Short Communication

Study of the interactions of Pd,In with SiO_2 and Al_2O_3 mixed supports as catalysts for the hydrogenation of nitrates in water

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ABSTRACT

This paper shows that the combination of Al_2O_3 and SiO_2 as supports of Pd and In allows the modulation of the catalytic properties of nitrate hydrogenation in water in order to improve nitrate conversion and decrease the formation of ammonia. Mechanical mixtures of monometallic catalysts subjected to reduction in hydrogen at 450 °C are efficient catalysts when Pd is supported on Al_2O_3 and In is supported on SiO_2, thus showing considerably high activity and selectivity to gaseous nitrogen compounds when the proportions are 75 wt.% of Pd/Al_2O_3 and 25 wt.% of In/SiO_2. When these monometallic catalysts are reduced separately and then mixed *in situ* in the batch reactor, a moderate activity for nitrate reduction is obtained, suggesting that either some migration of In or Pd occurs in solution generating the bimetallic sites that are necessary to activate nitrate ions, or that a loose contact between In and Pd is enough to initiate the reaction. This contact could be favored by the opposite pzc of both supports.

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1. Introduction

In the last three decades, since the publication of Horold et al. [1], the elimination of nitrates and nitrites by catalytic hydrogenation has been deemed possible. Several catalyst formulations and process configurations have been investigated with the aim of improving the efficiency to reduce nitrates and, at the same time, avoid ammonia formation. Most of the catalysts reported in the literature have been prepared over different supports using Pt or Pd as the main active metal and adding a second metal such as Cu, Sn or In [1–3] as promoter. Monometallic catalysts based on noble metals are inactive for nitrate reduction and the presence of promoters is necessary to initiate the reaction [3–8].

In a recent work, Salomé et al. [9], using several physical mixtures with mono and bimetallic catalysts composed of Rh, Pd, Pt and Cu, were able to demonstrate that the presence of bimetallic sites in the initial catalyst is not mandatory to promote the reduction of nitrate; it is sufficient that the metals become in close contact during the reaction.

On the other hand, in a previous work [10], we reported that Pd, In/Al_2O_3 catalysts are highly active to abate nitrates in water, and that the optimum Pd:In weight ratio is 1:0.25. Similar activity and selectivity results with other catalyst compositions were reported by Prusse et al. [11,12] and Krawczyk et al. [13]. We also observed that SiO_2 supported catalysts, despite their lower activity, are more

selective to N_2 than Al_2O_3 supported ones [15–16]. Thus, the aim of this work is to combine the support properties mentioned above in order to improve catalytic efficiency and to gain further insight into the nature of the metal-support interactions. To this end, we used solids with 1 wt.% Pd and 0.25 wt.%. In supported on different mechanical mixtures of SiO_2 and Al_2O_3. Dynamic CO chemisorption, TPR, XRD, and FTIR of adsorbed CO were chosen as characterization tools and the activity measurements were carried out in a stirred batch reactor with an on-line pH control.

2. Experimental

2.1. Catalyst preparation

A series of monometallic (Pd or In) and bimetallic catalysts (Pd,In) were prepared by wet impregnation. Aqueous solutions of Pd (10 mg.mL^{-1}) dissolved in concentrated HCl and/or aqueous solutions of In_2O_3 (4.6 mg.mL^{-1}) dissolved in concentrated HCl were added to SiO_2 (AESAR Large Pore, surface area: 300 m^2.g^{-1}, pore volume: 1 mL.g^{-1}) or Al_2O_3 (Keene CK300, surface area: 180 m^2.g^{-1}, pore volume: 0.5 mL.g^{-1}) at room temperature in order to obtain concentrations of 1wt.% Pd and 0.25wt.% In.

Bimetallic catalysts were mechanically mixed in order to obtain different Al_2O_3:SiO_2 weight ratios: 100:0, 75:25, 50:50, 25:75, 0:100. Those catalysts were labeled as 100 m, 75 m, 50 m, 25 m, and 0 m, respectively (see Table 1). Other catalyst series were prepared by co-impregnating both metals over the support mixture with 75:25, 50:50 and 25:75 weight ratios and they were labeled as "c" (see Table 1). Those samples probably had the highest Pd–In contact due

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Table 1
Nomenclature assigned to catalysts.

