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Effect of the Support on Tin Distribution in
Pd-Sn/Al₂O₃ and Pd-Sn/SiO₂ Catalysts for
Application in Water Denitration

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Abstract

The reduction of nitrate to nitrogen is a key process for nitrate removal in water. Among others bimetallic, palladium tin catalysts are well suited for this purpose. In the present study Pd-Sn catalysts are used and characterized in the mentioned process. Alumina and silica supported catalysts were prepared by deposition of tin onto palladium particles by using controlled surface reaction. The accessibility of palladium and the amount of reducible tin are tested by $O_2/H_2/O_2$ titration. The structural characterization is based on ^{119}Sn Mössbauer spectroscopy, TEM, XRD, and catalytic performances are tested in nitrate and nitrite reductions at room temperature. Remarkably, the properties of Pd-Sn/ Al_2O_3 and Pd-Sn/ SiO_2 are different, although they were prepared according to the same procedure. Namely, the silica supported catalyst is more stable and selective, but is less active than the alumina supported one. This could be explained by the difference of (i) the interaction between the two metals and (ii) the affinity of tin with the support depending on the support used. The characterization results are interpreted with respect to the catalytic behavior of the materials.

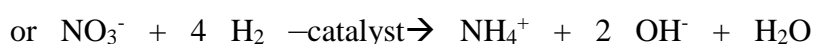
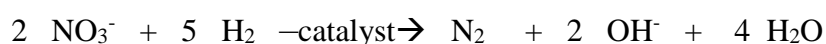
Keywords: Pd-Sn catalysts ; catalytic reduction in water ; bimetallic catalyst ; ^{119}Sn Mössbauer spectroscopy ; support effect

INTRODUCTION

Ground and surface water pollution by harmful nitrogen-containing compounds is a growing environmental problem. In surface it contributes to river and sea eutrophication. In ground water they are potentially harmful compounds for human health (blue baby syndrome, cancer...). Nitrate is one of the most problematic and widespread among the potential groundwater contaminants. Sources of nitrate in groundwater originate from four categories: (i) natural sources (ii) waste materials (iii) row crop agriculture and (iv) irrigated agriculture (1).

Biological and physicochemical treatments allow an effective removal of nitrates but have several economical and ecological disadvantages. Catalytic reactions constitute also promising approaches for the destruction of pollutants in water. Since the first paper of Tacke and Vorlop (2) on the use of palladium-copper bimetallic catalysts for nitrate reduction, numerous studies have been aimed to the development of suitable catalysts for the selective reduction of nitrate into nitrogen gas (2-20). Their application in various reactor types such as suspended-bed reactor, hollow fibers (5), batch recycle reactor (11) and membrane reactors (13) has been studied.

Nitrate reduction for drinking water treatment demands very active catalysts because the reaction has to be performed at the temperature of the groundwater. Moreover, a high selectivity is necessary to avoid the production of ammonium ions by over-reduction of intermediates of the stepwise nitrate hydrogenation. This selectivity is directly controlled by the hydrogen coverage of the precious metal. The global reaction is the following:



The reduction of nitrate leads to the formation of hydroxide ion, which causes an increase of the pH value up to 10, which could be avoided by using a buffering system as controlled addition of hydrochloric acid or carbon dioxide (4,7,15).

Palladium catalysts have proved to be active and the most selective for nitrite reduction. To reduce nitrate, it is necessary to activate the noble metal by addition of a second metal of group 11, 12, 13 or 14. Mostly, copper was used as a promoting second metal (2-15,17,20), but other suitable promoters, such as tin, indium or zinc (4-5,11,14-19) have demonstrated interesting performances. Whereas the addition of a promoter to the noble metal is necessary to reduce nitrates, it leads to contrasting results for the activity and the selectivity. Indeed, depending to the operating condition and to the preparation method, tin or copper leads to the best selectivity toward ammonium ion (4,9,11).

Moreover, in the case of Pt-Cu/ γ -Al₂O₃ bimetallic catalyst, it was demonstrated that the preparation methods involved different behaviors in nitrate abatement. Precisely, the preparation method by catalytic reduction led to the most active catalysts compared to those resulting from classical methods such as co-impregnation or successive impregnation (20).

Then, the highest activity and selectivity for nitrate removal under controlled addition of carbon dioxide should be observed with Pd-Sn bimetallic catalysts prepared by catalytic reduction. In order to correlate the catalytic performances of this type of catalyst with the metal-metal interaction, it is of major importance to localize tin species. But the characterization of tin is a challenge, due to its high oxidability in air. Some studies on Pt-Sn/Al₂O₃ and Pt-Sn/SiO₂ catalysts (21,22) gave interesting results on the different phases of tin present in the catalyst and their influence on the activity and the selectivity of the catalyst for n-hexane rearrangement reactions or for the 1,2-dichloroethane dechlorination. A study (23) on Pd-Sn/SiO₂ evidenced by XPS and CO adsorption a modification of electronic configuration of Pd due to the effective interaction between Pd and Sn. Some authors (19)

used ^{119}Sn Mössbauer spectroscopy to characterize tin based catalysts supported on alumina for nitrate reduction in water. Other studies (24,25) proved that the types of tin species are very dependent on the support and on the preparation method. The Pt-Sn catalyst is the most studied tin based catalyst in the literature, but for catalytic nitrate reduction the Pd-Sn catalyst is more attractive.

The aim of the present study is to characterize mono- and bi-metallic Pd-Sn catalysts prepared by controlled surface reaction, favoring the deposition of tin on palladium particles, and deposited on alumina or silica with ^{119}Sn Mössbauer spectroscopy TEM, EDS, XRD and $\text{O}_2/\text{H}_2/\text{O}_2$ titration. The characteristics of these materials are compared with their catalytic performances in nitrate and nitrite reduction, chosen as test reaction since it is very sensitive to the metallic distribution.

1. EXPERIMENTAL

2.1. Catalyst preparation

2.1.1. Monometallic catalysts

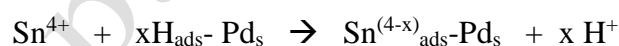
A powdered γ -alumina from Procatalyse (surface area (BET method): $216 \text{ m}^2.\text{g}^{-1}$; pore volume: $0.55 \text{ m}^3.\text{g}^{-1}$; isoelectric point: 7) and a silica from Degussa (surface area (BET method): $175 \text{ m}^2.\text{g}^{-1}$; pore volume $0.47 \text{ m}^3.\text{g}^{-1}$; isoelectric point : 3) were used as support. First, they were ground and then sieved to retain particles with sizes between 0.04 and 0.08 mm.

Monometallic catalysts were prepared by impregnation of the support with the precursor salt $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ (Johnson Matthey, 99.9%) in an aqueous solution brought to pH 11 by

addition of ammonia. This pH value was chosen to ensure the cationic exchange between the precursor salt and the support surface (26). The mixture was stirred for 12h and then ammonia and water were evaporated by heating on a sandbath. After drying overnight at 120°C, catalysts were calcined in flowing air (80mL.min⁻¹) at 400°C (6°C.min⁻¹) for 4 h, and cooled to room temperature under N₂. Finally the catalysts were reduced by flowing hydrogen (60mL.min⁻¹) at 400°C (6°C.min⁻¹) for 6 h. Monometallic catalysts Pd/γ-Al₂O₃ and Pd/SiO₂ have a metal loading of 5 wt. %. In the following, these catalysts are identified by their respective notation, Pd5A and Pd5S.

2.1.2. Bimetallic catalysts

Bimetallic catalysts were prepared by a controlled surface reaction. In order to favor metal-metal interactions, the second metal was deposited by a redox reaction occurring between the hydrogen chemisorbed on the pre-reduced noble metal and the oxidized modifier (27,28). A palladium monometallic catalyst was modified by a surface reaction between chemisorbed hydrogen and the second metal, according to the overall reaction



A known amount of a monometallic catalyst was placed in an atmospheric glass reactor. The reactor was flushed with a counter current nitrogen flow for 15 min at room temperature. Afterwards the catalyst was reduced by a hydrogen stream at a temperature rising to 400°C and then cooled to room temperature. At the same time, the desired amount of SnCl₄ (Aldrich, 99%) modifier, chosen in order to obtain 1.5 wt.% of tin in the bimetallic catalyst, was dissolved in hydrochloric acid solution and degassed by bubbling with N₂. The solution was then added to the monometallic catalyst and maintained under stirring by hydrogen flow for 2h. The pH value of the resulting mixture was equal to 0.7. The bimetallic catalyst was

separated from the aqueous solution via a filter at the bottom of the reactor, and washed. Afterwards, the resulting material was dried overnight under a nitrogen stream at 80°C.

In this study, each bimetallic catalyst is identified by its specific support A for alumina and S for silica. The catalyst is noted PdSnA or PdSnS.

