catalyst, which is of the same order as for the fresh catalyst. However, considering the uncertainty and the lower precision on the dispersion of this aged solid, we have kept for the following the value of an OD of 1 per gram of catalyst for 2.0 μmol Rh_s per gram of catalyst. This value is much lower than that obtained with the alumina supported rhodium catalyst (6.5 μmol Rh_s per gram of catalyst) (1). As indicated above, it could originate from the redox nature of the ceria–alumina support which facilitates the total oxidation of the rhodium. Consequently, the method appears more sensible when rhodium is supported on ceria–alumina.

After the treatment under NO, the adsorption of CO was performed at room temperature (Fig. 1, spectrum d). The spectrum is modified like for Rh/Al_2O_3. The intensity of the 1912 cm^{-1} band decreases and there is formation of two bands at 2100 and 2028 cm^{-1} due to Rh^I–$(CO)_2$ gem–dicarbonyl species. An additional νCO band is also evidenced at 2115 cm^{-1}. It could correspond to CO adsorbed on a Rh^{2+} ion (11).

3.1.3. Determination of the relation between the optical density of the 2075 cm^{-1} νCO band and the number of surface platinum atoms in Pt/CeO_2–Al_2O_3 catalysts following NO adsorption at 473 K. The adsorption of NO at 298 K on the $0.5Pt/CeO_2$–Al_2O_3 solid leads to a spectra with three bands at 1912, 1810, and 1700 cm^{-1}. The 1912 cm^{-1} band was not observed with alumina as support. It can be ascribed to the formation of Pt^{2+}–NO species. After heating at 473 K under NO and evacuation at room temperature, there is no more infrared band in the wavenumber domain corresponding to nitrosyl complexes adsorbed on platinum, i.e., 1700–1900 cm^{-1} (Fig. 2). The formation of gaseous N_2O is observed, but with a higher concentration than when platinum was supported on alumina, and also the presence of gaseous CO_2 (2350 cm^{-1}). After the heating at 473 K, nitrate species are also formed as for the rhodium catalyst.

After the treatment under NO, CO was adsorbed at 298 K. Two bands appear in the νCO domain at 2115 and 2072 cm^{-1} but with a very low intensity. The first one should correspond to Pt^{2+}–CO (11–13) and that at 2072 cm^{-1} to the adsorption of CO on metallic platinum (12, 14–16). Thus, the oxidized platinum atoms appear to be slightly reduced by the CO probe. On the basis of a dispersion of 60%, the relation between the optical density at 2072 cm^{-1} and the number of platinum surface atoms has been calculated as an OD of 1 per gram of catalyst corresponds to 87 μmol Pt_s per gram of catalyst. As for rhodium, this value is very different from that obtained with alumina as support (18 μmol Pt_s) which stresses again the important effect of the support.

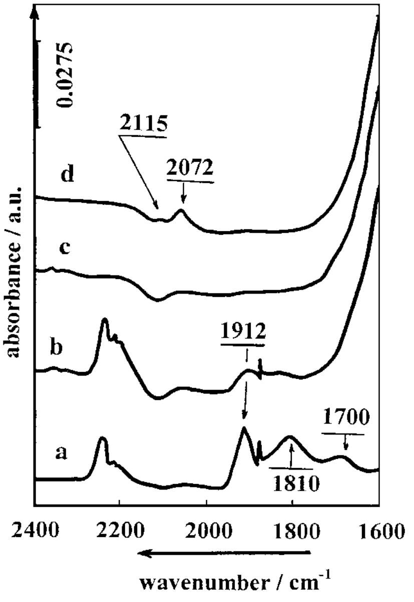

FIG. 2. Adsorption of NO at 298 and 473 K on the $0.5Pt/CeO_2$–Al_2O_3 catalyst. (a) NO at 298 K ($P = 1.5$ k*Pa*); (b) after one night under NO at 473 K, NO at 298 K ($P = 1.5$ k*Pa*); (c) vacuum, 298 K; (d) after adsorption of 2.7 kPa CO at 298 K; vacuum, 298 K.

