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XAFS Study of Dried and Reduced PtSn/C Catalysts: Nature and Structure of the Catalytically Active Phase

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Bimetallic PtSn/C catalysts, prepared on two activated carbon supports of different surface chemistry by two different preparation procedures, have been analyzed by XAFS spectroscopy. The main goal is to identify the effect of the support surface oxidation and the preparation procedure (coimpregnation or successive impregnations) in the interaction of platinum with the support and/or with tin atoms. XAFS results reveal the effect of the mentioned variables in the structure of the supported phase. It has been found in dried samples that the interaction of the platinum species with the support is stronger if the carbon surface is oxidized. The two-step impregnation, compared with the coimpregnation method, renders samples with a stronger platinum−support interaction. Such an interaction determines the distribution of the active phase on the support particles. The structure of the metallic phase after reduction is quite different for samples prepared with the oxidized and nonoxidized carbon support and is also dependent on the preparation procedure. From the XAFS data, the presence of the following platinum containing structures is suggested: PtSn alloy, Pt−O−Sn^{2+} species and pure Pt clusters. The relative proportion of these structures in the catalysts and their distribution on the support determine the catalytic activity for cyclohexane dehydrogenation.

1. Introduction

In addition to aspects traditionally analyzed in mono-metallic catalysts, the characterization of bimetallic catalysts includes the elucidation of the nature of the interaction between the metals and between the metals and the support, and the identification of the electronic states of the metals and their geometrical arrangement in the catalyst. Obtaining such insights is an arduous task that requires the collection and assimilation of information from several analytical techniques and test reactions. Of the available techniques, X-ray absorption spectroscopy provides structural information on an atomic level. X-ray absorption fine structure (XAFS) spectroscopy is extremely useful for studying the structure of supported small particles because it is sensitive to short range ordering. If the supported metal particles are small enough, then there is a large fraction of metal atoms in contact with the support, and the contribution from the metal−support interface is large enough to be detected in the bulk XAFS spectrum. Therefore, XAFS spectroscopy not only provides information about particle sizes (and in some cases about particle structure) but also about the structure of the metal−support interface.[1−4]

Knowledge of the structure of the metal−support interface is indispensable for the understanding of the metal−support interaction, a parameter that, usually, has a noticeable effect on the catalytic activity as it may determine the nature of the active phase. The preparation method may influence the interaction between metal and support; thus, the information about this aspect can be used to select or modify the preparation procedures to obtain the proper catalyst. Additionally, the reduction pretreatment may have an important influence on the structure of the metal−support interface and on the metal−support interaction.

Bimetallic PtSn catalysts are widely used for hydrocarbon reforming and dehydrogenation reactions. In these materials, tin improves the activity and stability of the catalyst. The characterization of bimetallic PtSn catalysts supported on alumina and/or silica has been well studied.[5−14] However, research on PtSn catalysts sup-

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ported on carbon materials is relatively scarce.[15−17] The use of carbon as the support provides several technological advantages, such as the stability in different reaction media and a high versatility in chemical and physical properties.[18] The PtSn/carbon catalysts studied in the present work have already been characterized by TPD, TPR, and XPS and tested in several catalytic reactions.[17] The results obtained revealed a striking and complicated mutual effect of Pt and Sn in their reducibility behavior. Although some interaction between Pt and Sn could be inferred, the actual nature was unclear. Previous studies of monometallic Pt/C catalysts[19,20] indicated a noticeable interaction of platinum with the support. A similar interaction could well be expected in the case of bimetallic catalysts.

The present paper deals with the analysis of the interaction of platinum with tin and with the support, both after drying and reduction stages. The main objective is to identify any effect of the support surface chemistry, the preparation method, and the hydrogen reducing treatment on the mentioned interactions. XAFS spectroscopy is the tool used because of its recognized power to characterize the local environment around heavy active metals.[1−4] The study carried out by XAFS spectroscopy complements the characterization of the PtSn/carbon catalysts achieved with more common techniques (XPS, H_2-chemisorption, TPD, TPR, test reactions).[17]

2. Experimental Section

2.1. Sample Preparation. The original carbon support is a commercial carbon (GA-160 from Carbonac) derived from peach pits. It was crushed and sieved to a final particle size between 100 and 140 mesh and then purified by acid treatment to an ash content of 0.16 wt %.[19] The purified carbon, designated here **C**, was subjected to an oxidation treatment with an aqueous solution (20 v/v %) of H_2O_2 at room temperature for 48 h. The oxidized carbon is designated **C−HP**. These two carbons (**C** and **C−HP**) were used as contrasting supports for the investigation of the role of the support surface chemistry on the final state of Pt and Sn. The determination of the oxygen surface groups on these supports was done by TPD experiments. Samples were heated at 20 K/min, in a He flow (60 mL/min) up to 1200 K. The analysis of desorbed products was carried out by mass spectrometry. The amounts of CO and CO_2 evolved in the TPD experiments are shown in Table 1. These results are discussed below.

Precursors of the bimetallic PtSn/carbon catalysts were prepared by two different impregnation procedures: (a) coimpregnation (CI) of both supports with a solution of H_2PtCl_6 and $SnCl_2$ in 0.4 M HCl, and (b) two-step or successive impregnations (SI). In SI, the support was first impregnated with a solution of $SnCl_2$ in 0.4 M HCl, followed by a drying step at 393 K, after

Table 1. CO and CO_2 Evolution from Supports C and C−HP during a TPD Experiment

support	CO (μmol/g)	CO_2 (μmol/g)
C	259	91
C−HP	663	133

Table 2. Platinum and Tin Content (in wt %), H_2 Chemisorption Values (H/M), and Surface Sn/Pt Ratio Estimated by XPS

catalyst	%Pt	%Sn	H/M (mmol H_2 g_{Pt}^{-1})	Sn/Pt
PtSn/C (CI)	0.78	0.36	0.57	16.1
PtSn/C (SI)	0.86	0.42	0.75	24.3
PtSn/C-HP (CI)	0.81	0.38	0.57	23.3
PtSn/C-HP (SI)	0.89	0.39	0.68	27.0
Pt/C	0.85	0	1.01	—
Pt/C-HP	0.84	0	1.15	—

which the support was impregnated with an aqueous solution of H_2PtCl_6. In all cases, the proportion between the volume of impregnating solution and the carbon weight was 30 mL g^{-1}. Concentrations of H_2PtCl_6 and $SnCl_2$ in the impregnating solutions were chosen to have about 1 wt % Pt and a molar ratio of Pt/Sn close to 1. Impregnations were carried out by keeping the support in contact with the solution, under stirring, at 298 K for 5 h. Afterward, the solid was separated by filtration and dried at 393 K for 24 h. Monometallic Pt/carbon and Sn/carbon catalysts were also prepared by similar procedures. The platinum and tin loading in the different catalysts are shown in Table 2.

