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Laser Raman Studies of the Preparation of Platinum and Iridium Catalyst Systems

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Steps in the preparation of Pt, Ir, and Pt–Ir on alumina catalysts have been followed by laser Raman spectroscopy. The samples investigated were prepared by impregnation of alumina with the appropriate chloroplatinic acid and chloroiridic acid solutions. The resulting materials were then heated in air at varying temperatures. Laser Raman spectra indicated significant differences in the nature of the surface species remaining when Pt/Al_2O_3 and Ir/Al_2O_3 preparations were subjected to such thermal treatments. After a drying step at 110°C, the Pt/Al_2O_3 preparation exhibits Raman bands at frequencies very close to those at which bands have been reported for the $PtCl_6^{2-}$ ion, whereas the Ir/Al_2O_3 preparation yields a spectrum significantly different from that reported for the $IrCl_6^{2-}$ ion. With increasing temperature, both the platinum and the iridium species decompose with loss of chlorine ligands. After being heated in air at 500°C, the Ir/Al_2O_3 sample exhibits a Raman spectrum characteristic of crystalline IrO_2. The presence of platinum in the bimetallic Pt–Ir/Al_2O_3 sample inhibits the formation of crystalline IrO_2 to some degree.

INTRODUCTION

In the preparation of a supported metal catalyst, the deposition of a metal precursor on a carrier and the subsequent thermal decomposition of the precursor are important steps (*1, 2*). The conditions employed can be crucial for attaining high catalytic activity. Thus, in the preparation of supported iridium catalysts, it is important to avoid heating (calcining) the material in air at too high a temperature. For example, in the presence of air at 500°C, large crystallites of IrO_2 are formed. On subsequent treatment with hydrogen, the IrO_2 is reduced to large iridium crystallites, which are characterized by an undesirably low surface area. The problem is also encountered with platinum–iridium catalysts, in which oxidative agglomeration of the iridium interferes with the formation of highly dispersed bimetallic clusters of platinum and iridium. However, the problem is less severe with these catalysts than with those containing iridium alone, since the platinum inhibits the oxidative agglomeration of iridium to some degree. These conclusions have been derived with the aid of data from chemisorption isotherms, X-ray diffraction, and Mössbauer effect spectroscopy (*3–7*).

Further information related to the surface chemical processes occurring in the preparation of platinum and iridium catalyst systems has been obtained with the use of probes such as temperature-programmed reduction, transmission electron microscopy, and electron diffraction (*8, 9*). Another probe of potential interest for studies of these catalysts is laser Raman spectroscopy (LRS). This type of spectroscopy has the capability of identifying the types of ligands surrounding a metal atom, without the extensive interference from the catalyst support which is encountered with infrared spectroscopy. The utility of LRS for studies of catalytic materials has been demonstrated by the work of Chan *et al.* (*10–14a*). In the present paper we report the results of an investigation employing LRS to follow the surface chemistry involved in the prep-

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aration of Pt/Al_2O_3, Ir/Al_2O_3, and $Pt–Ir/Al_2O_3$ catalysts.

II. EXPERIMENTAL

A. Preparation of Catalysts

A sample of γ-Al_2O_3 obtained from Engelhard was used as the support in all of the catalysts. It was precalcined at 550°C and was ground to a fine powder. The surface area was approximately 180 m^2/g. The Pt/Al_2O_3 and Ir/Al_2O_3 samples were prepared by contacting the alumina with aqueous solutions of chloroplatinic and chloroiridic acids, respectively. The solutions contained 0.1 g of platinum or iridium per milliliter. A mixed solution of the acids was used in the preparation of the bimetallic $Pt–Ir/Al_2O_3$ sample. The materials were all dried in air at 110°C for 16 h. One part of each preparation was calcined for 4 h in air at 270°C, while another was calcined for 2 h at 500°C. For Raman spectroscopy measurements, about 0.2 g of sample was pressed in a 13-mm die (at a pressure of approximately 500 atm) to form a wafer. The amount of chlorine in each of the catalyst preparations was determined by X-ray fluorescence analysis.

