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# Catalytic reduction of nitrates using Pt/$CeO_2$ catalysts in a continuous reactor

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ABSTRACT

The increasing pollution of natural sources of drinking water encourages the development of new emerging technologies and processes for water remediation. The present study demonstrates that monometallic Pt catalysts provide high conversion on the nitrate reduction reaction when ceria is used as support. However, the presence of ammonium was detected in all the catalysts. In order to control the formation of ammonium, the acid–base character of the support was modified, introducing several fluoride species into the $CeO_2$, using two different methods: impregnation and combustion. The introduction of fluoride species in the $CeO_2$ support by combustion produces a slight decrease in the reduction of nitrates. However, an important decrease in ammonium formation was observed. The capability of the reduction of surface $CeO_2$ and the acid–base properties of the support, after the addition of fluoride species, play an important role in the control of both activity and selectivity. The incorporation of fluoride species into the $CeO_2$, represents an alternative way to improve the selectivity of nitrate reduction toward nitrogen without the use of additional molecules such as $CO_2$ to control pH.

## 1. Introduction

Nitrate is a priority pollutant of groundwater in many countries due to both its toxicity and its widespread presence. The main sources of nitrate pollution are associated to intensive agricultural activities including fertilizer application as well as livestock exploitation. Excessive levels of nitrate in water are detrimental to human health. Besides causing problems with blood pressure, it causes methemoglobinemia in infants and studies suggest that nitrate is a precursor of carcinogenic nitrosamines. The accepted level of nitrate in water is in the range of 50 mg/l depending on local legislation (http://reports.eea.eu.int.).

A large number of physicochemical and biological processes have been developed for removing nitrate from contaminated water, although these processes might be either marginally cost-effective or detrimental due to potential side-effect on water quality. In an attempt to overcome these disadvantages catalytic denitrification have emerged as the most promising, efficient and flexible technique. In this process, nitrate ions are reduced using hydrogen over bimetallic catalyst to nitrite as an intermediate and then to nitrogen or ammonia as the final products [1]. One of the advantages of the catalytic reduction of nitrate containing effluents is that the reaction is performed in mild conditions, at room temperature and atmospheric pressure [2–6].

Previous studies were demonstrated that nitrites are reduced by hydrogen on various hydrogenation catalysts, such as palladium or platinum supported on alumina, whereas these catalysts are inactive for nitrate reduction. To reduce nitrates, it is necessary to activate the precious metal by addition of a promoter. Normally the research on catalytic reduction has focused on the use of bimetallic catalyst [2–8], but more recently, studies involving monometallic catalysts have appeared [9–12] following the idea that nitrate reduction could be catalyzed by some catalyst containing a noble metal able to chemisorb hydrogen and a support with redox properties [9,11,12]. In this sense, Epron et al. used $CeO_2$ as an active support [9]. Pd/$CeO_2$ catalysts showed high activity in reducing nitrates but poor selectivity to nitrogen (ammonia was 80% of the product). The reaction mechanism suggested that the oxygen vacancies are involved as active sites for reducing nitrates. Although these catalysts present high activity the selectivity to ammonia as a by-product is too high, which is undesirable in drinking water.

Whereas a step-wise reaction seems to be the most accepted mechanism for nitrate reduction [13,14], there are different opinions about the mechanism of ammonium formation. Wărnă et al suggested that the key intermediate on the noble metal could be $NO_{(ads)}$. Yoshinaga et al. [15] went further and described the possible chemical environment of the active sites on the basis of the kinetic measurements and the hydrogenation power of the species involved. Recently, ATR-IR has been used to monitor in situ the ability of Pd/$Al_2O_3$ catalyst to reduce nitrite [16]. The results showed that the adsorption of $NO^{-}_{2(aq)}$ on H–Pd/$Al_2O_3$ produced

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$NO_{(ads)}$, $NH_{2(ads)}$ and $NH_4^+$. These species are originated from the reaction with hydrogen on the palladium surface. Subsequent hydrogenation showed that $NO_{(ads)}$ is converted into $N_2$, whereas the hydrogenation of $NH_{2(ads)}$ yields $NH_4^+$. Ebbesen et al. proposed a reaction scheme in which nitrogen and ammonia are formed via two parallel step-wise hydrogenation processes.

The $NH_4^+$ formation is accepted to be related with a pH increase due to the formation of hydroxide during the reduction of nitrates. Furthermore, basic pH induces a polarization of the support and has repulsive effect on nitrates and nitrites, inducing a decrease of the activity and the selectivity to nitrogen [17]. Different solutions have been used to reduce the formation of hydroxides [18–22] using a pH buffer as carbon dioxide or formic acid. The main drawbacks of these alternatives are a negative impact on the inner wall of a reactor and on the global environment by the use of the acids and the decrease in the nitrate reduction activity. Thus it is necessary to find an ecological friendly method of pH control of the system, instead of buffers used before. One of the possibilities for green chemical control of pH is to use a catalyst with acid–base character. However, the effect of the acid–basic properties of the catalyst on the nitrate reduction reaction has not been studied until now.

