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State of Pt in Dried and Reduced PtIn and PtSn Catalysts Supported on Carbon

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The state of platinum in carbon-supported bimetallic PtSn and PtIn catalysts, prepared by two different methods,
coimpregnation and successive impregnation, has been investigated by X-ray photoelectron spectroscopy,
X-ray absorption fine structure (XAFS), transmission electron microscopy (TEM), and a catalytic test. An
important effect of the nature of the second metal in the state of platinum, related to the preparation conditions,
has been found. Different states of platinum are found, mainly platinum metal and binary intermetallic
compounds with the second metal. The preparation method has a clear effect on the state of platinum in
reduced PtSn samples, while it is much lower in the reduced PtIn catalysts. As deduced from TEM, in general
in the bimetallic catalysts the mean particle size is smaller and the particle size distribution is narrower than
in the monometallic Pt/C catalyst, and there is an effect of the preparation method. In general, PtIn catalysts
are more homogeneous than PtSn. Because of the mentioned differences, catalytic activity for cyclohexane
dehydrogenation, a structure insensitive test reaction, depends on the second metal and preparation method.

Introduction

It is known that the addition of a catalytically inactive metal,
like Sn, In, Re, or Ge, to an active metal like platinum is a way
to modify the catalytic properties of the noble metal.[1,2] The effect
of the second metal, which can be interpreted from both a
geometrical and an electronic point of view, can be analyzed
by investigating the structure of the supported metal particles.

Sn and In are both additives of platinum catalysts for
hydrogenation and dehydrogenation reactions,[3−9] particularly
in the dehydrogenation of light paraffins. They usually produce
a decrease of catalytic activity but an interesting modification
of selectivity. There are some papers devoted to the analysis of
the differences between Sn and In as additives[3−5] that obtain,
mainly from catalytic activity results, interesting conclusions
about the structure of the active phase. In the case of PtSn
catalysts, the formation of PtSn bimetallic phases is usually
reported,[10] although for PtIn catalysts the existence of PtIn
bimetallic phases is reported by some authors[11] but rejected by
others.[12,13]

The present paper deals with the characterization of carbon-
supported PtSn and PtIn catalysts prepared by two different
procedures: coimpregnation and successive impregnation. The
preparation conditions can determine the formation of bimetallic
clusters. It has been already reported in the case of the
calcination temperature[14] and of acidic treatment[15] and also on
the platinum to second metal ratios and chlorine content.[16] In
this work, to examine the state and the environment of platinum
X-ray absorption fine structure (XAFS) and X-ray photoelectron

spectroscopy (XPS) techniques have been used. It must be
pointed out that for such an investigation, the XAFS technique
is especially useful[17,18] because it provides information about
the local structure of the bimetallic particles and the electronic
state of the element under investigation. In bimetallic catalysts,
curve fitting for a quantitative analysis is fairly troublesome,
mainly because of the lack of suitable references. A transmission
electron microscopy (TEM) analysis was also performed with
the objective of determining the particle size and the catalyst
dispersion, and cyclohexane dehydrogenation was used as a test
reaction to get information on the active sites.

Experimental

1. Catalysts Preparation. The support used in this work was
obtained from a commercial activated carbon (GA-160, Car-
bonac) after purification (acid treatments and H_2 heat treatment)
and size reduction (to 100−140 mesh)[19] with its textural
properties being $S_{BET} = 987$ m^2 g^{-1} and $V_{pore} = 0.33$ cm^3 g^{-1}.
The resulting material was labeled "C". The preparation of
PtSn/C catalysts has been previously reported,[19] and the same
method was used for the preparation of PtIn/C catalysts. In
summary, the catalysts were prepared by two different impreg-
nation procedures: (a) coimpregnation (method CI) with an
aqueous solution of H_2PtCl_6 and $SnCl_2$ or $In(NO_3)_3$ and (b) two-
step or successive impregnation (method SI). By the SI method,
the catalysts were first impregnated with an aqueous solu-
tion containing the In or Sn salts, dried as 393 K, and then
impreganted with an aqueous solution of H_2PtCl_6. In both cases
(CI and SI methods), the impregnating solution containing $SnCl_2$
was HCl (0.4 M) to avoid hydrolysis of the tin precursor. A
monometallic Pt/C sample was also prepared by impregnation
with an aqueous solution of H_2PtCl_6. The supports were
maintained in contact with the impregnating solution (30 mL/g

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carbon) under stirring at 298 K for 5 h, then the solid was separated by filtration and dried at 393 K for 24 h. The nominal total content of platinum was about 0.8 wt %, while indium and tin contents were about 0.6 wt % and 0.4 wt %, respectively, corresponding to atomic ratios of Pt/In = 0.78 and Pt/Sn = 1.22.