The experimental nominal composition of each catalyst was verified by elementary analysis. Generally, the experimental error was within 5 %.

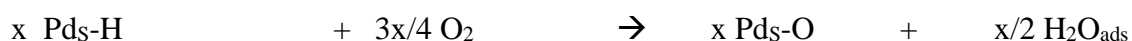
2.2. Characterization methods

2.2.1. O₂/H₂/O₂ titration

O₂/H₂/O₂ titration was performed in order to estimate the palladium accessibility in the mono and bimetallic catalysts (29,30) and the amount of reducible tin in the bimetallic catalyst (29). After reduction in H₂ at 400°C, the catalyst was flushed for 30 min with argon at the same temperature to remove adsorbed hydrogen, and then cooled to 80°C. The experiment was conducted at 80°C to avoid the formation of β-PdH (31-34). Before O₂/H₂/O₂ titration, the sample was saturated by hydrogen and then purged by flushing argon for 10 minutes. The same flushing under argon was performed between each titration cycle.

After pretreatment, pulses of oxygen were introduced until the full saturation of the catalyst was achieved to determine the oxygen uptake OT1. The chemisorbed oxygen was then titrated by hydrogen to determine HT. Afterwards a second oxygen titration (OT2) was carried to confirm the HT value. On the monometallic Pd catalyst, the reactions involved during the titration are the following:

(1) Titration of chemisorbed hydrogen by oxygen (OT1)

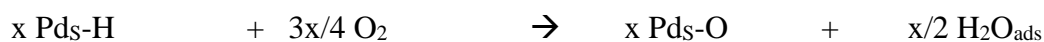


where x is the number of palladium surface atoms Pd_s

(2) Titration of chemisorbed oxygen by hydrogen (HT)



(3) Titration of chemisorbed hydrogen by oxygen (OT2)



The palladium dispersion in the monometallic catalyst was calculated from the value of hydrogen uptake assuming that the surface stoichiometry of the irreversibly chemisorbed hydrogen is unity. The average particle size of palladium was calculated from the dispersion values, assuming cubic shapes for the palladium particles.

2.2.2. TEM measurements

TEM measurements were carried out with a Philips CM120 electron microscope operating at 120kV with a resolution of 0.35nm. The powder was ultrasonically dispersed in ethanol, and the suspension was deposited on an aluminum grid coated with a porous carbon film. The particle size distribution was obtained from TEM pictures calculating the surface average particle diameter from $d_p = \Sigma n_i d_i^3 / \Sigma n_i d_i^2$.

X-ray energy dispersive spectrometry (EDS) was performed on the metal, on the support and on the vicinity of the metal for each sample using the STEM mode of the microscope using a Si-Li Super UTW detector.

2.2.3. Powder X-Ray Diffraction

Powder-XRD was used for crystallites identification. The diffractograms were obtained at room temperature with a Siemens D500 diffractometer equipped with a copper target. All the catalysts were pre-reduced before measurement. The spectra were acquired with the software DIFFRAC and evaluated with the software EVA. The databank used comes from the International Centre for Diffraction Data (ICDD).

2.2.4. ^{119}Sn Mössbauer spectroscopy

^{119}Sn Mössbauer spectra were recorded at 77 and 300K in an cell (35) built to allow treatments in various gas atmospheres, with a pellet supported by a thin Be plate. The use of two different temperatures can give important information about the nature of the tin species environment (36). The pellet was made from a powdered catalyst sample (ca. 0.5 g) by pressing (100 MPa). Spectra were obtained for as-prepared samples. Each sample has been tested as received to identify the various oxidation states of tin present in the sample, and thereafter reduction in a H_2 flow at 400°C (2 h, 10 mL.min⁻¹, $p_{\text{H}_2} = 1$).

The sample was isolated in an in situ cell, and was kept in the atmosphere of treatment during collection of spectra. After treatments, spectra were obtained at room temperature first, then at 77K.

Mössbauer spectra were recorded with a constant acceleration KFKI spectrometer equipped with $\text{Ba}^{119}\text{SnO}_3$ source (300 MBq). For fitting purposes, components of the Lorentzian line shape were assumed, and no isomer shift parameters were initially constrained. Successive iterations were applied to obtain a better fit to the experimentally generated data. The estimated accuracy of positional parameters is $\pm 0.03 \text{ mm.s}^{-1}$. The isomer shift values are referred to SnO_2 (room temperature).

f_A (recoilless fraction) values were also approximated by calculating $\phi_A = -d \ln(A_{300}/A_{77})/dT$ data, where A_{300} and A_{77} are the actual absorption areas of components in the spectra recorded at 300 and 77K, respectively. f_A is connected to the probability of the Mössbauer effect. It provides a rough estimation of the bonding strength of particular species, the smaller the temperature dependence, i.e. ϕ_A , the stronger the bond.

2.3. Nitrate and nitrite reduction

Nitrate and nitrite reduction reactions were performed in a semi-batch reactor, at atmospheric pressure and 25°C. In a typical experiment, 64 mg of the powdered catalyst was used. The catalyst is at first reduced under hydrogen (180°C; 0.5 h). During this time 90 mL of ultra pure water (18.2 M Ω) is placed in a vial purged with nitrogen. When the catalyst is stabilized in temperature the ultra-pure water is added over the reduced catalyst. Then, the catalyst is maintained in water under bubbling hydrogen for 30 min before introduction of the reactant, in order to be aged. The catalyst was mixed to water by the gas bubbling. This treatment is sufficient to avoid any metal dispersion modification during the reaction (20).

The catalytic test was carried out under CO₂ in order to buffer the pH solution at a value of 5. The buffering began 10 minutes before the reaction to stabilize the pH. Afterwards, 10 mL of a solution (16 mmol.L⁻¹) of nitrate (KNO₃) or nitrite (KNO₂) were introduced in the reactor to start the reaction. The catalyst dispersion in the aqueous medium was achieved by the gas flowing ($p_{H_2} = 0.5$ bar, $p_{CO_2} = 0.5$ bar, flow rate = 250 mL.min⁻¹) through a porous glass located at the bottom of the reactor. It was checked that the hydrogen flow and the resulting stirring were sufficient to ensure that the reaction was not rate-limited by reactant diffusion. To monitor the progress of the reaction, representative aqueous samples were periodically

taken out and immediately separated by filtration and then analyzed as described in the following section.

“Tested catalysts” are fresh catalysts after one catalytic nitrate reduction test. “Blank catalysts” are catalysts submitted to the same treatment as the catalytic test (same pretreatment, same time, same medium and same gases) but without nitrate or nitrite. The tested catalysts are either characterized or next activated according to a procedure similar to the one used for fresh catalysts, and a new catalytic test was performed.

2.4. Analysis

The reaction components were analyzed by High Performance Liquid Chromatography (HPLC). Nitrate and nitrite concentrations were determined after separation on a C18 grafted phase column using an UV detector at $\lambda=210$ nm. Ammonium ions were quantified using an Alltech Universal Cation column coupled with a conductivity detector. The acidic mobile phase (oxalic acid) used provided the complete conversion of the ammonia basic form into ammonium ions. The gas phase was analyzed by on-line gas chromatography using a GIRA GC10C equipped with an automated gas sample valve, a TCD detector and a Porapak Q column.

Activities of catalysts, corresponding to the disappearance rate of nitrate and nitrite, determined at 75% conversion of the nitrite or the nitrate.

The initial concentration of $1.6 \cdot 10^{-3}$ mol.L⁻¹ of nitrate corresponding to a concentration of 100 mg.L⁻¹. 75% of conversion allows to obtain water corresponding to the European guideline for nitrates concentration in drinkable water (25 mg.L⁻¹).

The selectivity of the reaction, evaluated at 75% of nitrite and nitrate reduction, corresponds to the ratio between the amount of ammonium ion formed and the amount of converted reactant.

3- RESULTS AND DISCUSSION

The composition of the catalysts was determined by the central service of analysis of the CNRS (French national center of scientific research). The catalyst was initially dissolved in a solution of aqua regia and analyzed by ICP/AES (Perkin Elmer Optima 2000 DV). In the remaining part of this publication, the identifications mentioned in the Table 1 will be used.

3.1. Monometallic catalysts

The $O_2/H_2/O_2$ titration was performed on the monometallic catalysts, Pd5A and Pd5S, immediately after preparation (fresh catalysts Pd5AF and Pd5SF) and also after the catalytic test (Pd5AT and Pd5ST), in order to evaluate the modifications induced by the catalytic test. Results are summarized in Table 2.

The dispersion of palladium and the particle sizes determined from the hydrogen uptake are also reported in Table 2. The mean particle size of the fresh catalysts estimated from TEM pictures, not reported here, are identical to those determined by $O_2/H_2/O_2$ titration.