The aim of this work is to report the effect of the acid–base properties of the catalysts in the control of the selectivity in the nitrate reduction. Monometallic Pt catalysts supported on $CeO_2$ have been studied using a continuous reactor. In order to control the acid–basic properties of the catalysts to avoid the ammonium formation, the introduction of fluoride species using different protocols has been studied.

## 2. Experimental

### 2.1. Catalysts synthesis

Cerium nitrate was used as precursor of cerium oxide. In a Pyrex dish (500 ml), a mixture of cerium ammonium nitrate (7.50 g), Pluronic (0.21 g) and 4 ml of ethanol were introduced and stirred. When the mixture was homogeneous, it was introduced into a muffle furnace preheated to 350 °C. The solution boiled with foaming and frothing and ignited to burn with a flame yielding about 2.5 g voluminous oxide product within 5 min.

Two procedures have been followed for preparing fluorinated ceria. The first is a co-combustion method referred to as (C). The cerium nitrate, corresponding amount of ammonium fluoride and Pluronic were dissolved in ethanol and then combusted as described before. The second procedure is an impregnation method referred to as (I) which the aqueous solution of ammonium fluoride is impregnated on ceria already synthesized. The material is dried over night at 120 °C and then calcined in a muffle furnace preheated at 400 °C.

Ceria and fluorinated ceria were impregnated using the incipient-wetness technique with an ethanol solution of the corresponding metal salt ($H_2PtCl_6$). After that, the samples were dried at 120 °C for 24 h and then reduced at 350 °C in hydrogen flow for 3 h.

### 2.2. Characterization

Powder X-ray diffraction patterns of the different samples were obtained on a Siemens D5000 diffractometer using nickel-filtered Cu K$\alpha$ radiation. The patterns were recorded over a range of $2\theta$ angles from 10° to 90° and crystalline phases were identified using the Joint Committee on Powder Diffraction Standards (JCPDS) files.

Temperature programmed reduction (TPR) studies were performed using a TPD/R/O 1100 (ThermoFinnigan) equipped with a thermal conductivity detector (TCD) and coupled to a mass spectrometer QMS 422 Omnistar. Before reduction, the sample (around 100 mg) was dried under flowing helium at 120 °C for 24 h. The reduction was carried out between room temperature and 800 °C at a heating rate of 10 °C/min flowing a gas mixture of 5% $H_2$ in argon (20 ml/min total flow).

Hydrogen chemisorption analysis were carried out in a Micromeritics ASAP 2010 apparatus. Samples were previously reduced in the same conditions in which the catalysts were prepared. After reduction, the hydrogen on the metal surface was removed with 30 ml/min of He for 30 min at 410 °C. The sample was subsequently cooled to room temperature under the same He stream. The chemisorbed hydrogen was analyzed at 70 °C using the adsorption–backsorption isotherm method.

BET analysis was carried out in a Micromeritics ASAP 2010 apparatus. The surface BET area was determined by $N_2(g)$ adsorption at a single and multi-point partial pressures of $N_2(g)$. Prior to the physisorption measurements, the samples were outgassed for at least 30 min at 120 °C under He.

Fourier transform infrared (FTIR) spectra were recorded on a Bruker IFS 28 spectrometer equipped with an MCT detector at a resolution of $4\,cm^{-1}$. The measurement cell is connected to a vacuum system working in the $10^{-6}$ mbar range and allows in situ pre-treatments of samples. The catalysts were pressed into self-supporting wafers and were reduced in 500 mbar of pure $H_2$ at 300 °C. After keeping the catalyst in hydrogen atmosphere at that temperature for 30 min, the cell was evacuated under vacuum for another 30 min at the reduction temperature. CO adsorption measurements were carried out at 20 °C using 5 mbar of pure CO, followed by evacuation of the gas phase of CO at 20 °C.

### 2.3. Catalytic activity

A simplified diagram of the experimental setting is shown and explained in previous work [23]. The reactor was filled with 0.5 g of catalyst. The catalytic reduction of nitrate was performed in a fixed-bed reactor. The liquid feed solution with 60 mg/l of nitrate ions was introduced by a pump (70 ml/h). The hydrogen flow is adjusted by a mass flow controller (3 ml/min) and the catalytic system worked at ambient temperature and pressure. The reaction products were analyzed by HPLC coupled with conductivity detector (Shimatzu). Nitrate and nitrite concentration were determined after separation on a Shim-pack IC-A1S column at 40 °C. Ammonium ions were quantified using a Shodex IC YK-421 column at 40 °C. The reaction time for all the experiments has been for 24 h. No change in both catalytic activity and selectivity has been observed during this reaction time.