2. XPS. XPS of PtSn/C catalysts were obtained with a Fisons ESCALAB MkII 200R electron spectrometer, while the XPS analysis of PtIn/C catalysts were carried out with a VG-Microtech Multilab electron spectrometer. In both cases, the source employed was the Mg K_α (1253.6 eV) radiation of twin anode in the constant analyzer energy mode. Pressure of the analysis chamber was maintained below 10^{-9} Torr. The binding energy scale was regulated by setting the C 1s transition. Peak areas were estimated by calculating the integral of each peak after subtraction of the background and fitting the experimental peak by a combination of Lorentzian/Gaussian (L/G) curves. Measurements were carried out on both dried and reduced samples. The reduced samples (treatment in H_2 flow, 60 mL/min at 623 K for 12 h) were handled in N_2, and then they were further reduced in situ under the same conditions for 1 h.

3. XAFS. The XAFS measurements were performed in Japan at the Photon Factory in the National Laboratory for High-Energy Physics (KEK-PF) (2.5 GeV electron storage ring, stations BL-7C, BL-9A) and at the SPring-8 facility, managed by the Japan Synchroton Research Institute (8.0 GeV electron storage ring, station BL1B101). A Si(111) double crystal was used to monochromatize the X-ray beam from the 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. After a reduction treatment (H_2, 60 mL/min, 623 K, 12 h) the samples were transferred without exposure to air to a glove box where they were vacuum packed in the form of pressed pellets or inside glass tubes. XAFS was measured on the packed samples. This means that it is not really an in situ characterization, but handling, packing, and measurements have been done very carefully to avoid contact with air.

Data were analyzed using the program Athena (version 0.8.041).[20] The Fourier transform (FT) was performed on k^3-weighted extended XAFS (EXAFS) oscillations over the range of 3-12 Å^{-1}. Data fitting was carried out using the program Artemis (version 0.8.000)[20] which is based on the FEFF code.[21,22] Fits were performed in R space considering the possible single scattering paths in clusters of 6 Å. Fittings with both k^1- and k^3-weighting were done to verify the validity of the fits. Single values of σ^2 (Debye-Waller factor, mean-square displacement of path distance in R, or second cumulant), S_0^2 (amplitude reduction factor), ΔR (change in half path length or first cumulant), and ΔE_0 (E_0 shift of the path) for all the paths are used in the fitting. N_{ip} was the number of independent points. R-range and k-range delimit the range used in the fit. Different constraints assuming coherent dislocations of the atoms were considered but they did not improve the fits significantly.

Using the phase diagrams of Pt-Sn[23,24] and Pt-In[25] mixtures, taking into account the reduction temperature used and the atomic percentage of each metal, and supposing a homogeneous distribution of the metals, it is concluded that the bimetallic phases likely present in the reduced catalysts are: PtSn, Pt_3Sn, Pt_2In_3, Pt_3In_2, and Pt_3In. Thus, Pt metal and the mentioned bimetallic phases were considered for data fitting. Some data about their structure can be found in Table A included as Supporting Information. It must be noted that paths with a R_{eff}

TABLE 1: XPS Analysis of Catalysts Pt/C, PtSn/C, and PtIn/C: BE (eV) and Atomic Sn/Pt and In/Pt Ratios in Dried and Reduced Samples

sample	BE Pt $4f_{7/2}$ (eV)	BE Sn $3d_{5/2}$ (eV)	BE In $3d_{5/2}$ (eV)	M/Pt[a]
Pt/C	72.1 (60%) 73.7 (40%)			
Pt/C red	71.9			
PtSn/C (CI)	72.0 (54%) 73.7 (46%)	487.7		
PtSn/C(CI) red	71.8	486.4 (17%) 487.7 (83%)		16.10
PtSn/C (SI)	72.0 (62%) 73.9 (46%)	487.7		
PtSn/C (SI) red	71.8	486.5 (12%) 487.8 (88%)		24.40
PtIn/C (CI)	72.1 (47%) 73.8 (53%)		446.1	
PtIn/C (CI) red	71.3		444.3	1.06
PtIn/C (SI)	72.0 (62%) 73.2 (38%)		446.7	
PtIn/C (SI) red	71.2		444.9	2.14

[a] M = Sn or In.