B. Laser Raman Apparatus

Laser Raman spectra were recorded under ambient conditions on a Spex Ramalog, Model 14018, equipped with triple gratings and a water-cooled RCA GaAs photomultiplier for photon counting. An argon ion laser (Spectra Physics, Model 165) was tuned to the 514.5-nm line for excitation. A prism filter monochromator (Anaspec, Model 300S) with 0.4-nm bandwidth was used to filter out laser plasma lines. The sample wafer was mounted on a holder which could be spun at a speed of about 1500 rpm to minimize sample degradation or oxidation due to the heat or light from the laser radiation. The incident angle of the laser was about 45° with respect to the wafer. The Raman radiation was collected in backscattering geometry by an F/1.2 lens with an optical axis oriented at an angle of about 45° with respect to the wafer surface. The laser power ranged from 10 to 50 mW at the location of the sample. It was varied with the aid of suitable filters. The slits of the spectrometer were chosen to give a spectral resolution of 2 cm^{-1}. The scan rate of the grating was 0.5 cm^{-1}/s.

III. RESULTS AND DISCUSSION

A Raman spectrum obtained on the pure γ-Al_2O_3 used as the support in the samples showed no vibrational bands in the range 50 to 1000 cm^{-1}. Consequently, any bands observed with the samples in this region are not complicated by contributions from the support.

Raman spectra for Pt/Al_2O_3, Ir/Al_2O_3, and $Pt–Ir/Al_2O_3$ samples after various thermal treatments are shown in Figs. 1–3. The Pt/Al_2O_3 and Ir/Al_2O_3 samples contained 2 wt% Pt and 2 wt% Ir, respectively. The sample with both platinum and iridium present contained 3 wt% of each of these elements.

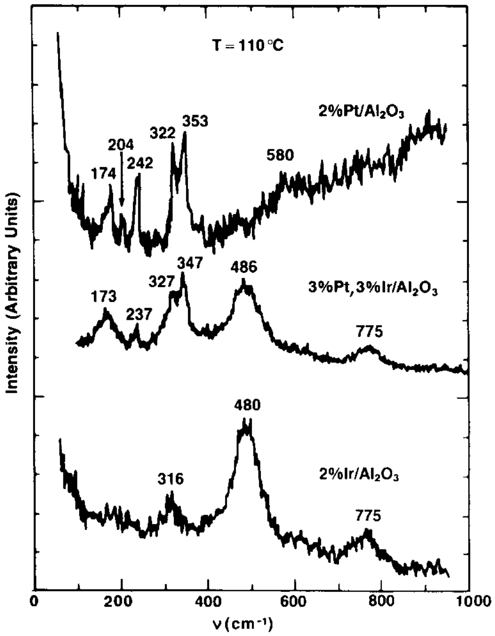

FIG. 1. Comparison of Raman spectra for Pt/Al_2O_3, Ir/Al_2O_3, and $Pt–Ir/Al_2O_3$ samples dried in air at 110°C.

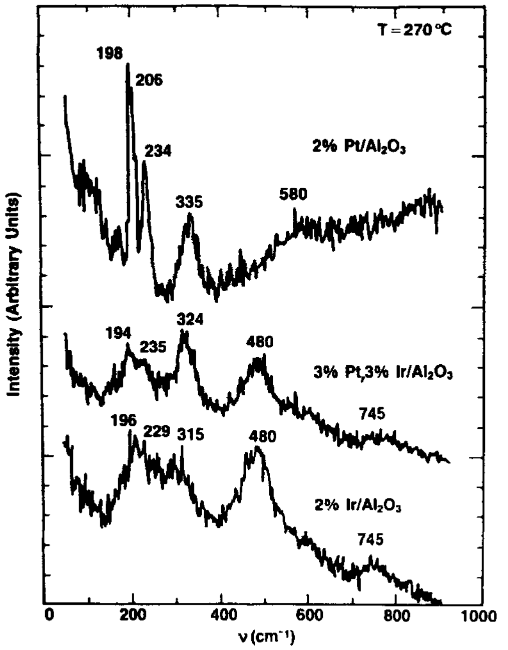

FIG. 2. Comparison of Raman spectra for Pt/Al_2O_3, Ir/Al_2O_3, and Pt–Ir/Al_2O_3 samples heated in air at 270°C.

