



## Spectroscopic and catalytic characterization of Pd–In and Pt–In supported on Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, active catalysts for nitrate hydrogenation

F.A. Marchesini<sup>a</sup>, S. Irusta<sup>b</sup>, C. Querini<sup>a</sup>, E. Miró<sup>a,\*</sup>

<sup>a</sup> Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE (FIQ UNL-CONICET), Santiago del Estero 2829, 3000 Santa Fe, Argentina

<sup>b</sup> Departamento de Ingeniería Química y Tecnologías del Medio Ambiente, Facultad de Ciencias, Universidad de Zaragoza, Pedro Cerbuna 12, Zaragoza, Spain

### ARTICLE INFO

#### Article history:

Received 7 March 2008

Received in revised form 11 June 2008

Accepted 16 June 2008

Available online 28 June 2008

#### Keywords:

Nitrates

Nitrites

Catalytic reduction

Bimetallic catalysts

### ABSTRACT

Bimetallic Pt–In and Pd–In catalysts supported on alumina or silica were studied for the reduction of nitrate to N<sub>2</sub> in water, using H<sub>2</sub> as reducing agent. Characterization results indicate that bimetallic particles with the surface enriched in indium, metallic crystals of Pt or Pd, and oxides of Pt or Pd and In<sub>2</sub>O<sub>3</sub> are the main surface species present in the catalysts.

Several catalysts studied in this work could fulfill the requirements usually established as limit values: 50 ppm of NO<sub>3</sub><sup>−</sup>, 0.1 ppm of NO<sub>2</sub><sup>−</sup> and 0.5 ppm of NH<sub>4</sub><sup>+</sup>. The reaction rate is strongly influenced by either the Pt:In or the Pd:In ratio, the optimum being observed at low contents of In. Of all the catalysts studied in this work, Pd(1 wt.%)In(0.25 wt.%)Al<sub>2</sub>O<sub>3</sub> is the most active one, but unfortunately, it presents an undesirable high selectivity towards ammonia when nitrate conversion reaches 100%. Pt(1.0%)In(0.25%)/Al<sub>2</sub>O<sub>3</sub> presents a high initial activity but it fastly deactivates during reaction. In general, Pd–In catalysts are more active for nitrate conversion than Pt–In, and alumina is a better support than silica.

The composition of the catalysts changes both after reduction and after contacting the liquid reaction media. These changes have been observed by XPS and TEM. In general, the samples used in the reaction have lower dispersion of metallic phases than the fresh-calcined ones. For most of the catalysts used in this work, the Pt:In or Pd:In surface ratio is lower than the bulk ones, this probably being the reason for the low amount of In that is sufficient to have an optimal performance for nitrate conversion.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

The contamination of water due to both intensive fertilization and waste effluents from industries has produced an increase of nitrate concentration in groundwater. Nitrates are reduced to nitrites in the digestive system, affecting hemoglobin and impairing its function as oxygen-carrier, thus causing the “blue baby syndrome”. They are also related to several kinds of cancer, e.g. ovarian and prostate cancers.

At present, the most widespread technologies for the removal of nitrates are biological denitrification and physical chemical processes: ion exchange, reverse osmosis and electro dialysis. However, they present serious problems, e.g. the bacterial process includes handling difficulties, low reaction rates, removal of by-products, low space velocities. Physical–chemical processes only remove the nitrate into brine which has to be treated afterwards or disposed of. Moreover these technologies can be very expensive.

Therefore, increasing attention has lately been paid to a novel technology, still in its development stages: catalytic denitrification [1,2] which employs solid bimetallic catalysts. In this catalytic process, nitrates are reduced to nitrogen using hydrogen; however, undesirable products such as nitrite and ammonium are also formed.

Several solid catalysts have been presented by various authors [3–5]. The catalysts were prepared over different mesoporous supports such as massive oxides, alumina or silica, with the addition of noble metals as Pt or Pd as the main metal, and some second metal such as Cu, Co or In as promoter metal. The possible mechanism for the catalytic reduction is through the combination of active sites in the bimetallic catalyst [6] where the nitrate is reduced to nitrite over the bimetallic particle, and then the nitrite produced is reduced over the noble metal particle to nitrogen or ammonium depending on site selectivity and environmental conditions. Ammonia is a side product which is obtained due to overreduction, and to avoid this a strict control of the reaction media is necessary. Nitrate reduction produces hydroxide ions, and the local accumulation of these could produce a loss of selectivity and activity. The pH can be successfully controlled by adding little volumes of a HCl solution [7].

\* Corresponding author. Tel.: +54 342 4536861; fax: +54 342 4536861.  
E-mail address: [emiro@fiqus.unl.edu.ar](mailto:emiro@fiqus.unl.edu.ar) (E. Miró).

In a previous communication [8] we reported that for Pt–In catalysts, bimetallic particles with the surface enriched in indium, probably  $\text{Pt}_2\text{In}_3$  and/or  $\text{Pt}_3\text{In}_7$  species, are the active sites for nitrate reduction. In this work, we present a complete study in which Pd–In and Pt–In catalysts are compared with the aim of relating their catalytic activity and selectivity with physicochemical properties. To this end, we used a series of solids with various metal compositions and different supports ( $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ). XPS, XRD and TEM were chosen as characterization tools, activity and selectivity measurements being carried out in a stirred batch reactor with an on-line pH control.

We have chosen the Pt–In and Pd–In metallic couples because In promoted catalysts have good activity for nitrate conversion and a potential high selectivity to  $\text{N}_2$ , as reported by other authors [1,6]. Prüsse et al. [6] presented a second generation of nitrate-reducing catalysts which included In as promoter, also describing new concepts such as the use of formic acid as reductant instead of hydrogen. The results obtained in the present work could also be useful to better understand the behavior of bimetallic catalysts in an ionic reaction media, in which bimetallic particles can undergo transformations due to both the reaction itself and the contact with the ionic solution.

## 2. Experimental

### 2.1. Catalyst preparation

The catalysts were prepared by dry impregnation. Aqueous solutions of  $\text{PtCl}_4\text{H}_2$  ( $10.0 \text{ mg mL}^{-1}$ ) or  $\text{PdCl}_2$  ( $10.0 \text{ mg mL}^{-1}$ ), and  $\text{InCl}_3$  ( $4.6 \text{ mg mL}^{-1}$ ) were added to 20–40 mesh particles of  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  at room temperature in order to obtain concentrations between 0.5 and 1.5 wt.% of Pt or Pd and between 0.05 and 1.8 wt.% of In. The solids were dried overnight at 393 K and calcined for 2 h, at 773 K in air flow. The supports used were 20–40 mesh  $\text{Al}_2\text{O}_3$  pellets (Ketjen CK300, surface area:  $180 \text{ m}^2 \text{ g}^{-1}$ , pore volume:  $0.5 \text{ cm}^3 \text{ g}^{-1}$ ) or 20–40 mesh  $\text{SiO}_2$  pellets (AESAR Large Pore, surface area:  $300 \text{ m}^2 \text{ g}^{-1}$ , pore volume:  $1 \text{ cm}^3 \text{ g}^{-1}$ ).

### 2.2. Catalyst characterization

#### 2.2.1. X-ray photoelectron analysis (XPS)

The X-ray photoelectron analysis (XPS) was performed with an Axis Ultra DLD (Kratos Tech.) instrument. The samples were mounted on a sample rod placed in the pretreatment chamber of the spectrometer and then evacuated at room temperature. The spectra were excited by the monochromatized Al  $\text{K}\alpha$  source (1486.6 eV) run at 15 kV and 10 mA. For the individual peak regions, a pass energy of 20 eV was used. The survey spectrum was measured at 160 eV pass energy. Analyses of the peaks were performed with the software provided by the manufacturer, using a weighted sum of Lorentzian and Gaussian component curves after background subtraction. The binding energies were referenced to the internal C 1s (285.0 eV) standard.

#### 2.2.2. X-ray diffraction analysis (DRX)

X-ray diffractometer patterns were acquired with an XD-D1 Shimadzu instrument, using Cu  $\text{K}\alpha$  radiation at 30 kV and 40 mA. The scan rate was  $1^\circ \text{ min}^{-1}$  in the  $2\theta = 10\text{--}80^\circ$  range.

#### 2.2.3. TEM images

Supported metal particles were observed with a Jeol Electronic Microscopy, Model 100 CX II operating at 100 kV with 6 Å resolution. The powder was ultrasonically dispersed in ethanol, and the suspension was deposited on a copper grid.

### 2.3. Nitrate hydrogenation experiments

The reaction test was performed in a three-necked round bottom flask (volume 250 mL) equipped with a magnetic stirrer (700–800 rpm). The pH value was controlled using an automatic pH controller unit. Experiments were carried out at room temperature, pH 5 and atmospheric pressure. Hydrogen was fed by a tube into the solution using a flow rate of  $400 \text{ mL min}^{-1}$  to ensure the maximum possible hydrogen concentration in solution.