## 3. Results and discussion

### 3.1. Catalysts characterization results

Table 1 summarizes some properties of the catalytic materials. The BET surface area of the resulting $CeO_2$ material was 103 $m^2/g$. The introduction of around 1 wt.% of fluoride species in the support using the combustion method (C) results in a slight decrease in the BET area (91 $m^2/g$). When the amount of fluoride species increased up to 5 wt.%, similar BET area was obtained (93 $m^2/g$). However, using the impregnation method (I) a substantial decrease of surface area is observed for the sample containing 1 wt.% of fluoride species (59 $m^2/g$). Further decrease in surface area is obtained increasing the amount of fluoride species (38 $m^2/g$ for the sample containing 5 wt.% of fluoride species). From these results, the deposition of the fluoride species on the ceria surface is expected using the impregnation method, whereas by combustion method is expected to introduce the species in the ceria matrix. The fluoride species located on the surface of the $CeO_2$, could block

**Table 1**
BET surface area, metal dispersion and reduction degree of the samples.

| Sample | BET ($m^2/g$) | Metal dispersion (%) | TPR reduction degree of $CeO_2$ (%) |
|---|---|---|---|
| $CeO_2$ | 103 | – | 4 |
| 1% F–$CeO_2$ (C) (combustion) | 91 | – | 5.5 |
| 5% F–$CeO_2$ (C) (combustion) | 93 | – | 3.5 |
| 1% F–$CeO_2$ (I) (impregnation) | 59 | – | 5 |
| 5% F–$CeO_2$ (I) (impregnation) | 38 | – | 3 |
| 0.2% Pt/$CeO_2$ | – | 110 | 14 |
| 0.5% Pt/$CeO_2$ | 80 | 70 | 18 |
| 1% Pt/$CeO_2$ | 70 | 70 | 27 |
| 1% Pt/1% F–$CeO_2$ (C) | 82 | 36 | 21 |
| 1% Pt/1% F–$CeO_2$ (I) | 55 | 30 | 13 |

the pores decreasing the surface area, whereas the introduction of fluoride species in the ceria matrix (up to 5 wt.%) does not produce important changes in the porosity. The BET results confirm the hypothesis showing a loss in surface area in the impregnated sample but not for the combustion ones. These results are in agreement with previous works where the introduction of doping agents in $CeO_2$ materials by combustion method, produces a substantial increase of the BET surface area [24].

The introduction of Pt in the $CeO_2$ catalysts produced an important decrease in the surface area (see Table 1). Probably due to the acid character of the platinum metal salt ($H_2PtCl_6$) used as precursor. However the incorporation of platinum in the F–$CeO_2$ catalysts, only produce a slight decrease in the surface area.

The platinum dispersion of the samples, obtained by hydrogen chemisorption, is also shown in Table 1. When the amount of platinum increased in Pt/$CeO_2$ samples, a slight decrease of the dispersion was observed. The dispersion of the 0.2% Pt/$CeO_2$ sample was 110% whereas for the 1% Pt/$CeO_2$ sample was 70%. Probably, some part of the hydrogen chemisorbed could be related with spill over of hydrogen on the ceria surface leading higher dispersion values. However, an important decrease in metal dispersion is observed when platinum is deposited on the fluoride samples. This fact could be related with the absence of spill over of hydrogen in the fluoride ceria surface.

Fig. 1 displays the XRD patterns of the samples. $CeO_2$ obtained by the combustion method has the typical fluorite-type structure. Basal reflections at $2\theta = 28.6°, 33.1°, 47.5°$ and $56.5°$ are related, to the planes (1 1 1), (2 0 0), (2 2 0) and (3 1 1) respectively, and there are in agreement with previous studies [25]. In the fluorinated samples, obtained by combustion, a little shift of the diffraction lines for the F–$CeO_2$ samples compared to pure $CeO_2$ was observed. This indicates that F is incorporated into the ceria lattice by the substitution of oxygen [26]. In addition, with high amount of F an increase in the crystallinity is observed. However, the $CeO_2$ samples before and after fluorination showed the same XRD pattern in the case of impregnation.

TPR profiles and reduction degrees of the $CeO_2$, F–$CeO_2$, Pt–$CeO_2$ and Pt–F–$CeO_2$ samples are displayed in Fig. 2 and Table 1, respectively. $CeO_2$ materials usually have two distinct features in hydrogen TPR, a wide peak around 450 °C assigned to a surface reduction process and a broad peak at higher temperature (near to 750 °C) assigned to the bulk reduction [27–29]. The TPR profile for the $CeO_2$ support is in agreement with these results, showing a first peak at 500 °C, that indicates that around a 4% of the $Ce^{4+}$ is reduced to $Ce^{3+}$, and a second peak at 850 °C. The incorporation of metals can catalyze the surface reduction process, as it has been observed in previous works [24,28,30,31], shifting the first wide peak to lower temperatures and sharpening its features, probably without affecting bulk ceria reduction [28]. This behaviour is indeed observed in Fig. 2(A) for TPR profiles of catalyst with several loadings of Pt. Different peaks between 200 °C and 450 °C, being related to the reduction of both platinum and $CeO_2$ are present. Small peaks around 200 °C could be attributed to reduction of platinum and ceria in the vicinity of Pt crystallites, as it has been suggested by Panagiotopoulou et al. [24]. The main peak detected around 300 °C is mainly due to the reduction of the $Ce^{4+}$ on the surface of the $CeO_2$ to $Ce^{3+}$ promoted by the addition of platinum. Around a 14% of $CeO_2$ is reduced to $Ce^{3+}$ for the $CeO_2$ containing 0.2 wt.% of platinum, whereas around 27% of $CeO_2$ is reduced when the amount of platinum was 1 wt.%. Furthermore, small reduction peaks between 400 and 450 °C that could be related to the reduction of surface ceria that is not in contact with platinum are also observed [30].

