Catalysis Letters 21 (1993) 309–320

Pt–Sn / Al_2O_3 sol–gel catalysts: metallic phase characterization

R. Gomez [1], V. Bertin, P. Bosch, T. Lopez
Department of Chemistry, Universidad Autonoma Metropolitana-I, PO Box 55-534, Mexico 09340 DF, Mexico

P. Del Angel and I. Schifter
Instituto Mexicano del Petroleo-IBP, Eje Central Lazaro Cardenas 152, Mexico 07300 DF, Mexico

Received 5 May 1993; accepted 9 July 1993

Highly dispersed platinum was found in Pt–Sn/Al_2O_3 catalysts prepared by the sol–gel method, i.e., cogelation of aluminum tri-sec-butoxide and tetrabutyltin and subsequent impregnation with hexachloroplatinic acid. X-ray diffraction studies showed that the cell parameter of pure platinum is not modified in bimetallic Pt–Sn samples. Moreover, energy dispersive X-ray analysis studies (EDX) showed that platinum, but not tin, was detected in the catalysts where tin was incorporated by the sol–gel coprecipitation of tin and aluminum. Incorporation of tin into the alumina network is suggested.

Keywords: Sol–gel catalysts; platinum–tin catalysts; platinum dispersion; X-ray diffraction; energy dispersive X-ray analysis; EDX analysis

1. Introduction

The need of continuous regenerations of metal supported catalysts to produce high octane number gasolines, has renewed the importance of Pt–Sn/Al_2O_3 catalysts. Consequently, a great number of papers has been devoted to the characterization of the Pt–Sn/Al_2O_3 catalysts [1–5]. Interest has been focused on the alloy formation and numerous papers have been written to define the type of alloys and the amount of alloyed metal, using techniques like infrared spectroscopy [6], X-ray photoelectron spectroscopy [7], transmission electron microscopy [8], ion scattering spectroscopy and Auger electron spectroscopy among others [9].

Both hydrogen chemisorption and catalytic activity, decrease drastically alloy-

---

[1] To whom correspondence should be addressed.

ing platinum with tin [10,11]. Tin, in these alloys, acts as a diluent of the platinum clusters [12]. Hydrogenolysis as well as deactivation values decrease as a consequence of the division of the platinum surface into small ensembles of platinum atoms which cannot hydrogenolyse [13]. In most cases, the preparation method is the wet coimpregnation of the alumina support with solutions of $SnCl_4$ and hexachloroplatinic acid. The use of Pt–Sn complexes like $[Pt_3Sn_8Cl_{20}]^{2-}$ [14] or $[PtCl_2SnCl]_3^{2-}$ [15–17] as impregnating precursors has also been studied and similar results to those obtained using the co-impregnation method have been reported.

In the industrial preparation of Pt–Sn/Al_2O_3 catalysts, tin precursor, often $SnCl_4$, is added during the synthesis of the alumina support, i.e., tin compounds are mixed with aluminum nitrate in basic medium. Hence, the use of aluminum gels has been proposed [18]. In preparations close to the industrial procedure, interesting papers have been written. The formation of chemically stable compounds like tin aluminates or tin oxides are mentioned as responsible of the high performance of Pt–Sn/Al_2O_3 catalysts [1,19–23]. It is clear, then, that alloy, tin oxides or tin aluminate formation is determined by the preparation procedure.

The understanding of the role of tin in platinum catalysts is a hard work: Does it modify the metal activity? Does it modify the support properties through the formation of tin oxide or tin aluminate or both? If, as a large number of publications claim, platinum–tin alloys are inactive, it is clear, then, that tin, in bimetallic Pt–Sn supported catalysts, essentially acts as a dope into the support. The main effect of tin has to be found in the modifications of the textural and structural properties of the support rather than in the modification of the metallic phase.