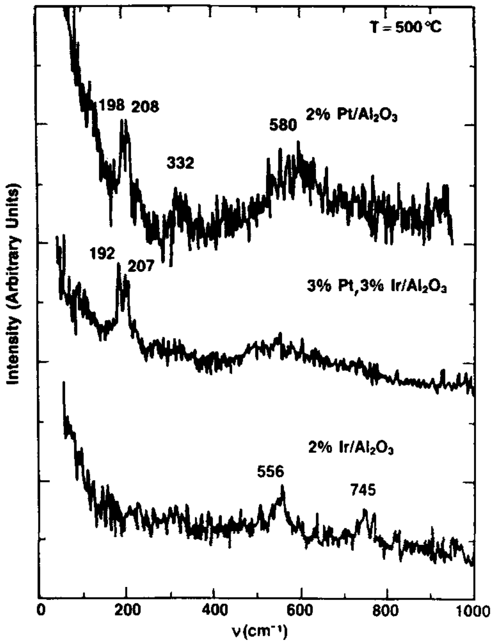

FIG. 3. Comparison of Raman spectra for Pt/Al_2O_3, Ir/Al_2O_3, and Pt–Ir/Al_2O_3 samples heated in air at 500°C.

The spectra in Fig. 1 were obtained after the samples had been dried in air for 16 h at 110°C subsequent to their preparation via contact of the alumina with an aqueous solution of the appropriate acid (i.e., chloroplatinic acid, chloroiridic acid, or a mixture of the two acids). The spectrum for the Pt/Al_2O_3 sample includes five Raman bands at frequencies in the range 174 to 353 cm^{-1} (Table 1). Data on the octahedral $PtCl_6^{2-}$ ion reported in the literature show three Raman bands and two infrared bands in this same range of frequencies (*15, 16*), as summarized in Table 2. However, for the Pt/Al_2O_3 sample there appears to be another band at about 580 cm^{-1} which is not observed for the $PtCl_6^{2-}$ ion. It would appear that the chloroplatinic acid on the

TABLE 1

Frequencies of Raman Bands for Pt/Al_2O_3, Ir/Al_2O_3, and Pt–Ir/Al_2O_3 Samples

Sample	Thermal treatment	Raman frequencies (cm^{-1})
Pt/Al_2O_3	Air, 110°C	174, 204, 242, 322, 353, 580
	Air, 270°C	198, 206, 234, 335, 580
	Air, 500°C	198, 208, 332, 580
Ir/Al_2O_3	Air, 110°C	316, 480, 775
	Air, 270°C	196, 229, 315, 480, 745
	Air, 500°C	556, 745
Pt–Ir/Al_2O_3	Air, 110°C	173, 237, 327, 347, 486, 775
	Air, 270°C	194, 235, 324, 480, 745
	Air, 500°C	192, 207

TABLE 2

Frequencies of Raman and Infrared Bands for $PtCl_6^{2-}$, $IrCl_6^{2-}$, and $PtCl_4^{2-}$ Ions

Ion		Frequencies (cm^{-1})		Reference
		Raman	Infrared	
$PtCl_6^{2-}$	(K^+ salt)	171, 318, 348	183, 342	(*15*)
	(K^+ salt)	171, 320, 349		(*16*)
	(in solution)	159, 322, 343		(*16*)
$IrCl_6^{2-}$	(K^+ salt)	190, 225, 352	184, 333	(*18–20*)
$PtCl_4^{2-}$	(K^+ salt)	196, 306, 333	168, 191, 321	(*21–23*)
	((n-butyl)$_4N^+$ salt)	173, 305, 328	147, 165, 313	(*24*)
	(in solution)	171, 312, 330		(*24*)
	(in solution)	170, 314, 332		(*16*)

alumina does not decompose at 110°C, in agreement with reported observations on the effect of heating pure chloroplatinic acid in air at a comparable temperature (*17*). The two extra Raman active bands observed for the Pt/Al_2O_3 sample are presumably related to some distortion of the $PtCl_6^{2-}$ structure as a consequence of interaction with the alumina.

The spectrum for the Ir/Al_2O_3 sample in Fig. 1 is very different from that for the Pt/Al_2O_3 sample. Three Raman bands are clearly observed, and they are much broader than the bands for the Pt/Al_2O_3 sample. Moreover, two of the three bands occur at frequencies of 480 and 775 cm^{-1} (Table 1), which are significantly higher than those corresponding to the three Raman and two infrared bands for the octahedral $IrCl_6^{2-}$ ion (*18–20*) given in Table 2. The latter are in the range 184 to 352 cm^{-1}. In this range of frequencies, there is only one clear band (at 316 cm^{-1}) in the spectrum for the Ir/Al_2O_3 sample. It appears that chloroiridic acid on alumina undergoes significant change under the conditions of the drying step. The differences in the behavior of the chloroiridic and chloroplatinic acids on alumina are attributed in part to a stronger interaction of the former with alumina. However, we cannot say anything definitive about the detailed nature of the interaction.