For both types of catalysts, a decrease of the palladium dispersion between the fresh and the tested catalysts, due to a sintering of palladium particles, is observed. Indeed the dispersion values are 12.2% for the fresh and 3.4% for the tested alumina supported catalyst and respectively 5.1% and 2.1% for the silica supported one. The same results are observed in

absence of nitrite (blank monometallic catalyst) that means that (i) the sintering is favored by the presence of both water and hydrogen, (ii) the catalytic nitrite reduction may not contribute to the sintering. This sintering phenomenon occurring in the presence of hydrogen and water has already been observed for Pt/Al₂O₃ catalysts (20,37,38) and for Pd/Al₂O₃ (39). Then the modification of the palladium accessibility occurs in the reaction media before the introduction of nitrite, when the catalyst, water and hydrogen are in contact. So, when the fresh catalyst is put in water under hydrogen bubbling before the catalytic test, the palladium dispersion at the beginning of the reaction is similar to the one of the tested catalyst in the same conditions. These results also demonstrate that the low dispersion values are observed on both supports, which could be explained by the high metal loading (5 wt %).

The catalytic performances for nitrite reduction were determined for the fresh and tested catalysts. Catalytic properties of the monometallic catalysts are summarized in Table 3. The activities of the fresh and tested catalysts are similar. As the palladium dispersions in the two catalysts are similar before the introduction of nitrites that means that the TOF is identical.

The silica supported catalysts, fresh or already used, are the most active and selective. The higher selectivity towards nitrogen for the silica supported catalysts, than the one obtained for alumina, could be linked to the difference of the particles size, the formation of N-N binding being favored on large particles (40). Then, in accordance with the results presented in (4), silica is the most suitable catalyst for nitrite reduction.

3.2. Bimetallic catalysts

3.2.1. Characterization

The Pd-Sn catalyst supported on alumina and silica were characterized by O₂/H₂/O₂ titration, TEM coupled with EDS, XRD and ¹¹⁹Sn Mössbauer spectroscopy.

3.2.1.1. Characterization by O₂/H₂/O₂ titration

The O₂/H₂/O₂ titration was performed on the bimetallic catalysts, PdSnA and PdSnS, immediately after preparation and also after catalytic test in order to localize the tin on the palladium particle surface. Indeed, if tin is deposited on the noble metal, a decrease of the hydrogen uptake, as compared to the one obtained in the monometallic catalyst, should be observed, since the presence of tin on palladium ensembles will decrease the number of palladium sites accessible to hydrogen.

The different results of oxygen and hydrogen uptakes are summarized in Table 4 for the fresh (F) and the tested (T) catalysts. As the presence of tin in interaction with palladium could modify the chemisorption stoichiometry of hydrogen on palladium sites and as the pretreatment under hydrogen could modify the tin distribution on palladium particles (41), the palladium dispersion was not calculated for the bimetallic catalysts.

The number of oxygen involved (OT1) corresponds to the amount of oxygen chemisorbed on accessible palladium surface and also on metallic tin atoms, especially those in interaction with palladium atoms. Indeed, it is well known that oxygen can be chemisorbed on metallic tin but not on ionic tin such as Sn²⁺ and Sn⁴⁺, and only tin species in interaction with palladium are likely to be reduced to Sn⁰ during the pretreatment (42,430). Then, during the first oxygen titration (OT1), the oxygen chemisorption on reduced tin atoms could occur according to the following reaction, assuming an approximate stoichiometry of one oxygen atom per tin atom (29):

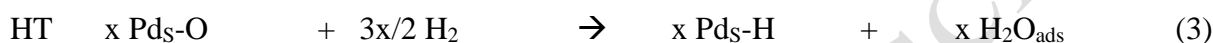


where y is the number of reduced tin atoms in interaction with palladium.

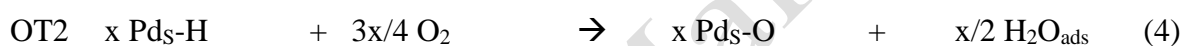
Then for the titration reactions, the first oxygen uptake would correspond to the formation of SnO (1) and to the titration of the hydrogen chemisorbed on palladium (2):



During the introduction of hydrogen, after outgassing, there is a titration of the oxygen chemisorbed on palladium (3) but not of the one chemisorbed on tin.



Finally, after outgassing, the introduction of oxygen allows the titration of hydrogen atoms chemisorbed on palladium (4).



Then, it can be inferred from these reactions that (i) the amount of oxygen uptake during the first titration by oxygen OT1 is not equal to the amount determined during the second titration by oxygen OT2 and (ii) that OT2 is equal to half the amount of hydrogen uptake HT.

This is in accordance with the values of OT1, HT and OT2 reported in Table 4. Then, the amount of reducible tin, y , in interaction with palladium is simply given by $y = \text{OT1} - \text{OT2}$.

The values of oxygen and hydrogen uptakes are only used for comparison. For both types of support, the HT value of the fresh catalyst is almost identical to the one of the tested catalyst. Moreover the HT value before and after catalytic test is higher in the bimetallic catalyst than in the corresponding blank or tested monometallic one whereas it has been demonstrated in paragraph 3.1 that the catalytic test leads to a sintering of palladium particles with an important decrease of the hydrogen uptake after catalytic test. Then, it can be inferred that the deposition of tin restricts the sintering of palladium particles which occurs when the

monometallic catalyst is immersed in an aqueous solution under hydrogen atmosphere. The presence of chlorine could also account for this result. The same behaviour has already been observed after introduction of tin on Pt/Al₂O₃ (44). In addition, for the silica supported catalyst, the HT value is higher in the bimetallic than in the fresh monometallic catalyst. This larger hydrogen uptake in the bimetallic as compared to the monometallic Pd5SF can be explained by a redispersion of palladium favoured by the presence of tin. Indeed, a change in the hydrogen chemisorption stoichiometry on palladium, due to the presence of tin, can not explain the difference obtained, the hydrogen uptake being 1.6 times higher in the fresh bimetallic than in the fresh monometallic catalyst. The same result has already been obtained for Pt-Sn/Al₂O₃ catalysts (45) with low tin loadings (10% and 50% of tin in the bimetallic phase). It was proved by transmission electron microscopy that platinum particles were two times smaller in the bimetallic than in the corresponding monometallic catalyst. However in that case the bimetallic was prepared by coimpregnation (45). It can also be considered that the chemisorption properties of Pd-Sn alloys could explain the higher hydrogen uptake of the bimetallic catalysts.

From the estimated value of reducible tin reported in table 4, which contributes to the oxygen uptake OT1, it seems that the catalytic test leads to a decrease of the amount of accessible tin in interaction with palladium on the alumina supported catalyst, although these data are only a rough estimation and should be taken with precaution. This could be explained by a migration of tin from palladium on the alumina support during the catalytic test. Indeed, tin stabilized on the support is not reducible and then cannot chemisorb O₂. On silica supported catalysts, the amount of oxygen chemisorbed on metallic tin is lower than on alumina catalysts, and is not affected by the catalytic test.

To conclude this part, the results on O₂/H₂/O₂ titration do not prove that tin is deposited on palladium particles since the hydrogen uptake of the bimetallic catalysts is identical or larger

as compared to the corresponding monometallic catalyst, which could be linked to a redispersion of palladium during tin deposition. On the contrary, the values of the oxygen uptake should indicate that metallic tin is present on the bimetallic catalyst after reduction, which could be an indication of the presence of bimetallic palladium-tin entities. In addition, it seems that the catalytic test induces some modifications in the tin distribution on the catalyst surface, especially for the alumina supported catalyst.

3.2.1.2. TEM, EDS and XRD

TEM coupled with EDX was carried out to collect more information on metallic particles in terms of particle size and composition. The TEM pictures of the two bimetallic catalysts are presented in Figure 1 for the fresh catalysts and in Figure 2 for the tested ones, and the distribution of the particle size estimated from the TEM pictures are reported in Figure 3.

If one refers to the particle size in the fresh and tested catalysts (Figure 3) one can see that these values are lower than those determined in the corresponding blank or tested monometallic catalyst. This confirms that the presence of tin would limit the sintering of palladium particles, in accordance with the hydrogen uptake values obtained during $O_2/H_2/O_2$ titration.

As far as the composition of bimetallic particles is concerned, the EDS results evidenced an heterogeneity in the tin distribution, with tin rich and tin poor particles. The EDS study showed also that for PdSnS, fresh or tested, tin is always associated with palladium, whereas PdSnA presents a lot of isolated tin particles on the support.

The XRD technique was used on pre-reduced catalysts to determine the composition of crystallized compounds. Figures 4a and 4b show the X-Ray diffraction patterns of PdSnSF and PdSnAF respectively. For the silica based catalyst the diffraction peaks correspond to two

principal definite structures, metallic palladium (Pd) and Paolovite (Pd_2Sn), and also to a palladium silicon tin, structure such as $\text{Pd}_{2,5}\text{Si}_{4,5}\text{Sn}_{4,5}$.