The reducibility of this system is also affected by introducing fluoride species. The TPR profiles for 1% F–$CeO_2$ by combustion (C) and impregnation (I) are showed in Fig. 2(B). The profiles are characterized by a broad high temperature peak above 850 °C related to the reduction of bulk ceria which remain constant for all the samples except for 5% F–$CeO_2$ (C) that is shifted to higher temperature. The peak related to the surface reduction (around

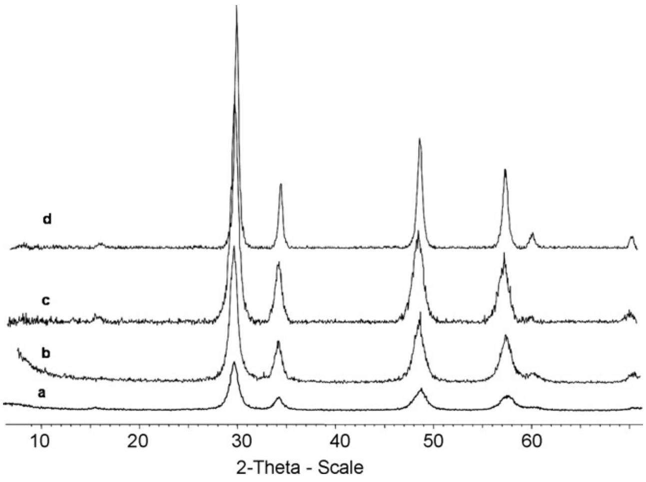

**Fig. 1.** XRD profiles of fluorinated ceria catalysts by combustion method [(a) $CeO_2$; (b) 0.5% Pt/1% F–$CeO_2$; (c) 1% F–$CeO_2$ and (d) 5% F–$CeO_2$].

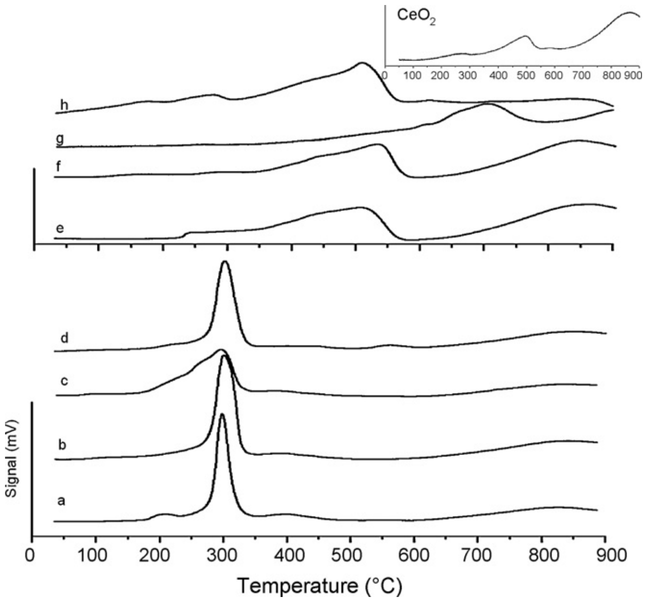

**Fig. 2.** TPR profiles. (a) 0.2Pt/$CeO_2$; (b) 0.5Pt/$CeO_2$; (c) 1Pt/$CeO_2$; (d) 1Pt1F$CeO_2$ (C); (e) 1F$CeO_2$ (I); (f) 5F$CeO_2$ (I); (g) 1F$CeO_2$ (C); (h) 5F$CeO_2$ (C).

500 °C) is present in all the samples, however the 5% F–$CeO_2$ (C) sample, showed this surface reduction at higher temperature (708 °C). This fact could be related with a requirement of higher reduction temperature for this material, probably due to the fluoride species incorporated in the ceria matrix. Table 1 shows the reduction degree of the $CeO_2$ surface for several samples. The reduction degree of the 1% F–$CeO_2$ samples obtained by combustion and impregnation was slightly higher than for the $CeO_2$. Probably the introduction of fluoride species generates some vacancies on the $CeO_2$ surface improving the reducibility. However, when the amount of fluoride species increased from 1 wt.% up to 5 wt.%, a slight decrease in the reduction degree with respect to $CeO_2$, was observed.

Furthermore, the introduction of Pt in the F–$CeO_2$ samples decreases the reduction temperature in similar way as observed for the Pt–$CeO_2$ samples. However a reduction degree of ceria surface of around 18% and 13% were obtained for 1% Pt/1% F–$CeO_2$ (C) and 1% Pt/1% F–$CeO_2$ (I), respectively. These values are lower than the obtained for 1% Pt/$CeO_2$ (around 27%).

