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# Structural aspects of $PtSn/\gamma$ - $Al_2O_3$ catalysts prepared through surface-controlled reactions: Behavior in the water denitrification reaction

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ABSTRACT

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#### 1. Introduction

Of all the water present on the earth surface, only 4.9% is available for human consumption. Of this minimum percentage 68% is present as groundwater, making it one of the main supplies for domestic use and irrigation for 50% of the population [1]. Today, part of this water is contaminated with concentrations of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> well above the maximum levels allowed by the U.S. Environmental Protection Agency (50 mg/L NO<sub>3</sub><sup>-</sup> and 1 mg/L NO<sub>2</sub><sup>-</sup>). While both NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> are part of the N<sub>2</sub> cycle and are present in water, soil and plants, their levels in the environment, especially in groundwater, have been increasing due to human activity [2]. The levels of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> are important indicators of water quality and their increase has been associated with pollution from eutrophication [3,4].

Elevated concentrations of nitrate in water sources lead to a potential risk to human health because nitrate is reduced to nitrite in the body. The toxicity of nitrite is primarily due to the fact that

0926-860X/\$ - see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.apcata.2012.12.034 it can react with secondary or tertiary amines present in human body to form nitrosamines, which are known to be carcinogens, and nitrite can react with iron(III) of hemoglobin to produce methe-

Sn added had a pronounced influence on the activity of the catalysts, being PtSn<sub>0.25</sub> catalyst the one with

the best performance. An explanation for this behavior is given in terms of the electronic and geometric

moglobinemia disease. [5,6]. Research and development of technologies to remediate contaminated water with  $NO_3^-$  have been steadily increasing over the past 20 years [7–11]. Different approaches have been proposed for the elimination of nitrates from groundwater. These include membrane separation [10], ionic exchange [8,12] and biological denitrification processes [13]. A potentially effective and economical alternative is based on the catalytic hydrogenation of  $NO_3^-$  to  $N_2$ . The catalysts currently used are based on bimetallic systems that are composed of a noble metal usually from groups 8, 9 and 10 (Pd, Rh, Ru or Pt) and a second metal such as Cu, Ag, Fe, Hg, Ni, Zn, Sn or In supported on different materials ( $Al_2O_3$ ,  $SiO_2$ , C, *etc.*) [14–18].

The activity and selectivity in the denitrification reaction of the bimetallic catalyst are highly dependent on the interaction between the metals, a fact that can be controlled by the preparation method, the nature of the promoter, the metal/promoter ratio and the operation conditions [18,19]. In this sense, the objective of this work is the study of PtSn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> bimetallic catalysts and, in order to obtain well-defined bimetallic catalysts, tin was introduced by means of







This research focuses on the controlled preparation and characterization of  $PtSn/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts and their activity and selectivity in water denitrification by reduction of  $NO_3^-$  and  $NO_2^-$  ions with hydrogen. The bimetallic PtSn catalysts were active in the hydrogenation of both  $NO_3^-$  and  $NO_2^-$  and the amount of

effects that the addition of tin exerts on Pt.

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Surface Organometallic Chemistry on Metals (SOMC/M) techniques [20,21]. The bimetallic catalysts so obtained are used in the water denitrification reaction. The activity and selectivity of the systems are analyzed as a function of the content of tin added.

# 2. Experimental

### 2.1. Catalyst preparation

The monometallic catalyst was prepared by ion exchange, using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as support (Air Products, surface area 190 m<sup>2</sup>/g; pore volume 0.50 m<sup>3</sup>/g), previously calcined at 500 °C for 2 h. The support was crushed and sieved in order to retain particles with mesh sizes between 60 and 100. The solid was contacted with an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> in an appropriate concentration so as to obtain 1 wt% Pt in the resulting catalyst. After 24 h of exchange at room temperature, the solid was repeatedly washed with distilled water, dried at 105 °C, calcined in air at 500 °C and reduced in H<sub>2</sub> at the same temperature, leading to the monometallic Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. After the reduction step, the Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was washed several times with ammonia solution (0.1 M) at room temperature, until negative reaction to chloride in the washing water.

The bimetallic PtSn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were prepared according to SOMC/M techniques. A portion of reduced Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was allowed to react with tetrabutyltin (SnBu<sub>4</sub>) in a paraffinic solvent. The reaction was carried out in H<sub>2</sub> atmosphere at either 90 °C in n-heptane or 120 °C in n-decane, depending on the amount of tin to be loaded. After 4 h of reaction, the liquid phase was separated and the solid was repeatedly washed with n-heptane. The material was then dried in N<sub>2</sub> at 90 °C and finally reduced in flowing H<sub>2</sub> at 500 °C for 2 h. The bimetallic catalysts were designated PtSn<sub>y</sub>, *y* being the Sn/Pt atomic ratio (*y* = 0, 0.25, 0.4 and 0.9). The chemical composition and nomenclature of all the catalysts prepared are listed in Table 1.