In this context, the sol–gel method, i.e., the addition of a metal precursor (tin in this case) to an aluminum alkoxide, seems to be a good alternative as it has been reported in a previous work [24]. With this purpose in mind, in the present work, Pt–Sn/Al_2O_3 catalysts were prepared from aluminum tri-sec-butoxide, tetrabutyltin and hexachloroplatinic acid. The metallic phase characterization was performed by H_2–O_2 chemisorption, X-ray diffraction, electron microscopy and energy dispersive X-ray analysis (EDX). The catalytic properties of these sol–gel preparations will be reported in a subsequent paper.

2. Experimental

2.1. CATALYST PREPARATION

Sol–gel catalysts were prepared adding to a solution containing *n*-butanol and tetrabutyltin (ICN K&K 99.9%) another solution containing aluminum tri-sec-butoxide (Aldrich 99%) in *n*-butanol. The homogeneous solution was refluxed and hydrolysis was obtained adding water. After gelling, the solids were dried at 70°C and calcined at 300°C and later impregnated with an aqueous solution containing $H_2PtCl_6 \cdot 6H_2O$. The water excess was evaporated and then the solids were dried and calcined in air for 3 h at 500°C. The reduction was accomplished in hydrogen flow at 500°C for 3 h. The amounts of tetrabutyltin and hexachloroplatinic acid were calculated to obtain tin and platinum concentrations between 0.3 and 1.0 wt%. The catalysts prepared by this method were labeled Pt–Sn-0.0–0.0 where the figures indicate the platinum and tin concentration respectively.

Two reference catalysts were obtained by wet impregnation of commercial alumina (Rhone Poulenc SCS 250, BET area 250 m^2/g). Monometallic platinum reference was obtained by impregnation of the alumina support with an aqueous solution of hexachloroplatinic acid, afterwards the solid was dried and calcined at 500°C. Reduction was accomplished under hydrogen flow at 500°C for 3 h. A bimetallic reference catalyst was prepared by successive impregnation. A *n*-butanol solution of tetrabutyltin was used to impregnate the alumina support. The resulting solid was dried and calcined at 300°C, later impregnated with an aqueous solution containing hexachloroplatinic acid. The final slurry was then dried and calcined at 500°C. As in the sol–gel preparation, reduction was accomplished in hydrogen flow at 500°C for 3 h. These catalysts were labeled Pt–I-0.3 and Pt–Sn–I-0.3–0.3 where the figures are the metal content of platinum and tin respectively.

2.2. CHEMISORPTION

Hydrogen–oxygen chemisorption and carbon monoxide sorption were used to determine metallic dispersion. Samples of the reduced catalysts were reactivated in situ at 400°C in a Cahn electrobalance under hydrogen flow for 2 h and, then, evacuated at 10^{-5} Torr. Dispersion measurements were obtained from the hydrogen–oxygen titration method [15,25]. Irreversible gas uptakes were determined at 70°C. A hydrogen pressure (10 Torr) was introduced into the gravimetric system and then evacuated. Irreversible adsorbed hydrogen was then titrated by oxygen under a pressure of 100 Torr. In separated reduced samples, carbon monoxide was adsorbed at 25°C. A carbon monoxide pressure (100 Torr) was introduced and then evacuated.

2.3. ELECTRON MICROSCOPY

The metal characterization was performed using a JEOL 100 CX electron microscope equipped with a STEM (scanning transmission electron microscope) attachment and an X-ray detector. The X-ray signal was transferred to a Tracor Northern 500 computer which recorded the spectra and performed both quantitative and qualitative data manipulation. Samples were prepared dispersing ultrasonically the catalyst powders in absolute isopropanol. The sample was placed in a coated copper grid and then exposed to the electron beam for their study. The particle size determinations were carried out measuring randomly the size of approximately 500 particles in the STEM micrographs. The quantitative analysis of the

EDX (energy-dispersive X-ray microanalysis) spectra was carried out using a standardless-thin-film technique. Integrated intensities of the platinum and tin X-ray lines were obtained using a least-squares-digital filter routine.