(half length of the path used in the FEFF calculation) far outside the fitting range were not always considered because they do not improve the fit.

4. Transmission Electron Microscopy (TEM). TEM images were obtained with a JEOL JEM-2010 microscope using an acceleration voltage of 200 kV. Samples were placed on the copper grids by using suspensions of the catalysts in ethanol.

5. Cyclohexane Dehydrogenation. Cyclohexane dehydrogenation is a structure insensitive test reaction. It has been carried out with the objective of getting information on the number of active sites, that is, the amount of accessible or electronically active platinum atoms.

Prior to any catalytic test, the catalysts were reduced in situ with H_2 at 623 K for 4 h. Catalytic tests were performed at atmospheric pressure in a differential flow reactor with a molar ratio H_2/C_6H_{12} = 29 and a molar flow of 0.056 mol/h C_6H_{12}. The activation energy was obtained by measuring the catalytic activity at 543, 558, and 573 K. The mass of catalyst used was appropriate to obtain a hydrocarbon conversion lower than 7%. The progress of the reaction was followed by gas chromatography.

Results and Discussion

1. XPS Analysis. Table 1 shows the XPS results obtained. As it can be observed, in the dried catalysts investigated about half of the platinum atoms are found as Pt(II) (binding energy (BE) about 72.0 eV), while tin remains in an oxidized (II) or (IV) state[19] (no distinction can be done from XPS data) and indium is completely in the (III) oxidation state. It must be added that in all cases Cl as chlorine (BE = 198.3-198.4 eV), together with some organic Cl (BE = 199.0-200.1 eV) that is part of the carbon support, is observed.

The reduction of chloroplatinic acid upon impregnation onto activated carbon has been previously observed[26-28] and explained by the reaction of the platinum compound with a reducing site on the support surface. According to van Dam and van Bekkum,[26] the reduced platinum species is coordinatively bound to the support by π-complex structures or oxygen-containing complex structures located at the basal plane edges of the carbon material.

After the reduction treatment, platinum is entirely in the zerovalent state in both PtSn and PtIn catalysts, and tin is
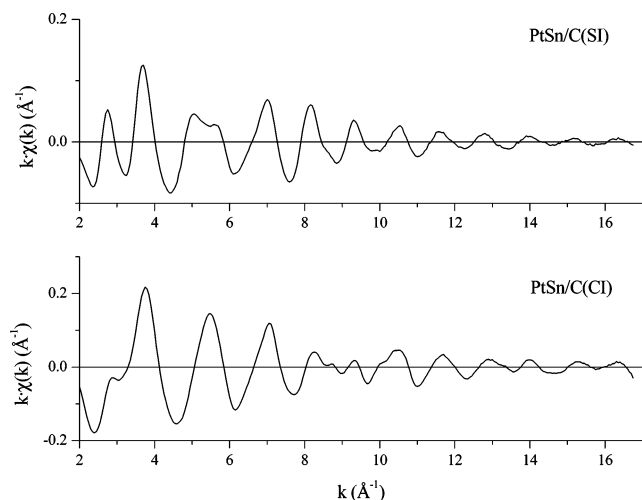
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Figure 1. Experimental EXAFS spectra of PtSn/C catalysts.
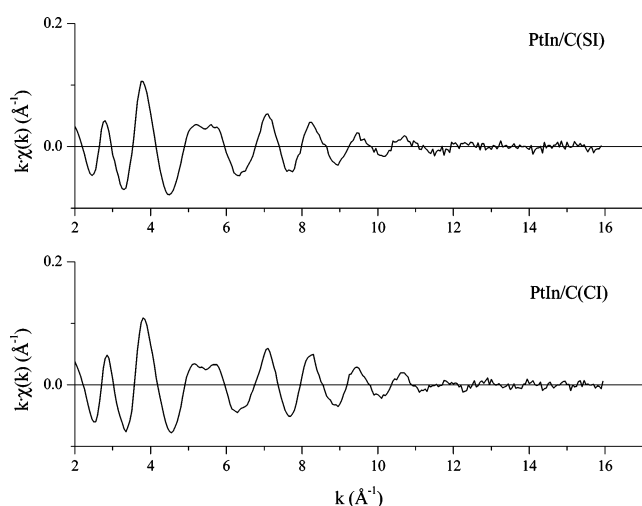
Figure 2. Experimental EXAFS spectra of PtIn/C catalysts.

Figure 3. Fourier Transform of the EXAFS oscillations (magnitude) of the carbon-supported reduced PtSn samples.