#### 2.2. Catalyst characterization

The platinum and tin contents were determined by atomic absorption spectroscopy (Varian Spectra AA55). The tin content of bimetallic catalysts was also measured by GC analysis, measuring the difference between the initial and the final concentration of tetra n-butyl tin in the impregnating solution. A good agreement was found between both methods. The gas chromatograph used was a Varian CP-3800 equipped with a flame ionization detector and a capillary column FactorFour CP8907 (VF-1 ms, 15 m × 0.25 mm ID, DF=0.25).

Temperature-programmed reduction (TPR) tests were carried out in a conventional reactor equipped with a thermal conductivity detector with a feeding flow of  $25 \text{ cm}^3 \text{ min}^{-1}$  (5% H<sub>2</sub> in N<sub>2</sub>) at a heating rate of  $10 \degree \text{C} \text{ min}^{-1}$ .

H<sub>2</sub> chemisorption measurements were performed in a static volumetric apparatus at ambient temperature. The method of the double isotherm was employed.

The size distribution of metallic particles was determined by transmission electron microscopy (TEM) using a JEOL 100 CX instrument. The samples were ground and ultrasonically dispersed in distilled water. For determining the particle size distribution histograms over 200 Pt particles were measured from micrographs taken directly from the screen using the clear field imaging. The mean particle size was obtained from the following expression (average volume-area diameter):

$$d = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$

where  $n_i$  is the number of particles with  $d_i$  size. This diameter is directly related to chemisorption measurements.

X-ray photoelectron spectra (XPS) were acquired with a multitechnique system (SPECS) equipped with an Al-K $\alpha$  100W X-ray source and a hemispherical electron analyzer PHOIBOS 150, operated in fixed analyzer transmission (FAT) mode. The spectra were collected at an energy pass of 30 eV. The powder samples were pressed to form a disk and mounted onto a manipulator that allowed their transfer from the pretreatment chamber to the analysis chamber. In the pretreatment chamber, the samples were reduced for 1 h at 400 °C in flowing H<sub>2</sub>. The spectra were recorded once the pressure in the analysis chamber reached a residual pressure of less than  $5 \times 10^{-9}$  mbar. As internal standard, the binding energy (BE) of the Al 2p peak at 74.5 eV was taken. The intensities were estimated by calculating the integral of each peak after subtracting the S-shaped background and fitting the experimental peak to a Lorentzian/Gaussian mix of variable proportion, using the Casa XPS program (Casa Software Ltd., UK).

#### 2.3. Catalytic test

The reaction was carried out in a 200 mL Pyrex glass semi-batch reactor equipped with a magnetic stirrer. In a typical run 200 mg of catalysts previously reduced under a flow of H<sub>2</sub> at 500 °C was loaded in the reactor that contained 90 mL of degassed distillated water. The reaction started when 10 mL of 1000 ppm NO<sub>3</sub><sup>-</sup> (precursor salt: NaNO<sub>3</sub>) or 1000 ppm NO<sub>2</sub><sup>-</sup> (precursor salt: NaNO<sub>2</sub>) was introduced in the reactor. The experiment was carried out at atmospheric pressure, at a temperature of 25 °C and a hydrogen flow of 400 mL min<sup>-1</sup>. The total time of a typical run was 3 h. To monitor the progress of the reaction, 1 mL of sample was taken periodically. The sample was filtered and then analyzed in an ion chromatograph (Metrohm 790 Personal IC) to determine NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> concentration. Ammonium ions were determined by potentiometry using a selective electrode, once the reaction had finished. The pH value for each sample was also measured.

### 3. Results and discussion

# 3.1. Preparation of bimetallic catalysts through SOMC/M techniques

The synthesis of bimetallic catalysts can be represented by the following global reaction:

$$Pt/\gamma - Al_2O_3 + ySnBu_4 + \frac{1}{2}yH_2 \xrightarrow{500\,^{\circ}C} PtSn_y/\gamma - Al_2O_3 + 4yBuH$$
(1)

The reaction between the monometallic Pt catalysts and SnBu<sub>4</sub> was followed by gas chromatography, which permitted establishing the total reagent consumption, and consequently, the *y* value that appears in Eq. (1). The amount of SnBu<sub>4</sub> fixed on the Pt catalyst is deduced from the difference between the initial concentration of SnBu<sub>4</sub> and the concentration after the reaction has been completed, that is when the concentration of SnBu<sub>4</sub> remains constant [22]. In order to study the specificity of the interaction between the monometallic Pt catalysts and SnBu<sub>4</sub>, blank experiments were conducted, in which SnBu<sub>4</sub> was contacted with the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. No detectable tin amounts on the support were observed [23].

The amount of tin fixed on platinum by SOMC/M techniques is a function of the SnBu<sub>4</sub> concentration used and the reaction temperature [24]. In order to obtain the Sn/Pt atomic ratios of 0.25 and 0.4, a reaction temperature of 90 °C (using n-heptane as solvent) was adequate to deposit the amount of SnBu<sub>4</sub> indicated in Table 1. To achieve the highest values of Sn/Pt atomic ratios studied in this paper (Sn/Pt  $\geq$  0.9), it was necessary to use a higher reaction temperature (120 °C) [21]. The treatment in hydrogen at 500 °C causes

#### Table 1

Chemical composition, nomenclature, metal dispersion and metal particle size of the catalyst studied.