2.2. XAFS Analysis. The X-ray absorption experiments were performed at the BL-7C station of the Photon Factory in the National Laboratory for High Energy Physics (KEK-PF) in Tsukuba, Japan. A Si(111) double crystal was used to monochromatize the X-ray beam from the 2.5 GeV electron storage ring. The Pt L_{III}-edge absorption spectra were recorded in the transmission mode at room temperature, in a range of photon energy extending from 11 300 to 12 700 eV. A Fourier transform was performed on k^3-weighted EXAFS oscillations over the range of 3−12 Å^{-1} (FT-EXAFS). The physical basis, data processing, and numerous applications of XAFS spectroscopy have been reported elsewhere.[1−4] It must be emphasized that the EXAFS oscillations mainly depend on bond length, ligand type (especially atomic number), coordination number, Debye−Waller factor, temperature of measurement, Debye temperature of the material, and the phase shift. All these factors must be taken into account through the use of appropriate reference compounds to obtain quantitative information. This is not always possible in complex systems and the fitting of the EXAFS spectra may lead to wrong interpretations.

XAFS measurements were carried out on the samples after the drying step ("dried samples") and after the reduction treatment ("reduced samples"). Wafers for XAFS experiments were prepared by pressing a homogeneous mixture of the catalyst and polyethylene. Samples were then sealed with a polyethylene film to prevent air contact during handling.

The reduced samples (obtained by treatment in H_2 flow, 60 mL min^{-1}, at 623 K for 5 h) were transferred, without exposure to air, to a glovebox where the polyethylene wafers were prepared. Afterward the samples were packed under vacuum also inside the glovebox.

Several bulk platinum compounds were analyzed in order to have reference spectra. Those compounds are Pt foil, PtO_2, H_2-$PtCl_6$, and $[Pt(NH_3)_4]Cl_2$.

Most of the XAFS figures presented in the Results and Discussion section have been plotted including an offset for each curve, either in the abscissa or ordinate axis, for a better observation of the differences.

2.3. H_2 Chemisorption and Catalytic Activity Measurements. The H_2 chemisorption measurements were carried out at 298 K in volumetric equipment. Catalysts were reduced in situ by flowing H_2 (60 mL min^{-1}) at 623 K for 5 h. Afterward, the samples were outgassed (vacuum close to 10^{-4} Torr) at the same temperature for 1 h. Then, the samples were cooled to 298 K. The hydrogen dosage included several points of equilibrium

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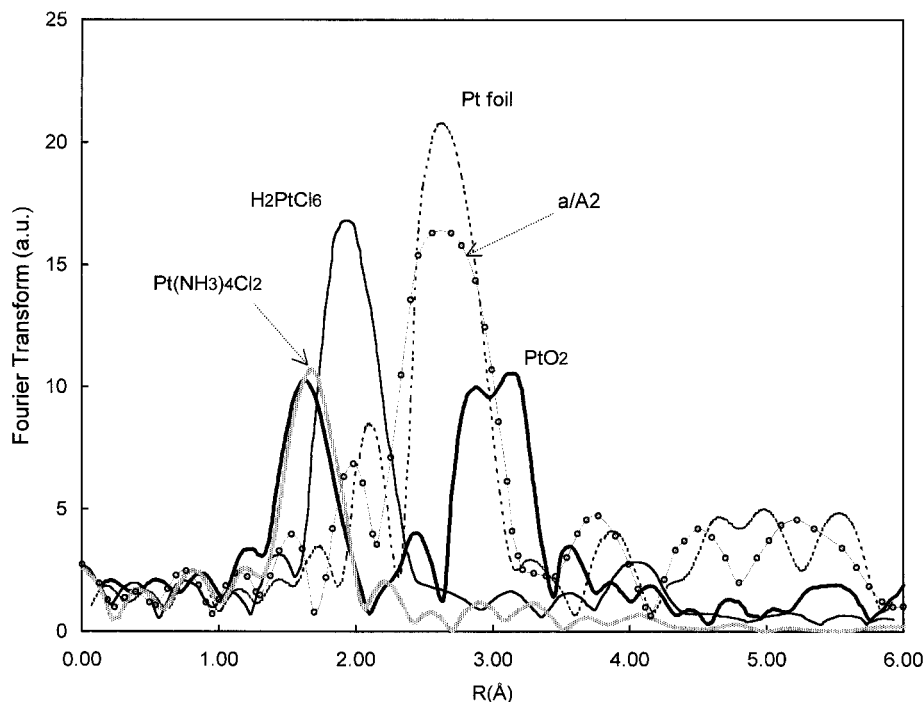
Figure 1. FT-EXAFS profiles for Pt foil, a/A2 catalyst, PtO_2, H_2PtCl_6 and $[Pt(NH_3)_4]Cl_2$ reference compounds.
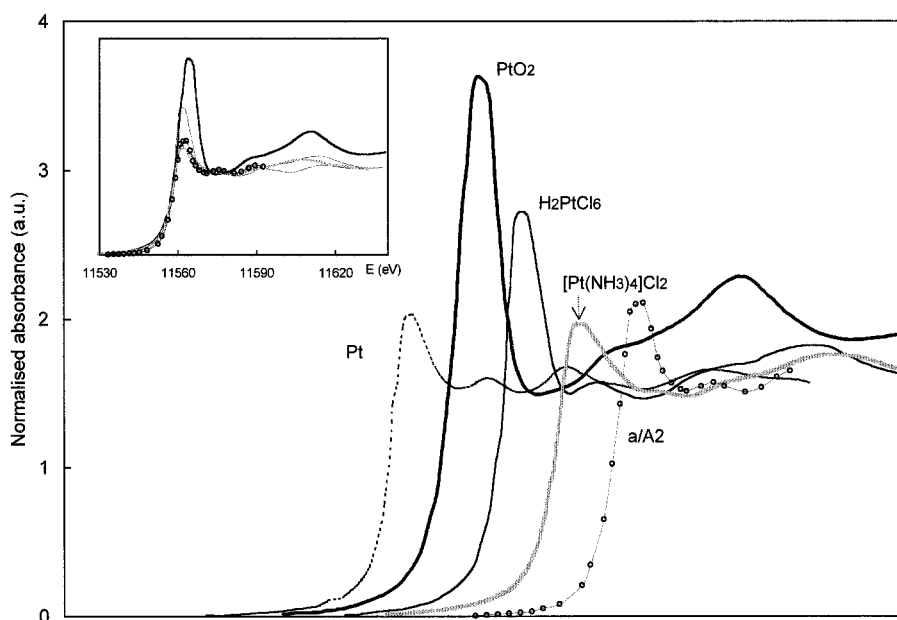