2.4. X-RAY DIFFRACTION

The X-ray diffraction measurements were obtained with a Siemens D500 X-ray diffractometer and a diffracted beam monochromator which selected the Kα copper radiation. The (111) platinum reflexion was measured introducing an internal standard (corundum), from this interplanar distance the platinum cell parameter was estimated. From the diffraction peak a mean diameter can be obtained, but, if the intensity profile is considered, the crystallite size distribution is provided, as shown by Alvarez et al. [26,27]: as the Pt content was very low and the alumina peak masks the Pt (111) peak, only the mean diameter is reported.

3. Results

3.1. METAL DISPERSION

Platinum dispersion was estimated from hydrogen titration by oxygen [28]. Under the chosen experimental conditions, one can assume that all the oxygen consumed for the hydrogen titration refers to platinum, according to the following reaction: $\text{Pt–H} + \frac{3}{4}O_2 \rightarrow \text{PtO} + \frac{1}{2}H_2O$. The dispersion values obtained by this method are reported in table 1. Dispersion was also estimated from carbon monoxide adsorption. Table 1 shows that, in low platinum content catalysts, the H_2–O_2 tritation gives dispersion values lower than those obtained by carbon monoxide adsorption. Although a part of the oxygen could be consumed in reacting with Sn(0), at high platinum content (1.0 wt%) both methods are in good agreement. It

Table 1
Platinum dispersion and mean particle size obtained from H_2–O_2 titration and carbon monoxide adsorption

Catalysts	H_2–O_2		Carbon monoxide	
	dispersion (%)	particle size (Å)	dispersion (%)	particle size (Å)
Pt–Sn-0.3–0.3	50	20	90	10
Pt–Sn-0.5–0.3	43	23	90	10
Pt–Sn-1.0–0.3	50	20	50	20
Pt–Sn-0.3–0.5	40	25	40	25
Pt–Sn-0.3–1.0	90	10	90	10
Pt–I-0.3	–	–	63	16
Pt–Sn–I-0.3–0.3	–	–	50	20

seems, then, that the hypothesis of oxygen consumed by tin is not probable in these samples. Using either H_2–O_2 titration or CO adsorption, the catalysts were found highly dispersed in both preparations, sol–gel and impregnation. The corresponding mean crystallite size was calculated assuming a spherical shape for platinum particles.

3.2. PARTICLE SIZE DISTRIBUTION DETERMINED BY STEM

The particles size distributions for the various catalysts were obtained from the STEM micrographs. The maximum of the particle size distribution is found around 30 Å. The particle size was calculated and reported in table 2 using the ratio volume/surface, $\sum nD_i^3 / \sum nD_i^2$, calculation which provides the most representative mean particle diameter [28]. The mean diameter is around 30 Å, a value which is not so far from the one obtained by gas chemisorption in high Pt metal content catalysts.

3.3. X-RAY DIFFRACTION

The mean volume crystallite size was calculated from X-ray spectra by the method reported in refs. [26,27]. The results are summarized in table 2. Mean volume crystallite sizes are larger than those obtained from electron microscopy histograms and chemisorption. X-ray diffraction provides D_v values which are always larger than mean surface crystallite size. The method is not very sensitive to very small particles.

Selected X-ray spectra using a corundum standard are shown in fig. 1, the position of the platinum peak is shown. No shift is observed in anyone of the catalysts. In bimetallic catalysts the platinum cell parameter is $a_0 = 3.92$ Å, this value agrees with the cell parameter of the monometallic sample. If this value is compared with the value reported in the JCPDS 4-0802 card ($a_0 = 3.9231$ Å) no difference is observed in the error range (±0.01 Å).