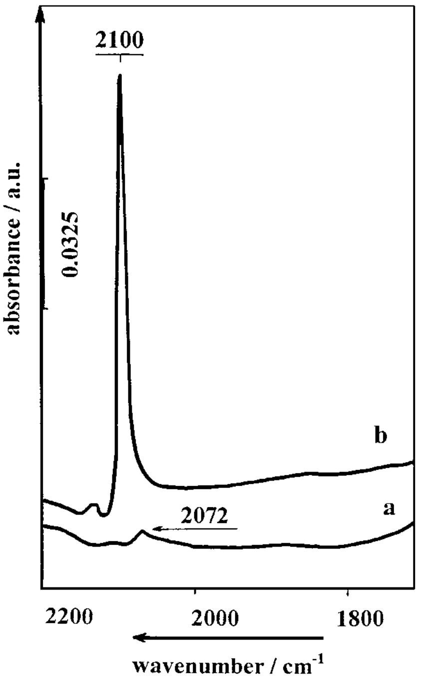

FIG. 3. Irreversible adsorption of CO at 298 K following treatment at 473 K under 1.5 kPa NO. (a) $0.5Pt/CeO_2$–Al_2O_3; (b) $2Pt/CeO_2$–Al_2O_3.

However, the absorbance of the νCO band is very weak compared to the case of $0.5Pt/Al_2O_3$. That makes imprecise the determination of the calibration coefficient. Consequently, to improve the quality of the spectrum, we have increased the platinum content from 0.5 to 2 wt%. Since the dispersion decreased from 60 to 36%, the number of platinum surface atoms was in fact multiplied by a factor of 2.4 (3). The related spectra after the successive adsorption of NO and CO and a final evacuation at room temperature are given in Fig. 3. For the $2.0Pt/CeO_2$–Al_2O_3, the most important point is the observation of an intense band near 2100 cm^{-1}, characteristic of CO bound to partially oxidized platinum. There is a notable shift of the wavenumber, 2100 instead of 2085–2065 cm^{-1} for Pt/Al_2O_3 or 2072 cm^{-1} for $0.5Pt/CeO_2$–Al_2O_3. Thus, in the case of the $2Pt/CeO_2$–Al_2O_3 solid, the calculated calibration coefficient for the 2100 cm^{-1} band corresponds to 11 μmol Pt_s per gram of catalyst for an OD of 1 per gram of catalyst.

It results that the calibration coefficients for platinum vary widely with the platinum content. We have seen that the presence of cerium favors the decomposition of NO in N_2O, but also the formation of NO_x resulting in nitrates species. These nitrates probably modify the chemisorption properties of the platinum atoms and inhibit strongly the subsequent adsorption of CO, since CO does not seem to displace those species at room temperature. This would be particularly true for the platinum low loaded solid which has the highest dispersion. In this case, most of the platinum surface atoms are at the interface with the support and the association of platinum and ceria sites would constitute the adsorption sites for NO_2. With this model, only a small fraction of the platinum surface is able to adsorb CO, which then would explain the high calibration value. With the $2Pt/CeO_2$–Al_2O_3, a greater part of the platinum surface will be able to adsorb CO, thus lowering the calculated calibration coefficient.

3.1.4. Conclusion. Due to the presence of ceria in the support, the successive adsorption of NO and CO on Pt or Rh/CeO_2–Al_2O_3 leads to several modifications in the infrared spectra compared to the case of pure alumina. At 473 K, NO oxidizes the reduced ceria and numerous nitrate species bound to the support are formed. NO oxidizes also platinum and rhodium. On rhodium, the oxidation of Rh^0 in Rh^I seems more complete than it was observed on alumina. It is probable that the proximity of the labile ceria oxygen ions favor its oxidation. On a quantitative point of view, the infrared band at 1912 cm^{-1}, corresponding to Rh^I–NO^+ species, is not perturbed by the presence of ceria. For platinum, there is practically no band at this wavenumber value. Therefore, it is justified to use the optical density of this band to dose the surface rhodium atoms.

On the contrary, the subsequent CO adsorption after the interaction with NO at 473 K shows that the chemisorption properties of platinum towards CO are strongly modified by the presence of ceria. There is probably a deep oxidation of the metal particles with formation of stable nitrate species and the results vary with the platinum loading. Consequently, contrary to the case of platinum on alumina, this sequence of CO adsorption after the treatment at 473 K under NO is unable to dose the platinum surface atoms when supported on ceria–alumina.