In order to study the impact of the Pt particles on the ceria, FTIR with adsorption of CO was performed (Fig. 3A). The Pt/$CeO_2$ catalysts spectra are characterized by the presence of bands between 2120–2130 and 2080–2070 $cm^{-1}$. The strong bands observed at around 2068 and 2083 $cm^{-1}$ are attributed to CO linearly bonded to surface-exposed metal Pt atoms [30,32]. However, the bands assignment in the region 2130–2110 $cm^{-1}$ is a matter of controversy. The bands between 2120 and 2130 $cm^{-1}$ may have different origins, but it is mainly attributed to the presence of oxidized Pt in Pt/$CeO_2$. It is well known that Pt is bonded to surface lattice oxygen and this kind of bond is not fully reducible even at high reduction temperature. Since the vibrational frequency of adsorbed CO is higher when the state of metal is more positive, the bands between 2120 and 2130 $cm^{-1}$ may be due to CO linearly adsorbed on Pt atoms interacting with oxygen; i.e., Pt atoms are in a more unsaturated coordination state ($Pt^{\delta}$), probably created by a strong metal–support interaction (SMSI) [32]. On the other hand, these bands may also be attributed to the adsorption of CO on $Ce^{3+}$, as well as to the presence of species like Cl. The presence of Cl species could arise from the precursor salt of platinum ($H_2PtCl_6$) [33]. In order to clarify, the CO-FTIR spectrum of the 0.5% Pt/$CeO_2$ catalyst was recorded at different reduction temperatures (Fig. 3B). Fig. 3B shows that increasing the reduction temperature the intensity of the band around 2078 $cm^{-1}$ increases. This fact could be related to an increase in the reduction of platinum. Furthermore, an increase in the intensity of the band between 2120 and 2130 $cm^{-1}$ is also observed when the reduction temperature of the sample increased. In this way the band between 2120 and 2130 $cm^{-1}$ could be related with CO on $Ce^{3+}$ due to the surface reduction of the support observed by TPR. This band disappears in the spectrum of Pt–5F$CeO_2$ (C) catalyst (Fig. 4) where the interaction of Pt–$CeO_2$ is modified by the fluorine species decreasing the reduction of the surface of the $CeO_2$, above discussed. Furthermore, for this sample, the band related with $Pt^0$ sites (around 2083 $cm^{-1}$) is shifted to lower wavenumber (at around 2074 $cm^{-1}$). This shift to lower wavenumber of the band could be related with an increase in the platinum particle size [38,39].

Ammonia is probably the most frequently used probe molecule for acidity assessment, because it can interact with both Brönsted acidic sites (by forming ammonium anions) and Lewis acid sites (by forming acid–basic adducts) [34]. In order to confirm an increase of the acidity properties of the samples by fluorination process, FTIR spectra for ammonia adsorption on $CeO_2$ and F–$CeO_2$ have been performed (Figs. 5 and 6). It is generally believed that the IR bands around 1393, 1450,1680 and 3300 $cm^{-1}$ are due to the vibrations of $NH_4^+$ produced by the $NH_3$ adsorption on Brönsted acid sites, whereas the peaks around 1610 and 1230–1260 $cm^{-1}$ are due to the coordinatively adsorbed $NH_3$ on Lewis acid sites [35,36]. $CeO_2$ spectra did not show any band of $NH_3$ adsorption, presenting a basic character. This result is in agreement with previous studies that showed that ceria of high surface has mainly a basic character [37]. On the other hand, F–$CeO_2$ sample presents several bands at 1250, 1610 and 3232 $cm^{-1}$ assigned mainly to Lewis acid sites. However, peaks between 1300 and 1500 $cm^{-1}$, related with Brönsted sites, could be overlapped with the sample spectrum. In this way, it is demonstrated that by fluorination process is possible to enhance the surface acidity of the ceria.

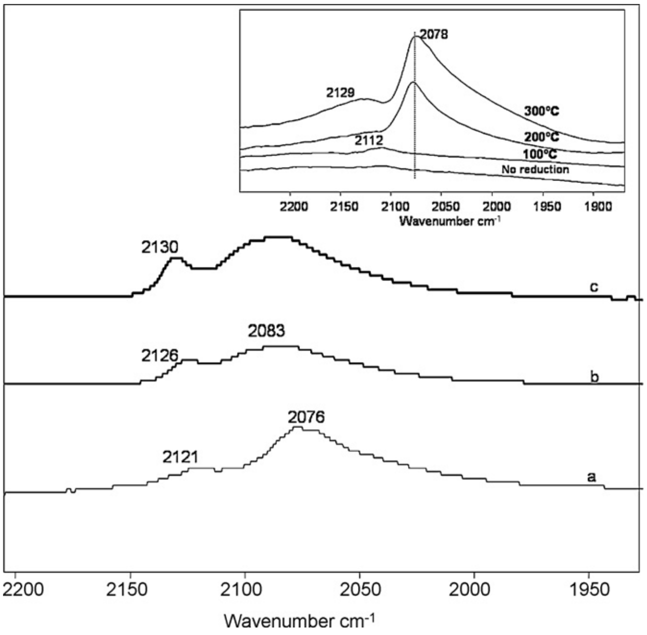

**Fig. 3.** FTIR profiles of Pt/$CeO_2$ catalysts. Profile of CO adsorption followed by short evacuation at room temperature. (A): (a) ceria; (b) 0.2% Pt; (c) 0.5% Pt and (d) 1% Pt. (B): 0.5% Pt/$CeO_2$ reduced at several temperatures.