For the alumina based catalyst, peaks corresponding to Pd-Sn and Pd-Sn-Al species are also observed but it was impossible to correlate the peaks with a particular composition referenced in the JSPER base.

3.2.1.3. ^{119}Sn Mössbauer spectroscopy

The Mössbauer spectra of the reduced PdSnAF and PdSnSF at 77 and 300K are presented on Figure 5. The corresponding Mössbauer parameters and the different chemical species identified are presented in Table 5. The Table 6 summarizes the composition and the relative intensity of each measured tin compound.

a) Alumina supported catalyst

It was demonstrated by Mössbauer spectroscopy (19,45) that on Pd-Sn/ Al_2O_3 catalysts, a large amount of tin, between 41 and 80%, is deposited on the support whatever the preparation method. Then, to favor the characterization of all tin species (metallic and oxide) by this technique, the tin loading chosen was 6% for Pd-Sn/ Al_2O_3 catalyst. It was verified, by catalytic test, that this catalyst was representative of the samples PdSnAF and PdSnAT used in this study, the same activity being obtained for nitrate reduction.

Fresh catalyst

For all alumina based catalysts before reduction the tin phase is characterized by a doublet with an Isomer Shift (IS) close to 0 and a Quadrupole Splitting (QS) around $0.6 \text{ mm}\cdot\text{s}^{-1}$, that is

only characteristic of a Sn^{4+} species such as SnO_2 (45). This result proves that all tin species are oxidized in Sn^{4+} during the storage of the catalyst.

After reduction of the catalyst the best fitting of the spectra is obtained for three different species. One corresponds to oxidized tin in Sn^{2+} form (20% of the relative intensity), the two others are attributed to metallic tin associated with palladium, one tin poor phase Pd-Sn(a) and one tin rich phase Pd-Sn(b). Contrary to the results reported by Sales and al (24), no Sn^{4+} species such as SnO_2 or Sn^{4+} species interacting with the alumina support are identified on the reduced samples.

The peak corresponding to the Sn^{2+} state has an IS close to 4 and a QS close to 0.3, that is characteristic of Sn^{2+} with chloride ligands. This phase is likely to be SnCl_2 (47) or an oxo-chlorinated species of tin. This compound resulting from the precursor salt SnCl_4 used for the preparation is known to be very stable on alumina and then irreducible at low temperature.

The tin poor phase Pd-Sn(a) has an IS close to 1.4 which could be attributed to a solid solution of tin in palladium, such as $\text{Pd}_{(x>3)}\text{Sn}$ (48,49). The major characteristics of this solid solution is the Isomer Shift lower than 1.46. It is impossible to determine the relative quantity of tin in this compound. The tin rich phase Pd-Sn(b) has an IS close to 2.2 attributed to an alloy between tin and palladium with 57 at% of tin (Pd_3Sn_4). If one calculate the ratio between the tin rich and the tin poor phase, one obtain a value close to 1.6, indicating that the tin rich phase is predominant. Contrary to Berndt et al. (19), the presence of significant proportions of metallic tin was not evidenced. In addition, the amount of oxidized tin species is lower in our study than the lowest value presented in (18) obtained with a $\text{Pd}(5\%)\text{Sn}/\text{Al}_2\text{O}_3$ catalyst with a low tin content (0.5%) and prepared by incipient wetness method, for which 41% of oxidized tin (Sn^{2+} and Sn^{4+}) was found. Then it can be inferred that the deposition of tin by catalytic reduction is more convenient to favor the formation of bimetallic Pd-Sn entities on alumina support and to avoid strong tin support interactions.

Tested catalyst

After the catalytic test, and without pre-reduction, tin is for the major part in an oxide phase. From the calculation of φ_A corresponding to the bond strength between tin and alumina, it can be deduced that the interactions between tin and the support are less important after catalytic test, the value being 1.2 before and 2.1 after. Therefore, it can be assumed that the tin oxide phase deposited on the palladium is aggregated.

After reduction, 20% of tin is Sn^{4+} oxide species, corresponding to SnO_2 . Then it seems that the catalytic test, the reduction of nitrates in water, leads to an increase of the amount of tin deposited on the support. As no Sn^{4+} was present on the fresh catalyst after reduction, it appears that the Sn^{4+} form is more irreducible after the catalytic test, probably due to the lower quantity of tin in interaction with palladium. This evolution of the tin phase after the catalytic test may induce a deactivation of the catalyst by loss of reduced and then active tin in interaction with palladium. Considering the mechanism proposed in (20), the decrease of tin in interaction with palladium after the catalytic test is logical, since, during the reaction tin, is oxidized by NO_3^- and then goes in solution. Then, a part of this tin is likely to be redeposited on alumina in form of SnO_2 , rather than on palladium.

The amount of chlorinated Sn^{2+} species is almost not modified by the catalytic test. This result confirms the high stability of this tin species.

After reduction, two Pd-Sn phases are also observed, but the corresponding alloys or solid solution of the tested catalyst are not identical to those observed directly on the fresh reduced catalyst. The tin poor phase Pd-Sn(a) corresponds to an alloy Pd_3Sn , resulting from a slight decrease of the palladium content in this phase during the catalytic test, since the palladium content in this type of phase was higher before the test ($\text{Pd}_{(x>3)}\text{Sn}$). This could be explained by

a segregation between palladium and tin leading to the apparition of monometallic palladium particles on the support.

For the tin rich phase Pd-Sn(b), the Isomer Shift value of 2.51-2.53 is very close to that of β tin (2.58 mm.s⁻¹ (48,49)), indicating that in the bimetallic particles, tin might be aggregated at the surface of palladium particles and considered as unalloyed metallic tin.

On alumina based catalyst, the most important results are that the ratio between tin rich and tin poor phase is higher after catalytic test (1.62) than before (0.75), indicating that the tin distribution is modified by the test in water. It seems that tin is aggregated with itself or is deposited as large particles on free palladium. The interactions between the metallic phase and the support decrease after catalytic test. The values of ϕ_A increase from 5.5 to 6.3 and from 3.4 to 4.3 respectively for the tin poor and the tin rich phases, indicating that in both cases tin is less in interaction with the palladium and could be aggregated with itself. Then, the dispersion of tin in bimetallic particles is decreased by the catalytic test, in accordance with the results obtained by O₂/H₂/O₂ titration.

Then, the catalytic test induces an important modification of the palladium and tin distribution on the alumina surface with (i) an increase of tin oxide species in interaction with the support and (ii) a segregation between tin and palladium in bimetallic particles.

b) Silica supported catalyst

Fresh catalyst

For the catalysts characterized as prepared, the only phase detected is the oxide phase SnO₂. The calculation of ϕ_A gives a value of 6.2 indicating that the tin is weakly bonded with the support compared to the alumina based catalyst. And then, in this oxide phase, tin is not in

interaction with the support, but included in large particles over palladium. The value of φ_A is characteristic of an alloy (47).

After reduction the best fit of the spectra was obtained for two different species. A tin poor Pd-Sn(a) and a tin rich Pd-Sn(-b) phase. The tin poor phase is identical to that observed on alumina, corresponding to a solid solution of tin in palladium. The tin rich phase Pd-Sn(b) is an alloy with an Isomer Shift close to 1.8, corresponding to Pd₂Sn. This phase is the same than the one observed by XRD. This phase has a relative area of 77%, and the ratio between the relative quantity of the tin rich and tin poor phases, is about 3. This value is very high compared to the 1.6 observed on the alumina supported fresh catalyst.

Tested catalyst

After catalytic test and without prereduction before measurement, the Pd-Sn/SiO₂ catalyst contains 25% of a metallic phase Pd₃Sn and 75% of the SnO₂ oxide phase. This large amount of metallic phase, after catalytic test and contact with air, demonstrates a good stability of metallic tin in this alloy

The calculation of the bond strength between tin and silica gives 5.5, indicating that the oxidized tin could be aggregated (weak metal-support interaction). For the metallic phase of Pd₃Sn, the calculation of the φ_A gives 2.5, this value is close to that of pure tin.

Once more, after reduction, no tin oxide phase is identified. This demonstrates the good stability of the bimetallic entities over silica. The tin poor phase Pd-Sn(a) is an alloy with an isomer shift close to 1.5, characteristic of the Pd₃Sn phase (48, 49). The comparison of this composition to the composition of the tin poor phase before the catalytic test (solid solution with less than 18 at% of tin), shows that the catalytic test leads to an enrichment of tin of this phase.