Figure 4. Fourier Transform of the EXAFS oscillations (magnitude) of the carbon-supported reduced PtIn samples.

partially reduced; only about 15% of the total measured tin is in the zerovalent state, and indium shows only one electronic state determined by a binding energy (In $3d_{5/2}$) of 444.3 and 444.9 eV for samples PtIn/C (CI) and PtIn/C (SI), respectively. According to the literature[29] and considering that the binding energy measured in the same apparatus for a In foil reference is 444.0 eV, it can be derived that in the H_2 treated samples indium is in the zerovalent state but interacting with a more electronegative atom. This result can be interpreted as an indication of PtIn alloying.

The calculated surface atomic ratios Sn/Pt and In/Pt indicate that segregation of the second metal is clear in PtSn/C samples (high ratio Sn/Pt), while a higher homogeneity in the composition and structure of the bimetallic phase can be deduced for the PtIn/C catalysts (low surface ratio In/Pt).

2. XAFS Analysis. Figures 1 and 2 show the raw EXAFS oscillations obtained for PtSn/C and PtIn/C catalysts, respectively. The data quality is good for the range of fits used, especially in the case of PtSn/C catalysts.

Figure 3 depicts the FT-EXAFS profiles of the reduced PtSn/C (CI) and PtSn/C (SI) catalysts. Figure 4 shows analogous data corresponding to PtIn catalysts. In both cases and for the sake of comparison, the FT-EXAFS profiles obtained for the reduced monometallic Pt/C and platinum foil have been also represented.

Figures 3 and 4 clearly show an important decrease in the coordination of platinum in bimetallic catalysts with respect to
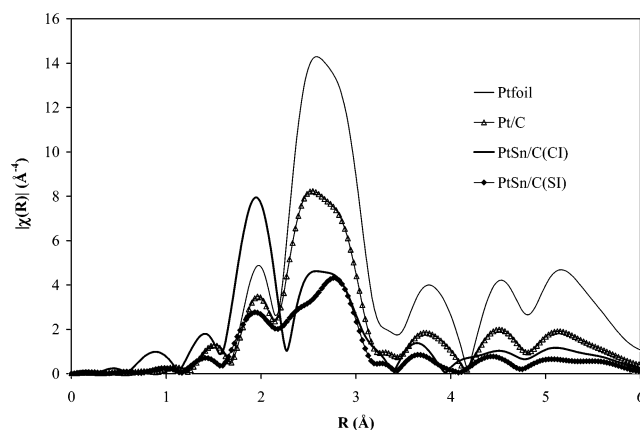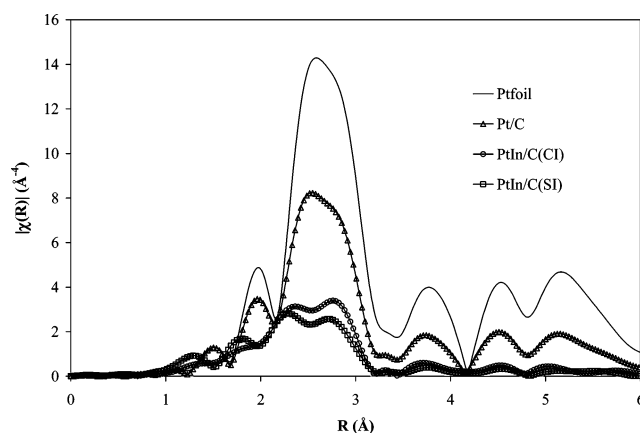
the monometallic one. That is, in reduced samples a very important effect of the second metal in the structure of platinum is observed. The second point is the large difference between the structure of platinum in PtSn and PtIn catalysts (compare Figures 3 and 4) that reveals a noticeable effect of the nature of the second metal.

In the case of the PtSn catalysts, the FT-EXAFS profiles (Figure 3) seem to be composed of three main peaks. Several authors who have studied bimetallic PtSn catalysts supported on Al_2O_3[30−32], graphite and activated carbon,[27,28,33] and SiO_2[13,34,35] have already observed FT-EXAFS profiles with three main peaks at the same distance ranges found in this work. There is, however, a lack of agreement in the literature to accurately determine the contribution of Pt−Pt and Pt−Sn interactions to the mentioned peaks. In previous publications, it was considered that the peaks observed from 2.35 to 2.80 Å (without phase shift correction) resulted from Pt−Pt and Pt−Sn bonds, while the peak at lower distances (below 2.10 Å) may be due to the interaction of platinum with the support.[28] As observed in Figure 3, the lower-distance peak is more intense and better resolved for the PtSn/C (CI) catalyst, suggesting a higher fraction of Pt-support interactions. The spectra shown in Figure 3 indicated that the catalytic surface of the reduced PtSn/C catalysts is a complex one that must be composed of several types of structures.[28] According to the comments presented above, it probably contains Pt−O(C) species (signifying the interactions of Pt with the support), Pt_xSn_y bimetallic phases, and monometallic particles. Similar studies on $PtSn/Al_2O_3$ catalysts[32]