Table 2
Comparative platinum particle size (Å), measured by chemisorption, STEM and X-ray diffraction techniques

Catalysts	CO chemisorption	STEM	X-ray diffraction
Pt–Sn-0.3–0.3	10	30	58
Pt–Sn-0.5–0.3	10	30	51
Pt–Sn-1.0–0.3	20	25	64
Pt–Sn-0.3–1.0	10	–	78
Pt–I-0.3	16	30	50
Pt–Sn–I-0.3–0.3	20	30	60

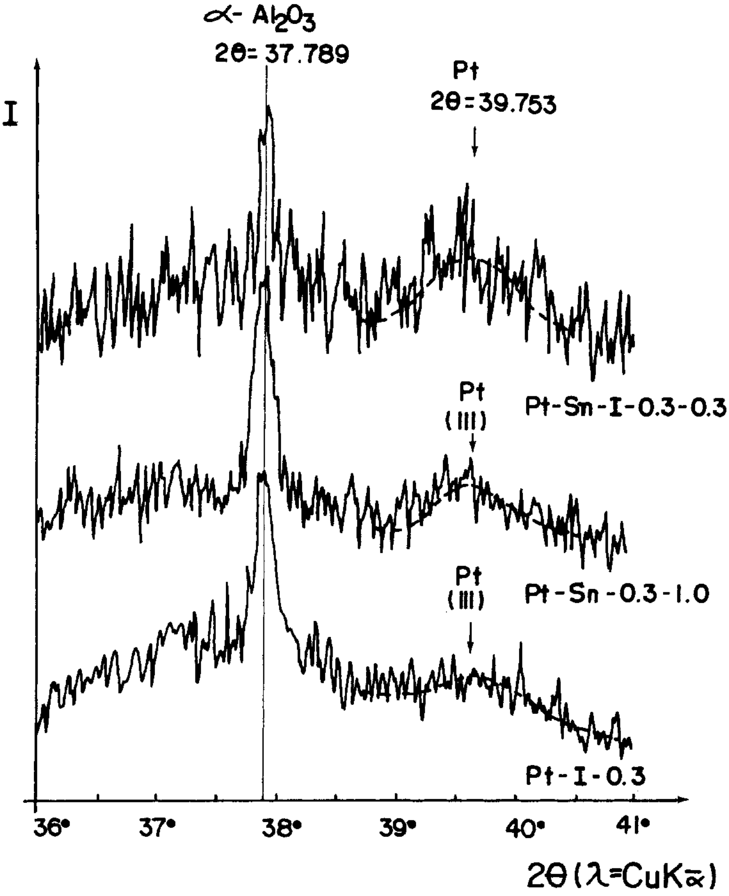

Fig. 1. The (111) platinum diffraction peak in Pt–Sn sol–gel catalysts.

3.4. EDX SURFACE ANALYSIS

EDX measurements on selected samples were obtained exposing the sample to the electron beam for 600 s. Typical EDX spectra are shown in figs. 2 and 3. The EDX spectra analyses were obtained analysing both "large zones" of about 7,500 μm^2 (labeled LZ) and "small zones" of 0.5 μm^2 (labeled SZ). The results are reported in table 3, where MLZ and MSZ are the mean values for large and small zones respectively.

The results of table 3 show that almost only platinum is detected in sol–gel preparations (large and small zones) while in the impregnated catalyst both platinum and tin are detected. The determination of the platinum metal concentration can be considered in good agreement with the nominal value if the limits of the technique are considered. However, the most significant result obtained by EDX is the appar-

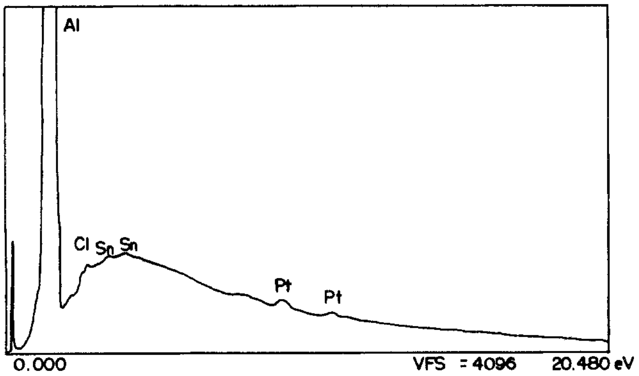

Fig. 2. Typical EDX spectrum for sol–gel Pt–Sn-0.3–1.0 alumina supported catalysts.

ent impossibility to detect tin X-ray emission in sol–gel preparations even if tin concentration reached 1.0 wt%, fig. 4.