The tin rich phase Pd-Sn(b) is also an alloy, with an IS close to 2.2, characteristic of Pd₃Sn₄ (48, 49). As in the tin poor phase, a global enrichment in tin of this metallic phase is observed. The φ_A calculation gives a value close to 7, so it can be inferred that the tin is in very large particles over palladium. As the only phases identified are Pd₃Sn and Pd₃Sn₄ alloys after the catalytic test with no isolated tin species, and as the catalytic test induces an enrichment in tin of these bimetallic species, it can be deduced that isolated palladium particles are likely to be present on the silica support, and that the number of palladium atoms involved in this bimetallic particles is decreased after catalytic test. From the comparison of the relative area of the two Pd-Sn phases it can be noticed that there is two times more of the tin poor phase than tin rich phase. This result, correlated with the high incorporation rate of tin in the palladium particles, can be explained by a migration of the tin in rich phase to the tin poor phase. This is likely to be due to the oxidation of tin during the nitrate reduction, and to a higher probability of re-deposition of this species in the poor phase.

c) Conclusion of the ¹¹⁹Sn Mössbauer study

To conclude, spectra of silica supported bimetallic PdSn catalysts, before and after catalytic test, after contact with air or reduced, present evidence that the formation of bimetallic entities is predominant on this type of support.

Contrary to the results obtained with the silica supported catalysts, it is difficult to prevent the deposition of tin on alumina, due to its high affinity for the support, even if the preparation method and the catalytic test, where hydrogen is chemisorbed on palladium particles, favors the catalytic reduction of Sn²⁺ or Sn⁴⁺ and then the formation of bimetallic particles. Then, it could be inferred that in the fresh bimetallic catalyst, tin species present in bimetallic entities are likely to be located at the interface between the support and the

palladium particles, which would favor the migration of tin from bimetallic particles to the support during the catalytic test leading to the unreducible SnO₂ species observed on PdSnAT.

3.2.2. Catalytic performances

In order to link the tin distribution with catalytic performances, samples were evaluated in nitrite and nitrate reduction.

3.2.2.1. Nitrite reduction

The catalytic performances for nitrite reduction were determined for the two different (PdSnA and PdSnS) fresh (F) or tested (T) catalysts. Results are reported in Table 7.

The alumina based catalysts are the most active, but the silica ones are the most selective, in accordance with (3). This could be explained by the difference of hydrogen adsorption capacity of the two types of catalysts. Indeed, the hydrogen uptake is higher on the alumina supported catalysts as compared to silica catalysts and then the accessibility of palladium sites and the probability of nitrite reduction by hydrogen on these sites is also more important on PdSn. This could also explain the selectivity in N₂, which is lower on the alumina than on the silica supported catalysts. Indeed, the more accessible palladium surface, the higher probability of meeting of four hydrogen and one nitrogen atoms, favoring the formation of NH₄⁺. However, the selectivity of the tested alumina supported catalyst is lower than the one of the corresponding fresh catalyst whereas its activity and its hydrogen uptake are lower. Then, the activity and selectivity of the bimetallic catalysts can not be only rationalized in terms of palladium accessibility to hydrogen, and the presence of tin has to be taken into account. The activity in nitrite reduction has been reported as a function of the number of oxygen atoms chemisorbed on metallic tin determined from the O₂/H₂/O₂ titration results

reported in Figure 6. This figure demonstrates that the activity of the catalysts for nitrite reduction could also be related to the number of metallic tin sites in interaction with palladium. It is well known that nitrite reduction occurs principally on metallic palladium sites (3,12). So the influence of the amount of metallic tin in interaction with palladium on the activity could be explained in terms of electronic effect. Indeed, the donating effect of tin toward palladium would reinforce its noble character and then its activity.

3.2.2.2. Nitrate reduction

The catalytic test was carried out with fresh and tested catalysts supported on alumina and silica. The results are presented in Table 7. During nitrate reduction no nitrite appeared in solution whichever the catalyst is, that is likely to be due to the higher activity of all the catalysts for nitrite than for nitrate reduction. As for nitrite reduction, the fresh alumina supported catalyst is more active but less selective than the fresh silica one. The same difference is observed between the tested catalysts. The figure 6 shows also that the activity in nitrate reduction could be correlated to the number oxygen atoms chemisorbed on metallic tin sites which could be oxidized by nitrate.

4- CONCLUSION

Then to conclude, it has been evidenced by Mössbauer spectroscopy that on silica supported catalysts, only Pd-Sn solid solutions or alloys are present, whereas on alumina supported catalysts, tin is present at the interface between the support and palladium, or alone on the support, due to its high affinity for alumina. The presence of tin in bimetallic catalyst restricts the sintering phenomenon occurring in water on monometallic palladium catalyst supported on alumina or silica. In addition, the estimated number of oxygen atoms chemisorbed on

metallic tin is very low on the silica supported catalysts whereas the amount of oxygen chemisorbed on tin is much more important in the alumina supported catalysts. It seems that the activity of the catalyst in nitrate and nitrite reduction is directly linked to the amount of reducible tin in interaction with palladium. This confirms a redox mechanism between nitrate and tin. For nitrite reduction, this could be explained by a reinforcement of the noble character of palladium.

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Table 1: Catalysts identification, metal loading and chloride content (in wt%) of fresh mono and bimetallic catalysts supported on alumina (A) or silica (S)

Catalyst	% Pd	% Sn	% Cl
Pd5AF	4.7	-	0
Pd5SF	4.7	-	0
PdSnAF	4.7	1.5	0.9
PdSnSF	4.7	1.5	0.9

Table 2: Oxygen and hydrogen atom uptakes, dispersion and particle size in the monometallic fresh (F) or tested (T) palladium catalysts supported on alumina (A) or silica (S)

Catalyst	OT1 ($\mu\text{mole.g}_{\text{cat}}^{-1}$)	HT ($\mu\text{mole.g}_{\text{cat}}^{-1}$)	OT2 ($\mu\text{mole.g}_{\text{cat}}^{-1}$)	Dispersion of palladium (%)	Particle size (nm)
Pd5AF	74	162	58	12.2	8.3
Pd5AT	22	46	24	3.4	28.8
Pd5SF	32	68	34	5.1	19.8
Pd5ST	14	28	12	2.1	47.5

Table 3: Activity and selectivity in nitrogen, at 75 % of nitrite conversion, of palladium catalysts supported on alumina or silica

Catalyst	activity ($\text{mmol.min}^{-1}\text{g}_{\text{cata}}^{-1}$)	Selectivity in N_2 (%)
Pd5AF	0.450	91.9
Pd5AT	0.440	97.0
Pd5SF	0.728	99.4
Pd5ST	0.725	>99.7

Table 4: Oxygen and hydrogen atom uptakes in palladium-tin catalysts supported on alumina or silica and estimated amount of metallic tin

<i>Catalysts</i>	OT1	HT	OT2	Amount of Sn ⁰
	($\mu\text{mole.g}_{\text{cat}}^{-1}$)	($\mu\text{mole.g}_{\text{cat}}^{-1}$)	($\mu\text{mole.g}_{\text{cat}}^{-1}$)	($\mu\text{mole.g}_{\text{cat}}^{-1}$)
PdSnAF	142	146	72	70
PdSnAT	98	140	68	30
PdSnSF	72	112	56	16
PdSnST	70	108	54	16

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Table 5 : Parameters of Mössbauer Spectra of the Pd-Sn catalysts supported on alumina or silica

Sample	Treatment ^a Temp. Mes.	Species ^b	IS ^c (mm.s ⁻¹)	QS ^d (mm.s ⁻¹)	FWHM ^e	RI ^f (%)	φ_A ^g (a.u.)			
PdSnAF	As prepared	Sn ⁴⁺	300K	0.02	0.57	0.96	100	1.2		
			77K	0.07	0.63	1.13	100			
	Reduced	Pd-Sn(a)	300K	1.43	-	1.33	38.7	5.5		
			77K	1.40	-	1.31	21.5			
		Pd-Sn(b)	300K	2.24	-	1.33	43.3	3.4		
			77K	2.21	-	1.70	56.8			
		Sn ²⁺	300K	4.01	0.26	0.75	18.0	5		
			77K	4.07	0.30	0.78	21.7			
	PdSnAT	As received	Sn ⁴⁺	300K	0.03	0.53	0.94	100	2.1	
				77K	0.07	0.57	1.03			
Reduced		Sn ⁴⁺	300K	0.05	0.54	0.80	27.2	3		
			77K	0.03	0.55	0.76	17.5			
		Pd-Sn(a)	300K	1.70	-	1.31	39.8	6.3		
			77K	1.69	-	1.18	32.5			
		Pd-Sn(b)	300K	2.51	-	1.06	20.9	4.3		
			77K	2.53	-	1.23	33.2			
		Sn ²⁺	300K	3.89	0.32	0.73	12.1	6.1		
			77K	3.97	0.33	0.72	16.8			
PdSnSF		As prepared	Sn ⁴⁺	300K	0.02	0.54	0.96	100	6.2	
				77K	0.05	0.56	0.95	100		
	Reduced	Pd-Sn(a)	300K	1.34	-	1.30	17.6	5.2		
			77K	1.33	-	1.08	27.9			
		Pd-Sn(b)	300K	1.81	-	1.45	82.4	3.8		
			77K	1.93	-	1.46	72.1			
		PdSnST	As received	Sn ⁴⁺	300K	0.01	0.53	0.94	70.9	5.5
					77K	0.04	0.55	0.90	79.0	
Pd-Sn(c)	300K		1.56	-	1.08	29.1	3.4			
	77K		1.62	-	1.04	21.0				
Reduced	Pd-Sn(a)		300K	1.53	-	1.28	76.9	2.9		
			77K	1.50	-	1.17	49.0			
	Pd-Sn(b)		300K	2.25	-	1.10	23.1	7		
			77K	2.12	-	1.50	51.0			

^a All the experiments for a given catalyst were performed with the same sample, which was treated in situ with H₂ at 400°C for 2 hours. The temperatures of the measurement (Temp. Mes.) are 77 or 300 K.