The catalysts were pretreated under a flow of  $\text{H}_2$  ( $100 \text{ mL min}^{-1}$ ) at 723 K with a heating rate of  $10 \text{ K min}^{-1}$ . Then, a stirred batch reactor was loaded with 80.0 mL of distilled water, 200 mg of catalyst, and 100 N-ppm of nitrate as initial concentration. Subsequently, a hydrogen flow of  $400 \text{ mL min}^{-1}$  was fed to the batch reactor. A pH of ca. 5 was maintained during the reaction time by the addition of small amounts of HCl [7].

Small samples were taken from the vessel for the determination of nitrate, nitrite and ammonium using Vis spectroscopy (Cole Parmer 1100 Spectrophotometer) combined with colorimetric reagents. In order to determine nitrates, the Cd Column method and then the colorimetric reaction were used. This colorimetric reaction is the same as the one employed in the assay for nitrites. Ammonium was analyzed by the adapted Berthelot method. The other nitrogen containing compounds were  $\text{N}_2$  and small amounts of  $\text{N}_2\text{O}$  in the gas phase, which were not measured.

## 3. Results and discussion

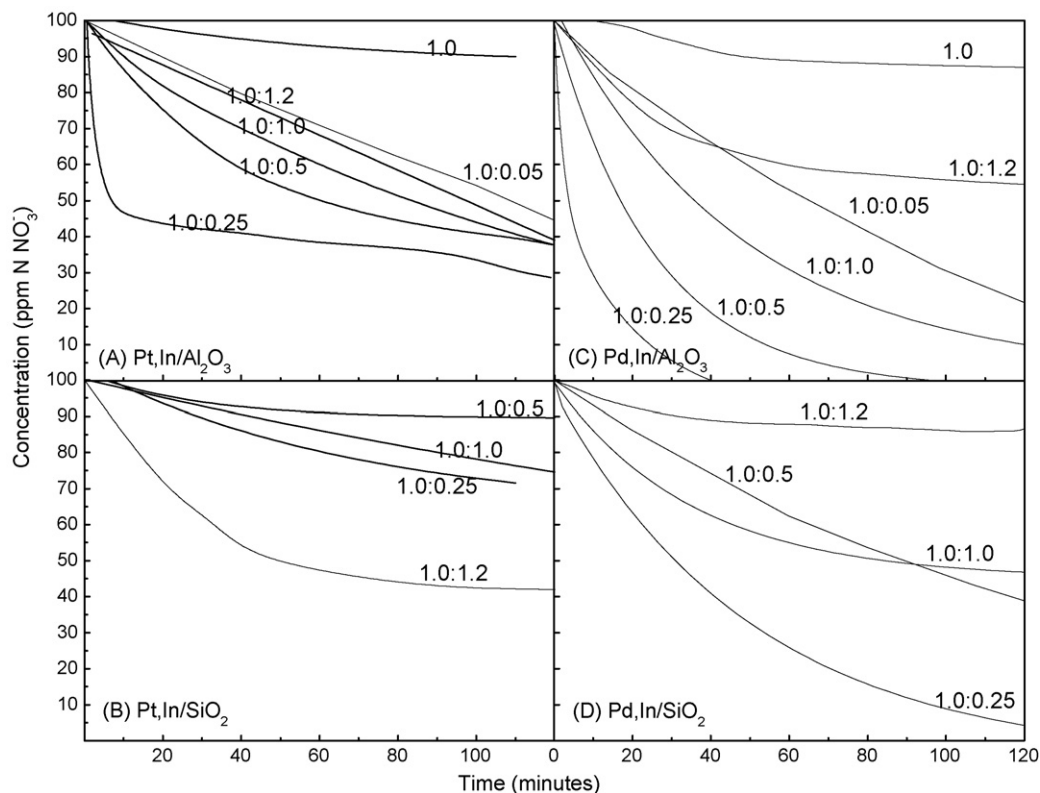
### 3.1. Reaction experiments

Fig. 1 shows reaction results for the catalysts studied in this work, containing 1 wt.% of noble metal and different In amounts, from 0.05 wt.% to 1.2 wt.%. In general, it can be seen that Pd–In catalysts reduce nitrates faster than Pt–In ones, and that alumina is a better support than silica, which could be due to the higher PZC value of silica, thus decreasing the rate of adsorption of nitrate ions.

Catalysts containing only noble metals (Pt or Pd), are almost inactive. The addition of a small amount of In (0.05 wt.%) to Pt/ $\text{Al}_2\text{O}_3$  and Pd/ $\text{Al}_2\text{O}_3$  increases nitrate conversion and is further increased with 0.25 wt.% of In. However, the addition of higher amounts of In results in lower conversions. A similar behavior is observed in terms of the reaction rate measured at low nitrate conversions; at intermediate In contents an optimum reaction rate is obtained.

In a previous communication [8], for Pt–In catalysts, we reported that the Pt(1.0%)In(0.25%)/ $\text{Al}_2\text{O}_3$  catalyst shows a very high initial conversion rate but after ca. 15 min, it decreases reaching only 67.7% of conversion at 100 min. The decrease in reaction rate occurred faster than with catalysts with lower Pt:In ratios [8], in such a way, that the initial reaction rate is the highest for the Pt(1.0%) In(0.25%)/ $\text{Al}_2\text{O}_3$  catalyst, whereas at 60% conversion, it is the lowest. For other catalysts with higher In loadings up to a 1.0:1.2 wt.% Pt:In ratio, both the initial reaction rate and the nitrate conversion decreased as the In loading increased. Note that none of the Pt–In catalysts reached 100% of nitrate conversion after 120 min of reaction. In the case of Pd–In catalysts such deactivation phenomena are not observed, at least in the experiments shown in Fig. 1. In fact, Pd(1.0%)In(0.25%)/ $\text{Al}_2\text{O}_3$  reaches 100% of nitrate conversion in 40 min.

In addition to nitrogen, certain undesirable products such as nitrites and ammonia were produced. Moreover, even though  $\text{N}_2$  is the main gaseous compound formed, nitrogen oxides can also be produced [7]. Daum and Vorlop [9] suggested that nitrogen oxides are reaction intermediates. In Figs. 2 and 3, nitrite and ammonia production against time are shown, respectively. Nitrite is a reaction



**Fig. 1.** Nitrate reduction on In promoted Pt and Pd catalysts supported on  $\text{Al}_2\text{O}_3$  (A) and (C) and Pt and Pd catalysts supported on  $\text{SiO}_2$  (B) and (D). For reaction conditions see Section 2.

intermediate; thus, in general it presents curves with a maximum at intermediate reaction times. The most active catalysts for nitrate reduction show the lowest nitrite formation because they are also active for nitrite reduction. However, results for ammonia production indicated that higher Pt:In or Pd:In ratios produce higher ammonia concentrations, reaching about 22–23 ppm.

As said above, the reaction rate measured at low nitrate conversions shows a maximum if plotted against Pt/In or Pd/In ratios. This behavior is shown in Fig. 4A for Pd, In/ $\text{Al}_2\text{O}_3$  catalysts, which are the most active among those studied in this work. The nitrate conversion reached at 100 min of reaction time is also depicted (Fig. 4B), showing a similar trend as the reaction rate. Unfortunately, the Pd(1.0%)In(0.25%)/ $\text{Al}_2\text{O}_3$  catalyst, the most active one for nitrate conversion, produces the highest ammonia concentration, indicating that formulations with an adequate balance between activity and selectivity are necessary.

In order to gain insight into the deactivation phenomena, an experiment was designed in which once nitrate is ca. totally converted, a new amount (pulse) of nitrate is introduced in the batch reactor. In this way, the catalyst is subjected to a higher time-on-stream, in which deactivation could be better observed. Results of this experiment for Pd(1.0%)In(0.25%)/ $\text{Al}_2\text{O}_3$  are shown in Fig. 5. It can be seen that in the second and third pulse of nitrate, the time necessary to reach 100% of conversion steeply increases. Fig. 6 shows the same experiments but with pulses of nitrite, and a similar behavior is observed. Thus, a slow deactivation is observed for the Pd–In catalyst, which is lower than that reported for the Pt–In one [8]. Steady state experiments with longer time-on-stream are planned to determine the extent of deactivation with time under practical conditions. Since no loss of metals has been detected in the solution (detection limit is ca. 0.1 ppm, which corresponds to 0.008 mg of weight loss from the catalyst), and taking into account the results obtained in a previous commu-