Catalysts	Label
Pd,In/Al₂O₃:Pd,In/SiO₂	
100:0	100 m
75:25	75 m
50:50	50 m
25:75	25 m
0:100	0 m
Pd,In/(Al₂O₃:SiO₂)	
75:25	75c
50:50	50c
25:75	25c
Pd/Al₂O₃:In/Al₂O₃ = 75:25	AA
Pd/Al₂O₃:In/SiO₂ = 75:25	AS
Pd/SiO₂:In/SiO₂ = 75:25	SS
Pd/SiO₂:In/Al₂O₃ = 75:25	SA

to the way they were prepared. Finally, monometallic Pd/Al₂O₃, Pd/SiO₂, In/Al₂O₃ and In/SiO₂ catalysts were mixed in order to obtain mixtures denoted as AS, AA, SA and SS (see Table 1). Those samples presented lower Pd–In contact also because of the way they were prepared.

The solids were dried overnight at 120 °C and calcined at 500 °C in air flow for 2 h. Before the hydrogenation reaction, the catalysts were reduced under H₂ flow at 450 °C for 1 h. In some special cases, monometallic catalysts were reduced at 700 °C.

2.2. Catalyst characterization

Temperature-Programmed Reduction (TPR) experiments were performed on 50 mg of fresh samples in an Okhura TS2002S instrument equipped with a TCD detector using a heating rate of 10 °C/min in a flow of 5%H₂/Ar (50 mL/min). Dynamic CO chemisorption measurements were carried out by sending 250 μL pulses of 2.5% CO/N₂ on 0.10 g fresh catalysts, after reduction in H₂ for 1 h at 450 °C. X-ray patterns were acquired with a Shimadzu XC-D1 diffractometer using CuKα radiation and a monochromator with a scan velocity of 1°/min. CO adsorption followed by FTIR analysis was carried out using an IR cell made of glass with CaF₂ windows. The infrared spectrometer was a Shimadzu IR Prestige 21 instrument and the spectra were collected at a resolution of 8 cm⁻¹.The standard wafer pretreatment was a reduction in H₂ at 400 °C for 1 h. Afterwards, the reductant gas was stopped and the system was evacuated at 10⁻⁶ Torr during 30 min maintaining the temperature at 400 °C. After collecting a reference spectrum for background subtraction at room temperature, the disk was exposed to an 8 Torr of CO. Then, the spectra were collected. This step was repeated at higher CO pressures: 16, 40 and 90 Torr.

2.2.1. Nitrate hydrogenation experiments

A stirred batch reactor was loaded with 80.0 mL of distilled water, 200 mg of catalyst, and 100 N-ppmNO₃⁻ as initial concentration. Subsequently, a hydrogen flow of 400 mL/min 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. The catalysts were treated by H₂ bubbling in water before introducing nitrates or nitrites [5]. Experiments performed at different stirring rates between 500 and 1000 rpm showed that the reaction was mass-transfer limited below 600 rpm. Between 600 and 1000 rpm external diffusion limitations were overcome and similar activities were observed. Consequently, 800 rpm was chosen for all experiments.

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
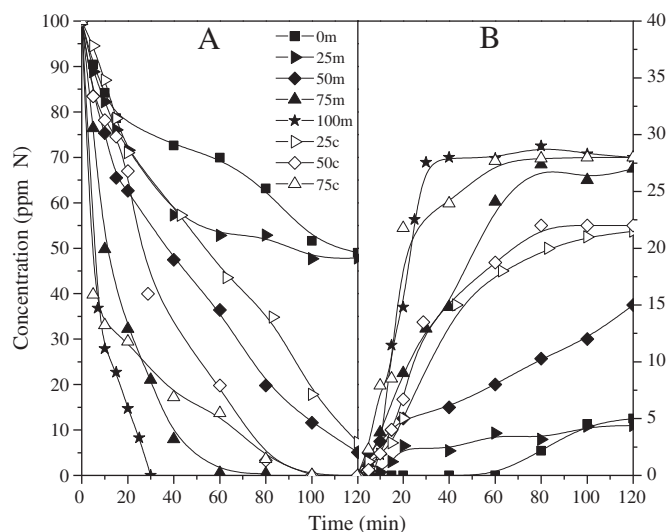

Fig. 1. Nitrates conversion (A), Ammonia production (B). For reaction conditions see Experimental section.

colorimetric reaction were used. This colorimetric reaction is the same reaction employed in the assay for nitrites. Ammonium was analyzed by the adapted Berthelot method.