Figure 2. XANES profiles for Pt foil, a/A2 catalyst, PtO_2, H_2PtCl_6 and $[Pt(NH_3)_4]Cl_2$ reference compounds (the data have been plotted with a shift of 10 eV between each XANES profile). The inset shows the actual position of the curves.

pressure ranging from 50 to 250 Torr. The amount of hydrogen chemisorbed was estimated by extrapolation of the linear part of the isotherm to zero pressure.[21]

The catalytic activity for cyclohexane (C_6H_{12}) dehydrogenation was determined at 573 K and atmospheric pressure in a differential flow reactor by using a H_2/C_6H_{12} molar ratio of 29 and a C_6H_{12} molar flow of 0.056 mol h^{-1}. The activation energy of this reaction was obtained from data of catalytic activity at 523, 558, and 573 K. The sample weight used in these experiments was appropriate for obtaining a cyclohexane conversion lower than 7%. Previous to the reaction, catalyst samples were reduced with H_2 at 573 K for 3 h. The only reaction product was benzene. The evolution of the reaction was monitored by gas chromatography.

3. Results and Discussion

3.1. Reference Compounds. The FT-EXAFS and XANES profiles of the reference compounds are presented in Figures 1 and 2, respectively. For a better comparison of the intensity of the white line, the XANES profiles have been represented with a shift of 10 eV between them (Figure 2). The figure also includes the XAFS results for a reduced Pt/carbon catalyst, sample a/A2, with a low platinum dispersion (about 0.2, which corresponds to a platinum particle size of about 5 nm).[20] As previously reported,[22] platinum particles of about 5 nm exhibit a structure similar to that of bulk metal but without the

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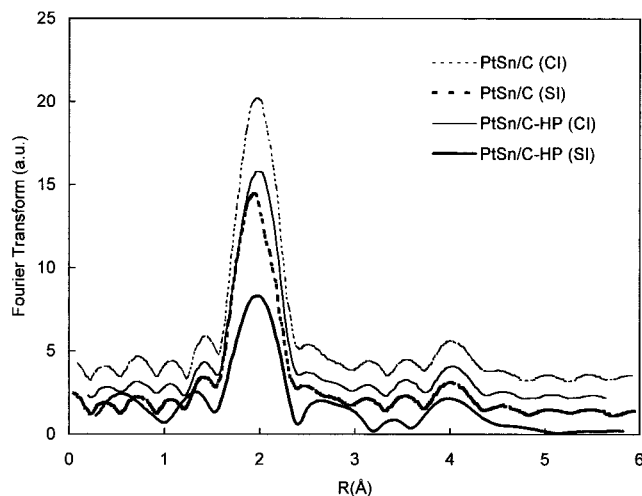
Figure 3. FT-EXAFS profiles for the dried bimetallic PtSn/ carbon catalysts (the FT-EXAFS profiles have been plotted with a shift of 1 unit between them in the *y*-axis).

problems related to thickness.[23] For this reason, the catalyst a/A2 can be considered as an appropriate reference. Figures 1 and 2 show that the XAFS spectra of the platinum foil and the Pt/carbon catalyst contain the same features although some differences can be observed which can be attributed to the influence of the carbon support. Figure 2 also shows that the intensity of the white line is related to the density of vacant d electronic states in platinum. It must be noted that the density of states depends not only on the oxidation state of the absorbing atom and its coordination sphere, but also on particle size[24] (see platinum foil and sample a/A2 in Figure 2).

The estimated phase shift correction is about 0.36 for data below 2.5 Å, and about 0.14 for data above 2.5 Å. The distances noted in the discussion are those directly observed in the FT-EXAFS data; that is, the value of the phase shift correction must be added to account for the real distances.

3.2. Dried Samples. Figure 3 depicts the FT-EXAFS profiles of the four dried PtSn/carbon samples, (PtSn/C (CI), PtSn/C(SI), PtSn/C−HP(CI), and PtSn/C−HP(SI)). These FT-EXAFS data are characterized by a main peak located at about 2 Å. The differences between the four spectra are mainly related to the variation of intensity of this peak. All the FT-EXAFS results contain essentially the same features as those of the reference compound H_2PtCl_6 (Figure 1). Thus, the peak located at about 2 Å in the spectra of Figure 3 is likely due to Pt−Cl bonds. A decrease in the intensity of that peak should be related to a change in the coordination of platinum from Cl atoms to other light scatterers.[1−4,25] In fact, it can be proposed that the chloride coordination of platinum decreases as a consequence of the interaction of the platinum atoms with oxygen or carbon atoms of the support. The interaction of platinum with oxygen is possible due to the important amount of surface oxygen complexes present in the supports.[17,19] The Pt−C interaction is also likely because, apart from the suitability of the carbon structure for coordination with platinum, the redox process that takes place during impregnation may lead to a close contact of platinum with the carbon surface atoms. This redox process between $PtCl_6^{2-}$ ions in solution and the carbon

surface produces a partial reduction of the platinum species.[17,20,26] Evidence of this redox process in the PtSn/ carbon system has been reported previously.[17] The redox reaction between the platinum precursor and the carbon surface can be explained by the mechanism proposed by Van Dam and Van Bekkum.[26] According to these authors, during the impregnation of an activated carbon with an aqueous solution of H_2PtCl_6, the $[PtCl_6]^{2-}$ species is reduced to $[PtCl_4]^{2-}$ by the support. This species subsequently or simultaneously interacts with a site S in the support surface giving a $[PtCl_3S]^-$ species. The process produces a change in the platinum coordination, chloride being removed from the first coordination sphere. There are two possibilities for the ligand site S in the carbon support: C=C structures in the carbon basal planes, and oxygen-containing functional groups on the basal plane edges.[26] Since it is not easy to discriminate between a Pt−O and a Pt−C interaction, both of them might be present. In fact, similar distances are found for Pt−O and Pt−C in Pt compounds in which platinum has a formal valence of (II) or (IV). For example, $[Pt(CH_3COO)_2]_4$ shows two Pt−O bonds 2.00 Å long and the other two 2.16 Å long,[27] the estimated Pt−O bond distance in PtO_2 from crystallographic data is 2.03 Å[28] and that reported from EXAFS measurement in a reference PtO_2 sample is 2.04 Å;[29] and in $[Pt(\eta^2\text{-}C_2H_2)Cl_3]^-$ and $[Pt(\eta^2\text{-}C_2Ph_2)(PPh_3)_2]$ the stated Pt−C bond distance is 2.02 Å.[30]