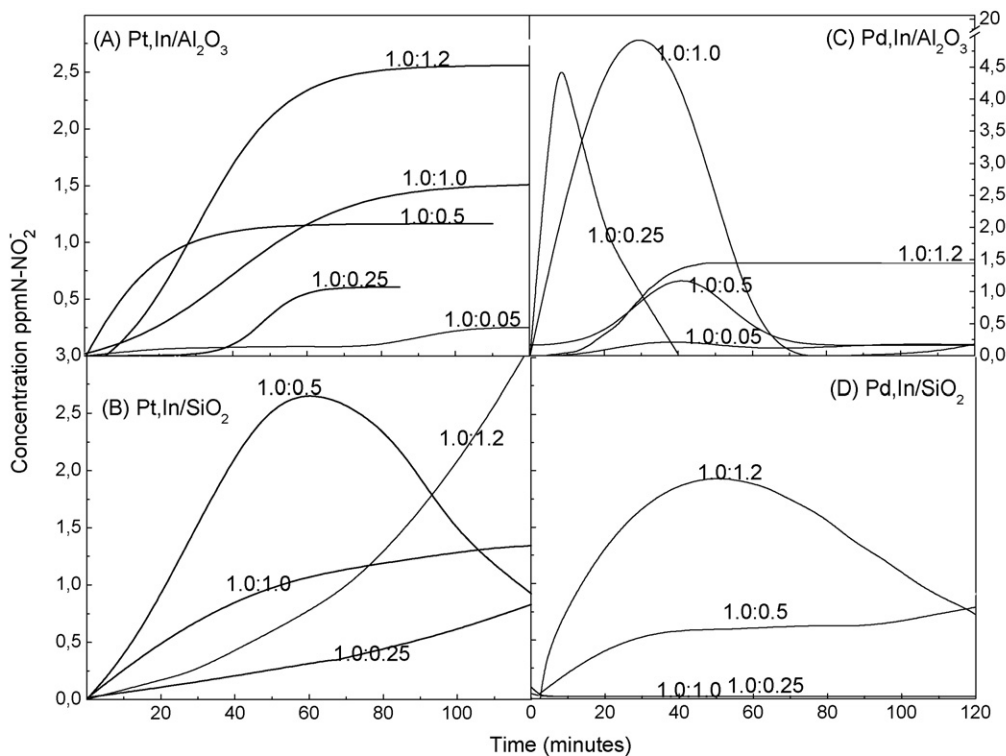
nication [8], a loss of the intimate contact between the active ingredients of the catalyst could be responsible for this slow loss in activity; thus, the possibility of catalyst regeneration could be considered. Table 1 shows a summary of catalytic results for the different catalysts studied in this work.

### 3.2. Catalyst characterization

#### 3.2.1. XPS results

The chemical state of elements and their relative proportions were determined by XPS. The binding energies of Si 2p, Al 2p, Pd 3d, In 3d, O 1s and C 1s were recorded. The Pt 4f level was recorded for silica samples but this energy region was overshadowed by the presence of a very strong Al 2p peak. Instead, for aluminium supported samples, the Pt 4d lines were analyzed. For comparison, Table 2 shows the results obtained for calcined samples of monometallic catalysts. Tables 3–6 show results for fresh-calcined bimetallic catalysts and after reaction (used) for selected samples. In the case of Pd–In catalysts, some results for reduced samples are also included.

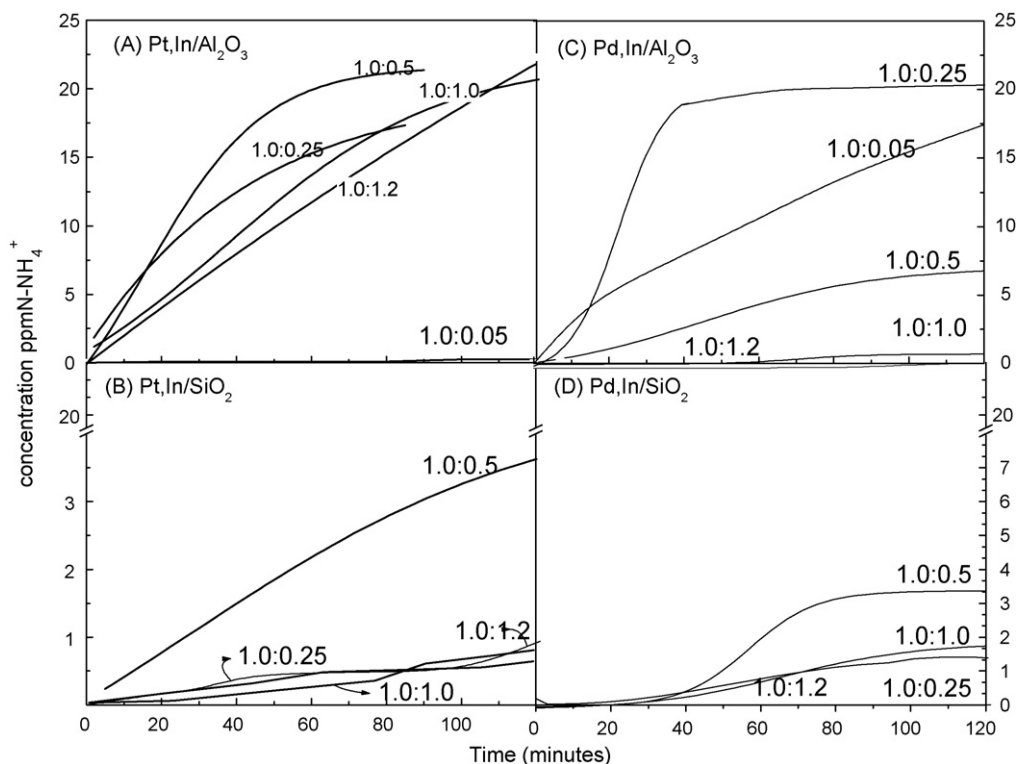
**3.2.1.1. Pt–In catalysts.** The corresponding values for fresh or calcined and used Pt, In/ $\text{Al}_2\text{O}_3$  solids are listed in Table 3. The peak analysis of In 3d exhibited two peaks at around 445.5 and 453 eV (not shown) with a FWHM in the range of 1.7–2.2 eV. These peaks can be attributed to In  $3d_{5/2}$  and  $3d_{3/2}$ , respectively, associated with the presence of  $\text{In}_2\text{O}_3$  [10]. In most of the used samples a second component can also be observed with peaks around 444.4 and 452.2 eV (FWHM in the range of 1.6–2.0 eV) that could be related to the presence of metallic In [10]. These peaks could also be attributed to  $\text{In}_x\text{Pt}_y$  intermetallic compounds, since it was found that for Pt–In metal-ionic clusters with an electronic deficient state of  $\text{Pt}^{\delta+}$  In, 3d peaks are observed at lower BEs [11].



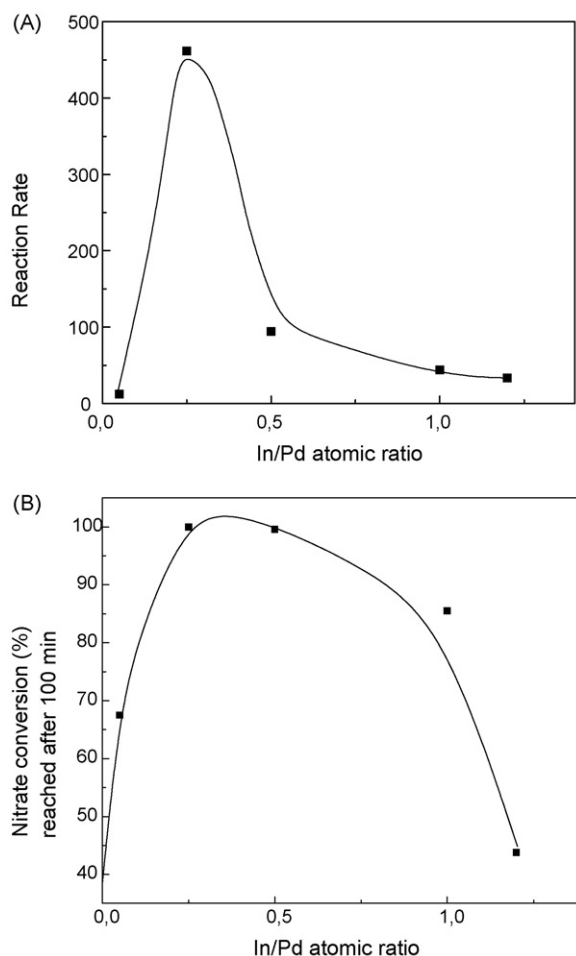
**Fig. 2.** Nitrite production on In promoted Pt and Pd catalysts supported on Al<sub>2</sub>O<sub>3</sub> (A) and (C) and Pt and Pd catalysts supported on SiO<sub>2</sub> (B) and (D). For reaction conditions see Section 2.