Sample	Nomenclature	Pt (wt.%)	Sn (wt.%)	Sn/Pt (at/at)	H/Pt <sup>a</sup>	$d_{\text{TEM}}\left(\text{nm}\right)$	$D^{\mathbf{b}}$
$Pt/\gamma - Al_2O_3$	Pt	1.0	-	0	0.70	1.9	0.75
$PtSn_{0.25}/\gamma - Al_2O_3$	PtSn <sub>0.25</sub>	1.0	0.15	0.25	n.d.	2.0	0.73
$PtSn_{0.4}/\gamma - Al_2O_3$	PtSn <sub>0.4</sub>	1.0	0.24	0.4	0.20	2.0	0.73
$PtSn_{0.9}/\gamma-Al_2O_3$	PtSn <sub>0.9</sub>	1.0	0.54	0.9	n.d.	2.1	0.68

<sup>a</sup> Dispersion of Pt, number of hydrogen atoms chemisorbed to the total number of Pt atoms.

<sup>b</sup> Dispersion of Pt, measured from TEM data (for the procedure, see the text).

the detachment of all the organic fragments mainly as n-butane (butenes were observed only at trace levels) due to the hydrogenolysis of the Sn—C bonds, as has been determined in previous work [25].

As a result of the preparation procedure, a PtSn bimetallic catalyst is obtained, with a strong interaction between both metals, as suggested by the use of a controlled method of preparation, based on the specific chemical reaction between the precursors (Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SnBu<sub>4</sub>).

#### 3.2. Temperature-programmed reduction (TPR)

Fig. 1 shows TPR profiles of the monometallic and the different PtSn<sub>y</sub> bimetallic catalysts studied. Two peaks appear in the monometallic Pt catalyst profile: the main peak at low temperature, centered around 180 °C, and a second peak centered at 450 °C. Literature data indicate that this profile is due to two types of Pt oxides in the monometallic catalyst, one in weak and the other in strong interaction with the support [26]. This reduction profile is in agreement with others previously published [27], and is characteristic of a Pt/Al<sub>2</sub>O<sub>3</sub> system subject to a chloride removal process after the impregnation step.

Sn-modified systems (Fig. 1) show a shift toward lower temperatures of the high-temperature peak, which can be assigned to the reduction of both platinum oxides and a fraction of Sn oxides. In all the cases the reduction of tin oxides occurs at temperatures much lower than those in the literature, where temperatures above  $630 \,^{\circ}$ C are reported for SnO<sub>2</sub> [28]. The selectivity of the preparation reaction leads to a close relationship between Pt and Sn atoms; Pt atoms generate atomic hydrogen by dissociative adsorption, these hydrogen atoms being able to reduce a fraction of tin oxides closely related to transition metal atoms. Thus, the reaction temperature of Pt is the one that controls the global reduction process.



Fig. 1. TPR patterns of (a) Pt; (b) PtSn<sub>0.25</sub>; (c) PtSn<sub>0.4</sub> and (d) PtSn<sub>0.9</sub> catalysts.

# 3.3. Hydrogen chemisorption and transmission electron microscopy (TEM)

The dispersion of the catalysts presented in this paper was analyzed by TEM and H<sub>2</sub> chemisorption. TEM results indicate that the systems obtained presented a narrow distribution of particle sizes as is shown in Table 1. Fig. 2 presents the particle size distributions for the monometallic Pt catalyst and the bimetallic with the highest tin content, PtSn<sub>0.9</sub> and there it can be seen that distribution for the bimetallic catalyst followed that of the monometallic catalyst, with a slight increase in the mean size of the supported metal particles. This latter observation is consistent with the hypothesis that Sn is deposited on Pt or at its periphery. From literature data and simple geometrical estimates, Pt aggregates with a size between 1.8 and 2.4 nm are formed by between 150 and 400 atoms, so that when *ca.* 30–150 Sn atoms are selectively deposited on Pt (according to a Sn/Pt = 0.2–0.4), the expected increase in the original particle size must be of the order of a few tenths of nm [29].

Similarly, literature results reported for RhSn/SiO<sub>2</sub> prepared by SOMC/M techniques indicated an increase in the average size of the particles with respect to Rh/SiO<sub>2</sub> of *ca*. 0.4–0.6 nm [30]. In the same work, by applying scanning TEM nanoarea elemental analysis (EDX) it was verified that the X-fluorescence signals of Rh and Sn were always associated, confirming that this preparation method causes an important interaction between both metals.