This difficulty can be overcome by considering that the surface composition of a bimetallic PtRh catalyst can be deduced if we know the total number of surface metal atoms obtained by hydrogen chemisorption and if we can deduce precisely the number of surface atoms of one metal population, either platinum or rhodium. As shown above, this can be obtained for rhodium by infrared, using NO as probe molecule after reaction at 473 K. In the case of platinum, the adsorption of CO, just after reduction and before the adsorption of NO can be considered also as a possible solution, but only when the rhodium surface content is low, because the overlap of the CO infrared bands ascribable to platinum and to rhodium respectively brings some limitation to the precision of the method (1). We tested these two approaches with one model and two commercial three-way catalysts. The measurements presented below were carried out both on fresh and aged catalysts in order to precise the evolution of the catalyst and to assess the limitations of the method when the physicochemical characteristics of the catalysts are strongly damaged.

3.2. Surface Composition of a Model $1Pt0.2Rh/CeO_2$–Al_2O_3 Catalyst

3.2.1. Measurement by hydrogen chemisorption and infrared spectroscopy of adsorbed NO. We have measured the rhodium surface atoms Rh_s by using the infrared technique of the adsorption of NO at 473 K. In parallel, hydrogen chemisorption allowed to dose the total number of surface metal atoms $Pt_s + Rh_s$. This procedure was applied to the 1% $Pt0.2Rh/CeO_2$–Al_2O_3 catalyst in a fresh or aged state.

Table 2 gives the number of atoms Rh_s deduced from the optical density of the 1912 cm^{-1} band of the Rh^I–NO^+ complex (Fig. 4). The total numbers of surface metal atoms $(Pt_s + Rh_s)$ determined directly by hydrogen chemisorption values are also given. For the fresh catalyst, the atomic ratio Pt_s/Rh_s calculated from these values is 2.55. It is lower but not very different from $Pt/Rh = 3.13$, the value obtained from the bulk chemical analysis. A slight superficial enrichment in rhodium is possible, as was already observed for $PtRh/Al_2O_3$ catalysts (1).

As shown on Fig. 4 (spectrum b), there is practically no νNO band ascribable to rhodium after aging. The deduced

TABLE 2

Comparison between the Number of Surface Metal Atoms Obtained on the $PtRh/CeO_2$–Al_2O_3 Catalysts by Hydrogen Chemisorption (Hc) and by FTIR of Adsorbed NO or CO

Catalyst	1Pt–0.2Rh/ CeAl-fresh	1Pt–0.2Rh/ CeAl-aged
Volumetric adsorption		
H/M (%)	37	2.6
$(Pt + Rh)_s$ (μmol g^{-1})	28.3	2.0
FTIR spectroscopy		
Rh_s (μmol g^{-1}) deduced from IR NO	8.0	0.05
Pt_s (μmol g^{-1}) deduced from mixed method (Hc and IR NO)	20.3	1.95
Pt_s (μmol g^{-1}) deduced from IR CO	25.0	1.0
$(Pt + Rh)_s$ (μmol g^{-1}) deduced from IR (NO and CO)	33.0	1.05
Pt/Rh atomic ratio		
Bulk	3.13	3.13
From mixed method (Hc and NO)	2.55	39
From IR (NO and CO)	3.14	20

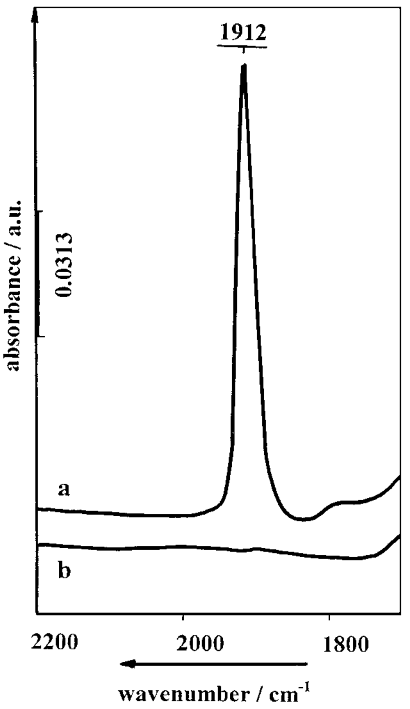

FIG. 4. Irreversible adsorption of NO at 298 K on 1Pt0.2Rh/CeO_2–Al_2O_3 catalysts, fresh (a) and aged (b), following treatment at 473 K under 1.5 kPa NO.

number of Rh_s is very low (0.05 μmol Rh_s g^{-1}) and the Pt_s/Rh_s ratio increases considerably, meaning a high depletion in rhodium at the surface. In these conditions, practically all the surface metal atoms would be platinum atoms. To check this point, we have measured the number of Pt_s by infrared spectroscopy of CO adsorbed directly after the reduction, i.e., without pretreatment at 473 K under NO.