In the calcined samples, the Pt 4d peak allows the deconvolution into two components, a major one at higher BE (316.6–317.1 eV) associated with the presence of oxidized platinum species. Romanovskaya et al. [11] reported an increase of Pt

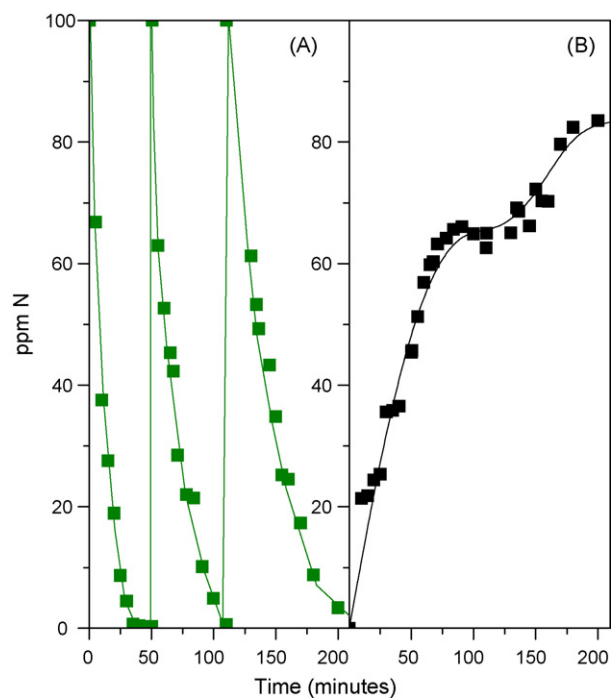
binding energies due to the formation of Pt containing inter-metallic compounds; so, the Pt 4d<sub>5/2</sub> line with high BE may also be caused by the presence of Pt–In clusters with the partial charge transfer from Pt to In, the minor component at lower binding



**Fig. 3.** Ammonia production on In promoted Pt and Pd catalysts supported on Al<sub>2</sub>O<sub>3</sub> (A) and (C) and Pt and Pd catalysts supported on SiO<sub>2</sub> (B) and (D). For reaction conditions see Section 2.



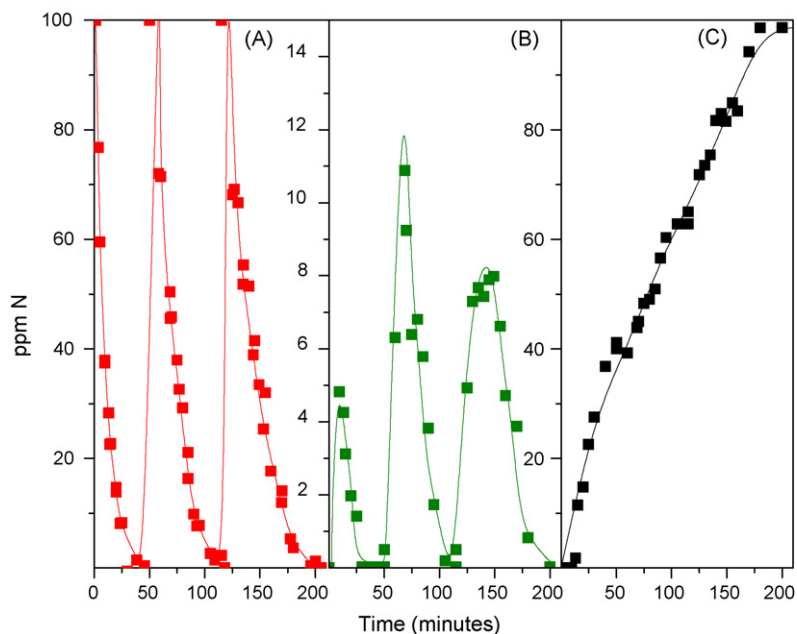
**Fig. 4.** (A) Reaction rate ( $\mu\text{mol of nitrate converted}(\text{min})^{-1}(\text{g catalyst})^{-1}$ ) as a function of the In/Pd atomic ratio. (B) Relationship between % nitrate conversion after 100 min of reaction and the In/Pd atomic ratio.



**Fig. 6.** (A) Nitrite reduction on Pd(1%)In(0.25%)/Al<sub>2</sub>O<sub>3</sub> catalyst after successive pulses of 100 N ppm from nitrite and (B) ammonia production on Pd(1%)In(0.25%)/Al<sub>2</sub>O<sub>3</sub> catalyst after successive pulses of 100 N ppm from nitrate. For reaction conditions see Section 2.

energies (314.0–314.3 eV) signifying the presence of metallic platinum [12]. It is interesting to notice that in the used samples only the high binding energy peak remains.

Table 4 shows XPS results for Pt–In catalysts supported on SiO<sub>2</sub>. In general, the results are in line with those described for Al<sub>2</sub>O<sub>3</sub> catalysts. Interestingly, despite the support used, the Pt:In surface ratio is lower than the bulk value except for the catalysts with higher indium content on Al<sub>2</sub>O<sub>3</sub> support. In Fig. 7, the surface Pt:In



**Fig. 5.** (A) Nitrate reduction on Pd(1%)In(0.25%)/Al<sub>2</sub>O<sub>3</sub> catalyst after successive pulses of 100 N ppm from nitrate. (B) Nitrite production on Pd(1%)In(0.25%)/Al<sub>2</sub>O<sub>3</sub> catalyst after successive pulses of 100 N ppm from nitrate and (C) ammonia production on Pd(1%)In(0.25%)/Al<sub>2</sub>O<sub>3</sub> catalyst after successive pulses of 100 N ppm from nitrate. For reaction conditions see Section 2.

**Table 1**  
Summary of reaction results

Catalyst	Residual N-ppm <sup>a</sup>			C <sub>NO<sub>3</sub><sup>-</sup></sub> <sup>a</sup>	S <sub>NH<sub>4</sub><sup>+</sup></sub> <sup>b</sup>	S <sub>NO<sub>c</sub></sub> <sup>c</sup>	TR50% <sup>d</sup> (min)	Reaction rate <sup>e</sup>	Reaction rate <sup>f</sup>
	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>						
Pt, In Al <sub>2</sub> O <sub>3</sub>									
1.0, 1.2	48.4	2.4	18.3	51.6	35.5	59.9	98	2.2	12.8
1.0, 1.0	44.9	1.6	19.7	55.1	35.8	61.3	86	2.9	16.5
1.0, 0.5	41.9	1.3	22.0	58.1	37.9	59.9	60	2.5	14.5
1.0, 0.25	40.5	0.6	17.1	59.5	28.7	70.3	5	31.5	180.4
1.0, 0.05	45.8	0.3	10.7	45.7	23.4	75.9	110	4.1	23.2
Pt, In SiO <sub>2</sub>									
1.0, 1.2	42.7	2.1	0.5	57.3	0.9	95.5	48	6.6	37.6
1.0, 1.0	78.1	1.8	1.3	21.9	5.9	85.8	NR <sup>g</sup>	1.3	7.6
1.0, 0.5	90.1	1.8	3.3	9.9	33.3	48.5	NR	0.2	1.4
1.0, 0.25	73.2	1.9	1.0	26.8	3.7	89.2	NR	1.6	9.3
Pd, In Al <sub>2</sub> O <sub>3</sub>									
1.0, 1.2	56.2	1.4	ND <sup>h</sup>	43.8	ND	96.8	NR	5.9	33.5
1.0, 1.0	14.5	ND	0.7	85.5	0.8	99.2	35	7.7	43.9
1.0, 0.5	0.4	ND	6.4	99.6	6.4	93.6	16	16.5	94.5
1.0, 0.25	ND	0.1	19.6	100.0	19.6	80.3	14	80.7	461.2
1.0, 0.05	32.5	0.2	15.3	67.5	22.7	77.0	64	2.1	12.2
Pd, In SiO <sub>2</sub>									
1.0, 1.2	91.4	ND	ND	8.6	ND	100.0	NR	2.4	13.7
1.0, 1.0	48.0	1.1	1.6	52.0	3.1	94.8	86	7.4	42.5
1.0, 0.5	47.3	0.4	3.3	52.7	6.3	93.0	95	2.4	13.5
1.0, 0.25	9.2	ND	1.3	90.8	1.4	98.6	30	5.2	50.7

<sup>a</sup> Measured after 100 min of time-on-stream.<sup>b</sup> Selectivity to NH<sub>4</sub><sup>+</sup>, defined as NH<sub>4</sub><sup>+</sup> formed/nitrate converted.<sup>c</sup> Selectivity to gaseous nitrogen compounds (mainly N<sub>2</sub>).<sup>d</sup> TR50%: time to reach 50% of conversion.<sup>e</sup> (N-ppm)(min)<sup>-1</sup>(g catalyst)<sup>-1</sup>.<sup>f</sup> (μmol of nitrate converted)(min)<sup>-1</sup>(g catalyst)<sup>-1</sup>.<sup>g</sup> NR: no reaches this conversion.<sup>h</sup> ND: no detectable.

ratio is plotted against the bulk one, showing the mentioned effect. The scattering in the points could be ascribed to the presence of complex mixtures of different phases. On used solids, there is a decrease in both indium and platinum superficial concentrations probably related to an increase in particle size. This effect occurs for both alumina and silica supported Pt–In catalysts, the only exception being the catalysts with high In content. There seems to be a different behavior for solids with low Pt:In ratio.