^b Pd-Sn(a), tin poor Pd-Sn alloys ; Pd-Sn(b), tin rich Pd-Sn alloys ; Pd-Sn(c), tin phase stable in the air

^c Isomer Shift relative to SnO₂.

^d Quadrupole splitting.

^e Full width at half maximum.

^f Normalized relative intensity. Because the probability of the Mössbauer effect (recoilless fraction) is different for the various Sn species (49), the RIs do not strictly correspond to concentrations.

^g $\varphi_A = -d \ln (A_{300}/A_{77})/dT \times 10^{-1}$, where A₃₀₀ and A₇₇ are the actual absorption areas of components in the spectra recorded at 300 and 77 K, respectively.

Table 6 : Tin species identified for reduced bimetallic catalysts supported on alumina or silica before (PdSnAF and PdSnSF) and after (PdSnAT and PdSnST) catalytic test with the estimated relative amount of this tin phase

Sample	Sn ⁴⁺	Pd-Sn(a)	Pd-Sn(b)	Sn ²⁺
PdSnAF	SnO ₂	Pd _(x>3) -Sn	Pd ₃ -Sn ₄	SnO _x Cl _y
	0 %	30%	50%	20%
PdSnAT	SnO ₂	Pd ₃ -Sn	β Sn/Pd	SnO _x Cl _y
	22%	36%	27%	15%
PdSnSF	SnO ₂	Pd _(x>3) -Sn	Pd ₂ -Sn	SnO _x Cl _y
	0 %	23%	77%	0 %
PdSnST	SnO ₂	Pd ₃ -Sn	Pd ₃ -Sn ₄	SnO _x Cl _y
	0%	63%	37%	0%

Table 7: Activity and selectivity towards nitrogen at 75 % of conversion for nitrite and nitrate reduction in the presence of palladium-tin catalysts supported on alumina or silica

Catalyst	Nitrite reduction		Nitrate reduction	
	Activity (mmol.min ⁻¹ g _{cata} ⁻¹)	Selectivity in N ₂ (%)	Activity (mmol.min ⁻¹ g _{cata} ⁻¹)	Selectivity in N ₂ %
PdSnAF	0.576	97.1	0.049	92.8
PdSnAT	0.396	94.3	0.040	84.6
PdSnSF	0.334	> 99.7	0.034	93.2
PdSnST	0.315	> 99.7	0.031	90

Figure captions

Figure 1 : TEM pictures of the fresh Al_2O_3 and SiO_2 supported Pd-Sn bimetallic catalysts, PdSnAF (a) and PdSnSF (b)

Figure 2 : TEM pictures of tested Al_2O_3 and SiO_2 supported Pd-Sn bimetallic catalysts, PdSnAT (a) and PdSnST (b)

Figure 3 : Histograms of particle sizes of the alumina supported catalysts (a) PdSnAF (■) and PdSnAT (■) and silica supported catalysts (b) PdSnSF (■) and PdSnST (■) determined from TEM pictures.

Figure 4 : XRD spectra of reduced PdSnSF (a) and PdSnAF (b) 25 to 85° 2 θ scale

Pd syn (—) PdSn (—→) Pd₃Sn₂ (·····→)

Figure 5 : ¹¹⁹Sn Mössbauer spectra of the reduced PdSnSF (a) and PdSnAF (b) measured at 77 K (▲) and 300 K (■).

Figure 6 : Activity in nitrite (▲) and nitrate (■) reduction as a function of the estimated number of oxygen atoms chemisorbed on metallic tin in interaction with palladium.