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TABLE 2: Parameters Obtained for the Fitting (k^3-Weighted) of PtSn/C Samples for Different Possible Structures[a]

sample	PtSn/C (CI)	PtSn/C (SI)	PtSn/C (SI)
structure fitted	Pt + Pt$_3$Sn	Pt + PtSn	Pt$_3$Sn
ΔE_0 (eV)	11.4 ± 5.3	5.8 ± 4.4	8.2 ± 3.1
S_0^2	0.09 ± 0.04	0.13 ± 0.06	0.35 ± 0.12
ΔR (Å)	0.00 ± 0.02	0.03 ± 0.02	−0.02 ± 0.02
σ^2 (Å^2)	0.0021 ± 0.0022	0.0009 ± 0.0027	0.0063 ± 0.0021
R-factor	0.0233	0.0225	0.0237
χ^2_{red}	1586.9	930.1	698.9
N_{ip}	6.12	6.12	6.99
high correlations (>0.85)	σ^2 and S_0^2	σ^2 and S_0^2	σ^2 and S_0^2
	ΔR and ΔE_0	ΔR and ΔE_0	ΔR and ΔE_0
k-range (Å^{-1})	3.29−12.01	2.93−11.95	2.93−11.95
R-range (Å)	2.27−3.39	2.17−3.27	2.17−3.41

[a] ΔE_0: E_0 shift of the path. S_0^2: amplitude reduction factor. ΔR: change in half path length or first cumulant. σ^2: Debye−Waller factors, mean-square displacement of path distance in R or second cumulant. χ^2_{red}: reduced chi-square. N_{ip}: number of independent points. R-range and k-range delimit the range used in the fit.

TABLE 3: Parameters Obtained for the Fitting (k^3-Weighted) of PtIn/C Samples for Different Possible Structures[a]

sample	PtIn/C (CI)	PtIn/C (CI)	PtIn/C (SI)
structure fitted	Pt + Pt$_3$In$_2$	Pt + Pt$_3$In	Pt + Pt$_3$In
ΔE_0 (eV)	4.6 ± 1.5	5.7 ± 1.1	2.4 ± 1.5
S_0^2	0.28 ± 0.04	0.28 ± 0.03	0.30 ± 0.05
ΔR (Å)	−0.05 ± 0.01	−0.05 ± 0.01	−0.08 ± 0.01
σ^2 (Å^2)	0.0080 ± 0.0010	0.0102 ± 0.0008	0.0120 ± 0.0012
R-factor	0.0082	0.0040	0.0094
χ^2_{red}	35.4	17.4	13.4
N_{ip}	6.72	6.72	6.78
high correlations (>0.85)	σ^2 and S_0^2	σ^2 and S_0^2	σ^2 and S_0^2
	ΔR and ΔE_0	ΔR and ΔE_0	ΔR and ΔE_0
k-range (Å^{-1})	3.04−12.11	3.04−12.11	2.95−11.93
R-range (Å)	2.00−3.21	2.00−3.20	2.00−3.24

[a] ΔE_0: E_0 shift of the path. S_0^2: amplitude reduction factor. ΔR: change in half path length or first cumulant. σ^2: Debye−Waller factors, mean-square displacement of path distance in R or second cumulant. χ^2_{red}: reduced chi-square. N_{ip}: number of independent points. R-range and k-range delimit the range used in the fit.

found that in the reduced sample about 80% of Pt is in the form of small crystallites and the remaining 20% is forming a PtSn alloy.

