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Activated Carbon Supported Metal Catalysts for Nitrate and Nitrite Reduction in Water

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Abstract Ten monometallic and 13 bimetallic catalysts supported on activated carbon were assessed, the former in the reduction of nitrate or nitrite and the latter in the nitrate reduction. Under the conditions used, nitrite was shown to be reduced by monometallic catalysts. With exception of Ru, only some of the bimetallic catalysts were able to reduce nitrate. Rh–Cu shows the highest conversion, but Pd–Cu is the most promising catalyst if selectivity into nitrogen is also considered.

Keywords Nitrate · Nitrite · Hydrogen · Metal catalysts · Activated carbon

1 Introduction

The increasing pollution of natural sources of drinking water encourages the development of new emerging technologies and processes for water remediation. Nitrate concentrations in surface water and especially in groundwater have increased in many locations in the world. Nitrate anion is potentially harmful because it can be transformed into nitrite in the human body, which can cause blue baby syndrome, and it is also a precursor of the carcinogenic nitrosamines [1–4]. In addition, nitrates can originate eutrophication in rivers and lakes. The main sources of nitrates are the overuse of fertilisers in agriculture as well as the effluents from certain industries. Most of the nitrate salts are soluble in aqueous medium so that nitrate ions are easily spread over the groundwater sources [3]. For these reasons, the European Community limit values for nitrate, nitrite and ammonium concentrations in drinking water are 50, 0.5 and 0.5 mg/L, respectively, and for the discharge of wastewater are 50 and 10 mg/L for nitrate and ammonium concentrations, respectively.

Nitrates can be removed from water by physicochemical, biological and catalytic methods. The main disadvantage of the physicochemical treatments (ion exchange, reverse osmosis and electrodialysis) is the fact that nitrate is not converted into harmless compounds but only concentrated; then it must be treated afterwards or disposed of [3–5]. Biological denitrification is recognized as a useful method for the selective conversion of nitrate into harmless gaseous nitrogen. However, this process has several disadvantages since it is difficult to handle and leads to the production of undesirable by-products [1]. In addition, there are concerns about possible bacterial contamination, the presence of residual organics in the treated water and the possible increase in the chlorine demand of purified water [6].

The catalytic reduction of nitrate has been suggested in the literature as a promising method for nitrate removal from water without the drawbacks of the conventional methods [2, 5–9]. This process was reported for the first time by Vorlop and Tacke [10] and consists in the reduction of nitrate anion to nitrogen over bimetallic catalysts in the presence of a reducing agent. Nitrite as intermediate and ammonium as by-product are considered the major limitations of this process [9, 11]. Previous studies on the heterogeneous catalytic nitrate reduction have shown that bimetallic catalysts are much more efficient than the monometallic ones. The catalyst is usually composed of a noble metal, mainly Pd or Pt but also Ru, Rh or Ir, and a transition metal, such as Cu, Sn, Ag, Ni, Fe or In on

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different supports (alumina, silica, titania, activated carbon, polymers) [1–22]. Pd and Pt as noble metal and Cu and Sn as promoter metal were the most studied catalysts and have been considered as the most actives and selectives. Among them, Pd–Cu, Pd–Sn and Pt–Cu, seem to be the most effective for nitrate reduction, but are still inadequate in terms of selectivity towards nitrogen [4, 5, 7, 9, 16].