3.2.2. Measurement of the number of platinum surface atoms by infrared spectroscopy of adsorbed CO. It is well known that the direct adsorption of CO at 298 K on a supported platinum catalyst followed by infrared constitutes a tool for quantitative analysis of platinum surface atoms (17). We underlined above that, for bimetallic PtRh systems, a routine use of this method is questionable, because there is an overlap of the linearly bound Pt–CO (νCO at 2075 cm^{-1}) with the bands attributed to CO bound to rhodium at around 2105, 2040, and 2060 cm^{-1} (1). The first two are due to Rh^I–$(CO)_2$ gem–dicarbonyl species, whereas the last one corresponds to Rh°–CO. Therefore, it is necessary to adjust the spectra profiles with appropriate software in order to deconvolute the carbonyl band of CO adsorbed on platinum and thus calculate the number of platinum surface atoms. Due to the multiplicity of bands on rhodium, the same curve adjustment cannot be done for measuring the number of surface rhodium atoms Rh_s.

We have applied this procedure to the fresh and aged bimetallic catalysts, focusing only on the linearly bound Pt–CO. The spectra of the νCO band corresponding to the irreversible adsorption of CO at 298 K directly after the reduction at 573 K are presented in Fig. 5. A main band is observed at 2076 and 2058 cm^{-1} for the fresh and aged catalysts, respectively. A software adjustment of the spectra was done assuming a gaussian shape for each band and with the hypothesis that the spectra were constituted by four bands corresponding to the two linear CO bands on platinum and rhodium and the two gem–dicarbonyls bands formed on isolated Rh^I atoms, respectively. This fitting procedure is not very accurate and does not fully account for the shoulder in the low wavenumber region (<2000 cm^{-1}). However, the νCO band of CO adsorbed on platinum being only considered, the measurement of its optical density was thus used to determine the number of platinum surface atoms. It is clear that other fitting procedures could have modified the absolute optical densities for the νCO platinum band. However, the error on the optical density and thus on the values obtained for the number of Pt_s can be considered as limited, and, as specified after, the deduced dispersion values are in reasonable agreement with those obtained by hydrogen chemisorption.

After deconvolution, there is a small shift in the calculated νCO for platinum at 2080 and 2059 cm^{-1}. The first value is in agreement with the positions 2070–2078 cm^{-1} previously reported for platinum supported on ceria–alumina (18–20). Concerning the shift from 2080 to 2059 cm^{-1} between the fresh and the aged catalyst, it can be associated to the elimination of chlorine during the aging treatment. This hypothesis is supported by the observation of a shift in the platinum νCO band from 2071 to 2058 cm^{-1}

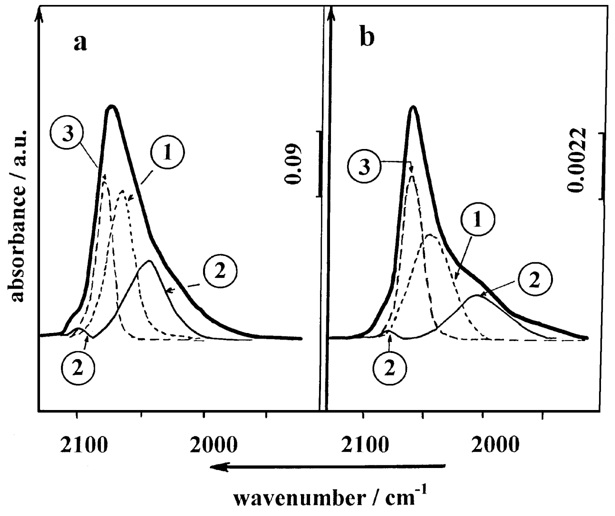

FIG. 5. Curve adjustment of the νCO band observed on the 1Pt0.2Rh/CeO_2–Al_2O_3 catalysts, fresh (a) and aged (b), corresponding to the irreversible adsorption of CO at 298 K after reduction under hydrogen and evacuation at 573 K. The main band, at 2076 and 2058 cm^{-1} for the fresh and aged catalysts, respectively, was considered as resulting from three species: (1) Rh°–CO, (2) Rh^I–$(CO)_2$ (2 bands), and (3) Pt°–CO.

when replacing H_2PtCl_6 by a solution of platinum acetylacetonate during the impregnation of the ceria–alumina support (20). The numbers of Pt_s atoms calculated from the deconvoluted platinum νCO band are given in Table 2, i.e., 25.0 and 1.0 μmol Pt_s g^{-1} for the fresh and the aged catalysts, respectively.