To analyze the presence of Pt metal and Pt$_x$Sn$_y$ bimetallic compounds, data fitting was performed in the region centered at 2.7 Å. To determine the acceptability of a fit, the following criteria have been considered: $\sigma^2 > 0$, R factor close to or lower than 0.02,[36] and consistency with the k^1 weight fit. The criterion employed to check if two fits are consistent is: the fitted parameters in both fits (k^1 and k^3 weights) should have uncertainty ranges that overlap. For the PtSn catalysts, the fitting has been done considering the presence of PtSn or Pt$_3$Sn bimetallic compounds, Pt metal, or a combination of Pt metal and a bimetallic compound. Table 2 contains the parameters and the details of the best fits (k^3-weighted) obtained. The structures indicated are those corresponding to the fits that are acceptable according to the criteria indicated above. Curve fitting is shown in Supporting Information: Figures A and B, and Table B. These results indicate that the state of platinum in the reduced sample PtSn/C (CI) corresponds to a combination of Pt metal and the Pt$_3$Sn bimetallic compound, while sample PtSn/C (SI) contains the Pt$_3$Sn bimetallic compound and/or a mixture of Pt metal and PtSn bimetallic compound. The low values of S_0^2 (<0.8) for all supported bimetallic catalysts are indicative of small particle size and the effective reduction of coordination. It must, however, be taken in mind that this technique is insensitive to polydispersity.[37]

The FT-EXAFS profiles obtained for the reduced PtIn/C catalysts (Figure 4) in both CI and SI samples contain two main maxima centered at about 2.3 and 2.7 Å, respectively. This means that the structure of platinum in these samples is quite different from that in monometallic Pt/C and in PtSn/C catalysts.
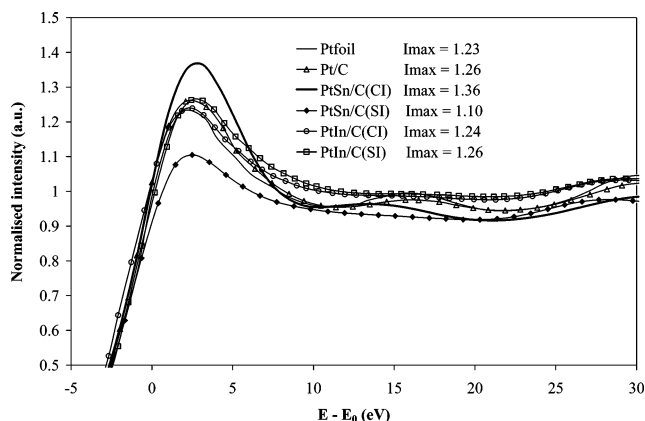
Figure 5. XANES spectra of the carbon-supported reduced samples.

In this case, different fits were done considering the presence of platinum metal, Pt$_2$In$_3$, Pt$_3$In$_2$, and Pt$_3$In bimetallic compounds, and the following combinations: Pt + Pt$_2$In$_3$, Pt + Pt$_3$In$_2$, and Pt + Pt$_3$In. Good fits for the PtIn/C (CI) reduced sample were obtained with Pt + Pt$_3$In$_2$ and Pt + Pt$_3$In structures with the best fit being the one obtained with a combination of Pt and Pt$_3$In structures. EXAFS data of reduced PtIn/C (SI) only fit well with a combination of Pt and Pt$_3$In structures. Curve fitting is included as Supporting Information: Figures C and D and Table C. According to the analysis carried out, the presence of the Pt$_2$In$_3$ bimetallic compound is rejected in both samples. Thus, it can be concluded that reduced catalysts PtIn/C (CI) and PtIn/C (SI) mainly contain Pt metal and bimetallic Pt$_3$In. Table 3 contains the parameters and the details of the three best fits obtained (by the use of k^3-weighting). Although there are some differences between PtIn samples because the sample
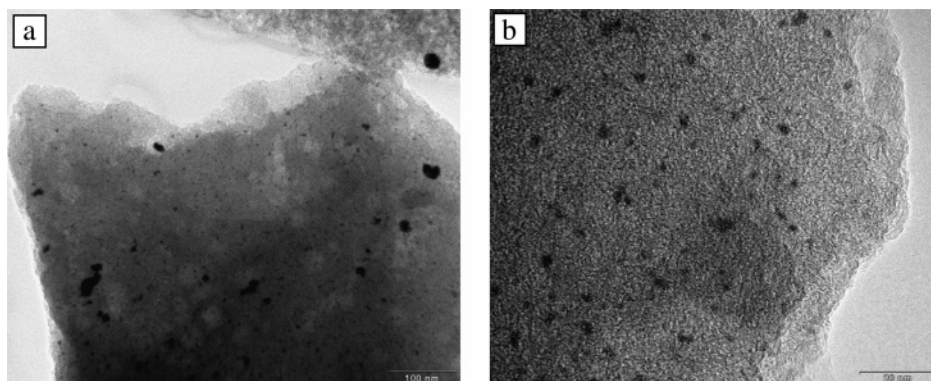
Figure 6. (a,b) TEM images of the sample PtSn/C (SI) reduced, with low magnification (a) and high magnification (b).
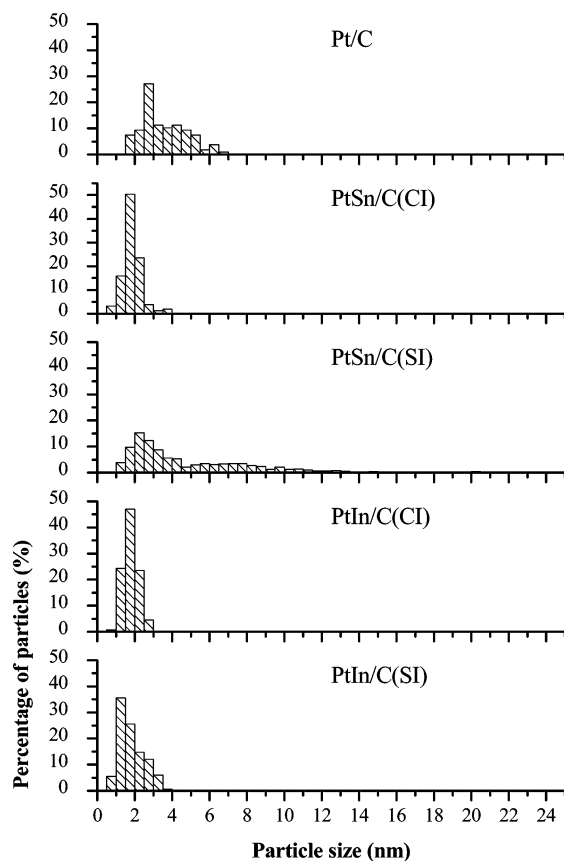