The FT-EXAFS profiles obtained for the four PtSn samples (Figure 3) do not reveal the presence of any Pt− Sn and Pt−Pt interactions. According to the literature, the Pt−Sn distance in an alloy is about 2.7 Å[16,31] and about 2.5 Å in a $[Pt(SnCl_3)_5]^{3-}$ complex[32] (similar to the one that could be formed in the solution used for coimpregnation[33]). None of these distances appear in the obtained FT-EXAFS profiles. The absence of a Pt−Sn interaction can also be deduced from the comparison of the results shown in Figure 3 with those obtained for the monometallic Pt/C and Pt/C−HP catalysts (Figure 4). There is a significant similarity between the data in Figures 3 and 4, which could be evidence for a similar atomic environment of platinum in both cases.

The data in Figure 4 indicate that the state of platinum in dried monometallic catalysts is influenced by the support surface chemistry. In fact, for the catalyst prepared with the oxidized support (Pt/C−HP), the intensity of the main peak is lower than that for the sample prepared with the original carbon (Pt/C). These results can be explained by a higher coordination of Pt with O and C atoms from the oxidized support. A similar effect of the support surface chemistry is also observed with the bimetallic catalysts. Thus, comparing the data obtained for the dried PtSn/C(CI) and PtSn/C−HP(CI) samples (Figure 3), a lower intensity of the main peak (close to 2 Å) can be observed for the sample prepared with the oxidized support. For the catalysts obtained by successive

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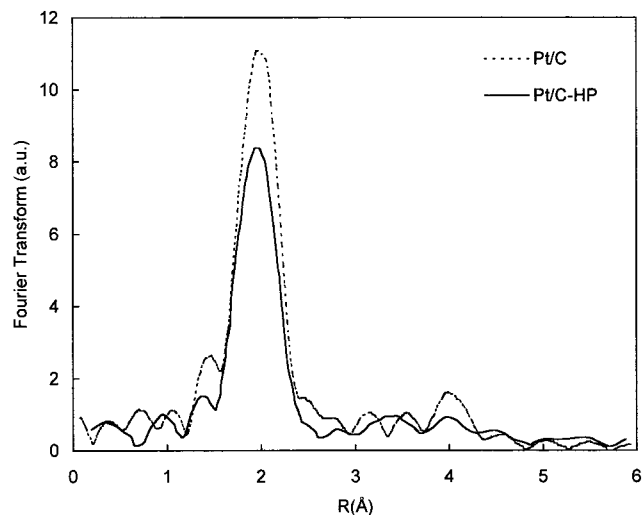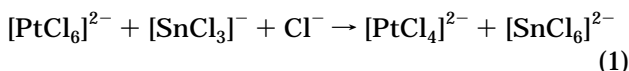(25) Bazin. D.; Triconnet, P.; Moureaux, P. *NIM B* **1995**, *97*, 41.

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Figure 4. FT-EXAFS profiles for the dried monometallic platinum catalysts, Pt/C and Pt/C−HP.

impregnation, PtSn/C−HP(SI) and PtSn/C(SI), the change in the Pt coordination toward Pt−O or Pt−C bonds is even larger than in the samples previously commented. This means that the interaction of the platinum species with the support is stronger with increasing support surface oxidation, independent of both the tin presence and the preparation method.

Regarding the effect of the preparation method, the comparison of the FT-EXAFS profiles corresponding to samples PtSn/C(CI) and PtSn/C(SI) (Figure 3) shows that the intensity of the main peak (close to 2 Å) is lower for the catalyst prepared by successive impregnations (PtSn/C (SI)). A similar behavior, but to a greater extent, was found for samples prepared with the oxidized support, PtSn/C−HP(CI) and PtSn/C−HP(SI) (Figure 3). These observations indicate that platinum species interact more effectively with the surface of the support in catalysts prepared by successive impregnations. The effect of the preparation method on the interaction of Pt species with the support can be explained as follows. For samples prepared by coimpregnation, a redox reaction takes place when H_2PtCl_6 and $SnCl_2$ are put in contact in hydrochloric acid solution, resulting in the formation of a PtSn complex[33]

$$[PtCl_6]^{2-} + [SnCl_3]^- + Cl^- \rightarrow [PtCl_4]^{2-} + [SnCl_6]^{2-} \tag{1}$$

$$[PtCl_4]^{2-} + 2[SnCl_3]^- \leftrightarrow [PtCl_2(SnCl_3)_2]^{2-} + 2Cl^- \tag{2}$$

The impregnation solution contains a mixture of the above written species. However, since Pt and Sn are in a 1:1 molar ratio in the solution, the $[SnCl_3]^-$ ion will be preferentially consumed in reaction 1 and the $[PtCl_2(Sn-Cl_3)_2]^{2-}$ ion will have a very low concentration. That is, we can consider that the coimpregnating solution contains mainly $[PtCl_4]^{2-}$, $[SnCl_6]^{2-}$, and Cl^- anions, and small amounts of the $[PtCl_2(SnCl_3)_2]^{2-}$ complex. In the case of successive impregnations, $PtCl_6^{2-}$ is added in the second step after loading $SnCl_2$.

Additionally, the coimpregnation is done in the presence of Cl^- ions in the solution (0.4 M HCl); while the H_2PtCl_6 solution used in the second step of successive impregnations is purely aqueous. The presence of Cl^- ions can modify the interaction of Pt with the carbon surface. In fact, Van Dam and Van Bekkum[26] reported that when hydrochloric acid or potassium chloride is added to the chloroplatinic

acid solution, the adsorption strength of the platinum species on the carbon surface decreases. A possible explanation for this behavior is that in a hydrochloric solution, the chloride-containing Pt complexes are more stable and, as a consequence, the loss of chloride ligands would be less. That is, the presence of chloride ions in the solution during the coimpregnation may partially hinder the interaction of the $[PtCl_4]^{2-}$ ions with the S support sites.