By adding the number of Pt and Rh surface atoms obtained in each case by infrared spectroscopy (CO and NO), it is possible to calculate the total dispersion of the metallic phase. It is 43 and 1.4% for fresh and aged catalysts, respectively. These values are not very far from those obtained by H_2 chemisorption, i.e., 37 and 2.6%.

Concerning the surface composition, the calculated atomic ratio $Pt_s/Rh_s = 3.14$ is identical to the bulk composition ($Pt/Rh = 3.13$), which suggests a good homogeneity of the system. After aging, the ratio remains very high ($Pt_s/Rh_s = 20$) as it was deduced from the mixed method (from Hc and NO) for which the atomic ratio was equal to 39. Considering the very low surface rhodium content, these values can be considered of the same order and indicate a quasi-disappearance of rhodium at the surface with a strong enrichment in platinum. It has been established that, for unsupported PtRh single crystals, high temperature treatments lead to Pt-rich alloy surfaces (21, 22). In the present case, there is no indication of the presence of an alloy after aging. This near absence of metallic rhodium atoms can be more easily interpreted as due to a large sintering of the rhodium particles and/or to the formation of oxidized rhodium, not reducible in our temperature conditions, possibly as Rh^{3+} in the alumina structure.

3.2.3. Discussion. It has been often emphasized that the surface composition of bimetallic particles may vary as a function of temperature and also under the influence of the gas phase environment. For example, Van Delft *et al.* (21), working on Pt–Rh alloy single crystals, have observed that Rh-rich surfaces are more reactive toward NO that the Pt-rich surfaces. They have concluded that under reaction conditions, both temperature and chemisorption can alter the surface composition. Beck *et al.* (22) have also established that, under reducing conditions, the surface composition of a $Pt_{10}Rh_{90}(111)$ single crystal is enriched in platinum. The 30% Pt in the surface layer was close to that obtained after annealing in vacuum at 1273 K. Opposing this, under oxidizing conditions, the surface layers become enriched in rhodium, with oxidation of Rh to Rh_2O_3. Thus, although Pt and Rh remain well mixed in these model single crystals alloys, there is possibly a surface reconstruction into Pt and Rh islands following the successive reduction and oxidation treatments.

For bimetallic supported catalysts, the low metal content and the interactions with the support are not favourable to the formation of a homogeneous alloy. Bimetallic particles of different compositions are probably formed and modifications of the surface composition may occur following NO and CO adsorption. However, in the case of PtRh/alumina catalysts, the results of the quantification method have shown a good agreement between the total numbers of surface atoms determined by the infrared method and those obtained by hydrogen adsorption. As already pointed out, a slight rhodium enrichment was measured for the initial catalysts compared to the nominal composition. It could be attributed to a surface rhodium segregation after the treatment under NO at 473 K, but it could be also inherent to the catalyst itself. Thus, it is valuable to discuss the present results obtained with model $PtRh/CeO_2–Al_2O_3$ catalysts.

The same techniques were used to measure the superficial contents of platinum and rhodium. From the infrared of NO at 473 K and CO at 298 K, it has been possible to calculate the number of surface rhodium atoms (Rh_s) and platinum atoms (Pt_s). The examination of Table 2 shows that the total ($Pt_s + Rh_s$) is very close to the value obtained directly by hydrogen chemisorption, which again supports the validity of the methods. However, it must be remarked that, for the number Pt_s, less reliable results may be obtained in the presence of a high surface rhodium content compared to platinum. Indeed, the adsorption of CO at 298 K would lead to a spectrum for which a precise curve deconvolution may become critical. In this case, it seems better, in order to obtain a more reliable Pt/Rh ratio, to deduce the number of surface platinum atoms only by the difference between the data of hydrogen chemisorption and that obtained for rhodium by infrared of NO adsorbed at 473 K.

Concerning the catalyst, in the fresh state, the surface composition is close or identical to the bulk composition determined by chemical analysis. This result gives certainly more support to the validity of the method. Opposing this good homogeneity of the fresh catalysts, the application of these methods to the aged catalyst indicates a strong heterogeneity of the solid with a high surface enrichment in platinum at the expense of rhodium. The two metals are probably present in different segregated particles. Although we cannot eliminate the possibility, there is no direct evidence to support the formation of a sintered alloy with the surface highly enriched in platinum.