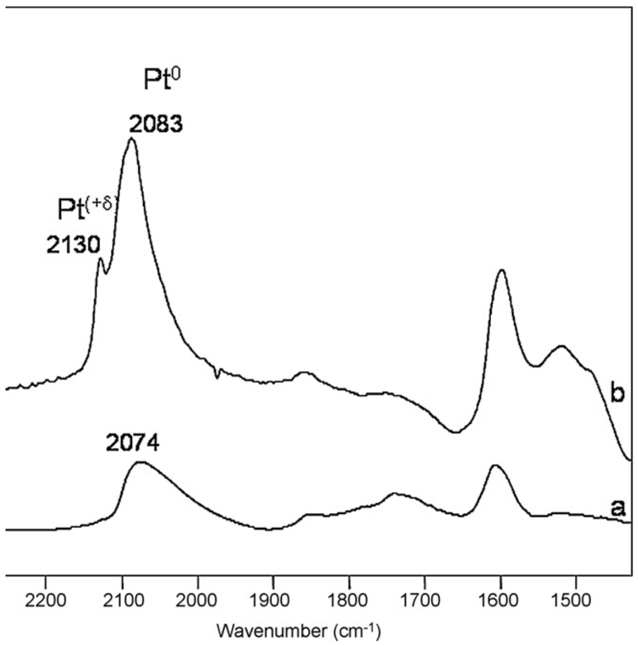

**Fig. 4.** FTIR CO adsorption profiles of 1% Pt/$CeO_2$ (a) and 1% Pt/F–$CeO_2$ (C) (b).

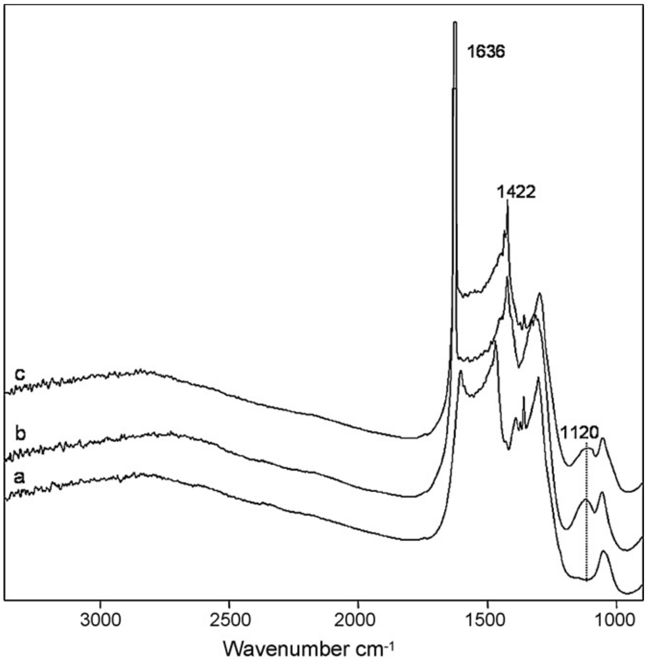

**Fig. 5.** FTIR $NH_3$ adsorption profiles $CeO_2$ [(a) sample; (b) after absorption and (c) after evacuation].

### 3.2. Catalytic activity

The catalytic activity in the hydrogenation reaction of nitrates in water using Pt–$CeO_2$ catalysts in a continuous reactor has been studied. The results of the nitrate conversion and the selectivity to nitrite and ammonium are plotted in Fig. 7 and summarize in Table 2. $CeO_2$ showed slight activity in the reduction of nitrates (20%) being the main product $NH_4^+$ (80%) and $NO_2^-$ (18%). The active sites could be related to the oxygen vacancies on the surface of the ceria supports that have some activity for nitrates reduction [9]. The introduction of platinum increases the nitrate conversion but maintaining a high selectivity to ammonia formation. The increase in the activity could be explained by an increase of the surface ceria reduced by the introduction of the platinum particles, as it has been observed by TPR results. The reduction of the coordination number of unsaturated surface $Ce^{3+}$ leads to a positive charging of the surface, which makes these sites favourable for nitrate sites [9,40].

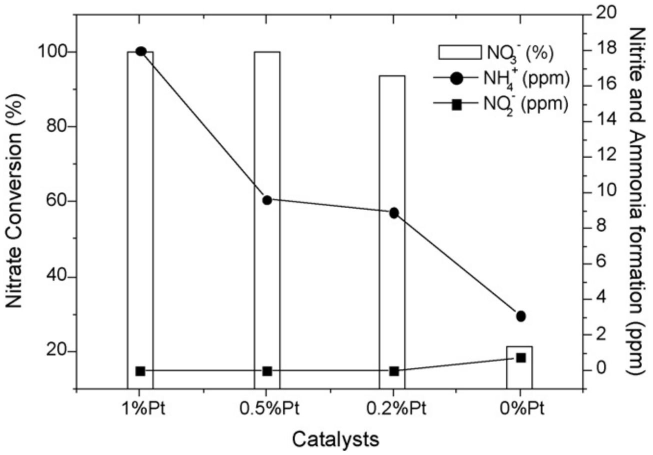

**Fig. 7.** Catalytic activity and selectivity of monometallic Pt/$CeO_2$ catalysts [(□) nitrate conversion; (■) nitrite concentration and (●) ammonia concentration].