The absorption edge corresponding to the four bimetallic dried catalysts and the platinum foil has been plotted in Figure 5. There are clear differences in the intensity of the white line of platinum in the different samples. The energy of the Pt L_{III} resonance is similar, within the limits of experimental uncertainty. To interpret these results, it must be remembered that, the more intense the white line, the more electron deficient are the platinum species.[34,35] As expected, the data in Figure 5 indicate that the concentration of vacant d-electron states is higher for platinum in the PtSn catalysts than in the platinum foil (the same conclusion is obtained if the reference sample a/A2 is used, see Figure 2). According to Figure 5 there are slight differences between the state of platinum in the different bimetallic catalysts. Thus, the electron deficiency of Pt atoms decreases in the following order:

PtSn/C (CI) > PtSn/C−HP (CI) > PtSn/C (SI) >
PtSn/C−HP (SI)
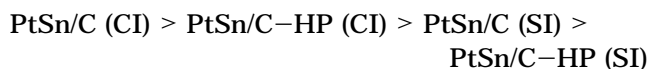
The results also reflect the effect of the surface oxidation of the support. For a given preparation method, platinum atoms in catalysts prepared with the nonoxidized support are more electron deficient (i.e., the intensity of the white line is higher). Comparing samples prepared with the same support, platinum is more electron deficient in catalysts prepared by coimpregnation. This behavior can be related to the weaker interaction of Pt species with the support that results in a smaller degree of reduction of platinum by contact with carbon. These conclusions are in complete agreement with the EXAFS data discussed above.

A comparison of the absorption edge of bimetallic and monometallic catalysts indicates that the electronic state of platinum is not highly modified by tin addition (Figure 6a and 6b). The intensity of the white line for the monometallic catalysts is between those corresponding to the bimetallic ones; either for samples prepared with the original carbon or with the oxidized one. This indicates that tin does not affect the electronic state of platinum atoms very much in dried samples.

In summary, the FT-EXAFS profiles (Figure 3) and the intensity of the white line of the catalysts analyzed (Figure 5) show that support surface oxidation favors the removal of Cl from the platinum coordination sphere. Also, the conditions used in the coimpregnation method hinder to some extent the interaction of platinum species with the carbon surface. The XAFS results obtained on dried bimetallic catalysts do not reveal any interaction between Pt and Sn. However, according to previous results,[17] both metals should be in relatively close proximity because they greatly influenced the behavior of each other during a TPR experiment.[17] In those experiments, a large H_2 consumption peak was observed at about 623 K, thus indicating the co-reduction of platinum and a fraction of tin at this temperature.

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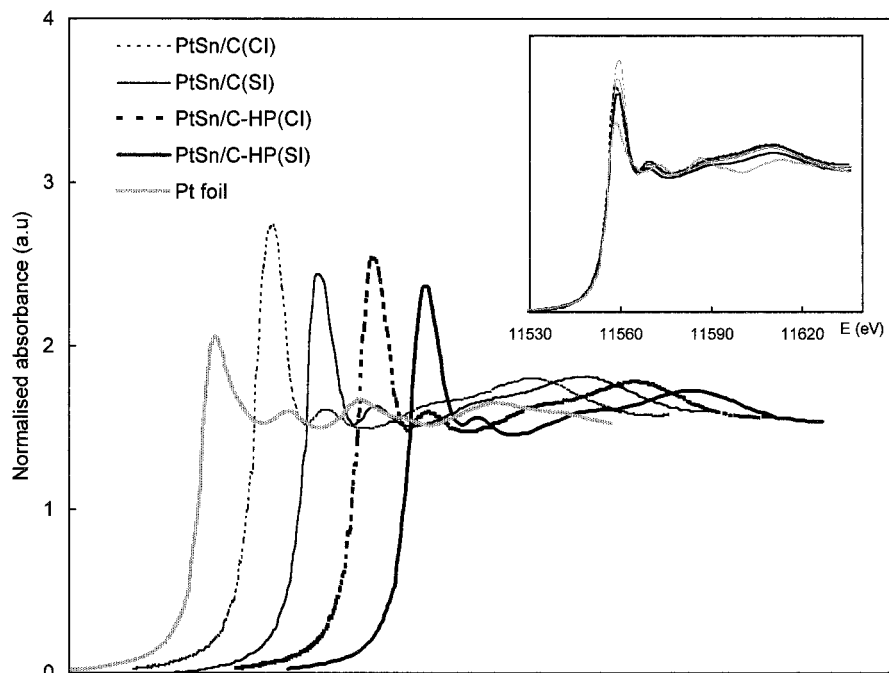(35) Bazin, D.; Sayers, D.; Rehr, J. J. *J Phys. Chem. B* **1997**, *101*, 11040.

Figure 5. XANES profiles for the dried bimetallic PtSn/carbon catalysts and platinum foil (the data have been plotted with a shift of 10 eV between each XANES profile). The inset shows the actual position of the curves.

3.3. Reduced Samples. Using the XPS technique, de Miguel et al. reported[17] that after a reducing treatment (in H_2 at 623 K for 3 h), platinum in the bimetallic PtSn/carbon catalysts is fully reduced, while more than 80% of tin remained as Sn^{2+} or Sn^{4+} (that is, only 20% of tin was reduced to the zero valent state). Although in the four bimetallic catalysts supported on carbon platinum is completely reduced, the FT-EXAFS profiles exhibit differences in the platinum coordination. The intensity of the white line also shows some differences in the electronic state of platinum in the reduced catalysts. Figure 7 contains the FT-EXAFS profiles obtained for the four PtSn catalysts supported on carbon. Also, data obtained for a PtSn/Al₂O₃(CI) catalyst have been included in this figure. The FT-EXAFS spectra indicate a noticeable effect of both the support surface chemistry and the preparation method on the platinum coordination after the reduction treatment. The FT-EXAFS profiles plotted in Figure 7 have three main peaks (which, in some cases, are not completely resolved) with differences in their relative intensities. These three peaks are located at the following distance ranges (without phase shift correction): 1.85−2.10 Å, 2.35−2.50 Å, and 2.65−2.80 Å (i.e., 2.21−2.46 Å, 2.71−2.80 Å, and 2.80−2.94 Å, respectively, after phase shift correction). Several authors who have studied bimetallic PtSn catalysts supported on Al₂O₃,[5,8] graphite,[16] and SiO₂[9] have already observed FT-EXAFS profiles with three main peaks at the same distance ranges. According to these data and to the reference FT-EXAFS spectrum for platinum foil (Figure 1), the signals observed from 2.35 to 2.80 Å in Figure 7 can be due to Pt−Sn and/or Pt−Pt interactions.