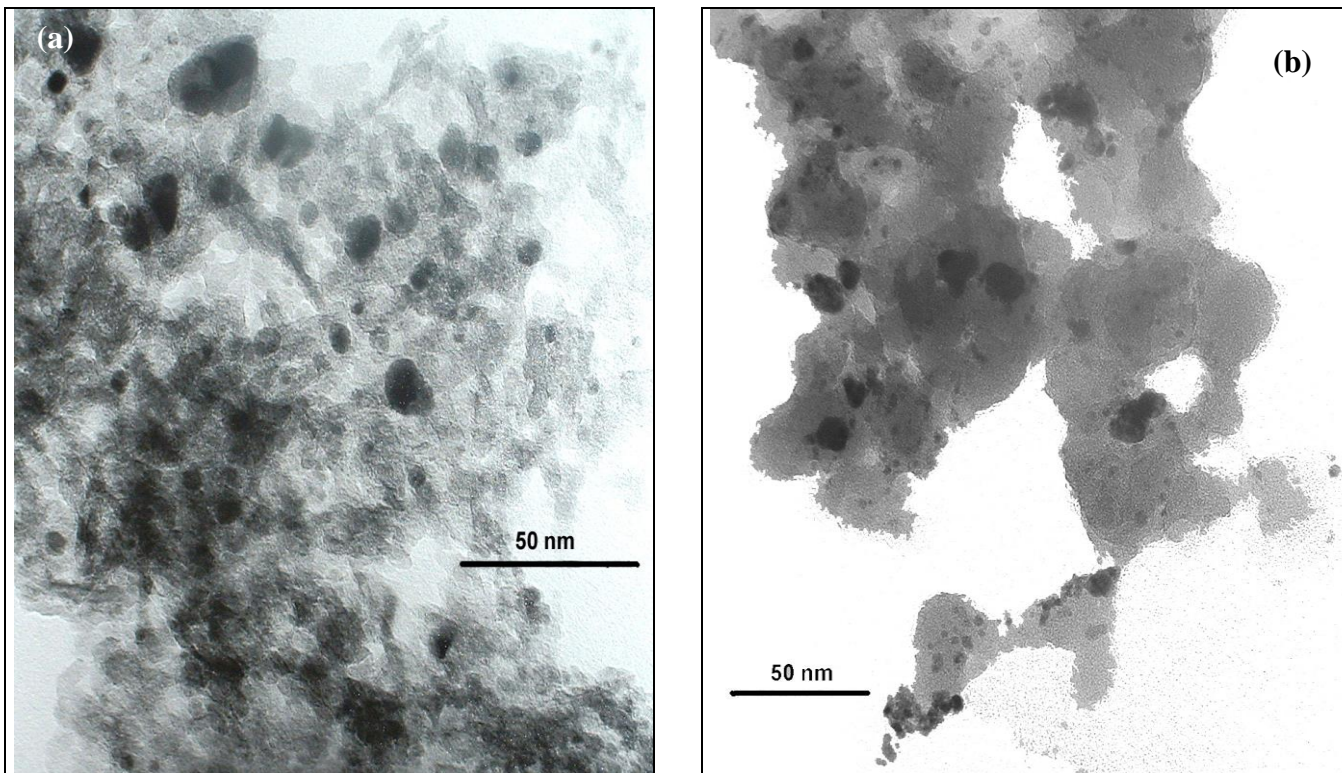


Figure 1

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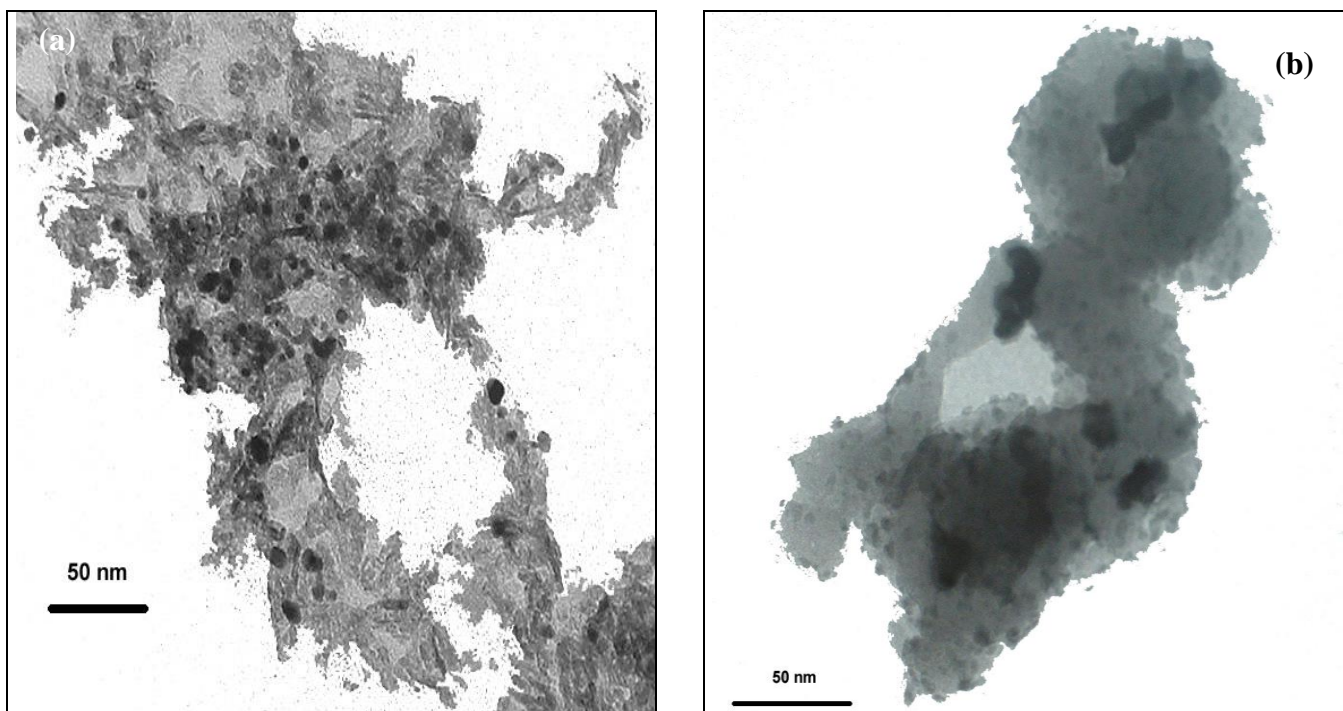


Figure 2

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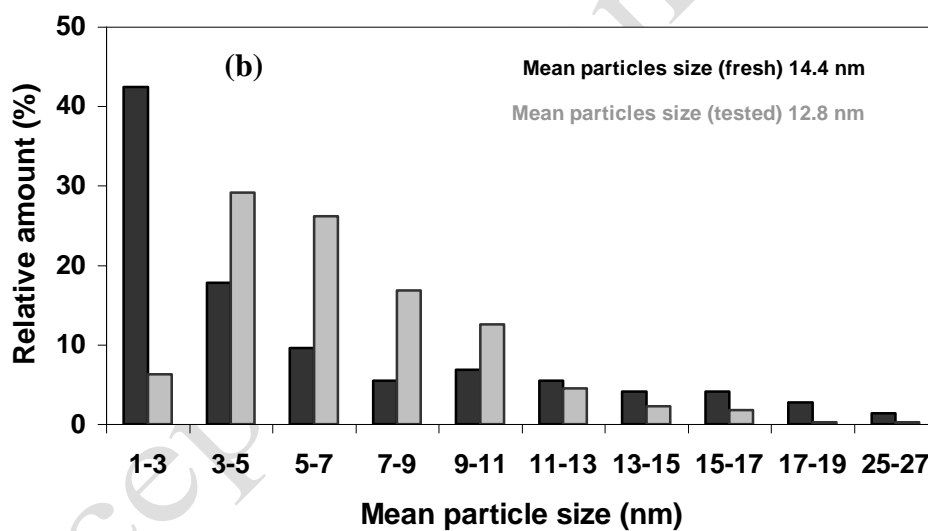
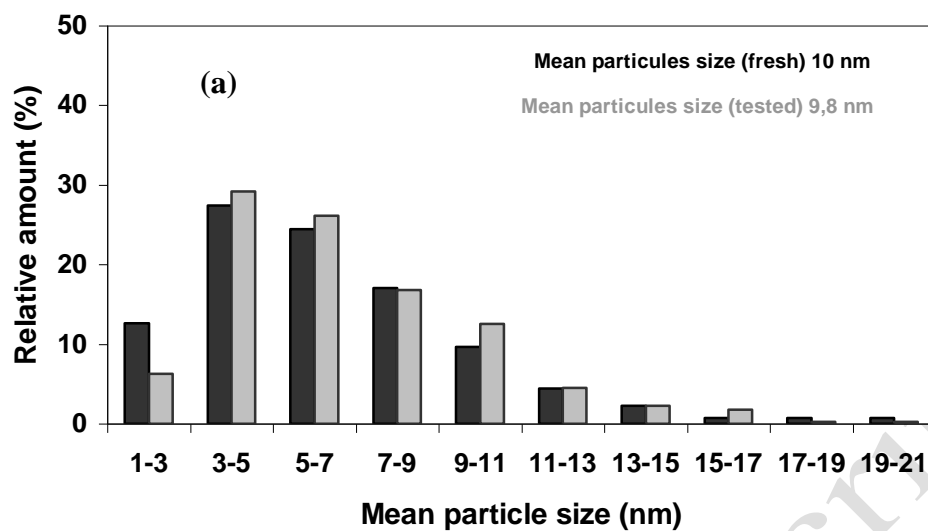


Figure 3

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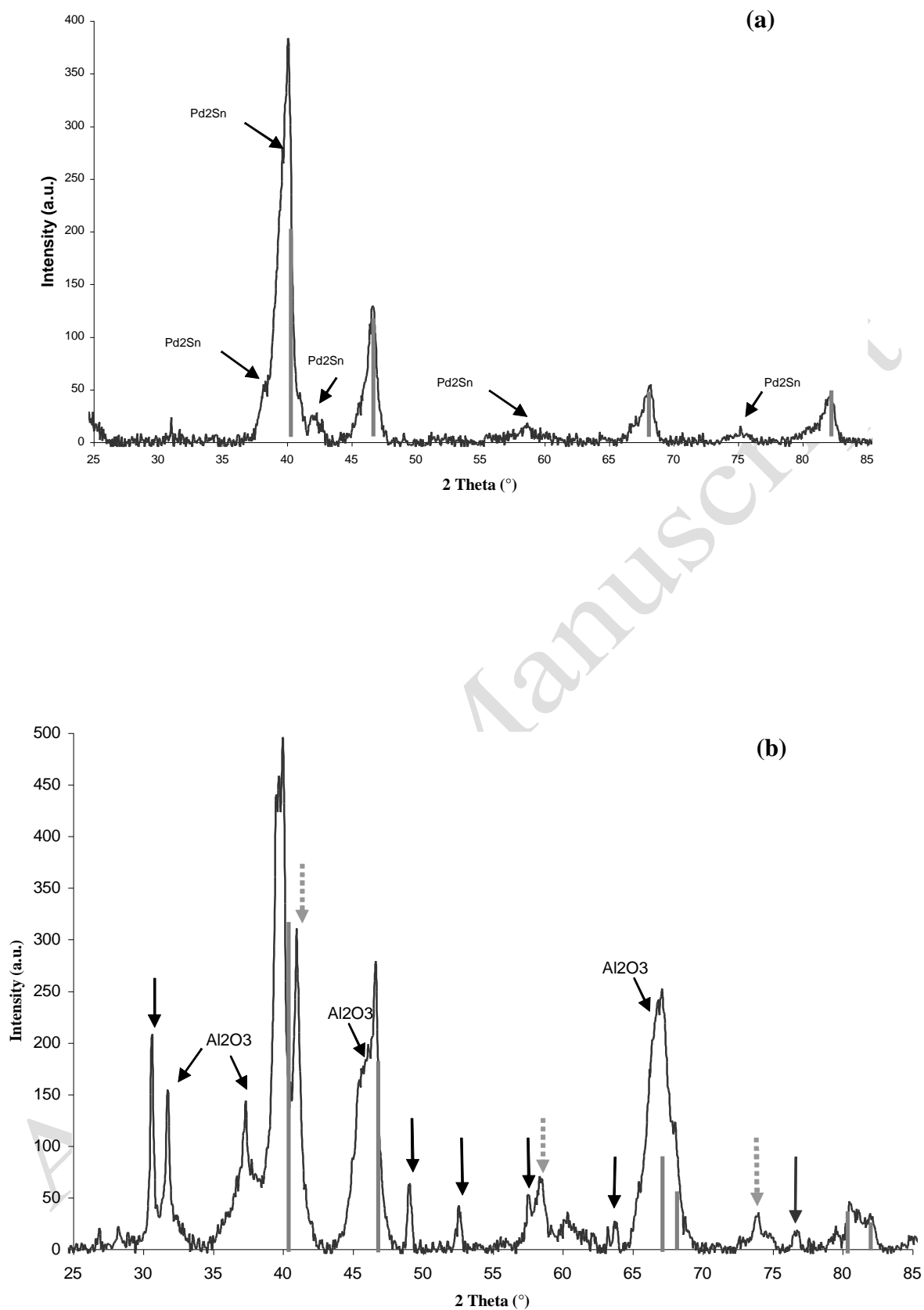