The metal dispersion (D) is calculated from the Pt particle size distribution obtained from TEM measurements by the following equation [31], assuming spherical particles:

$$D = \frac{6M_{\rm Pt}}{\sigma\rho_{\rm Pt}} \left(\frac{\sum_i n_i d_i^2}{\sum_i n_i d_i^3}\right)$$

where  $M_{\rm Pt}$  and  $\rho_{\rm Pt}$  are the molar mass (kg mol<sup>-1</sup>) and density  $(\text{kg}\,\text{m}^{-3})$  of Pt, respectively;  $n_i$  is the number of particles with a diameter  $d_i$ ,  $\sigma$  is the area occupied by 1 mol of Pt at the surface  $(3.75 \times 10^4 \text{ m}^2 \text{ mol}^{-1})$ . The global Pt dispersion obtained is shown in Table 1. From the analysis of the data obtained, it can be seen that the addition of tin affects in a small proportion the dispersion values with respect to the monometallic system. This is an indication of the specificity of the reaction between both metals. The data obtained for chemisorption experiments can be compared to those of TEM. Table 1 shows the values of H/Pt (hydrogen chemisorption) for the bimetallic and monometallic catalysts. As shown in this table, in the case of the monometallic system, the value of H/Pt ( $\approx$ 70%) is indicative of a high dispersion of the metallic phase. However, unlike what was shown by dispersion values calculated from TEM results for the bimetallic systems, there is a strong decrease in the amount of hydrogen chemisorbed. This drop in hydrogen chemisorption cannot be explained by the existence of sintering phenomena because, as shown by TEM, the addition of Sn slightly increases the average particle size. The decrease in H/Pt cannot be attributed to a simple geometric blocking effect of Pt atoms by Sn. The cause of this phenomenon should be interpreted by the simultaneous existence of changes of both geometric and electronic nature, which would be responsible for a decrease in the adsorption energy of hydrogen.



Fig. 2. Particle size distribution obtained by TEM: (a) Pt and (b) PtSn<sub>0.9</sub> catalysts.

Both effects generate changes in the dissociation of the H<sub>2</sub> molecule [32,33].

#### 3.4. Surface characterization by XPS

To carry out the surface characterization by XPS, the catalysts were always analyzed after a reduction step, and a subsequent "*in situ*" pretreatment in hydrogen at 400 °C for 30 min, so as to avoid any eventual reoxidation process.

Fig. 3 shows the spectra from the analysis of  $PtSn_{0.25}$  and  $PtSn_{0.9}$  bimetallic catalysts in the Sn  $3d_{5/2}$  binding energy region. The values of the binding energies (BE) of Pt  $4d_{5/2}$  and Sn  $3d_{5/2}$  for all the studied catalysts are reported in Table 2. There, it is shown that for Pt the BE value is around 314 eV, which is indicating that Pt is in the metallic state (Pt(0)), meaning that the catalyst is completely reduced.



**Fig. 3.** Sn XPS spectra (Sn  $3d_{5/2}$ ) of PtSn<sub>0.25</sub> (a) and PtSn<sub>0.9</sub> (b) catalysts. Samples treated at 400 °C in H<sub>2</sub>.

In the case of bimetallic systems, a decrease of *ca.* 1 eV in BE for the peak corresponding to Pt is observed. This effect is caused by the addition of Sn, and must be associated with the existence of changes in the Pt electronic nature, which in principle can be interpreted as an increase in the electron density on the transition metal.

These electronic modifications generated by Sn on Pt agree with the results published in the literature on PtSn catalysts [34,35]. Quantum calculation studies conducted by Shen *et al.* employing density functional theory (DFT) for Pt<sub>19</sub> and Pt<sub>16</sub>Sn<sub>3</sub> clusters indicated that Sn donates electrons to the 6*sp* and 5*d* orbitals of platinum [36]. Rodriguez et al. investigated PtSn alloy surfaces using high-resolution photoemission (synchrotron radiation) and self-consistent *ab-initio* calculations and concluded that Pt—Sn bonds involved both a Sn(5*s*,5*p*)  $\rightarrow$  Pt(6*s*,6*p*) charge transfer and a Pt(5*d*)  $\rightarrow$  Pt(6*s*,6*p*) rehybridization that localize electrons in the region between the metal centers [37]. Similarly, in a previous XANES Pt L2,3 study conducted on PtSn/SiO<sub>2</sub> catalysts, the existence of electronic effects was also explained by a *d*  $\rightarrow$  *sp* rehybridization process that takes place in small PtSn nanoclusters, leading to an increase in the number of Pt 5*d* holes [38].