The spectrum for the Pt–Ir/Al_2O_3 sample clearly reveals features characteristic of the Ir/Al_2O_3 sample, namely, the bands at 486 and 775 cm^{-1}. It also reveals bands in the region 173 to 347 cm^{-1}. This is the same range in which bands attributable to Pt–Cl bonds are observed in the spectrum for the Pt/Al_2O_3 sample and in which the Ir/Al_2O_3 sample exhibits a band at 316 cm^{-1}. However, a close inspection of the spectrum for the Pt–Ir/Al_2O_3 sample indicates that it is not a simple combination of the spectral features observed for the Pt/Al_2O_3 and Ir/Al_2O_3 samples, suggesting a possible interaction between complexes of platinum and iridium on the surface of the alumina.

When the samples are heated in air for 4 h at 270°C, there is clearly some decomposition of both chloroplatinic and chloroiridic acids, as shown by data on the amount of chlorine retained (Table 3). The initial chlorine contents of the Pt/Al_2O_3, Ir/Al_2O_3, and Pt–Ir/Al_2O_3 samples resulting from the use of chloroplatinic and/or chloroiridic acids in their preparation are 2.2, 2.2, and 6.6 wt%, respectively. The amounts of chlorine retained by the samples after a given heat treatment cannot be used for the quantitative determination of the number of chlorine atoms lost from the chloroplatinic and/or chloroiridic acids, since alumina itself retains a significant amount of the chlorine.

The Raman spectrum for the Pt/Al_2O_3 sample in Fig. 2 exhibits four bands in the

TABLE 3

Chlorine Retention of Samples after Various Thermal Treatments

Sample	Chlorine content (wt%)			
	Initial	After 16 h at 110°C	After 4 h at 270°C	After 2 h at 500°C
Chlorided Al_2O_3[a]	5.4	4.63	1.83	0.45
Pt/Al_2O_3 (2 wt% Pt)	2.2	2.05	1.69	0.67
Ir/Al_2O_3 (2 wt% Ir)	2.2	1.91	1.70	0.58
$Pt-Ir/Al_2O_3$ (3 wt% Pt, 3 wt% Ir)	6.6	5.20	3.05	0.76

[a] Prepared by impregnating alumina with a solution of HCl.

frequency range 198 to 335 cm^{-1} (Table 1), which is within the range expected for Pt–Cl bonds (Table 2). Again, however, the Pt/Al_2O_3 sample exhibits a band at about 580 cm^{-1} which is outside the range for Pt–Cl bonds given in Table 2. The spectrum for the Ir/Al_2O_3 sample in Fig. 2 exhibits five Raman bands (Table 1), three of which are within the range of frequencies given for Ir–Cl bonds in Table 2. The bands observed for the Ir/Al_2O_3 sample in this range are broad compared to the bands found for the Pt/Al_2O_3 sample. We note that two of the bands (at 196 and 229 cm^{-1}) for the Ir/Al_2O_3 sample either were not present in the spectrum of the sample after drying at 110°C or were very weak. If the bands are due to Ir–Cl bonds, it is not readily apparent why they were not also present in the spectrum in Fig. 1 for the sample heated at the lower temperature. We have no explanation for this finding. At higher frequencies, the band observed at 480 cm^{-1} is the same band seen in the spectrum obtained after the sample was simply dried at 110°C. The band at 745 cm^{-1} is somewhat lower in frequency than a similar band (at 775 cm^{-1}) for the dried sample.

As in Fig. 1, the spectrum for the $Pt-Ir/Al_2O_3$ sample in Fig. 2 reveals features which are clearly characteristic of the Ir/Al_2O_3 sample. However, the features observed for the Pt/Al_2O_3 sample are less evident. In particular, the sharp bands at 198 and 206 cm^{-1} are not observed for the $Pt-Ir/Al_2O_3$ sample. As suggested earlier, there appears to be an interaction between platinum and iridium complexes on the alumina.