The initial reaction rate at nitrate conversions lower than 10% was calculated. At low conversions, product concentrations are small; thus, the initial reaction rate (IRR) is an intrinsic property of the active sites towards the nitrate hydrogenation reaction.

3. Results and discussion

3.1. Reaction experiments

Figs. 1 and 2 show nitrate conversion and selectivity results for mixtures of bimetallic catalysts (m) and Pd,In impregnated on mixtures of supports (c). The corresponding values for Pd,In/Al₂O₃ (100 m) and Pd,In/SiO₂ (0 m) catalysts are also included for comparison. Values of conversions and selectivities measured at 100 min of TOS and the calculated initial rates are summarized in Table 2. As expected, the catalysts with higher alumina content are more active to convert nitrates, and as the proportion of SiO₂ increases, the selectivity to ammonia measured at 50% of conversion decreases, results that are in line with those reported in our previous work [14].
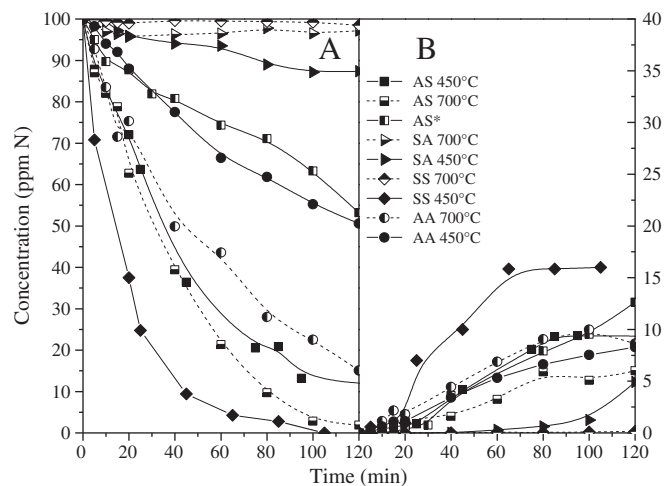

Fig. 2. Nitrates conversion (A), ammonia production (B). For reaction conditions see Experimental section.

Table 2
Reaction behavior of Pd,In 1:0.25 catalysts supported on different Al_2O_3–SiO_2 mixtures.

Catalyst	$T_{reduction}$ (°C)	t = 100 min				Reaction rate [e]
		% X^a	% S_{NH4}^b	% S_{NO2}^c	% S_{NC}^d	
100 m	450	100.0	25.0	0	75.0	48.5
75 m	450	100.0	37.9	0	62.1	22.5
50 m	450	88.4	13.6	0.9	85.5	16.5
25 m	450	52.3	8.3	1.3	90.4	10.5
0 m	450	50.9	8.9	0.3	90.8	8.5
75c	450	99.9	28.0	3.3	68.7	52.6
50c	450	99.9	22.0	0	78.0	17.0
25c	450	82.2	25.6	0	74.4	6.5

[a] Conversion at 100 min reaction.
[b] Selectivity to ammonia.
[c] Selectivity to nitrite.
[d] Selectivity to gaseous nitrogen compounds.
[e] (ppmN) (g catalysts)$^{-1}$ (min)$^{-1}$.

The initial reaction rates (IRR) are shown in Table 2. It can be noticed that the catalyst with the highest amount of Al_2O_3 presents the highest IRR and that it steeply decreases when the SiO_2 content increases. The IRR of alumina supported catalyst is so high that the OH produced could not be neutralized by the system and the reaction has a high selectivity to ammonia [2,15]. The IRR of SiO_2 supported catalysts is lower allowing OH neutralization; as a result, ammonia production is lower.

Interestingly, the conversion and selectivity of the 50c and 75c catalysts are similar to those of the 100 m catalyst. Moreover, nitrate conversions and ammonia selectivities are higher for the "c" catalysts than those for the "m" ones. These results can be related to a preferential impregnation of Pd and In on alumina particles for the "m" solids, which in turn is associated with the point of zero charge of alumina (pzc = 8). During the impregnation of Pd and In, the medium is strongly acid; thus, the alumina superficial charge is positive and the negative chloride complexes of palladium ($PdCl_4^{2-}$) [16] and indium ($InCl_4^-$) [17,18] could be preferentially adsorbed over alumina instead of SiO_2 (pzc = 2) [19]. As a result, the catalysts prepared on these mixed supports have properties similar to those prepared with alumina alone but with higher metal loading.