**Table 2**
Catalytic activity and selectivity during nitrate reduction using a continuous reactor.

| Catalysts | Conversion ($NO_3^-$) (%) | Selectivity ($NO_2^-$) (%) | Selectivity ($NO_4^+$) (%) | Selectivity $N_2$ (%) |
|---|---|---|---|---|
| $CeO_2$ | 21 | 7 | 83 | 10 |
| 0.2% Pt/$CeO_2$ | 93 | 0 | 54 | 46 |
| 0.5% Pt/$CeO_2$ | 99 | 0 | 55 | 45 |
| 0.5% Pt/$CeO_2$ $H_2$:$CO_2$ | 30 | 0 | 24 | 76 |
| 1% Pt/$CeO_2$ | 99 | 0 | 100 | 0 |
| 1% Pt/F–$CeO_2$ (C) | 90 | 0 | 21 | 79 |
| 1% Pt/F–$CeO_2$ (I) | 50 | 0 | 34 | 66 |

Higher platinum content in the catalyst, leads to an increase in the ammonia formation (50–100%, see Fig. 7). The increase in the selectivity toward ammonia with higher content of Pt in the catalysts could be related with the formation of hydroxyl groups from the water interaction with the oxygen vacancies. These hydroxyls would be liable for exchange in the presence of anions in solution leading to ammonia as main product [40].

In previous studies [14,41] it was demonstrated that nitrate might be reduced to nitrites over metallic copper following a redox reaction leading to the oxidation of copper species. Subsequently, the role of the noble metal was to activate hydrogen, enabling copper reduction. A similar type of mechanism is expected here

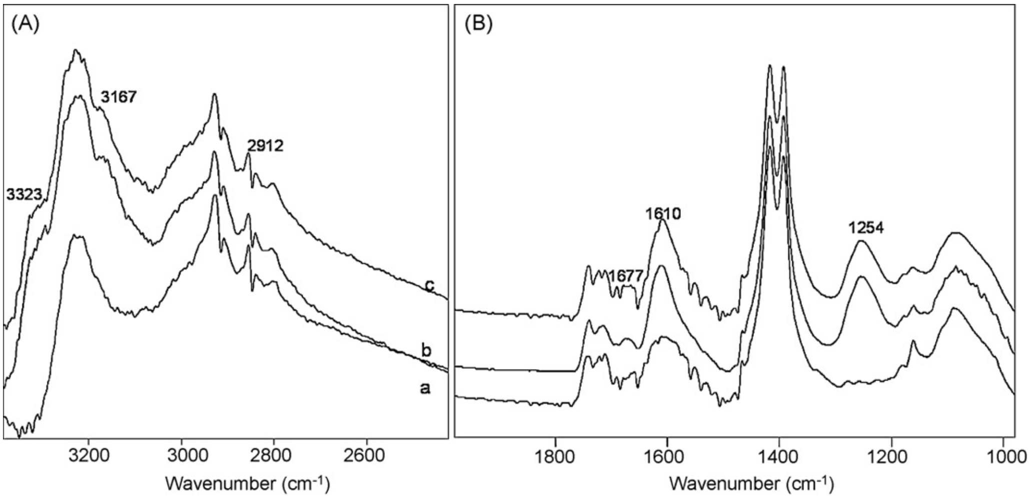

**Fig. 6.** FTIR $NH_3$ adsorption profiles 1% F–$CeO_2$ (C) [(a) sample; (b) after absorption and (c) after evacuation].

over monometallic Pt catalysts. In this case the promotion of the noble metal involves partially reduced species on the support [40]. Generally, this two-step process leads to a release of nitrite into the solution, which may be further reduced at a large stage. In this way a potentially relatively high concentration of nitrites in solution during reaction might exist for the bimetallic catalysts. However, the nitrite concentration in Pt/$CeO_2$ catalysts was null or very low. Sa and Anderson [40] showed that the nitrite adsorption on the catalyst occurs on the support via interaction of its nitrogen atom. It is likely that the sites are the same as those involved in the interaction with nitrate. In this way, the nitrites formed may be retained by the catalyst and subsequently hydrogenated rather than desorbing into solution followed by re-adsorption and reaction, as was observed in previous studies [12].