Heating the various samples in air at 500°C leads to marked decreases in the amount of chlorine retained (Table 3). Since the chlorine remaining could well be associated predominantly with the alumina, it appears that very few Pt–Cl or Ir–Cl bonds survive the treatment. Correspondingly, the Raman spectra for the samples (Fig. 3) are very different from the spectra obtained after the samples had been heated at 270°C. The change is most pronounced for the Ir/Al_2O_3 sample, for which the bands at 196, 229, 315, and 480 cm^{-1} have disappeared. Moreover, a new band is observed at 556 cm^{-1}.

For the Pt/Al_2O_3 sample, there is still some evidence of Pt–Cl bonds. However, the Raman bands are much less intense than the corresponding bands in Fig. 2, indicating that the Pt–Cl bonds have largely disappeared. It has been reported that pure chloroplatinic acid (unsupported) decomposes completely to metallic platinum when exposed to air at 500°C (*17*). Supporting chloroplatinic acid on alumina thus appears to retard the decomposition to some degree. It is probable that a longer exposure of the Pt/Al_2O_3 sample to air at 500°C would lead to complete decomposition. In this regard, it is known that the creamy yellow color of the sample disappears when the time of exposure is increased sufficiently.

The spectrum for the Pt–Ir/Al_2O_3 sample in Fig. 3 resembles that of the Pt/Al_2O_3 sample, in that Raman bands associated with Pt–Cl bonds are detected. Moreover, it differs from that of the Ir/Al_2O_3 sample, since bands at 556 and 745 cm^{-1} are not apparent. The state of the iridium in the sample containing both platinum and iridium must therefore be different from what it is in the sample containing iridium alone.

The Raman bands at 556 and 745 cm^{-1} observed for the Ir/Al_2O_3 sample heated in air at 500°C are attributed to the formation of IrO_2 crystallites. Previous X-ray diffraction studies of iridium-containing catalysts exposed to air at 500°C have shown that IrO_2 crystallites with sizes in the range 260–290 Å are present (*3, 4*). Furthermore, a Raman spectrum obtained on an IrO_2 powder (Fig. 4) shows two bands at frequencies similar to those at which bands are observed for Ir/Al_2O_3 samples heated in air at 500°C. In Fig. 4 the intensities of the bands for the Ir/Al_2O_3 samples are roughly proportional to the iridium content. However, the proportionality breaks down when the intensities of the bands for either Ir/Al_2O_3 sample are compared with those for the pure IrO_2 powder. The IrO_2 crystallites in the powder are much larger than those supported on the Al_2O_3. Furthermore, the IrO_2 powder is completely black while the Ir/Al_2O_3 samples are gray.

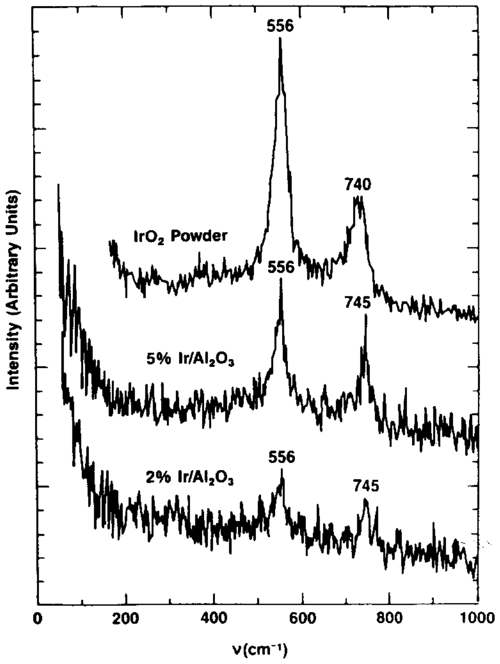

FIG. 4. Comparison of Raman spectrum for IrO_2 powder with spectra for Ir/Al_2O_3 samples heated in air at 500°C.

With regard to the state of the platinum in the Pt/Al_2O_3 sample heated in air at 500°C, we can say that it is present in a highly dispersed form. No lines attributable to platinum or PtO_2 crystallites are observed in an X-ray diffraction pattern, possibly because the crystallites are too small to be detected in a conventional diffraction experiment. If the platinum is present as very small metal clusters, one would still expect the platinum atoms in the clusters to be coordinated to oxygen present in a chemisorbed state, and possibly to oxygen in the alumina. When the sample is heated in air at 650°C an X-ray diffraction pattern reveals the presence of metallic platinum crystallites.