**3.2.1.2. Pd:In catalysts.** The corresponding values for fresh, reduced and used Pd, In/Al<sub>2</sub>O<sub>3</sub> solids are listed in Table 5. For the fresh or calcined samples the peak analysis of In 3d exhibits two peaks at around 445.4 and 453.5 eV with a FWHM in the range of 1.7–2.2 eV. Similarly to what was observed for the Pt–In samples, these peaks can be attributed to In 3d<sub>5/2</sub> and 3d<sub>3/2</sub>, respectively, associated with the presence of In<sub>2</sub>O<sub>3</sub>. Only in samples with a Pd:In ratio around 2 can a minor second component be observed with peaks at 443.5 and 452.2 eV (FWHM in the range of 1.6–2.0 eV) that could be related to either the presence of metallic In or In<sub>x</sub>Pd<sub>y</sub> intermetallic compounds.

In the calcined samples, the Pd 3d<sub>5/2</sub> peak exhibits two components around 336.1 and 337.6 eV. The component at higher binding energy could be associated with oxidized surface Pd species [13]. The component at low BE could not be related to metallic Pd, since values for Pd<sup>0</sup> in the literature are in the range of 334.6–335.6 eV [14]. On the other hand, the shift of the palladium peak to the higher binding energies side from the zero valent Pd metal value was observed in Pd, In/SiO<sub>2</sub> catalysts [15]. Besides, for the PdIn<sub>3</sub> phase the BE of the Pd 3d<sub>5/2</sub> peak was found to be 336.5 eV [16]. Since the presence of intermetallic compounds was also suggested by the In 3d peak in samples with a Pd:In ratio around 2, the presence of Pd–In intermetallic particles would be confirmed in these cases.

After reduction of the catalysts little or no change was observed in In 3d peaks while a small increase of the Pd component at lower BE, associated with the intermetallic compound, was found in solids with high indium loading. Only the 1.0:1.2 solid showed a peak at 335.3 eV that could be related to metallic Pd.

Important changes were detected in most of the used solids; the component of In 3d peaks at low BE was present in the spectra of all

**Table 2**  
XPS data for monometallic catalysts

Monometallic catalysts (wt.%)	In, Pt or Pd over Al or Si	Binding energies (eV)						
		Si 2p	Pd 3d <sub>5/2</sub>	In 3d <sub>5/2</sub>	Al 2p	Al 2s	Pt 4f	Pt 4d
In/Al <sub>2</sub> O <sub>3</sub> (0.5%)	0.0015	–	–	445.9	75.1	–	–	–
In/SiO <sub>2</sub> (0.5%)	0.0048	103.8	–	445.9	–	–	–	–
Pt/Al <sub>2</sub> O <sub>3</sub> (1.0%)	0.0042	–	–	–	74.7	119.5	–	315.6
Pt/SiO <sub>2</sub> (1.0%)	0.0032	104.0	–	–	–	–	73.3	–
Pd/Al <sub>2</sub> O <sub>3</sub> (1.0%)	0.0062	–	336.7	–	74.8	–	–	–
Pd/SiO <sub>2</sub> (1.0%)	0.0042	104.1	338.8	–	–	–	–	–

**Table 3**  
XPS results

Pt, In/Al <sub>2</sub> O <sub>3</sub>	Binding energies (eV)			Pt/Al	In/Al	Pt/In <sub>s</sub> <sup>a</sup>	Pt/In <sub>b</sub> <sup>b</sup>
	Al 2s	Pt 4d <sub>5/2</sub>	In 3d <sub>5/2</sub>				
1.0:0.25	119.7	314.1 (17%), 317.1 (83%)	445.5	0.011	0.006	1.9	2.3
Used	119.7	316.4	445.3	0.003	0.003	1.0	2.3
1.0:0.50	119.4	314.0 (24%), 316.6 (76%)	445.4	0.005	0.009	0.62	1.2
Used	119.5	317.0	445.5 (86%), 444.3 (14%)	0.002	0.005	0.50	1.2
1.0:1.0	119.7	314.0 (17%), 316.9 (83%)	445.6	0.004	0.011	0.38	0.59
1.0:1.2	119.5	314.0 (14%), 316.9 (86%)	445.6	0.007	0.012	0.55	0.49
Used	119.2	316.9	445.4 (79%), 443.9 (21%)	0.008	0.011	0.78	0.49

Surface features of Pt, In/Al<sub>2</sub>O<sub>3</sub> catalysts.

<sup>a</sup> s indicates surface.

<sup>b</sup> b indicates bulk.

**Table 4**  
XPS results

Pt, In/SiO <sub>2</sub>	Binding energies (eV)			Pt/Si	In/Si	Pt/In <sub>s</sub> <sup>a</sup>	Pt/In <sub>b</sub> <sup>b</sup>
	Si 2p	Pt 4f <sub>7/2</sub>	In 3d <sub>5/2</sub>				
1.0:0.25	104.9	74.6	446.3 (81%), 444.2 (19%)	0.0038	0.004	0.95	2.3
1.0:0.5	103.9	72.2, 73.5	445.9	0.0034	0.0072	0.47	1.2
1.0:1.0	103.6	71.9, 73.0	445.7	0.003	0.0168	0.19	0.59
Used	103.7	74.7	445.0	0.001	0.002	0.50	0.59
1.0:1.2	103.5	72.2, 73.5	445.7	0.0031	0.0214	0.14	0.49
Used	103.7	ND <sup>c</sup>	445.5 (76%), 443.5 (24%)	0	0.003	0	0.49

Surface features of Pt, In/SiO<sub>2</sub> catalysts.

<sup>a</sup> s indicates surface.

<sup>b</sup> b indicates bulk.

<sup>c</sup> Non-detectable.

catalysts. The palladium spectra showed an increase of the component at low BE after reaction; this, together with the In results, suggests an increase of the intermetallic phase.

The Pd/In superficial ratio of calcined catalysts is always lower than the bulk value. After reduction, samples show a decrease in Pd and In superficial concentration, indicating an increase in particle size. On the other hand, used solids even when they have lower superficial concentration of both metals than the fresh samples, could suffer some re-dispersion in the reaction mixture, since the atomic % of Pd and In as seen by XPS is higher than in the reduced solids. Probably, during reaction some extent of reoxidation could occur, giving place to the observed changes.

**Table 5**  
XPS results

Pd, In/Al <sub>2</sub> O <sub>3</sub>	Binding energies (eV)			Pd/Al	In/Al	Pd/In <sub>s</sub> <sup>a</sup>	Pd/In <sub>b</sub> <sup>b</sup>
	Al 2p	Pd 3d <sub>5/2</sub>	In 3d <sub>5/2</sub>				
1.0:0.25	74.6	336.3 (55%), 337.8 (45%)	445.4	0.0036	0.0020	1.75	4.3
Reduced	74.8	336.3 (55%), 337.4 (45%)	445.7	0.0012	0.0009	1.25	4.3
Used	74.7	335.4 (59%), 337.1 (41%)	445.1 (92%), 443.5 (8%)	0.0025	0.0015	1.67	4.3
1.0:0.50	74.6	336.3 (56%), 337.9 (44%)	445.2 (94%), 443.5 (6%)	0.0052	0.0037	1.41	2.1
Used	74.6	336.1 (72%), 337.9 (28%)	445.4 (93%), 443.6 (7%)	0.0020	0.0023	0.89	2.1
1.0:1.0	74.5	336.1 (46%), 337.6 (54%)	445.3	0.0056	0.0087	0.64	1.0
Reduced	74.2	336.0 (58%), 337.3 (42%)	445.1	0.0018	0.0043	0.42	1.0
Used	74.3	335.9 (67%), 37.5 (33%)	445.21 (95%), 43.3 (5%)	0.0031	0.0056	0.54	1.0
1.0:1.2	75.0	336.3 (59%), 37.9 (41%)	445.6	0.0054	0.0103	0.53	0.9
Reduced	74.7	335.3 (14%), 36.6 (66%), 37.8 (20%)	445.5	0.0016	0.0055	0.29	0.9
Used	74.8	336.0 (72%), 37.8 (28%)	445.6 (97%), 43.8 (3%)	0.0026	0.0069	0.38	0.9

Surface features of Pd, In/Al<sub>2</sub>O<sub>3</sub> catalysts.

<sup>a</sup> s indicates surface.

<sup>b</sup> b indicates bulk.

**Table 6** summarizes the XPS results of silica-based solids. Indium is mostly as In<sub>2</sub>O<sub>3</sub>, since the In 3d<sub>5/2</sub> peak showed one major component around 445.7 eV and in some cases a less important second component appeared (443.5–443.9 eV). This last peak would be associated with the presence of intermetallic In–Pd compounds.