Although there are some difficulties to distinguish accurately between the contribution of Pt−Pt and Pt−Sn interactions,[31] some authors tried to identify them separately. Thus, refs 5, 9, and 16 report that the Pt−Pt bond contributes to the larger distance range of the FT-EXAFS profile (at about 2.77 Å) while the contribution of the Pt−Sn bond appears at slightly lower distances (depending on the PtSn species formed in any case). However, Caballero et al.[8] assigned a peak at 2.68 Å to the Pt−Pt

bond and one at 2.93 Å to the Pt−Sn bond. There is also disagreement[16] about the assignment of the peak at lower distances (<2.10 Å, in Figure 7). Thus, Caballero et al.[8] assigned this peak to the interaction of platinum clusters with the support via Pt−O−Sn²⁺ species; Pinxt et al.[16] do not define clearly the origin of this peak and Stagg et al.[9,31] explain it as due to an interference phenomenon between the Pt−Pt and Pt−Sn bonds. All these discrepancies reveal the difficulty for an accurate quantification of the EXAFS oscillations and that the use of appropriate references and complementary techniques is necessary for a correct assessment of bond distances and coordination numbers.

In the present paper, for the PtSn catalysts analyzed, the peaks observed from 2.35 to 2.80 Å (without phase shift correction, Figure 7) are considered to result from Pt−Pt and Pt−Sn bonds. Additionally, the peak at lower distances (below 2.10 Å, Figure 7) has been assumed to proceed from the interaction of platinum with the support. Such an interaction can take place via O atoms of the surface of the support or C atoms from the carbon basal planes. These possible interactions have been previously proposed in the study of monometallic Pt/C catalysts.[20] Caballero et al.[36] also reported the existence of a Pt−C bond 1.94 Å long in Pt/Al₂O₃ catalysts containing carbon from hydrocarbon cracking. In any case, the contribution of Pt−O−Sn²⁺ structures cannot be discarded.

The FT-EXAFS profiles presented in Figure 7 show that the three peaks mentioned above have a similar intensity for the catalysts prepared with the oxidized supports (i.e., PtSn/C−HP(CI) and PtSn/C−HP(SI)). It must be pointed out that the FT-EXAFS profiles obtained for these two samples are very similar, which suggests that the preparation method does not produce significant differences in the state of the reduced metallic phase. It is interesting to emphasize that the three peaks of the FT-EXAFS spectrum for the PtSn/Al₂O₃(CI) catalyst have similar intensity. On the other hand, important differences

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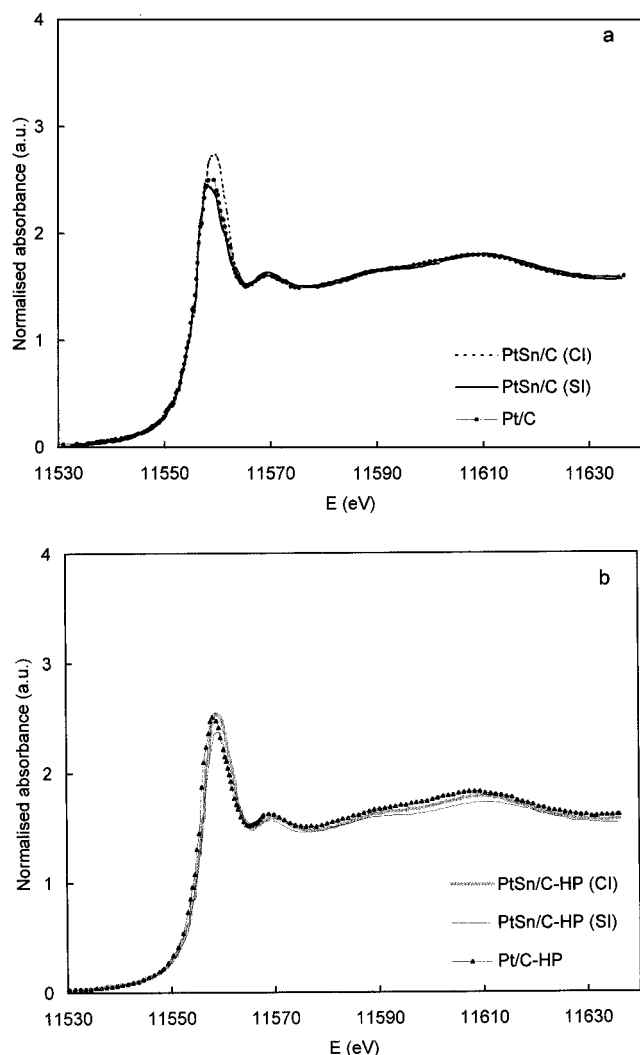
Figure 6. Comparison of the intensity of the absorption edge in mono- and bimetallic catalysts: a) catalysts prepared with the non-oxidized carbon and b) samples prepared with the oxidized carbon.

exist between the catalysts prepared with the nonoxidized support, and these differences indicate a significant influence of the preparation method on the structure of the metal particles. Thus, the peak at lower distances (from 1.85 to 2.10 Å in Figure 7) is more intense and better defined and resolved for the PtSn/C(CI) sample than for the PtSn/C(SI) catalyst. According to the criteria explained above, this means that the interaction of metallic platinum with the support (as Pt−C or Pt−O) or with tin through the Pt−O−Sn^{2+} species, is higher in the catalyst PtSn/C(CI). It must be remembered that the interaction of platinum species with the support is not strong for the dried PtSn/C(CI) sample (see Section 3.2.). It seems that in this sample, the platinum species interact more efficiently with other elements after the reduction treatment. Thus, we suggest that the FT-EXAFS signals observed below 2.1 Å come from Pt−O−Sn^{2+} species. This would have some relation with the mutual effect of tin and platinum found in TPR experiments.[17]

In summary, the surface chemistry of the carbon support and the preparation method of the catalysts influence the structure of metallic particles in the reduced catalysts. If the carbon surface is oxidized, both preparation methods (CI and SI) will produce a similar catalyst structure, which is also close to the structure of PtSn catalysts supported

on Al$_2$O$_3$. On the other hand, a different structure of the metallic phase is obtained depending on the preparation method, when nonoxidized carbon is used as support.