The absence of tin signal in sol–gel catalysts can be due to two effects: (i) tin particles are well dispersed on the alumina support, and hence the accumulative signal is too small or (ii) tin is incorporated into the alumina network and it cannot be detected, as the concentration is very low. Such is not the case in the impregnated sample: tin was incorporated by impregnation of the support and the interaction tin–alumina is limited to the surface layers of the support. In this case EDX analysis detects tin and the amount agrees with the nominal composition, fig. 5.

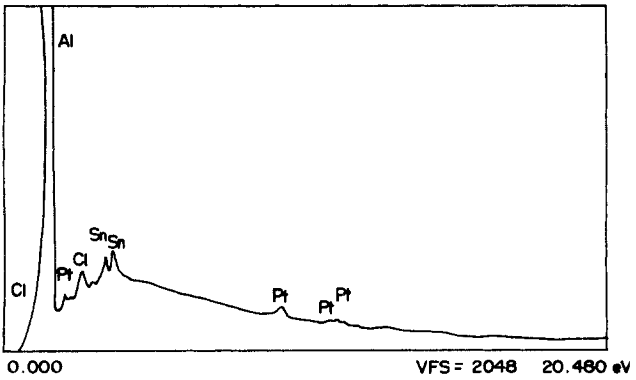

Fig. 3. Typical EDX spectrum for impregnated Pt–Sn–I-0.3–0.3 alumina supported catalysts.

Table 3
EDX mean zone analysis of the bimetallic Pt– Sn/Al_2O_3 catalysts

Catalysts	Large zone		Small zone	
	%Pt	%Sn	%Pt	%Sn
Pt–Sn-0.3–0.3	0.36	0.02	0.63	0.02
Pt–Sn-1.0–0.3	2.1	0.00	1.04	0.00
Pt–Sn-0.3–1.0	0.34	0.00	0.33	0.00
Pt–Sn–I-0.3–0.3	0.24	0.42	0.23	0.37

4. Discussion

In bimetallic catalysts the determination of the particle size is a difficult task, since it is not easy to discriminate particles from one metal or the other. Moreover, bimetallic particles have also to be considered. However, in the catalysts studied in this work, the determination of the particle size has been done using two selective techniques which determine only the platinum particle size: (i) hydrogen titration with oxygen and X-ray diffraction. Electron microscopy technique does not discriminate between platinum and tin at least for the particle size expected in our catalysts.

In table 1 dispersions obtained by hydrogen titration and carbon monoxide adsorption are reported. Recently Balakrishnan and Schwank [4], found that, in bimetallic Pt–Sn/Al_2O_3 catalysts, the carbon monoxide adsorption values are higher than those obtained by hydrogen chemisorption. The dilution of platinum atoms by tin may be a plausible interpretation. As hydrogen needs at least two sites

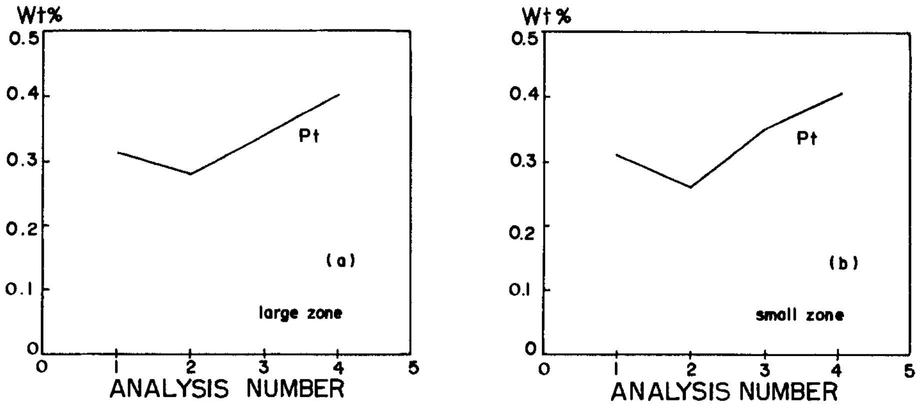

Fig. 4. EDX analysis for sol–gel Pt–Sn-0.3–1.0 alumina supported catalysts.