Figure 7. Particle size distributions of the reduced catalysts measured by TEM.

TABLE 4: Mean Particle Size, Reaction Rate, and Activation Energy for Cyclohexane Dehydrogenation

sample	mean particle size (nm)	reaction rate (mol/hg$_{Pt}$)	E_a (Kcal/mol)
Pt/C	3.6 ± 1.2	32.0	19.6
PtSn/C (CI)	1.8 ± 0.5	2.2	29.4
PtSn/C (SI)	4.9 ± 3.5	3.0	28.8
PtIn/C (CI)	1.8 ± 0.4	11.2	23.0
PtIn/C (SI)	1.8 ± 0.7	4.9	30.0

XPS and XAFS data reveal a higher homogeneity in the metallic phase formed in PtIn/C than in PtSn/C catalysts after the reduction treatment. In relation to this observation, Passos et al.,[3,4] comparing the behavior of PtSn and PtIn catalysts supported on Al_2O_3 in hydrogenolysis reactions, also concluded that Pt surface atoms were more homogeneously diluted or covered by In than by Sn. The XAFS data also show that the effect of the preparation method in the state and structure of platinum in the reduced samples is less important for PtIn/C than for PtSn/C catalysts.

In relation with the previous discussion, it must be mentioned that only XAFS data at the Pt L(III)-edge are available in this work, and therefore the information obtained about the bimetallic phase is not confirmed with results from the investigation of Sn and In edges.

3. TEM Analysis. Analysis of TEM images shows that with the exception of sample PtSn/C (SI) the particle size of bimetallic catalysts ranges between 0.5 and 4 nm. In the sample PtSn/C (SI), there are also larger particles of different size, up to about 25 nm. Figure 6a,b shows TEM images of this sample. In the monometallic catalyst (Pt/C), the particle size, ranges between 1.5 and 7 nm. Figure 7 shows the particle size distribution determined from TEM images for the five catalysts under investigation. Energy-dispersive X-ray (EDX) analysis confirms that the particles are composed of Pt and Sn or In. To determine the average particle size, statistical analyses have been performed with percentiles of 95%, uncertainties are the corresponding standard deviations, and thus ranges of particle size contain 95% of the total population. The results are shown in Table 4. These data indicate that in general (with the exception of sample PtSn/C (SI)) the addition of the second metal (Sn or In) produces a decrease of the mean particle size and a narrower particle size distribution. The preparation method (CI versus SI) also affects the average particle size and the particle size distribution. Thus, the CI method produces smaller particles and narrower distributions than SI. On the other hand, in general, PtIn samples have narrower particle size distribution and are more homogeneous than PtSn catalysts. We also observed these tendencies in XPS and XAFS results, and it seems that the surface composition and the state and structure

prepared by coimpregnation possesses also the Pt_3In_2 bimetallic compound, the preparation method (CI versus SI) influences the formation of different structures in a lesser extent than in the case of PtSn samples.