Regarding the oxidation state of Sn, XPS results show a band whose deconvolution in two peaks centered at BE values of ca. 484 and 487 eV (see Fig. 3) can be assigned to Sn(0) and Sn(II, IV), respectively. Table 2 lists these values for each of the bimetallic systems, as well as the calculated  $Sn(0)/Sn_{TOTAL}$  and Sn(0)/Pt ratios. The origin of ionic tin detected by XPS can be assigned to the migration of part of the tin initially deposited on platinum (via the reaction between SnBu<sub>4</sub> and Pt) to the platinum-support interface. The Sn(0) percentage (Table 2, column Sn(0)/Sn<sub>TOTAL</sub>) has a maximum value of about 40% and decreases as the tin content increases, whereas the Sn(0)/Pt ratio increases with the Sn content. Thus, for the PtSn<sub>0.9</sub> catalyst, the Sn(0)/Pt ratio does not exceed the value of 0.2. The presence of Sn in the metallic state, interacting with Pt, suggests the possibility of forming alloys, as is well known for PtSn systems. The literature reports the existence of different types of PtSn alloys: Pt<sub>3</sub>Sn, PtSn, Pt<sub>2</sub>Sn<sub>3</sub>, PtSn<sub>2</sub>, PtSn<sub>4</sub> [39]. From the XPS results, the values of Sn(0)/Pt ratio indicate the existence of 0.1–0.2 Sn atoms per

#### Table 2

Pt  $4d_{5/2}$  and Sn  $3d_{5/2}$  binding energies (eV) and XPS Sn(0)/Sn<sub>Total</sub> and Sn(0)/Pt atomic ratios for Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and PtSn<sub>y</sub> catalysts.

Catalyst	Pt 4d <sub>5/2</sub>	Sn 3d <sub>5/2</sub>	$Sn(0)/Sn_{Total}^{a}$	Sn(0)/Pt
Pt	314.8	-	-	-
PtSn <sub>0.25</sub>	3136	48684836	0.42	0.11
PtSn <sub>0.4</sub>	3136	48644845	0.34	0.14
PtSn <sub>0.9</sub>	3140	48724836	0.20	0.18

<sup>a</sup>  $Sn_{Total} = Sn(0) + Sn(II,IV)$ .



Fig. 4. Concentration profile as a function of time for the reduction of 100 ppm NO<sub>3</sub><sup>-</sup> over the studied catalysts.

atom of Pt, therefore the PtSn alloys that could be formed would be those with the lower Sn content.

### 3.5. Catalytic activity

Figs. 4 and 5 show the results of the hydrogenation of  $NO_3^-$  (Fig. 4) and  $NO_2^-$  (Fig. 5) for the different catalysts studied. The analysis of the data obtained for the monometallic Pt catalyst reveals that it is active for the reduction of  $NO_2^-$  but not for that of  $NO_3^-$ . This catalytic behavior is consistent with the bibliographic data: monometallic catalysts based on noble metals such as Pd or Pt are not active in the reduction of  $NO_3^-$  but they are active in nitrite reduction. It is widely accepted that to be active in  $NO_3^-$  reduction, a catalyst must possess a number of bimetallic sites as well as monometallic sites [16].

In order to study the influence that a promoter would have on the performance of the Pt catalyst for the hydrogenation of  $NO_3^-$ ,

in the present work we studied the influence of the addition of Sn, using techniques derived from SOMC/M. The metallic surface plays an important role in the catalytic reduction of nitrates, and the nature of the active sites (which can be tuned by the synthesis method employed) is crucial for the catalytic activity and selectivity.

The base monometallic catalyst was modified with increasing amounts of Sn. As shown in Figs. 4 and 5, the resulting bimetallic PtSn catalysts were active in the hydrogenation of both  $NO_3^-$  and  $NO_2^-$ . The amount of Sn added has a pronounced influence on the activity of the catalysts. Thus, the addition of a small amount of tin (PtSn<sub>0.25</sub> catalyst) significantly increases the conversion of  $NO_3^-$ , but further increases in the Sn concentration cause a decrease in the activity of the catalysts (Fig. 4). These results are in good agreement with those obtained by Soares et al. [18]. These authors studied a series of TiO<sub>2</sub>-supported PtSn catalysts containing different Pt/Sn atomic ratios in the water denitrification reaction and



Fig. 5. Concentration profile as a function of time for the reduction of 100 ppm NO<sub>2</sub><sup>-</sup> over the studied catalysts.



**Fig. 6.** Influence of the tin content expressed as Sn/Pt atomic ratio (see Table 1) on the  $NO_3^-$  and  $NO_2^-$  conversion of the studied catalysts. Conversion measured after 180 min. The reaction conditions are indicated in the text.

the best catalyst found corresponded to a Pt/Sn atomic ratio of 3:1, which allowed obtaining a  $NO_3^-$  conversion of 76% after 5 h of reaction.

Since Pt is almost inactive for this reaction, the addition of Sn should lead to the modification of the active sites, in which now  $NO_3^-$  ions can be reduced. A possible explanation for this behavior may be given in terms of the electronic and geometric effects that the addition of tin exerts on Pt. As indicated by XPS results, the addition of Sn leads to an electronic enrichment of Pt that could cause  $NO_3^-$  ions to be less strongly adsorbed on Pt, making bimetallic systems become active in this reduction reaction.

In order to explain the influence of tin addition, two aspects should be considered. On the one hand, the electronic effect is mainly due to the presence of Sn(0), which increases the electronic density on Pt (Table 2), favoring the reaction. On the other hand, the geometric effect decreases the size of the platinum ensembles, thereby inhibiting  $NO_3^-$  adsorption and its subsequent hydrogenation. As a result, the catalyst activity shows a maximum as a function of the Sn content, as shown in Fig. 6.