The best selectivity to gaseous nitrogen compounds is obtained when the SiO_2 proportion is 25% in "m" catalysts. As said before, it is remarkable that S_{NC} for "c" catalysts are lower than those obtained for "m" catalysts. This behavior could be partly explained by the lower activity of "c" catalysts to nitrite reduction or because the occupation of the active sites by nitrates avoids nitrite reduction [5]. Another possibility could be that the locally increased metallic load on alumina particles provokes that Pd–$NO_{(ads)}$, the clue intermediate [20], could meet another Pd–$H_{(ads)}$ species instead of a Pd–$NO_{(ads)}$ species, thus producing ammonia instead of $N_{2(g)}$.

Since it has been reported that bimetallic sites are responsible for the first step in the reaction mechanism of nitrate reduction [14], different mixtures of monometallic catalysts were evaluated in order to study the effect of different degrees of metal–metal and metal–support interactions. The mixtures were reduced either at 450 °C or 700 °C and they are denoted as AS, SA, SS and AA (see Table 1). A preparation was also performed by mixing previously reduced monometallic catalysts, which is labeled as AS*. Fig. 2 shows the reaction results, and despite the fact that most of these catalysts could not convert 100% of nitrates before 120 min, an interesting behavior was observed which helped us better understands the nature of this system.

In the case of the AS samples (Pd/Al_2O_3 + In/SiO_2 mixtures), the AS solid reduced at 450 °C showed good nitrate conversion, and when the reduction temperature was increased to 700 °C in order to promote In–Pd interactions, it showed a better selectivity to gaseous nitrogen compounds and the reaction rate was similar (See Table 3). For the AS* preparation, in which catalysts were reduced separately at 450 °C and introduced into the batch reactor, it was

expected that the lower degree of Pd–In interaction took place. Nevertheless, a considerable nitrate conversion was obtained (see Fig. 2).

Interestingly, an opposite behavior was observed for the SA samples (Pd/SiO_2 + In/Al_2O_3 mixtures). The SA catalyst reduced at 700 °C could not convert nitrates and SA reduced at 450 °C showed low conversion.

Finally, physical mixtures of the monometallic catalyst with the same support were evaluated (See Fig. 2 and Table 3). The SS mixture reduced at 700 °C was inactive to reduce nitrates. SS reduced at 450 °C reached 99% conversion in 100 min and its S_{NC} was 84%. Surprisingly, the latter mixture showed a better activity than the Pd, In/SiO_2 catalyst, with somewhat lower S_{NC}. On the other hand, the AA catalyst reduced at 450 °C was poorly active (see Table 3). It reduced less than 50% of nitrates. When reduced at 700 °C, it showed a somewhat better activity.

The results obtained show that by regulating the metal–metal and metal–support interactions, different catalytic behaviors are obtained. Since the interactions of Pd and In with Al_2O_3 are stronger than with SiO_2 [14], it can be suggested that Pd particles covered by In oxide is the better configuration in order to obtain active catalysts. This suggestion is supported by the results obtained for AS and SA mixtures. When In is supported on SiO_2, it has more mobility and after reduction treatments it can migrate towards the surface of Pd crystals that are deposited on Al_2O_3, yielding moderately active solids. The opposite occurs for SA mixtures that result in poorly active catalysts.

The mixture of monometallic catalysts supported on alumina (AA) shows some nitrate conversion only after reduction at 700 °C, indicating that a high reduction temperature is needed to obtain some degree of Pd–In interaction, which is due to the stronger metal–support interactions. On the contrary, the SS catalyst reduced at 700 °C is inactive, indicating that the extremely high mobility of the metals is harmful, probably due to the agglomeration of Pd crystals. A reduction of SS at 450 °C results in a catalyst that is indeed more active than Pd,In/SiO_2, showing that an optimum Pd–In interaction can be obtained by mechanically mixing the monometallic catalysts and reducing the mixture at moderate temperature.