Figure 4

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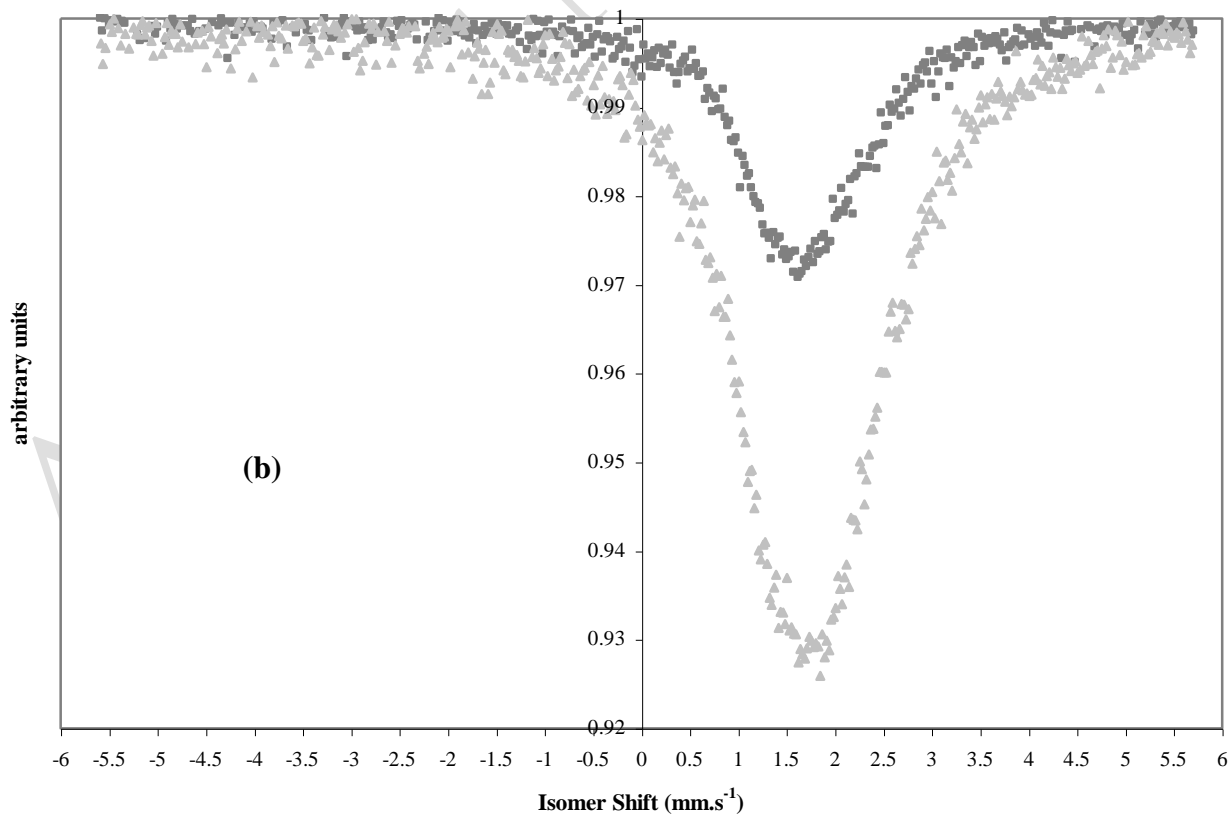
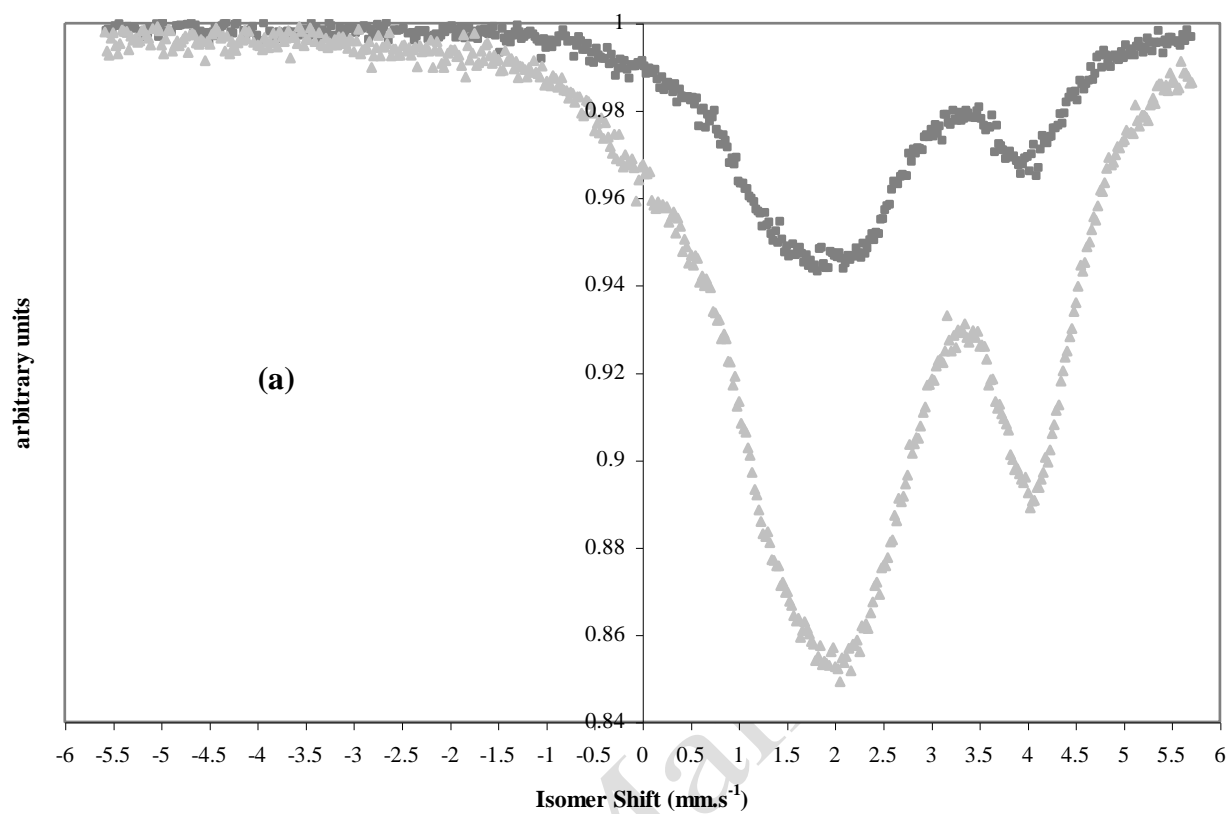


Figure 5

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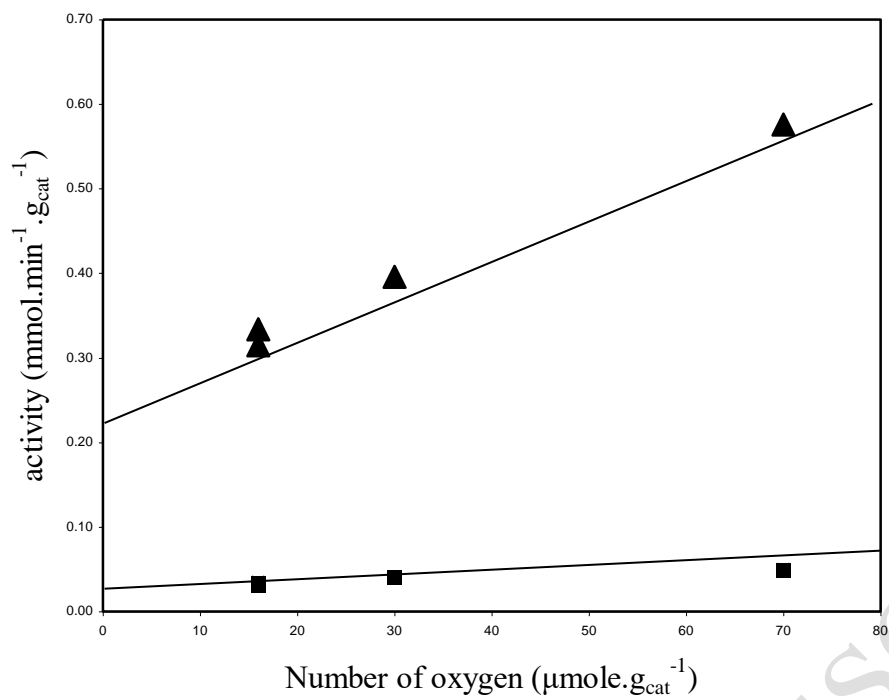


Figure 6

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