As in the case of alumina supported Pd–In, the Pd 3d<sub>5/2</sub> peak could be deconvoluted into two peaks for all catalysts. In these cases, the component at higher binding energy (337.9–337.0 eV) could also be associated with oxidized surface Pd species [13] and the peak at lower BE (336.0–335.3 eV) could be attributed to Pd–In intermetallic compounds. A third peak appeared in the catalysts

**Table 6**  
XPS results

Pd, In/SiO <sub>2</sub>	Binding energies (eV)			Pd/Si	In/Si	Pd/In <sub>s</sub> <sup>a</sup>	Pd/In <sub>b</sub> <sup>b</sup>
	Si 2p	Pd 3d <sub>5/2</sub>	In 3d <sub>5/2</sub>				
1.0:0.25 Used	104.1 104.1	337.9 (45%), 336.0 (55%) 337.4 (37%), 335.9 (63%)	445.5 (82%), 443.5 (18%) 445.3 (78%), 443.6 (22%)	0.0080 0.0030	0.005 0.002	1.4 1.7	4.3 4.3
1.0:0.5 Reduced Used	103.9 103.8 103.7	337.5 (81%), 335.7 (19%) 337.4 (40%), 335.3 (60%) ND <sup>c</sup>	445.5 445.7 (80%), 443.6 (20%) 445.8	0.0031 0.0005 0	0.001 0.004 0.003	1.25 0.28 0	2.1 2.1 2.1
1.0:1.0 Used	103.9 104.0	337.0 (75%), 335.7 (25%) ND	445.7 445.8	0.0027 0	0.006 0.003	0.47 0	1.0 1.0
1.0:1.2 Used	102.1 103.9	337.8 (15%), 335.9 (85%) 335.6	445.8 445.5 (62%), 443.5 (38%)	0.0013 0.0008	0.007 0.0011	0.20 0.75	0.9 0.9

Surface features of Pt, In/SiO<sub>2</sub> catalysts.

<sup>a</sup> s indicates surface.

<sup>b</sup> b indicates bulk.

<sup>c</sup> Non-detectable.

with 1.5 wt.% of Pd (not shown) at higher binding energy. In Ref. [17], the authors assigned one Pd component at a BE of 338.6 eV to highly dispersed and polarized Pd<sup>2+</sup> ions in the close vicinity of chloride anions. The same assignation could be made in this case, since the survey spectrum of the 1.5:0.9 solid showed the presence of chlorine contamination (0.8 at.%) that came from the catalyst preparation step.

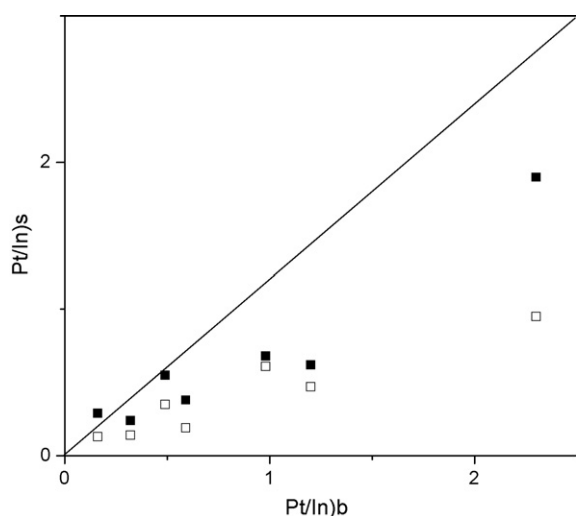
Small changes could be observed after reaction in most of the catalysts for both indium and palladium, even though, in the 1.5:0.5 (not shown) and 1.0:1.0 solids the Pd concentration went below the XPS range of detection. It is interesting to notice that in these two catalysts before reaction the palladium is mostly as PdO while for the other calcined solids the intermetallic compound concentration is higher than the oxide concentration. Besides, the In 3d<sub>5/2</sub> peak presents only one component related to the presence of In<sub>2</sub>O<sub>3</sub>, supporting the absence of intermetallic compounds in these two solids.

The Pd:Si ratio was lower after the catalysts were exposed to the reaction media, except for the 1.5:0.9 solids. This fact could be related to the presence of Pd associated with Cl<sup>-</sup> ions found in the calcined sample. The same trend is followed by the In superficial concentration. Thus, it is inferred that during reaction particle size would increase.

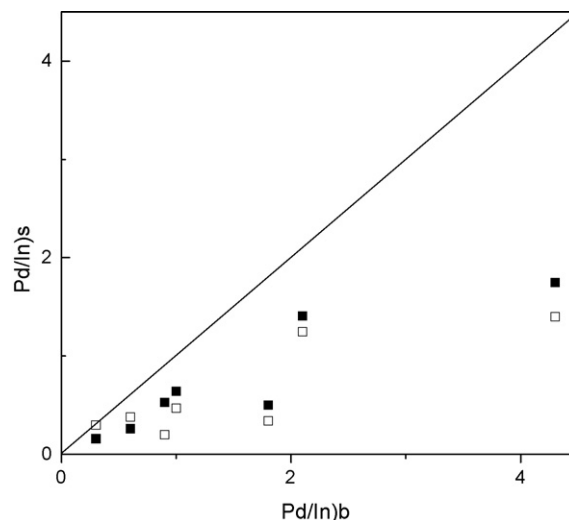
In line with the results shown above, the Pd:In surface ratio is lower than that of the bulk. Fig. 8 shows this effect.

### 3.2.2. XRD and TEM characterization

XRD and TEM experiments were conducted as additional techniques to further understand the structural properties of the catalysts used in this work. The XRD patterns of fresh-calcined Pt–In/Al<sub>2</sub>O<sub>3</sub> (not shown) present only the Al<sub>2</sub>O<sub>3</sub> characteristic peaks. Fig. 9 shows XRD patterns for Pd and Pd–In/Al<sub>2</sub>O<sub>3</sub> catalysts. The Pd(1.0%)/Al<sub>2</sub>O<sub>3</sub> calcined catalyst shows the peak characteristic of PdO at ca. 33.9° [18]. The same peak is observed, with a bigger size, in a Pd(5.0%)In(1.25%)/Al<sub>2</sub>O<sub>3</sub> catalyst, which was prepared increasing the metal loading for a better definition of the peaks, and maintaining the Pd/In ratio of the most active catalyst Pd(1%)In(0.25%)/Al<sub>2</sub>O<sub>3</sub>. It can be clearly seen that the peak of PdO shifts to a higher angle (ca. 40°) when the catalyst is reduced at 723 K, indicating the formation of metallic Pd. A similar pattern is observed when the metal loading is decreased to a half. However, none of the main characteristic peaks of In<sub>2</sub>O<sub>3</sub> (30.5°, 35.0° and 50.5°) are observed in the spectra, which suggests that In is either in the form of well-dispersed oxide species or forming an alloy with Pd. Hirano et al. [19] obtained a Pd–In alloy supported on SiO<sub>2</sub> after the reduction of a (5.0%) Pd with a molar ratio 1:1 with In at

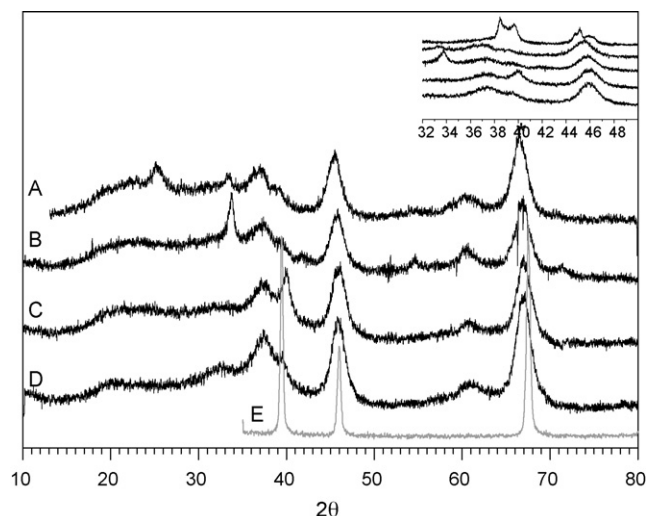


**Fig. 7.** Relationship between the Pt/In surface ratio and the Pt/In bulk ratio, (□) supported over Al<sub>2</sub>O<sub>3</sub>, (■) supported over SiO<sub>2</sub>.



**Fig. 8.** Relationship between the Pd/In surface ratio and the Pd/In bulk ratio, (□) supported over Al<sub>2</sub>O<sub>3</sub>, (■) supported over SiO<sub>2</sub>.