Carbon materials are finding an increasing number of applications in catalysis, either as supports for the active phases, or as catalysts on their own. They gather the desirable characteristics for a catalyst support: inertness; stability under reaction and regeneration conditions; adequate mechanical properties; possibility to adapt its physical form for a given reactor; high surface area and porosity [23]. In addition, it is possible to tailor both their texture and surface chemistry. The texture may be tailored to suit the specific application by adequate choice of the preparation procedure. In particular, it is possible to prepare carbons with different proportions of micro, meso and macropores. On the other hand, the nature and concentration of surface functional groups may be modified by suitable thermal or chemical post-treatments [23]. In water treatment processes, two additional advantages over inorganic supports must also be considered: activated carbon can play an additional important role as adsorbent since its effect in the adsorption of a vast range of micropollutants is well known; when used as a catalyst support for noble metals, as is the present case, the recovering of the metal just by burning the carbon material is very easy. This final advantage is of paramount importance to use this type of catalysts in industrial scale. Removal of nitrates from water is an important and developing area of research. Moreover, additional studies are still necessary to optimize the formulation of the catalysts and to get a better understanding about the influence of metals nature, in order to develop an effective catalytic process for purifying water streams. In this work, several metal catalysts supported on activated carbon were prepared, characterized and evaluated. Monometallic catalysts (Pt, Pd, Cu, Sn, Ru, Rh, Ni, Ir, Fe, and Zn) were considered for the study of the reduction of both nitrate and nitrite by hydrogen. Additionally, the bimetallic catalysts Pd–Cu, Pt–Cu, Rh–Cu, Ru–Cu, Pd–Ir, Pd–Sn, Pd–Fe, Pd–Ni, Pd–Zn, Ir–Cu, Rh–Sn, Pt–Sn and Pt–Fe, with 1 wt% of each metal, were selected for the study of nitrate reduction. To the best of our knowledge, this is the first systematic study for testing a wide range of monometallic and bimetallic catalyst using activated carbon as a support for the nitrate and nitrite reduction in water. A similar study was reported by Horold et al. [24], but only five monometallic and six bimetallic catalysts were tested, and using alumina as catalyst support in almost all cases. These screening tests represent the first step of a systematic investigation of metallic and bimetallic catalysts supported on activated carbon for nitrite and nitrate reduction, and were necessary to select the most promising catalytic systems for further developments.

2 Experimental

2.1 Preparation and Characterization of the Catalysts

The active metals were supported on a commercial activated carbon NORIT GAC 1240 PLUS (ACo) ground to a particle diameter between 0.1 and 0.3 mm. The catalysts were prepared by the incipient wetness method, and in the case of the bimetallic catalysts by co-impregnation, with aqueous solutions of the corresponding metal salts (H_2PtCl_6, $PdCl_2$, $Cu(NO_3)_2$, $SnCl_2$, $RhCl_3$, $RuCl_3$, $Ni(NO_3)_2$, $(NH_4)_3IrCl_6$, $Fe(NO_3)_3$, $ZnCl_2$). After that, the samples were dried at 100 °C for 24 h, calcined under a nitrogen flow at 400 °C for 1 h, and finally reduced at 400 °C in hydrogen flow for 3 h. The contents of both noble and promoter metals were maintained constant at 1 wt%.

Selected catalysts were characterized by H_2 chemisorption, N_2 adsorption at 77 K, temperature programme reduction (TPR) and X-ray diffraction (XRD). Metal dispersions were determined by chemisorption of H_2 at 30 °C and atmospheric pressure in an Altamira Instruments AMI-200 apparatus, using the pulse method, and assuming a stoichiometric ratio of $H_2/\text{metal} = 2$. Pulses of 58 μL (from a calibrated loop) were successively injected in the carrier gas (25 Ncm^3/min of Ar), which passes through a catalyst bed (150 mg), until saturation of the catalyst surface. The non-adsorbed hydrogen is measured with an online thermal conductivity detector. The amount of H_2 corresponding to saturation was calculated by summing the differences between the amounts injected and detected at outlet. TPR experiments were carried out in the same equipment; the sample (150 mg) was heated at 5 °C/min up to 600 °C under a flow of 5% (v/v) H_2 diluted in He (total flow rate of 30 Ncm^3/min). The H_2 consumption was followed by mass spectrometry (Dymaxion 200 amu, Ametek). The textural characterization of the materials was based on the corresponding N_2 equilibrium adsorption isotherms, determined at 77 K with a Coulter Omnisorp 100 CX apparatus. XRD spectra of platinum and palladium catalysts were recorded in the range $2\theta = 20$–$90°$ on a Philips X'Pert MPD diffractometer (Cu-Ka = 0.15406 nm). The average size of the metal particles was calculated from the half width of the diffraction peak using Scherrer equation.