The analysis of the Pt L$_{III}$ absorption edge can give us some additional information about the electronic state of platinum. Figure 8 shows this part of the XAFS spectrum for the four PtSn catalysts supported on carbon, the PtSn/Al$_2$O$_3$(CI) catalyst and the platinum foil. As can be observed, there is a negligible variation in the energy of the Pt L$_{III}$ resonance. However, the intensity of the white line exhibits significant differences. Thus, the intensity of the white line for the different samples increases in the following order

$$\text{PtSn/C(SI)} < \text{PtSn/Al}_2\text{O}_3\text{(CI)} \cong \text{PtSn/C−HP(CI)} \cong$$
$$\text{PtSn/C−HP(SI)} < \text{Pt foil} < \text{a/A2} \cong \text{PtSn/C(CI)}$$

That is, platinum in the sample PtSn/C(CI) is more electron deficient than in the catalysts studied or the platinum foil. This result agrees with the largest interaction of Pt with more electronegative atoms such as O (for example through the Pt−O−Sn^{2+} species or with the support). Platinum atoms have a similar electronic state in PtSn/C−HP(CI), PtSn/C−HP(SI), and PtSn/Al$_2$O$_3$(CI) catalysts. This observation is in agreement with the similar intensities of the main peaks of the FT-EXAFS profiles for these three samples (Figure 7). For the two bimetallic catalysts supported on oxidized carbon and for PtSn/Al$_2$O$_3$(CI) and PtSn/C(SI) samples, the intensity of the white line is lower than that for the platinum foil and reference sample a/A2 (Figure 2). A similar result was previously observed in a PtSn/Al$_2$O$_3$ catalyst by Caballero et al.[8] This effect is explained by the formation of a Pt−Sn bimetallic alloy that would produce an increase of the d-electron density of platinum atoms. Thus, the results shown in Figure 8 would indicate that the PtSn/C(SI) catalyst contains the largest amount of bimetallic PtSn alloy. Additionally, the PtSn bimetallic phase is formed in a similar extent for PtSn/C−HP(CI), PtSn/C−HP(SI), and PtSn/Al$_2$O$_3$(CI) samples.

The similarities between the results obtained for PtSn/C−HP(CI) and PtSn/C−HP(SI) samples seem to indicate that platinum develops a similar structure after the reduction treatment when the oxidized support is used, regardless of the preparation method. The results obtained with the catalyst supported on alumina suggest that the oxygen groups on the surface of Al$_2$O$_3$ play a role similar to that of surface oxygen complexes existing on the carbon support.

Further information on the state of the platinum metallic phase can be obtained by the analysis of the oscillations that appear after the absorption edge, in a range of about 60 eV. These oscillations are related to the atomic order around the absorbent atom. It has been stated[37] that the better defined the oscillations, the larger is the particle crystallinity. Accordingly, it can be deduced from data in Figure 8 that the metallic particles are more crystalline in catalysts prepared with the nonoxidized carbon (i.e., PtSn/C(CI) and PtSn/C(SI) samples). This is in agreement with the larger intensity of the peak corresponding to Pt−Pt distances in the FT-EXAFS profiles (located above 2.35 Å in Figure 7).

3.3. Catalytic Properties and Catalyst Structure. Many studies on PtSn catalysts have the objective to relate the catalyst structure and catalytic properties in hydro-

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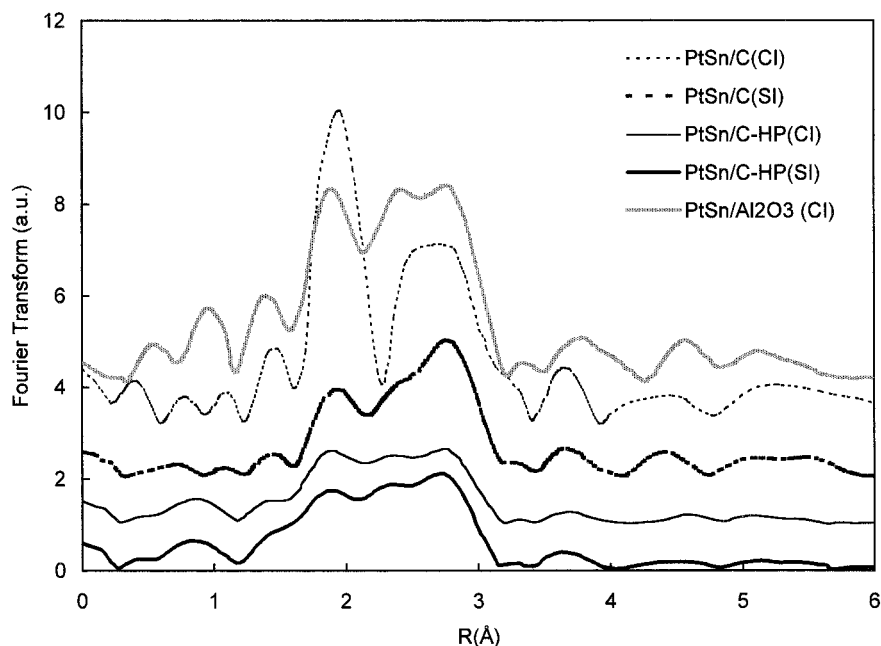
Figure 7. FT-EXAFS profiles of reduced bimetallic catalysts: PtSn/carbon and PtSn/Al$_2$O$_3$ samples (the FT-EXAFS profiles have been plotted with a shift of 1 unit between them in the *y*-axis).
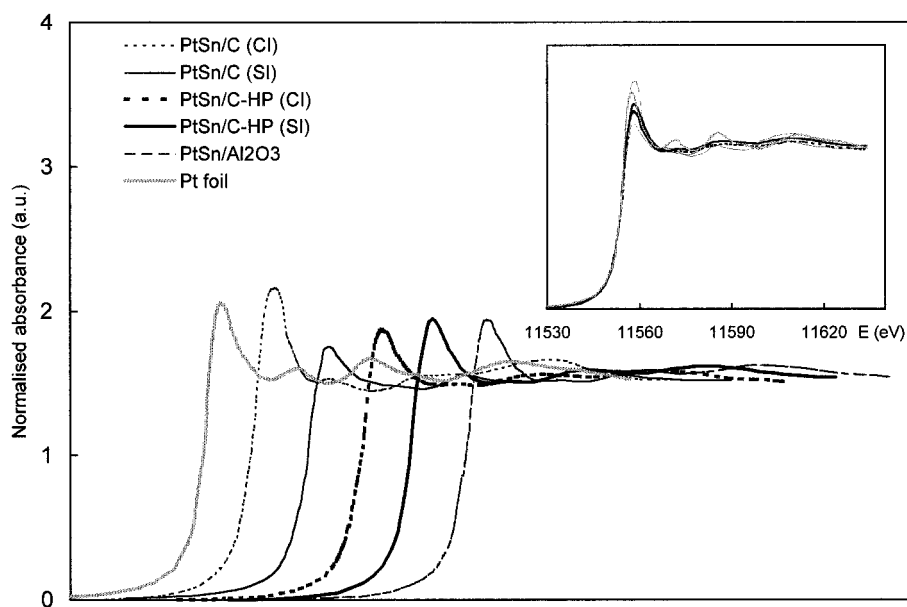

Figure 8. XANES profiles for the reduced bimetallic catalysts: PtSn/carbon and PtSn/Al$_2$O$_3$ samples, and for a platinum foil (the data have been plotted with a shift of 10 eV between each XANES profile). The inset shows the actual position of the curves.

carbon reactions.[38-41] The possible effect of Sn on the catalytic activity has been proposed to be either an electronic effect (electron transfer from Sn to Pt) that changes the bond strength between hydrocarbons and Pt surface atoms, or a geometric effect due to the dilution of the platinum atoms that results in a decrease of the cluster size.