About the mechanism of ammonium formation during the nitrate reduction reaction there are different opinions. The increase of the pH, due to the formation of hydroxide during the reaction, and the existence of different active sites are the causes for the formation of $NH_4^+$ decreasing the selectivity to nitrogen. The former has been verified by several authors that report a significant decrease in the ammonium concentration when a buffer, such as $CO_2$ [11,42,43], was co-fed in the reaction. On the other hand, Yoshinaga et al. [15] observed an increase in selectivity to $N_2$ with an increase in the Pd crystallite size, suggesting a structure-sensitivity of the process. Furthermore, noble metal with atoms of low coordination number (edges and corners positions) has high abilities for deep hydrogenation, leading to ammonia formation, while metal atoms on flat terrace sites yield nitrogen [44]. Sa and Anderson. [40] proposed that ammonia is formed via consecutive hydrogenation of NO, which is absorbed by both, the support and the noble metal but can be reduced exclusively by the noble metal. Summarizing, it is generally accepted that the ammonium formation is facilitated by the increasing pH of the solution, due to the formation of hydroxide ion, as well as the metal particle size and its electronic properties that consequently is related to the interaction between metal particle and the support. The effect of $CO_2$ co-feed in the selectivity of the reaction with the Pt/$CeO_2$ catalyst was studied. The results in Table 2 show that the introduction of $CO_2$ produces a control in the selectivity to ammonium but at the expenses of an important decrease in the activity. Previous work [9] has demonstrated the poisoning effect of the $CO_2$ leading to an activity decrease.

On the other hand, the nitrate reduction occurs through the interaction of oxygen atoms of nitrate with the oxygen vacancies, assisted by hydrogen in the interphase of Pt–$CeO_2$ [37], whereas, nitrite is reduced to nitrogen or over reduced to ammonium on the metal surface. Consequently, the high selectivity to ammonium can be related to the electronic properties of the metal. Besides, the chemical environment of Pt as the active component through an electronic interaction between metal and support can significantly change the activity and selectivity of the catalyst [45]. The surface reduced of $CeO_2$ is able to perform an electronic transfer to platinum that could increase the hydrogenation capacity of platinum.

Following this idea, the modification of the environment of the noble metal, as well as, the modification of the acid–base properties of the catalyst should affect the catalytic behavior of the material. In order to achieve it, fluorination process was applied to the ceria catalysts following two procedures (impregnation (I) and combustion (C)). The catalytic activity of these catalysts is shown in Fig. 8 and Table 2. The introduction of fluoride species decreases the ammonia formation in both cases. However, when the fluorination is performed by impregnation an important decrease in the nitrate reduction activity is observed (50%). This fact could be related with the deposition of the fluorine species on the surface of the ceria reducing the number of oxygen vacancies available as active sites as it was observed by characterization results. TPR results show a reduction degree of the $CeO_2$ surface of around 13%, that is lower compared to the Pt–$CeO_2$ sample (around 27%, see Table 1). On the other hand, when combustion method is applied, a comparable activity between non-fluorinated and fluorinated catalysts was observed. The amount of reduction degree of $CeO_2$ was also comparable (27% and 21%, respectively). This fact could indicate that the presence of reducible species on the surface of the $CeO_2$ could control the catalytic activity. Furthermore, the fluorinated catalysts showed higher selectivity to nitrogen that could indicates that the acid–base properties of the support could control the selectivity to nitrogen.

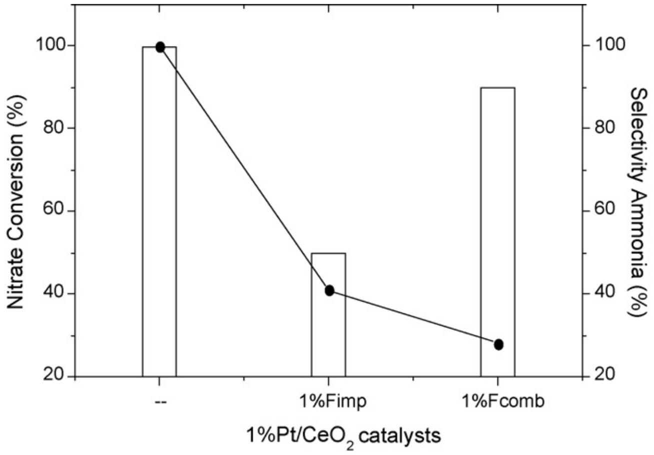

**Fig. 8.** Catalytic activity and selectivity of monometallic 1% Pt/$CeO_2$ catalysts without and with fluorination modification [(●) ammonia concentration and (☐) nitrate conversion].

## 4. Conclusions

Pt monometallic catalysts supported on ceria are active in the hydrogenation of nitrates reaction, meaning that the support is directly involved in the reaction due to the redox property of the material.

The addition of fluorine by combustion method in ceria can control the activity of the catalyst and the selectivity to nitrogen. Two possible causes for the ammonia formation are suggested: the increase of the pH of the media due to the $OH^-$ formation and the second, the over hydrogenation by the catalysts. This could be explained by the way that ceria as basic material transfer electronic density to the platinum sites, increasing the hydrogenation capacity, while in the fluorinated ones, fluorine as electronegative compound, removed electronic density from platinum, reducing the over hydrogenation process.

Further investigation is needed in order to clarify the ammonium formation mechanism during the nitrate reduction process using this type of catalysts, but in this preliminary study we conclude that the use of partially fluorinated ceria as support control the ammonia formation and represents a new alternative way to reduce nitrate with high selectivity to nitrogen gas.

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