The behavior obtained for the AS* catalyst, which was prepared by mixing the individually reduced monometallic catalysts, can be explained in terms of the interactions that take place during reaction in the aqueous media. At pH of 5, Al_2O_3 develops a positive charge over its surface, and the opposite occurs for SiO_2. This could make the support particles to interact between them due to electrostatic forces, giving place to weak Pd–In interactions that are enough to

Table 3
Reaction behavior for different mixtures of monometallic catalysts.

Catalyst	$T_{reduction}$ (°C)	t = 100 min				Reaction rate [e]
		% X^a	% S_{NH4}^b	% S_{NO2}^c	% S_{NC}^d	
AS	450	89.0	10.8	0	89.2	9.5
	450[f]	29.1	33.9	0.3	65.8	4.9
	700[g]	93.2	5.2	0	94.8	9.5
SA	450	12.4	39.1	0	60.9	0.9
	700	n.d.[h]	–	–	–	–
AA	450	44.7	17.4	0	82.6	2.8
	700	84.9	10.1	0	89.9	7.6
SS	450	99.9	16.0	0	84.0	27.8
	700	n.d.	–	–	–	–

[a] Conversion at 100 min reaction.
[b] Selectivity to ammonia.
[c] Selectivity to nitrite.
[d] Selectivity to gaseous nitrogen compounds.
[e] Initial reaction rate (ppm N) (min)$^{-1}$ (g catalyst)$^{-1}$.
[f] AS*: catalysts reduced separated at 450 °C.
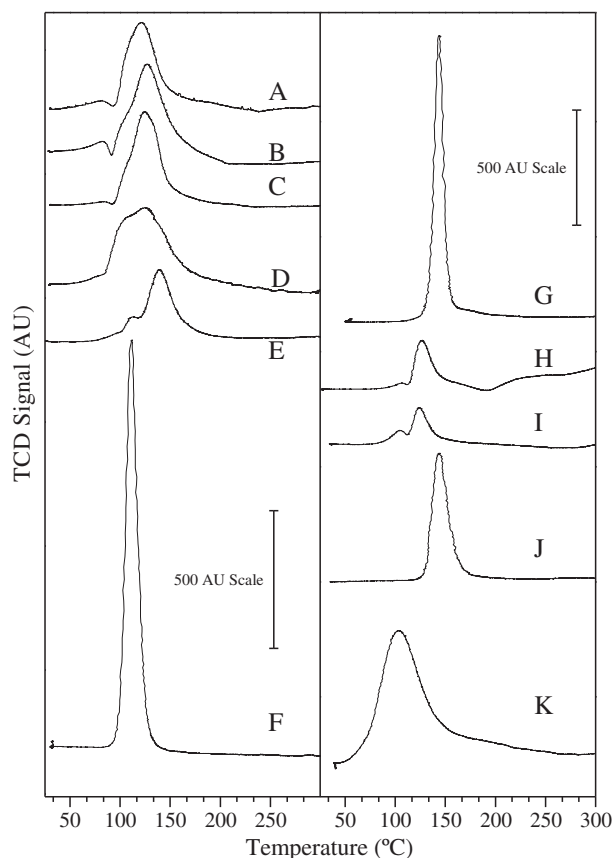[g] Catalysts reduced together at 700 °C.
[h] Not detected.

Fig. 3. TPR profiles of catalysts (A) 75 m, (B) 50 m, (C) 25 m; (D) 50c, (E) 25c, (F) 0 m, (G) SA, (H) AS, (I) AA, (J) SS, (K) 100 m. For analysis conditions see Experimental section.

make the reaction occur. A similar effect has been reported by Salomé et al. [9] using mixtures of catalysts composed by Pd, Pt, Rh and Cu.

3.2. Catalyst characterization

In order to confirm the findings about metal–support and metal–metal interactions described in the previous section, TPR experiments were carried out and the corresponding profiles are shown in Fig. 3. Those catalysts that have higher Al_2O_3 proportion present a peak at around 100–120 °C which corresponds to the reduction of Pd species [14], which is wider than that observed on catalysts with a higher proportion of SiO_2. This observation could be associated with a closer interaction with the support and a higher distribution of particle size in the catalysts.

TPR profiles of (c) catalysts are shown in Fig. 3 (D and E). It is worth noting that reduction peaks are wide, suggesting that Pd species are preferably situated over Al_2O_3 instead of over SiO_2.