The results obtained in this work go in the same direction as those reported for Pd-based catalysts modified with different amounts of Sn [40]. According to the published results, the surfaces of the PdSn catalysts used had ensembles of PdSn alloys along with pure Pd, their behavior being strongly dependent on the ratio between the two types of phases. A similar behavior has been observed by Marchesini et al. with PtIn/Al<sub>2</sub>O<sub>3</sub> catalysts, where the system with the lowest promoter metal loading was the most active in removing NO<sub>3</sub><sup>-</sup> from water [41]. The authors suggested that a large loading of the second metal may inhibit the access of the H<sub>2</sub> molecules to the Pt crystals, with the resulting decrease in the activity of the catalysts.

Regarding the selectivity of the reaction, with the Pt-based catalysts having Sn/Pt ratios below 0.9, neither the presence of

 $NO_2^-$  nor  $NH_4^+$  was detected, evidencing its high selectivity to nitrogen. Only for the  $PtSn_{0.9}$  catalyst was some increase in the concentration of  $NO_2^-$  detected. This catalyst was not very active in the elimination of  $NO_3^-$ , and the only product obtained was  $NO_2^-$ (it has been verified that the sum of the quantities of  $NO_2^-$  and  $NO_3^-$  remained constant and equal to the initial amount of  $NO_3^-$ ). A likely explanation for the low activity of the  $PtSn_{0.9}$  catalyst is that the high amount of Sn present in comparison with the rest of the  $PtSn_y$  catalysts, would cause an important diminution in the pure Pt clusters, thus almost inhibiting the reduction of  $NO_2^-$ . As has been previously published by Prüsse and Vorlop [16] the catalyst surface must possess bimetallic crystals, probably alloys, alongside with monometallic sites to be active in the reduction of  $NO_3^-$ . Without monometallic sites,  $NO_2^-$  reduction does not occur, as it happens with  $PtSn_{0.9}$  catalyst.

The selectivity of the different catalysts studied can also be explained through an analysis of the combination of geometric and electronic effects caused by the addition of Sn, associated with the adsorption of NO<sub>3</sub><sup>-</sup> ion. A detailed study on nitrate reduction on platinum has been obtained by Dima et al. when working with single-crystal platinum surfaces [42]. These authors have concluded that the nitrate reduction on platinum is structure-sensitive. Nitrate ions can be adsorbed on a metal surface either through one, two or three oxygen atoms (Fig. 7). In all three cases, the interaction with the surface would allow its reduction by means of the hydrogen present. The flat adsorption of NO<sub>3</sub><sup>-</sup> would lead to the simultaneous hydrogenation of the three oxygen atoms, generating N<sub>2</sub>without formation of NO<sub>2</sub><sup>-</sup> as an intermediate product (Fig. 7(a)). This adsorption geometry has been proposed for the interaction with different metal surfaces, such as Hg [43]. This orientation can be expected in the case of Au(111) surfaces, for example, because the distribution of atoms in the (111) surface plane for metals having face-centered cubic structure is particularly compatible with the adsorption of oxyanions of trigonal symmetry. Thus, IR spectroscopy has shown that this is the configuration that presents the ion  $HSO_4^-$  on a Pt(111) surface [44].

However, when analyzing the nitrate ion adsorption on the monometallic Pt catalyst, it appears that this is too strong, preventing its reduction which results in an almost inactive catalyst. A spectroscopic study of nitrate reduction at polycrystalline platinum conducted by Nakata et al. [45] has argued that the main species observed is adsorbed nitrate, more specifically a chelating bidentate nitrate chemisorbed on the Pt surface. Therefore, the presence of a second metal, tin in the present study, is mandatory to reduce nitrate.

As aforementioned, tin addition decreases the size of Pt ensembles. When they attain a certain value, the  $NO_3^-$  ion can no longer be planarly adsorbed and adsorption would basically be as indicated in Fig. 7(b), which explains the detection of  $NO_2^-$  in the course of the reaction.

This same type of behavior, that is, the non-generation of  $NO_2^$ during the hydrogenation of  $NO_3^-$ , was also observed by Mikami et al. [46] using Pt-promoted Ni catalysts. In the same sense, Barrabés et al. [47] reported as an important feature of the Pt–Cu catalysts studied by them that the liquid product was completely free of nitrite and ammonium ions, meaning that the reduced nitrate was completely transformed into nitrogen.