The present paper deals with supported PtSn catalysts in which different structures have been developed as a consequence of different preparation methods and different surface chemistry of the supports. To determine

how these differences in structure affect their catalytic properties, catalysts were tested in cyclohexane dehydrogenation, a structure-insensitive reaction that does not demand large ensembles of platinum atoms.[42]

Results on the catalytic activity (reaction rate in mol/h per gram of platinum and turnover frequency) and values of activation energy are presented in Table 3. The turnover frequency (TOF) has been calculated only for the monometallic catalysts on the basis of the number of active sites estimated by hydrogen chemisorption. TOF values were not calculated for bimetallic catalysts since the chemisorptive properties of metals can be strongly influenced by the interaction between metallic components (presence of alloyed particles, SMSI—strong metal support interaction—effects,[43] blockage of metal atoms, and dilution effects). Table 3 shows that the activities of bimetallic

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Table 3. Catalytic Activity for Cyclohexane Dehydrogenation

catalyst	r (mol h^{-1} g$_{Pt}^{-1}$)	TOF	E_a (kJ/mol)
PtSn/C (CI)	2.2	—	29.4
PtSn/C (SI)	3.0	—	28.8
PtSn/C-HP (CI)	9.9	—	30.1
PtSn/C-HP (SI)	7.7	—	26.1
PtSn/Al$_2$O$_3$	12.1	—	30.0
Pt/C	32.0	82	19.6
Pt/C-HP	86.2	192	21.6

catalysts are much lower than those of the monometallic ones (about 10 times for each series), and that there is an important increase of the activation energy (about 40%) when tin is present. In this sense, addition of tin to platinum produces a clear increase of the activation energy for C$_6$H$_{12}$ dehydrogenation. This effect can be attributed to an electronic modification of platinum by tin in the reduced bimetallic catalysts. An effect of the support surface chemistry is observed for both mono and bimetallic catalysts. Thus, catalysts prepared with the oxidized carbon are more active than those prepared with the original purified carbon. However, the different preparation method (in the case of bimetallic catalysts) does not make noticeable differences in catalytic activity.

Considering that cyclohexane dehydrogenation is a structure-insensitive reaction, similar TOF values should have been obtained for both monometallic catalysts. However, Pt/C and Pt/C−HP catalysts show different turnover frequencies. Similar results have also been observed in catalysts prepared with carbon supports subjected to different surface treatments,[19,44] and they have been related to differences in the location and accessibility of platinum particles depending on the support surface chemistry. In the case of catalysts Pt/C and Pt/C−HP, as discussed before,[19] it seems that with the oxidized support, and due to interaction with the surface oxygen groups of the support, platinum is located more externally and is more accessible to reactants. With the nonoxidized support, a fraction of platinum can reach the inner porosity and be anchored in a region accessible to hydrogen but not to the more voluminous cyclohexane molecule. In this way, not all the active sites determined by hydrogen chemisorption are actually active for cyclohexane dehydrogenation.

The differences between the catalytic activity of bimetallic catalysts prepared with oxidized and nonoxidized supports can be also explained with the arguments stated above. That is, with the oxidized supports the metal species are located more externally and therefore they are more accessible to the reactants.

In relation to the differences in structure found by EXAFS spectroscopy, it can be concluded that the catalysts with a higher catalytic activity have a similar FT-EXAFS profile and a similar intensity of the white line (i.e., catalysts PtSn/C−HP(C), PtSn/C−HP(SI), and PtSn/Al$_2$O$_3$(C)); that is, catalysts prepared with the oxidized

support and with alumina. This information confirms that these catalysts have a similar structure and electronic state of platinum.

Conversely, samples PtSn/C (CI) and PtSn/C (SI), which exhibit a similar low catalytic activity, seem to have, from XAFS results, a very different metallic structure and a different platinum electronic state. In this case, the above-suggested accessibility of the reactants to the metallic species can be considered the major factor responsible for diminished catalytic activity.

In any case, according to XAFS results, it must be indicated that the catalytic surface is a complex one, where PtSn alloy particles and Pt−O−Sn^{2+} species (with low catalytic activities) coexist with very active Pt particles. The final activity of the different catalysts is the result of the relative concentrations of these surface species, although it is very difficult to quantify their relative concentrations. Additional effects such as the Sn surface enrichment (which was observed in XPS measurements—Table 2), a different crystallinity of metallic particles and different distribution of the active phase within the support particles must be taken into account to explain the catalytic activity. It could be considered that there is an optimum combination of platinum and tin that gives a structure (including geometric arrangement and electronic state) that is most effective catalytically. The formation of such a structure, in which there is a fraction of bimetallic PtSn clusters, seems to be very dependent on the surface chemistry of the support.

4. Conclusions

(1) XAFS results reveal clear differences in the catalysts' structure that arise as a consequence of the preparation method and of the surface chemistry of the support.

(2) In dried samples, the interaction of the platinum is stronger with the oxidized support. The coimpregnation method results in a weaker interaction with the support for Pt than the successive impregnation method, probably because Cl$^-$ ions inhibit the adsorption process.

(3) XAFS results indicate that, in dried samples, tin does not affect the electronic state of Pt atoms.

(4) The XAFS analysis of reduced samples reveals differences in the structure of the metallic phase of the different catalysts in the following aspects: interaction with the support, concentration of bimetallic particles, and crystallinity of metallic particles. After reduction, samples prepared with the oxidized support show a very similar structure, regardless of the preparation method used. Conversely, when the original carbon is used as a support, the XAFS data reveal important differences between catalysts prepared by the different impregnation methods.

(5) The presence of bimetallic PtSn phases, Pt particles, and Pt−O−Sn^{2+} species can be suggested from XAFS results. The catalytic activity of bimetallic catalysts is determined by the relative concentrations of these surface species and their distribution in the support.

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