With respect to Indium species, it is known that there are two reduction zones. One from 300 °C to 400 °C assigned to the reduction of highly dispersed indium oxidized species and another zone which starts at 600 °C and is associated with the reduction of large particles of In_2O_3. Due to the low content of In, the high temperature peaks are not well defined; thus, TPR profiles are shown only in the 50–300 °C range.

In Fig. 3G, a narrow peak can be clearly observed, which is associated with Pd supported on SiO_2 the same as the peak observed in the TPR of the monometallic Pd/SiO_2 catalyst, but the former is situated at higher temperatures. In Fig. 3H, an interaction peak seems to appear representing indium particles which were interacting with Pd [14]. This observation could explain the presence of catalytic activity in this catalyst.

A broad reduction peak of indium oxide could be seen in the $Pd/SiO_2:In/SiO_2$ catalyst (between 200 and 500 °C), indicating that this species has mobility in this temperature range. This could explain the catalytic activity observed in SS (450 °C). Fig. 3J shows a low temperature reduction band of palladium species and high temperatures signals associated with indium species reduction.

Fig. 4 shows the XRD patterns of (m), (c), AS and SA catalysts. The profiles show the diffraction lines characteristic of the support with higher proportion in the mixture. In the SA catalyst (Fig. 4H) there appear refraction lines of InOCl (PDF 11–510) and InCl (PDF 26–765) between 25° and 35°. These compounds probably came from the precursors used in the catalysts preparation. There are signals of In_2O_3 (PDF 6–416) which could be associated with the metallic particle agglomeration.

In order to explain the low activity of SA (450 °C), its dispersion was determined using CO adsorption. The SA catalyst presented dispersion equal to 2%. The same determination in the AS (450 °C) catalyst results in a dispersion equal to 70%. These results indicate that Pd is agglomerated on the SiO_2 support after reduction at 450 °C, thus lowering the catalytic activity for nitrate reduction. Besides, due to the signals detected by DRX it is possible that Pd moves to support inner layers or probably In strongly interacts with palladium avoiding the adsorption of CO. An agglomeration effect also takes place, but to a lower extent, when the bimetallic catalysts are in contact with the aqueous reaction media, resulting in a partial deactivation, as we reported in previous articles [10,14].

In order to know the oxidation state of the active sites and their accessibility on the catalyst surface, CO adsorption was performed followed by FTIR analysis. The IR spectrum of CO adsorbed on AS is shown in Fig. 5. This catalyst presents an asymmetric band at 2080 cm^{-1} ascribed to CO linearly adsorbed (on top) on Pd^0 [21].
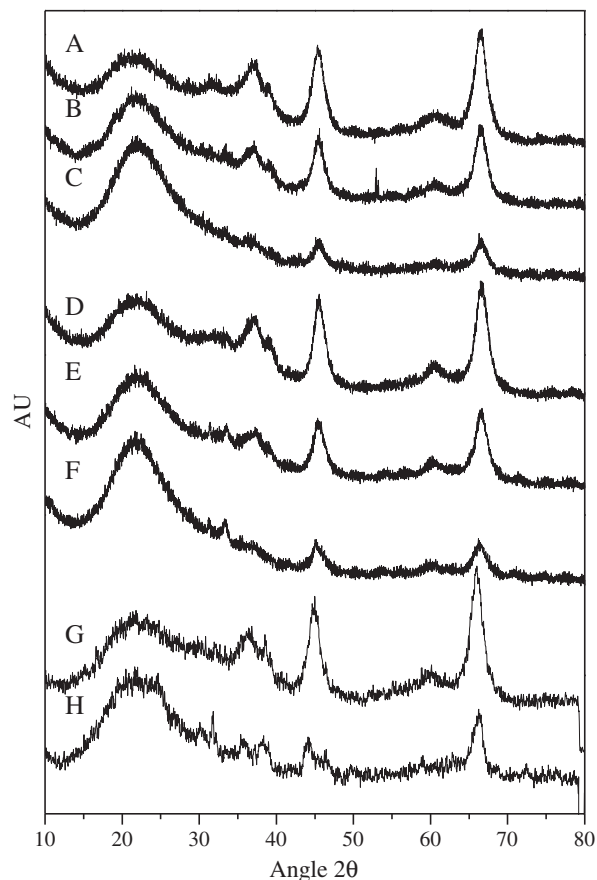