The catalysts evaluated in the removal of  $NO_3^-$ , were also employed in the reduction of  $NO_2^-$ . Fig. 5 presents the curves obtained for all the catalysts studied in this reaction, being appreciated that both the monometallic as well as the bimetallic have been active in the reduction of  $NO_2^-$ . Similarly to what happened with the reduction of  $NO_3^-$ , PtSn<sub>0.25</sub> catalyst was the most active. During the course of the reaction it was detected a significant increase in pH, associated to the reduction of  $NO_2^-$ . However, despite this increase in pH, NH<sub>4</sub><sup>+</sup> ion was not detected in the solution, indicating



Fig. 7. Possible adsorption modes of NO<sub>3</sub><sup>-</sup> on a metal surface: flat (a), through one oxygen atom (b), through two oxygen atoms (c).

a high selectivity of the reaction to  $N_2$ . The  $NO_2^-$  reduction process proposed, is therefore:

 $2NO_2^{-} + 3H_2 \rightarrow N_2 + 2H_2O + 2OH^{-}$ 

This route of  $NO_2^-$  reduction is in agreement with what is proposed in the literature [48].

The fact that no color has been observed in the solution allowed discarding the formation of NOx intermediates, both in the reduction of  $NO_2^-$  and  $NO_3^-$ .

## 4. Conclusions

The removal of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> ions present in drinking water can be performed by reduction in flowing H<sub>2</sub> (at room temperature and atmospheric pressure) using PtSn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> bimetallic catalysts. The preparation of these catalysts was carried out using SOMC/M techniques, which allow obtaining well defined solids in their composition and structure. The selectivity of the preparation reaction led to a strong interaction between Pt and Sn atoms, as evidenced by the results of TPR and XPS analysis. The activity of the bimetallic catalyst in the selective reduction of NO3- to N2 was found to be strongly dependent on the Sn content of the catalyst. Thus, the addition of a small amount of tin (PtSn<sub>0.25</sub> catalyst) significantly increased the conversion of NO<sub>3</sub><sup>-</sup>, but further increases in the Sn concentration caused a decrease in the activity of the catalysts. An explanation was given in terms of the electronic and geometric effects that the addition of tin exerts on Pt: the addition of Sn leads to an electronic enrichment of Pt that could cause NO<sub>3</sub><sup>-</sup> ions to be adsorbed on Pt less strongly, but the amount of tin added should be low enough to allow a planar adsorption of NO<sub>3</sub><sup>-</sup> on the Pt clusters, so that the simultaneous hydrogenation of its three oxygen atoms could happened, selectively generating N<sub>2</sub>.

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#### References

- Y. Bachmat, in: U. Zoller (Ed.), Ground Water Contamination and Control, Marcel Dekker, Inc., New York, 1994.
- [2] J.A.A. Jones, in: J.A.A. Jones (Ed.), Sustaining Groundwater Resources. A Critical Element in the Global, Springer, Dordrecht; London, 2011, p. 1.
- [3] J. Gabbay, Y. Almong, M. Davidson, A.E. Donagi, Analyst 102 (1977) 371-376.