**Fig. 9.** XRD of Pd/In/Al<sub>2</sub>O<sub>3</sub> samples (A) Pd(1%)/Al<sub>2</sub>O<sub>3</sub> calcined at 773 K during 4 h; (B) Pd(5%)In(1.25%)/Al<sub>2</sub>O<sub>3</sub> calcined 773 K during 4 h; (C) Pd(5%)In(1.25%)/Al<sub>2</sub>O<sub>3</sub> reduced in H<sub>2</sub> at 723 K during 10 h; (D) Pd(2.5)In(0.65)/Al<sub>2</sub>O<sub>3</sub> reduced 723 K during 10 h; (E) membrane of Pd used as reference.

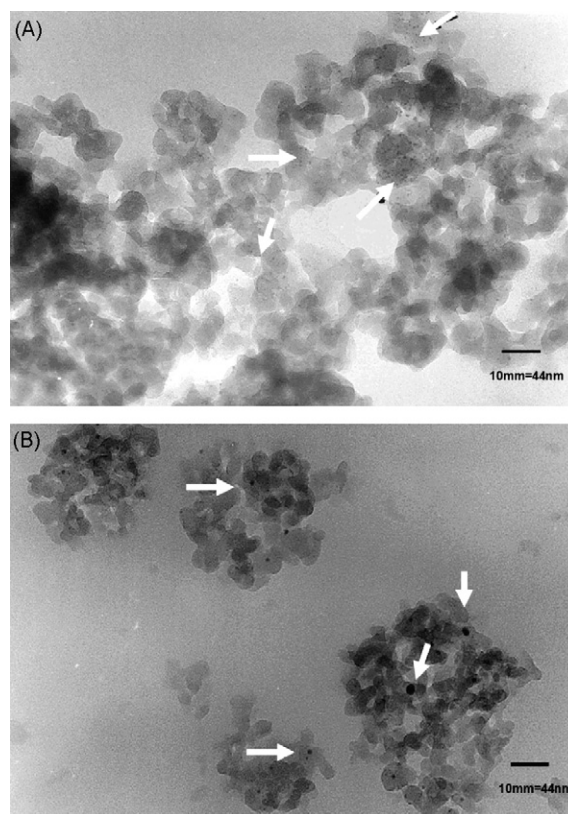
773 K during 10 h. The Pd<sub>0.48</sub>In<sub>0.52</sub> intermetallic compound has XRD characteristic peaks at  $2\theta = 39.2^\circ, 56.8^\circ, 70.9^\circ, 84.2^\circ$ . However, these peaks cannot be clearly distinguished in our catalysts, probably due to either the different support (Al<sub>2</sub>O<sub>3</sub> instead of SiO<sub>2</sub>) or the lower Pd:In ratio of our catalyst.

TEM images of alumina supported Pt(1.0%)In(0.25%) and Pd(1.0%)In(0.25%) catalysts, both fresh-reduced and used in reaction conditions are shown in Figs. 10 and 11, respectively. In both cases, for the fresh samples well dispersed Pt and Pd metallic particles can be observed, while after reaction their size increases.

### 3.3. Relationships between catalytic activity and surface properties

The results shown in Figs. 1–4 and Table 1 clearly indicate that there is a very strong effect of the Pt:In or Pd:In ratio on activity and product distribution. The support, either Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>, also has a major impact on the catalytic behavior. The European Community has established a limit value of 50 ppm of NO<sub>3</sub><sup>-</sup>, 0.1 ppm of NO<sub>2</sub><sup>-</sup> and 0.5 ppm of NH<sub>4</sub><sup>+</sup>. Therefore, there are several catalysts that could fulfill these requirements, for example Pd(1.0%)In(0.25%)/SiO<sub>2</sub> with 30 min TOS, Pd(1.0%):In(1.0%)/Al<sub>2</sub>O<sub>3</sub> at 70 min TOS. Other catalysts with very good activity (e.g. Pd(1.0%)In(0.25%)/Al<sub>2</sub>O<sub>3</sub>) when reaching the 50 ppm of NO<sub>3</sub><sup>-</sup> at short time on stream display a high value of NO<sub>2</sub><sup>-</sup>, and at longer TOS the NH<sub>4</sub><sup>+</sup> is out of specification. Therefore, within the set of catalysts under analysis in this work, a couple of formulations seem to be adequate to meet all the technical requirements regarding the concentration of nitrates, nitrites and ammonium. Several interesting observations can be drawn from the results shown above.

The concentration vs. time curve for NO<sub>2</sub><sup>-</sup> is typical for an intermediate compound, while for NH<sub>4</sub><sup>+</sup>, it is the curve that corresponds to a final product. However, the NH<sub>4</sub><sup>+</sup> production does not come directly from NO<sub>2</sub><sup>-</sup> reduction as can be seen for example in the case of the Pd(1.0%)In(0.25%)/SiO<sub>2</sub> and Pd(1.0%)In(1.0%)/SiO<sub>2</sub>, for which the maximum in NO<sub>2</sub><sup>-</sup> concentration occurs some time before the inflection point in the NH<sub>4</sub><sup>+</sup> curve. The rate of each step in the reaction network is strongly dependent on the hydrogen surface fugacity. Therefore, subtle differences in metal particle composition can be the key point in the development of active catalysts for this reaction. Pd:In catalysts have a higher

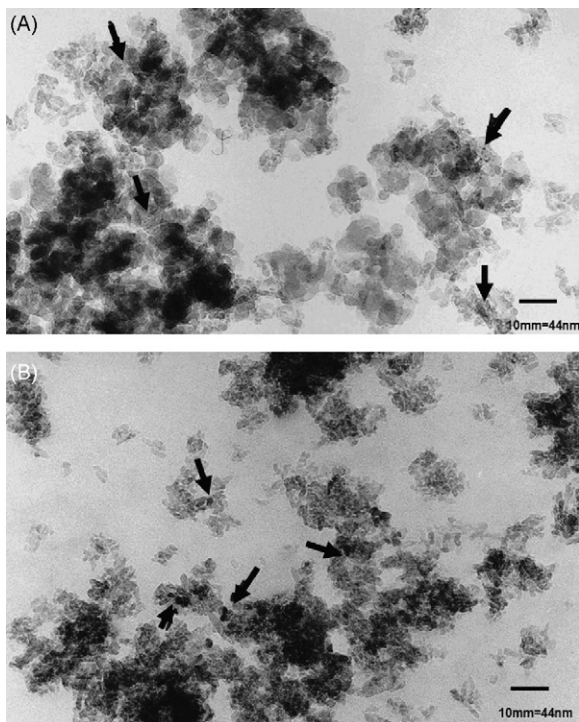


**Fig. 10.** TEM of Pt(1.0%)In(0.25%)/SiO<sub>2</sub> samples. Scale: 1 nm = 4.4 nm. Arrows show metallic particles: (A) fresh reduced catalyst; (B) used catalyst.

selectivity to NO<sub>2</sub><sup>-</sup> than to NH<sub>4</sub><sup>+</sup> at short reaction time, while Pt:In catalysts display the opposite behavior. This is specially noticeable on Pd(1.0%)In(0.25%)/Al<sub>2</sub>O<sub>3</sub> and Pd(1.0%)In(1.0%)/Al<sub>2</sub>O<sub>3</sub>. On Pt–In catalysts the selectivity to NH<sub>4</sub><sup>+</sup> is higher than to NO<sub>2</sub><sup>-</sup> from the beginning of the reaction, and does not follow the typical behavior for a final product coming from an intermediate product. This suggests that there might be an alternative reaction path in the formation of NH<sub>4</sub><sup>+</sup>, not going through the intermediate NO<sub>2</sub><sup>-</sup>, or the reduction of the latter is fast. Tables 3–6 show that Pt/Al<sub>2</sub>O<sub>3</sub> or Pt/SiO<sub>2</sub> surface ratios are higher than the Pd/Al<sub>2</sub>O<sub>3</sub> or Pd/SiO<sub>2</sub> ratios, respectively, even though the atomic composition of Pd containing catalysts is almost twofold that of Pt (molecular weight of Pd 106 and of Pt 195). This could be one of the reasons for the too high hydrogen availability on Pt catalysts that leads to a very high ammonium production. Note that the In/Al<sub>2</sub>O<sub>3</sub> or In/SiO<sub>2</sub> surface ratios are similar in both cases, i.e. catalysts with Pt or catalysts with Pd, and therefore one major difference between the bimetallic system is the noble metal dispersion.

As shown in Fig. 4, the reaction rate is strongly dependent upon the Pd:In ratio, both initial reaction rate and conversion at 100 min having a maximum as a function of this ratio. Since the reaction mechanism involves two different types of sites, these curves show that the maximum rate can be achieved at a rather low In:Pd ratio.