The bimetallic Pt–Ir/Al_2O_3 sample heated in air for 2 h at 500°C provides evidence of an interaction between platinum and iridium, since the IrO_2 Raman bands characteristic of the Ir/Al_2O_3 sample are not apparent. The presence of the platinum has the effect of inhibiting the formation of large IrO_2 crystallites during the heat treatment. However, this does not mean that oxidative agglomeration of the iridium is completely eliminated. Heat treatments on Pt–Ir/Al_2O_3 samples conducted for periods of 4 to 16 h at 500°C have provided clear evidence of oxidative agglomeration of the iridium (*3, 6*). Since increasing the time of treatment may increase the extent to which this process occurs, it is possible in the present work that a longer exposure of the Pt–Ir/Al_2O_3 sample to air at 500°C would have led to clear bands at 556 and 745 cm^{-1} in the Raman spectrum.

In all of the spectra for the Pt/Al_2O_3 sample, whether it had been heated at 110, 270, or 500°C in air, there appears to be a broad band at about 580 cm^{-1}. Also, in the spectra for the Ir/Al_2O_3 sample heated at 110 and 270°C, there is a band at 480 cm^{-1} which is no longer present when the sample is heated at 500°C. Since we have no information on such bands for platinum and iridium reference materials of known structure, we can only speculate on the nature of the surface species responsible for them. Since one effect of heating the samples is to change the ligands on platinum and iridium atoms from chlorine to oxygen, we suggest that oxychlorides or hydroxychlorides of platinum and iridium could be the intermediate surface species responsible for the Raman bands in question. Perhaps such a species is also responsible for the 775 cm^{-1} band for the Ir/Al_2O_3 and Pt–Ir/Al_2O_3 samples dried in air at 110°C.

The band at 745 cm^{-1} in the Raman spectra in Fig. 2 for the Ir/Al_2O_3 and Pt–Ir/Al_2O_3 samples heated in air at 270°C requires some comment. A band at this position is observed for large IrO_2 crystallites, as shown in Fig. 4 in the Raman spectrum for the IrO_2 powder. However, the bands at 745 cm^{-1} in Fig. 2 cannot be attributed to large IrO_2 crystallites, since heating the samples in air at 270°C is too mild a treatment for the formation of such crystallites (*3–7*). Furthermore, in the case of the Pt–Ir/Al_2O_3 sample, the band disappears when the temperature of treatment in air is increased from 270 to 500°C. If the band had been due to large IrO_2 crystallites, one would have expected the band to persist, or possibly become more intense, when the temperature of treatment was increased to 500°C. Therefore, we attribute the band to an intermediate species of the oxychloride type which differs in composition and/or structure from the species responsible for the band at 775 cm^{-1} in Fig. 1 for the samples dried in air at 110°C. The frequency of the band is apparently so close to that of the band for IrO_2 that we are unable to discern any difference.

When the Pt/Al_2O_3, Ir/Al_2O_3, and Pt–Ir/Al_2O_3 samples of the present investigation are to be used as catalysts, they are typically exposed to hydrogen at a temperature in the range of 400–500°C *in situ* in a reactor. After 2 h of such exposure, no Raman bands are observed for any of the samples. In the case of the platinum-containing samples, this indicates that hydrogen is more effective than oxygen in decomposing the platinum–chlorine complexes, since bands characteristic of Pt–Cl bonds are still observed after the samples are calcined in air for 2 h at 500°C. In the Pt/Al_2O_3 and Ir/Al_2O_3 samples, small clusters of platinum and iridium are formed on the alumina. In the sample containing both platinum and iridium, bimetallic clusters of the two elements are formed (*3*). Raman bands are therefore not observed when these elements are present solely in the form of dispersed metal clusters or metal crystallites.

Thus, the utility of Raman spectroscopy in the study of supported platinum and iridium catalysts is associated with the acquisition of information concerning the chemical changes occurring during the steps involved in the preparation of the catalysts, rather than the characterization of the metal clusters or metal crystallites present in the final catalysts. Nevertheless, the type of information obtained can be very useful for optimizing the preparation of such catalysts.

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