The analysis of the X-ray absorption near-edge structure (XANES) zone (Figure 5) shows, as well, a great similarity in the electronic state of platinum in both PtIn catalysts. The intensity of the white line is very close to the one corresponding to platinum foil, indicating that the deviation from the zerovalent state is low. Contrarily, in the case of the PtSn catalysts platinum is more electrodeficient in the sample prepared by coimpregnation. This result agrees with the largest interaction of platinum with more electronegative atoms like O, which results in a high-intensity peak in the FT-EXAFS at about 2 Å (Figure 3). The intensity of the white line in catalyst PtSn/C (SI) is lower than that in platinum foil. This can be explained by the presence of a large proportion of PtSn alloy in which the electron density in platinum atoms is higher.

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of catalyst particles are related with the particle size and particle size distribution.

4. Activity for Cyclohexane Dehydrogenation. Catalytic activity data of the mono- and bimetallic catalysts have been included in Table 4. As expected, the addition of the second metal produces a noticeable decrease of the catalytic activity. Such a decrease is more pronounced in the PtSn catalysts. The two PtSn samples show a similar catalytic activity for this structure insensitive reaction indicating that both contain a similar amount of active sites, that is, similar amount of exposed, electronically active, platinum atoms. The high Sn/Pt surface ratios determined by XPS (Table 1) point to an important blockage effect of tin. This could explain the low catalytic activity and the similar behavior of both PtSn catalysts. In the case of PtIn catalysts, there is not an important surface enrichment in indium. That is, a blockage effect can be ruled out, and the reduced catalytic activity must be a consequence of either different particle size or an electronic modification of Pt sites by interaction with In. The difference in catalytic activity between catalysts PtIn/C (SI) and PtIn/C (CI) could be related to the mean particle size in PtIn samples with the most active catalyst being the one with the smallest particles (low mean size and narrow size distribution, PtIn/C (CI)). Nevertheless, the small difference in the particle size (Table 4 and Figure 7) cannot explain a difference of more than twice in the catalytic activity. Therefore, it must be due to an electronic modification of platinum atoms. This is also supported by the higher E_a (observed activation energy) found for the bimetallic catalysts and particularly for catalyst PtIn/C (SI). A higher-catalytic activity of sample PtIn/C (CI) can be explained by differences in PtIn alloying in the two samples. As deduced from XAFS analysis, the main bimetallic phase in PtIn/C (SI) is Pt_3In, while in PtIn/C (CI) apart of Pt_3In, Pt_3In_2 may be also present. In summary, the higher activity of Pt in sample PtIn/C (CI) could be related to the presence of different type of alloyed species, particularly Pt_3In_2 (Table 3), or to a lower blockage of Pt by In (Table 1). In the case of Sn, the effect of the electronic modification of Pt by alloying is surely also present, but it seems that the blockage effect plays a more important role.

As a final consideration, it must be mentioned that the structure of the catalysts under reaction conditions can differ from that of the reduced samples. In the present case, however, because of the relatively mild reaction conditions, large differences are not expected.

Conclusions

The XAFS study of the bimetallic PtSn and PtIn carbon-supported catalysts reveals clear differences in the state of platinum related with the preparation procedure (CI or SI) and with the nature of the second metal. In the reduced PtSn/C and PtIn/C catalysts, platinum is found in several types of structures in different proportion depending on the preparation method. XAFS data reveal that together with platinum metal, Pt_3Sn and Pt_3In bimetallic compounds are the most common structures in PtSn and PtIn samples, respectively. There is not a direct correlation between the large differences in terms of elements distribution measured by XPS and the stoichiometry of the bimetallic compounds formed. The fact that several structures coexist in these catalysts complicates the analysis, the fit, and the interpretation of the XAFS data and emphasizes the heterogeneity of these samples. From the TEM analysis, it is concluded that, in general, in the bimetallic catalysts the mean particle size is smaller and the particle size distribution is narrower than in the monometallic Pt/C catalyst. There is also

an effect of the preparation method as the coimpregnation method produces smaller particles and narrower distributions than the successive impregnation. Moreover, PtIn catalysts have narrower particle size distribution than PtSn, and therefore they are more homogeneous. Results on the catalytic activity for cyclohexane dehydrogenation, a structure insensitive reaction, clearly reveal the blockage effect of tin in PtSn/C catalyts and the electronic modification of Pt by alloying in PtIn/C catalysts.

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