It has been established that In decreases the adsorption of hydrogen on platinum and on palladium [20]. As seen in Fig. 3, there is a general tendency: the higher the In content, the lower the NH<sub>4</sub><sup>+</sup> production, even though in some cases the total catalyst activity masks this result. However, what finally will modify the activity and selectivity is the real distribution of the noble metal and In. As shown in Figs. 7 and 8, the Pt:In and Pd:In average ratios are higher than the surface ratio as obtained by XPS. In other words, the curves in Fig. 4 would shift to higher In–Pd values if the



**Fig. 11.** TEM of Pd(1)In(0.25)/Al<sub>2</sub>O<sub>3</sub> samples. Scale: 1 mm = 4.4 nm. Arrows show metallic particles: (A) fresh reduced catalyst; (B) used catalyst.

surface concentration were used. Since the technique used is XPS, it could be argued that the In dispersion is higher than the Pd or Pt dispersion, and because of that the apparent metal:In ratio is higher in the bulk than in the surface. This could be observed even if no interaction between the metals takes place. This argument cannot be taken into account, since if this were the case, no change in catalytic behavior would occur. Clearly, as the In content is increased, the level of interaction between the metals also increases.

#### 3.4. Effect of reaction media on the catalyst structure

Important changes were detected in most of the used solids. On the Pd:In catalysts, the component of In 3d peaks at low BE was present in the spectra of all catalysts. The palladium spectra showed an increase of the component at low BE after reaction; this, together with the In results, suggests an increase of the intermetallic phase.

The Pd/SiO<sub>2</sub> ratio was lower after the catalysts were exposed to the reaction media, except for the Pd(1.5%)In(0.9%) solid (not shown). This fact could be related to the presence of Pd associated with Cl<sup>-</sup> ions found in the calcined sample. The same trend is followed by the In superficial concentration. Thus, it is inferred that during reaction the particle size would increase, as compared to the calcined sample.

TEM images of alumina supported Pt(1.0%)In(0.25%) and Pd(1.0%)In(0.25%) catalysts, both fresh-reduced and used in reaction conditions are shown in Figs. 10 and 11, respectively. In both cases, for the fresh samples well dispersed Pt and Pd metallic particles can be observed, while after reaction several particles with larger sizes are found.

After the reaction, XPS indicates that both Pd and In increase their average dispersion, even though Pd has a larger increase that leads to a higher Pd:In surface ratio, as compared to the reduced catalyst when supported on Al<sub>2</sub>O<sub>3</sub>. Therefore, it seems that according to both TEM and XPS, even though there are some

new particles that are formed during the reaction with an increase in the amount of intermetallic phase, also another change takes place leading to the overall increase in dispersion due to the stabilization of In and Pd small particles. According to these results, bimetallic particles increase the size, and monometallic particles are segregated during the reaction. This is not observed when Pd–In is supported on silica, since in this case the XPS analysis also reveals a decrease in dispersion after the catalyst is used in the reaction. These results also agree with those obtained by reaction cycles shown in Figs. 6 and 7. In these experiments, it is clearly shown that the catalytic activity decreases in each cycle.

It has to be emphasized that even though there is an increase in the amount of intermetallic compounds, as seen by XPS, this phase is now present as large particles with a low dispersion, and therefore a low activity is observed. On the other hand, there is an important amount of Pd and In that is not forming bimetallic particles but is present as small monometallic particles, as also suggested by the increase in the Pd:Al<sub>2</sub>O<sub>3</sub> and In:Al<sub>2</sub>O<sub>3</sub> ratios by XPS. This morphology change has a twofold effect: decrease in the dispersion of the active phase, and formation of inactive phases. Nevertheless, it can be observed that the rate of deactivation decreases. For example, to reach a level of 20 N ppm-NO<sub>3</sub><sup>-</sup>, it takes 17 min in the first cycle, 36 min in the second, and 43 min in the third. Therefore, the changes are more important during the first cycle, and then the modifications become less important as the cycles proceed. It could be possible, although it has not been verified yet, that the system reach a steady state, with no further changes in the metal distribution. If this is the case, there is room for catalyst optimization regarding its formulation, looking for an initial composition in order to obtain the best equilibrated catalyst.

#### 4. Conclusions

Among the catalysts studied in this work, those composed of Pd–In supported on Al<sub>2</sub>O<sub>3</sub> are the most efficient ones to abate nitrates in water. The reaction rate is strongly influenced by either Pt:In or Pd:In ratio, the optimum being observed at low contents of In. Pt(1.0%)In(0.25%)/Al<sub>2</sub>O<sub>3</sub> presents a high initial activity but it fastly deactivates during reaction. Pd(1.0%)In(0.25%)/Al<sub>2</sub>O<sub>3</sub> presents the best performance among Pd–In catalysts for nitrate conversion, and the deactivation is substantially lower than in the case of the Pt–In ones. Unfortunately, this catalyst presents an undesirable high selectivity towards ammonia when nitrate conversion reaches 100%.

With respect to the influence of the support, alumina is a better support than silica, which could be due to the higher PZC value of silica, thus decreasing the rate of adsorption of nitrate ions.

The surface of the bimetallic catalysts is composed of different phases: metallic Pt or Pd, oxides of Pt or Pd, In<sub>2</sub>O<sub>3</sub>, and intermetallic compounds. The presence of intermetallic compounds is important since it provides an intimate contact between the active phases. The deactivation observed is probably originated in the segregation of these bimetallic phases.

The composition of the catalysts change both after reduction and after contacting with the liquid reaction media. These changes have been observed by XPS and TEM. In general, the samples used in the reaction have lower dispersion of metallic phases than the fresh-calcined ones. For most of the catalysts used in this work, the Pt:In or Pd:In surface ratio is lower than the bulk ones, this probably being the reason for the low amount of In that is sufficient to have an optimal performance.

Several of the solids studied in this work are able to fulfill the requirements of the European Community about nitrates, nitrites and ammonia limit concentrations. This fact encourages further

studies to gain more insight into the reaction mechanism and active sites using Pd–In and Pt–In catalysts.

### Acknowledgements

The authors wish to acknowledge the financial support received from ANPCyT, UNL and CONICET. S.I acknowledges the support of a contract from “Ramón y Cajal” program. Thanks are given to Elsa Grimaldi for the English language editing.

### References

- [1] A. Pintar, J. Batista, *Catal. Today* 53 (1999) 35.
- [2] O. Ilinitch, P. Cuperus, L. Nosova, E. Gribov, *Catal. Today* 56 (2000) 137.
- [3] F. Deganello, L. Liotta, A. Macaluso, A. Venezia, G. Deganello, *Appl. Catal. B: Environ.* 24 (2000) 265.
- [4] Y. Matatov-Meytal, V. Barelko, I. Yuranov, M. Sheintuch, *Appl. Catal. B: Environ.* 27 (2000) 127.
- [5] G. Strukul, R. Gavagnin, F. Pinna, E. Modaferrri, S. Perathoner, G. Centi, M. Marella, M. Tomaselli, *Catal. Today* 55 (2000) 139.
- [6] U. Prüsse, M. Hahnlein, J. Daum, K. Vorlop, *Catal. Today* 55 (2000) 79.
- [7] A. Garron, K. Lázár, F. Epron, *Appl. Catal. B: Environ.* 59 (2005) 57.
- [8] F.A. Marchesini, S. Irusta, C. Querini, E. Miro, *Catal. Commun.* 9 (6) (2008) 1021.
- [9] J. Daum, K.D. Vorlop, *Chem. Eng. Technol.* 70 (1998) 1567.
- [10] A. De, P. Biswas, J. Manara, *Mater. Charact.* 58 (7) (2007) 629.
- [11] V. Romanovskaya, M. Ivanovskaya, P. Bogdanov, *Sens. Actuators B* 56 (1999) 31.
- [12] K. Persson, A. Ersson, K. Jansson, J.L.G. Fierro, S.G. Järås, *J. Catal.* 243 (2006) 14.
- [13] V. Narayana Kalevaru, A. Benhmid, J. Radnik, M.-M. Pohl, U. Bentrup, A. Martin, *J. Catal.* 246 (2007) 399.
- [14] A. Venezia, V. La Parola, B. Pawelec, J.L.G. Fierro, *Appl. Catal. A* 264 (2004) 43.
- [15] T. Hirano, Y. Ozawa, T. Sekido, T. Ogino, T. Miyao, S. Naito, *Appl. Catal. A* 320 (2007) 91.
- [16] T. Skalá, K. Veltruská, M. Moroseac, I. Matolínová, G. Korotchenkov, V. Matolín, *Appl. Surf. Sci.* 205 (2003) 196.
- [17] B. Pawelec, A. Venezia, V. La Parola, E. Cano-Serrano, J. Campos-Martin, J.L.G. Fierro, *Appl. Surf. Sci.* 242 (2005) 380.
- [18] K. Persson, A. Ersson, S. Colussi, A. Trovarelli, S.G. Järås, *Appl. Catal. B: Environ.* 66 (3–4) (2006) 175.
- [19] T. Hirano, Y. Osawa, T. Sekido, T. Ogino, T. Miyao, S. Naito, *Appl. Catal. A: Gen.* 320 (2007) 91.
- [20] F. Passos, D. Aranda, M. Schmal, *J. Catal.* 178 (1998) 478.