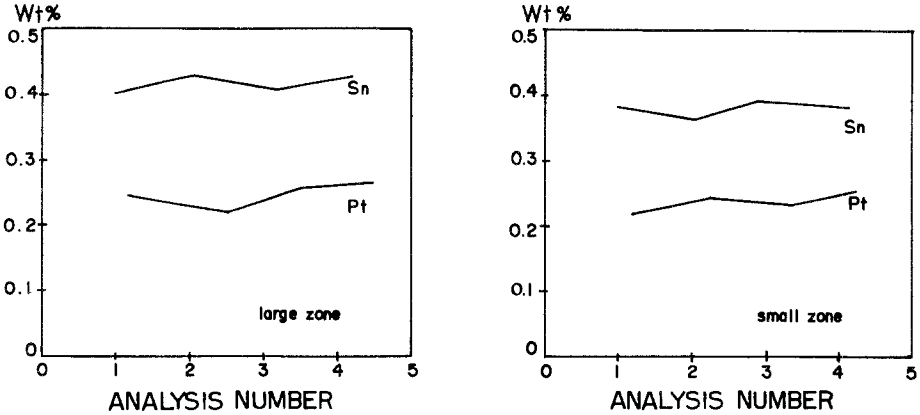

Fig. 5. EDX analysis for impregnated Pt–Sn–I-0.3–0.3 alumina supported catalysts.

for its dissociation and carbon monoxide needs only one, thus, carbon monoxide is less sensitive to dilution effects. The analysis of table 1 for sol–gel catalysts shows that carbon monoxide adsorption is higher than hydrogen titration. This result is in good agreement with those found by Balakrishnan and Schwank [4]. Note that in table 1 the hydrogen titration by oxygen determines correctly the number of hydrogen atoms preadsorbed on platinum atoms, since we do not obtain an increase in oxygen volume due to the increasing tin content [4]. Thus, oxidation of tin is not observed in sol–gel preparations.

Comparative results on particle size determination for mono and bimetallic catalysts are summarized in table 2. We will refer to the carbon monoxide chemisorption results, since it seems that this method is less sensitive to ensemble effects [4]. If adsorption values are used, the mean particle size is between 10 and 25 Å, no effect of tin is observed on platinum particle size. 0.3 or 1.0 wt% tin catalysts show the same platinum particle size. This result shows that the dispersive effect of tin in bimetallic Pt–Sn catalysts can be ruled out, at least in sol–gel preparations.

Electron microscopy histograms report a mean particle size diameter of around 30 Å. The disagreement between the small particles determined by chemisorption and the large ones obtained by electron microscopy, can be due to the resolution of the STEM microscope. The STEM JEOL 100 CX apparatus does not allow the observation of particles smaller than 20 Å. The mean particle size was calculated then from this value to higher ones. Nevertheless, note that the maxima in all the catalysts are found close to the detection limit. If this fact is taken into account the small particles measured by chemisorption must be the most representative. On the other hand X-ray diffractograms give values around 70 Å (volume mean crystallite size). Chemisorption calculations and electron microscopy observations report surface mean size values. Since from X-ray diffractograms a volume mean size is calculated, this disagreement is only apparent. If particles are isotropic, the diameter number distribution is clearly defined: $F_n(D)$ is the number of particles whose diameters lie between D and $D + dD$, and $\int F_n(D)\, dD = 1$. Likewise surface and volume particle size distributions are defined, $F_s(D)$ and $F_v(D)$; for instance $F_s(D)\, dD$ is the fraction of the total area of the sample due to particles whose diameters are comprised between D and $D + dD$. The mean diameter $\bar{D}_s$ is then defined as