Fig. 4. XRD patterns of catalysts: (A) 75c, (B) 50c, (C) 25c, (D) 75 m, (E) 50 m, (F) 25 m, (G) AS, (H) SA.
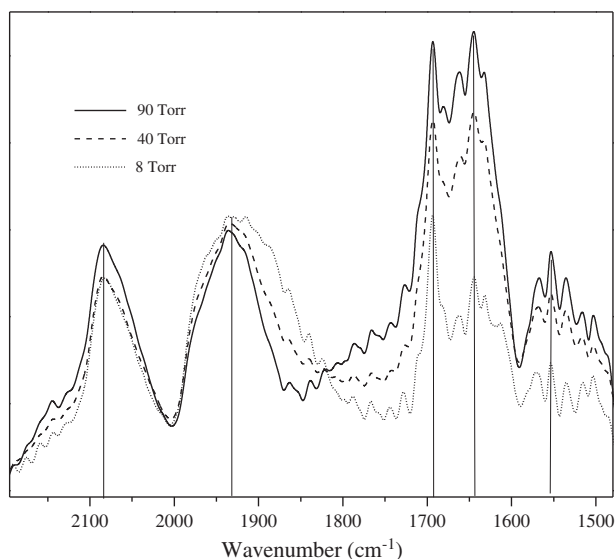
Fig. 5. IR spectra of CO adsorbed on reduced AS catalyst, $P_{CO} = 8, 40, 90$ Torr.

At the same time, the band between 2020 and 1800 cm^{-1} [14] with a maximum at 1930 cm^{-1} is assigned to CO in a bridged configuration bonding with Pd, forming a Pd^0–CO–Pd^0 complex with different coordination [22]. The absorption bands located in the 1630–1650 cm^{-1} range are assigned to the stretching frequency ($v_{C=O}$) of bridged carbonates. The band at 1650 cm^{-1} can also be associated with the adsorption of CO on the support surface (vCO–OH), as this band usually appears on the reduced Al$_2$O$_3$ without any supported metallic cation [14]. The formation of carbonate and bicarbonate species accounts for the existence of reactive surface oxygen which oxidizes CO to CO$_2$. The presence of CO$_3^{2-}$ and/or HCO$_3^-$ species on the surface of the impregnated solids indicates that they contain an amount of reducible cation. However, the presence of very little detectable signals in the 2100–2150 cm^{-1} range (2143 cm^{-1}) which is typical of adsorption of CO on oxidized Pd$^{\delta+}$ species, confirms that Pd is not fully reduced. It is important to highlight that for the SA catalyst characteristic adsorptions signals were not detected, which is in line with the CO uptake experiments.

4. Conclusions

It was found that (m) and (c) catalysts are active for nitrate and nitrite reduction using hydrogen as reductant agent. Particularly, those which have a higher proportion of Al$_2$O$_3$ have a higher nitrate conversion at 100 min of reaction. The best conversion and selectivity results were obtained with AS*. In this catalyst probably the net surface charge is optimum and the metallic particle found the appropriate interaction to reduce the nitrates to nitrites in a selective way.

With respect to the influence of the support, catalysts that have their Pd active sites on Al$_2$O$_3$ show the highest activity to reduce nitrates. It could be observed that the presence of SiO$_2$ improves the selectivity to gaseous nitrogen compounds, but in (c) catalysts this effect could be hidden because of the PZE effect during catalyst preparations. Al$_2$O$_3$ has a pI (isoelectric point) of 8 as the reaction media has a pH of 5. At this pH Al$_2$O$_3$ has a positive superficial charge which will produce a negative counterion layer (i.e. NO$_3^-$, NO$_2^-$), phenomenon that could explain the good activity. As the SiO$_2$ has a pI of 2, it presents a negative superficial charge producing a positive counterion layer (i.e. H$_3$O$^+$, NH$_4^+$). In equilibrium, the ammonia present in this layer could avoid the production of more ammonia. This excess of positive charge leads to the production of N$_{2(g)}$ as a final product instead of ammonia.

Characterization results show that Pd support interactions are determining for the reaction activity and selectivity and this could be ascribed to the different kinds of interactions obtained for each support and reduction temperature. Although the final concentrations of ammonia obtained were higher than the recommended level, the AS catalyst reduced at 700 °C offered closer values to regulations.

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