3.3. Surface Composition of Commercial Three-Ways Catalysts

Two commercial catalysts were studied also in the fresh and aged states. The surface composition was deduced from the dispersion measured by hydrogen chemisorption and from infrared data of NO adsorbed at 473 K as a probe molecule. The number of platinum surface atoms was also determined independently by infrared study of adsorbed CO. To make the comparison with the model catalyst easier, all the results concerning these commercial catalysts are given per gram of washcoat. The metal dispersions expressed as H/M vary between 33 and 1.3% (Table 3). There is a strong decrease of the accessible metallic area upon

TABLE 3

Comparison between the Number of Surface Metal Atom Values Obtained on the PtRh Commercial Catalysts by Hydrogen Chemisorption (Hc) and by FTIR of Adsorbed NO or CO

Catalyst (All data in $g^{-1}_{\mathrm{washcoat}}$)	COM1 fresh	COM1 aged	COM2 fresh	COM2 aged
Volumetric adsorption				
H/M (%)	33	2.7	26	1.3
$(Pt+Rh)_s$ (μmol g^{-1})	11.7	0.95	10.8	0.54
FTIR spectroscopy				
Rh_s (μmol g^{-1})	2.7	≈0	1.3	≈0
Pt_s (μmol g^{-1}) deduced from mixed method (Hc and IR NO)	9.0	0.95	9.5	0.54
Pt_s (μmol g^{-1}) deduced from IR CO		1.11		0.57

aging, which is attributed to a sintering of the precious metals.

The numbers of rhodium surface atoms are given in Table 3. In the case of the two aged systems, the adsorption of NO at 473 K gives no Rh^I–NO band at 1912 cm^{-1} and consequently zero values for Rh_s. The sensitivity limit being estimated to 0.01 μmol per gram of solid, there is no accessible surface rhodium after aging. This is in good agreement with the evolution observed for the aged model catalyst, for which the surface was depleted in rhodium. Under these conditions, the use of CO as a probe molecule for measuring the number of surface platinum atoms in aged catalysts becomes fully justified.

Thus, the adsorption of CO was performed on the two aged solids. The deduced surface platinum quantities are also given in Table 3. They are identical to those obtained from the hydrogen volumetric adsorption which does not discriminate between platinum and rhodium atoms. That clearly demonstrates the absence of accessible rhodium atoms at the catalyst surface.

The absence of rhodium was also confirmed by an XPS study performed on the two aged catalysts. Platinum and rhodium were not detected on the aged COM1 and very poorly detected for the aged COM2, especially for rhodium. After etching by neon bombardment, the XPS analysis revealed the presence of platinum in the underlayers, whereas rhodium was not detected.

4. CONCLUSION

The methodology previously developed for measuring the surface composition of PtRh/alumina catalysts was tested on similar bimetallic catalysts supported on ceria–alumina. It has been shown that due to the redox properties of the ceria–alumina support, the NO dismutation is favored and the formation of N_2O is observed at room temperature. At 473 K, a treatment under NO oxidizes the platinum and rhodium surface atoms. However, compared to alumina supported catalysts, the presence of ceria favors the total oxidation of Rh° in Rh^I and modifies the chemisorption properties of platinum toward CO.

For the determination of the number of surface atoms, the infrared band at 1912 cm^{-1} corresponding to the adsorption of NO at 473 K on rhodium (Rh^I–NO) is not perturbed by ceria and can be used to quantify the surface rhodium. However, for platinum, the method using CO adsorption at room temperature after the NO adsorption at 473 K could not be applied because the chemisorption properties of platinum toward CO are modified in the presence of the ceria–alumina and vary with the platinum loading. To overcome this difficulty, it has been possible to indirectly determine the number of surface platinum atoms by measuring the total number of metal atoms with hydrogen chemisorption and subtracting the number of Rh_s obtained by adsorption of NO.

These measurements were performed on model and commercial three-way catalysts. In the fresh solids, the surface composition in platinum and rhodium roughly reflects the global composition. However, in both cases, after aging at 1273 K under $N_2 + 10\%\ H_2O$, rhodium is practically not detected at the surface. This was confirmed by the good agreement obtained between the number of Pt_s measured by the direct adsorption of CO at room temperature and the total number of surface metal atoms by hydrogen volumetric adsorption.

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