$$\bar{D}_s = \int_0^{Dmax} F_s(D)\, dD = \sum nD^3 / \sum nD^2 ,$$

$$\bar{D}_v = \int_0^{Dmax} F_v(D)\, dD = \sum nD^4 / \sum nD^3 .$$

In the case of very broad or bimodal distributions, $\bar{D}_s$ and $\bar{D}_v$ may be very different. Chemisorption calculations use the sphere shape relationship $S = 6/\rho\, D_s$, electron microscopy estimation uses $\sum nD^3/nD^2$ and X-ray diffraction $\sum nD^4/\sum nD^3$. Thus, results of table 2, are in good agreement using the three methods, since the particle size follows the order: chemisorption < electron microscopy < X-ray diffraction. Moreover, if, in the results of table 2, the resolution limit of STEM microscope around 20 Å is considered, and that of X-ray diffraction around 35 Å, we can conclude that the mean particle sizes reported in the comparative table 2 define well the size of the platinum metal particles. Thus, to summarize, in monometallic or bimetallic Pt–Sn/Al_2O_3 catalysts prepared by the sol–gel method the platinum particles are highly dispersed.

In a recent paper, Srinivasan et al. [2] prepared Pt–Sn/Al_2O_3 catalysts by two methods: (i) coprecipitation of $SnCl_4$ and aluminum nitrate in basic medium and, then, impregnation with hexachloroplatinic acid and (ii) impregnation of an alumina support with a hexachloroplatinic acid and $SnCl_4$ solution. They observed by X-ray diffraction the formation of Pt–Sn alloys if the coimpregnation method was used. On the contrary, using coprecipitation method only platinum peaks are observed. X-ray diffraction patterns of sol–gel catalysts (fig. 1) show platinum peaks only. This result is in agreement with that obtained on a coprecipitated sample prepared by Srinivasan et al. [2]. However, the same effect is reported for our impregnated reference catalyst in opposition to the alloys observed in wet coimpregnated catalysts [2]. This disagreement may be attributed to the successive impregnation instead of coimpregnation method. Such result suggests that in both, sol–gel and impregnated catalysts, the formation of alloys does not occur, at least for low metal content catalysts.

The EDX analysis of the samples confirms the X-ray results. In fig. 4 the EDX analysis obtained in a sol–gel sample is shown. The elemental analysis of the surface does not reach zones in which tin and platinum coexist even if tin content is 1.0 wt%. EDX analysis has been shown to be an alternative technique to detect the possible formation of bimetallic clusters in supported Pt–Ru catalysts [29,30]. In our case the total absence of tin signal in sol–gel preparations suggests that in such catalysts the metal is not found on the support surface. Therefore it must be incorporated into the alumina network. The EDX analysis of the impregnated bimetallic catalysts shows that both tin and platinum are found coexisting on the support surface, fig. 5. However, this result does not confirm the formation of Pt–Sn alloys.

5. Conclusions

The results obtained by oxygen and carbon monoxide adsorption in bimetallic Pt–Sn / Al_2O_3 prepared by the sol–gel method or by impregnation show that in both preparations the platinum metal is highly dispersed. Such results were confirmed by X-ray diffraction and electron microscopy studies. Particle size obtained from these techniques agree well with chemisorption values if one considers that in the first case a volume particle size is obtained and for electron microscopy a surface mean diameter is reported. The determined particle size shows the expected sequence: chemisorption < electron microscopy < X-ray diffraction.

The study of bimetallic particles by X-ray diffraction and EDX analysis shows that in sol–gel preparations only platinum is detected. Tin must be incorporated into the alumina network. In the impregnated catalyst, platinum and tin are found coexisting on the support surface. However, they must be in phases apart i.e., tin oxide and platinum particles. These results suggest that, in the preparation of Pt–Sn / Al_2O_3 catalysts by the sol–gel method, the incorporation of tin into the alumina network occurs. The effect of tin, then, in sol–gel preparations must be found in the modifications of the support properties as acidity or texture rather than in the platinum activity. Such effect should modify the side reactions i.e. dealkylation, and deactivation, occurring in the reforming of naphta.

Acknowledgement

We acknowledge the support given by CONACYT, CNRS and NSF.