- [4] P. Mikuška, Z. Večeřa, Anal. Chim. Acta 495 (2003) 225–232.
- [5] R. Burakham, M. Oshima, K. Grudpan, S. Motomizu, Talanta 64 (2004) 1259–1265.
- [6] E.R. Jaffé, Clin. Haematol. 10 (1981) 99-122.
- [7] P.S. Barker, P.L. Dold, Water Res. 30 (1996) 769-780.
- [8] B.U. Bae, Y.H. Jung, W.W. Han, H.S. Shin, Water Res. 36 (2002) 3330-3340.
- [9] A.C.A de Vooys, R.A. van Santen, J.A.R. van Veen, J. Mol. Catal. A: Chem. 154 (2000) 203–215.
- [10] J.J. Schoeman, A. Steyn, P.J. Scurr, Water Res. 30 (1996) 1979–1984.
- [11] Y.H. Hwang, D.G. Kim, H.S. Shin, J. Hazard. Mater. 185 (2011) 1513-1521.
- [12] A. Pintar, J. Batista, J. Levec, Chem. Eng. Sci. 56 (2001) 1551-1559.
- [13] M.K. Firestone, in: F.J. Stevenson (Ed.), Nitrogen in Agricultural Soils, Soil Science Society of America, Madison, WI, 1985.
- [14] Y.H. Liou, S.L. Lo, C.J. Lin, C.Y. Hu, W.H. Kuan, S.C. Weng, Environ. Sci. Technol. 39 (2005) 9643–9648.
- [15] L. Calvo, M.A. Gilarranz, J.A. Casas, A.F. Mohedano, J.J. Rodriguez, Ind. Eng. Chem. Res. 49 (2010) 5603–5609.
- [16] U. Prüsse, K.D. Vorlop, J. Mol. Catal. A: Chem. 173 (2001) 313-328.
- [17] Y.H. Liou, C.J. Lin, S.C. Weng, H.H. Ou, S.L. Lo, Environ. Sci. Technol. 43 (2009) 2482–2488.
- [18] O.S.G.P. Soares, E.O. Jardim, Á. Reyes-Carmona, J. Ruiz-Martínez, J. Silvestre-Albero, E. Rodríguez-Castellón, J.J.M. Órfão, A. Sepúlveda-Escribano, M.F.R. Pereira, J. Colloid Interface Sci. 369 (2012) 294–301.
- [19] U. Matatov-Meytal, M. Sheintuch, Catal. Today 102 (2005) 121-127.
- [20] J. Margitfalvi, M. Hegedüs, S. Göbölös, E. Kern-Tálas, P. Szedlacsek, S. Szabó, F. Nagy, Proceedings of the 8th International Congress on Catalysis, West-Berlin, vol. 4, Verlag Chemie, Weinheim, 1984, pp. 903–914.
- [21] O.A. Ferretti, M.L. Casella, in: J.-M. Basset, R. Psaro, D. Roberto, R. Ugo (Eds.), Modern Surface Organometallic Chemistry, Wiley-VCH, Weinheim, 2009 (Chapter 6).
- [22] A.B. Merlo, B.F. Machado, V. Vetere, J.L. Faria, M.L. Casella, Appl. Catal. A 383 (2010) 43-49.
- [23] G.J. Siri, M.L. Casella, G.F. Santori, O.A. Ferretti, Ind. Eng. Chem. Res. 36 (1997) 4821–4826.
- [24] G.F. Santori, M.L. Casella, G.J. Siri, H.R. Adúriz, O.A. Ferretti, Appl. Catal. A 197 (2000) 141-149.
- [25] G.F. Santori, Ph.D. Thesis, Universidad Nacional de La Plata, Argentina, 2000.
- [26] H. Armendáriz, A. Guzmán, A. Toledo, M.A. Llanos, A. Vazquez, G. Aguilar-Ríos, Appl. Catal. A 211 (2001) 69–80.
- [27] S.A. Bocanegra, S.R. de Miguel, I. Borbath, J.L. Margitfalvi, O.A. Scelza, J. Mol. Catal. A: Chem. 301 (2009) 52-60.
- [28] V. Hughes, B. McNicol, J. Chem Soc, Faraday Trans. 75 (1979) 2165-2176.
- [29] R. Van Hardeveld, F. Hartog, Surf. Sci. 15 (1969) 189-230.
- [30] O.A. Ferretti, J.P. Bournonville, G. Mabilon, G. Martino, J.P. Candy, J.M. Basset, J. Mol. Catal. 67 (1991) 283-294.
- [31] J. Yang, V. Tschamber, D. Habermacher, F. Garin, P. Gilot, Appl. Catal. B 83 (2008) 229–239.
- [32] J. Volter, G. Lietz, M. Uhlemann, M. Hermann, J. Catal. 68 (1981) 42-50.
- [33] F. Passos, M. Schmal, M.A. Vannice, J. Catal. 160 (1996) 106–117.
- [34] P.D. Zgolicz, V.I. Rodríguez, I.M.J. Vilella, S.R. de Miguel, O.A. Scelza, Appl. Catal. A 392 (2011) 208–217.
- [35] G.J. Siri, J.M. Ramallo-López, M.L. Casella, J.L. García-Fierro, F.G. Requejo, O.A. Ferretti, Appl. Catal. A 278 (2005) 239–249.
- [36] J. Shen, J.M. Hill, R.M. Watwe, B.E. Spiewak, J.A. Dumesic, J. Phys. Chem. B 103 (1999) 3923–3934.
- [37] J.A. Rodriguez, S. Chaturvedi, T. Jirsak, J. Hrbek, J. Chem. Phys. 109 (1998) 4052–4062.
- [38] J.M. Ramallo-López, G.F. Santori, L. Giovanetti, M.L. Casella, O.A. Ferretti, F.G. Requejo, J. Phys. Chem. B 107 (2003) 11441–11451.

- [39] T.B. Massalskii, Binary Alloy Phase Diagrams, ASTM, Philadelphia, 1986.
- [40] J. Sá, D. Gasparovicova, K. Hayek, E. Halwax, J.A. Anderson, H. Vinek, Catal. Lett. 105 (2005) 209–217.
- [41] F.A. Marchesini, S. Irusta, C. Querini, E. Miró, Catal. Commun. 9 (2008) 1021-1026.
- [42] G.E. Dima, G.L. Beltramo, M.T.M. Koper, Electrochim. Acta 50 (2005) 4318-4326.
- [43] N.S. Marinković, J.J. Calvente, A. Kloss, Z. Kováčová, W.R. Fawcett, J. Electroanal. Chem. 467 (1999) 325–334.
- [44] P.W. Faguy, N.S. Marinković, R.R. Adžić, J. Electroanal. Chem. 407 (1996) 209-218.
- [45] K. Nakata, Y. Kayama, K. Shimazu, A. Yamakata, S. Ye, M. Osawa, Langmuir 24 (2008) 4358–4363.
- [46] I. Mikami, R. Kitayama, T. Okuhara, Appl. Catal. A 297 (2006) 24-30.
- [47] N. Barrabés, J. Just, A. Dafinov, F. Medina, J.L. García-Fierro, J.E. Sueiras, P. Salagre, Y. Cesteros, Appl. Catal. B 62 (2006) 77–85.
- [48] M. D'Arino, F. Pinna, G. Strukul, Appl. Catal. B 53 (2004) 161-168.