References

[1] R. Srinivasan and B.H. Davis, Platinum Metal Rev. 36 (1992) 151.
[2] R. Srinivasan, L.A. Rice and B.H. Davis, J. Catal. 129 (1991) 257.
[3] B. Coq and F. Figueras, J. Catal. 85 (1984) 197.
[4] K. Balakrishnan and J. Schwank, J. Catal. 127 (1991) 287.
[5] W. Unger, G. Lietz, H. Lieske and J. Volter, Appl. Surf. Sci. 45 (1990) 29.
[6] A.G.T.M. Bastein, F.J.C.M. Toolenaar and V. Ponec, J. Catal. 90 (1984) 88.
[7] Y.X. Li, J.M. Stencel and B.H. Davis, Appl. Catal. 64 (1990) 71.
[8] B.E. Handy, J.A. Dumesic, R.D. Sherwood and T.K. Baker, J. Catal. 124 (1990) 160.

[9] S.D. Gardner, G.B. Hoflund, M.R. Davison and D.R. Schryer, J. Catal. 115 (1989) 132.
[10] A. Palazov, Ch. Bonev, D. Shopov, G. Lietz, A. Sarkany and J. Volter, J. Catal. 103 (1987) 249.
[11] G.T. Baronneti, S.R. de Miguel, O.A. Scelsa and A.A. Castro, Appl. Catal. 24 (1986) 109.
[12] F.M. Dautzenberg, J.N. Helle, P. Biloen and W.M.H. Sachtler, J. Catal. 63 (1980) 119.
[13] B. Coq and F. Figueras, J. Mol. Catal. 25 (1984) 87.
[14] R. Srinivasan, R.J. de Angelis and B.H. Davis, J. Catal. 106 (1987) 449.
[15] A. Campero, M. Ruiz and R. Gomez, React. Kinet. Catal. Lett. 5 (1976) 177.
[16] V.H. Berndt, H. Mehner, J. Volter and W. Meisel, Z. Anorg. Allg. Chem. 429 (1977) 47.
[17] V.I. Kuznetsov, A.S. Beleyi, E.N. Yurchenko, M.D. Smolikov, M.T. Protasova, E.V. Zatolokina and V.K. Doplyaki, J. Catal. 99 (1986) 159.
[18] G.J. Antos and A. Heights, UOP, US Patent 3,929,683 (1975).
[19] R. Burch, J. Catal. 71 (1981) 348.
[20] R. Burch and L.C. Garla, J. Catal. 71 (1981) 360.
[21] G. Meitzner, G.H. Via, F.W. Lytle, S.C. Fung and J.H. Sinfelt, J. Phys. Chem. 92 (1988) 2925.
[22] S.R. Adkins and B.H. Davis, J. Catal. 89 (1984) 374.
[23] B.A. Sexto, A.E. Hughes and K. Foger, J. Catal. 88 (1984) 466.
[24] R. Gomez, V. Bertin, M.A. Ramirez, T. Zamudio, P. Bosch, I. Schifter and T. Lopez, J. Non-Cryst. Sol. 147/148 (1992) 748.
[25] R. Bacaud and F. Figueras, Compt. Rend. Acad. Sci. Ser. C 281 (1975) 479.
[26] A.G. Alvarez, R.D. Bonetto, D.M.A. Guerin, A. Plastino and L. Rebollo Neira, Powder Diffraction 2 (1987) 220.
[27] R.D. Bonetto, H.R. Viturro and A.G. Alvarez, J. Appl. Cryst. 23 (1990) 136.
[28] R. Gomez, S. Fuentes, F.J. Fernandez del Valle, A. Campero and J.M. Ferreira, J. Catal. 38 (1975) 47.
[29] G. Del Angel, S. Alerasool, J.M. Dominguez, R.D. Gonzalez and R. Gomez, Surf. Sci. 234 (1989) 407.
[30] G. Del Angel, V. Bertin, P. Bosch, R. Gomez and R.D. Gonzalez, New J. Chem. 15 (1991) 643.