The metallic dispersion and the average crystallite size of the monometallic catalysts that presented some activity are presented in Table 1. The results obtained by XRD, also presented in Table 1, are in agreement with those obtained by hydrogen chemisorption. The characterization

Table 1 Characterization of the monometallic catalysts

Catalyst	Dispersion (%)	Particle size (nm)
1%Pt_ACo	19.9 (7.3)	6.0 (13.9)
1%Pd_ACo	3.2 (3.7)	36 (30)
1%Rh_ACo	15.2	7.1
1%Ir_ACo	50	2.2

The values in brackets were obtained by XRD

of the support is presented in Table 2. A sample with 2% of Pd and 1% of Cu (a total metal loading higher than all the samples tested in this work) was also characterized by N_2 adsorption at 77 K and the textural parameters remained almost unchanged compared to the unloaded activated carbon. Therefore, we assume that the surface area of the activated carbon supported metal catalysts is not significantly different from the original activated carbon.

2.2 Catalysts Evaluation

Kinetic experiments were carried out in a semi-batch reactor, equipped with a magnetic stirrer and a thermostatic jacket, at room temperature and atmospheric pressure, and using hydrogen as reducing agent. Initially, 790 mL of deionised water and 400 mg of catalyst were fed into the reactor, the magnetic stirrer was adjusted to 700 rpm and the gas mixture of carbon dioxide and hydrogen ($H_2 + CO_2$ (1:1), $Q_{Total} = 200$ Ncm^3/min) was passed through the reactor during 15 min to remove oxygen; CO_2 acts as pH buffer (pH 5.5). After that period, 10 mL of a nitrate or nitrite solution, respectively prepared from $NaNO_3$ or $NaNO_2$, were added to the reactor, in order to obtain an initial NO_3^- or NO_2^- concentration equal to 100 ppm. Preliminary studies were carried out varying the stirring rate and it was checked that under the selected conditions there was no external diffusion limitations.

Small samples were taken from the reactor for determination of nitrate, nitrite and ammonium concentrations after defined periods. Nitrate and nitrite ions were simultaneously determined by HPLC using a Hitachi Elite Lachrom apparatus equipped with a diode array detector. The stationary phase was a Hamilton PRP-X100 column (150 mm × 4.1 mm) working at room temperature, under isocratic conditions. The mobile phase was a solution of 0.1 M NaCl/CH_3OH (45:55). Ammonium ions were determined by potentiometry using a convenient selective electrode. pH values were also measured.

The selectivities of nitrite, ammonium and nitrogen were calculated as:

$$S_{NO_2^-} = \frac{n_{NO_2^-}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \quad (1)$$

$$S_{NH_4^+} = \frac{n_{NH_4^+}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \quad (2)$$

$$S_{N_2} = \frac{2 * n_{N_2}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \quad (3)$$

where $n_{NO_3^-{}_i}$ is the initial amount of nitrate (mmol) and $n_{NO_3^-}$, $n_{NO_2^-}$, $n_{NH_4^+}$ and n_{N_2} are the amounts of the respective species (mmol) at time t (min). The amounts of nitrogen were calculated by a mole balance, assuming that the amount of NO_x produced is negligible [1, 12].

3 Results and Discussion

3.1 Monometallic Catalysts

The activity and selectivity of monometallic catalysts supported on activated carbon for the reduction of nitrates and nitrites were studied. A total of ten catalysts were evaluated, all containing 1 wt% of metal. For comparatives purposes, the catalytic activity of the support, activated carbon (ACo), and the possibility of nitrate and nitrite reduction only in the presence of hydrogen (blank) were also checked. Figure 1 shows the evolution of nitrate concentration and, under the experimental conditions used, it can be observed that the monometallic catalysts are practically inactive for the reduction of nitrate. Only Ru presents some activity, being nitrate mainly converted into ammonium. The Fe catalyst is not completely inactive, since it presents a nitrate residual conversion of 3% after 5 h. This indicates that probably nitrate can be reduced on monometallic sites but the degradation rate is very low. These results are in line with the literature, where it is generally accepted that monometallic sites are inactive for nitrate reduction [3, 5, 25].

Table 2 Textural characterization of the activated carbon (ACo)

S_{BET} (m^2/g)	$S_{meso}{}^a$(m^2/g)	$V_{micro}{}^a$(cm^3/g)	$W_{01}{}^b$(cm^3/g)	$W_{02}{}^b$(cm^3/g)	$L_1{}^c$(nm)
869	97	0.318	0.290	0.035	0.93

[a] Micropore volume (V_{micro}) and mesopore surface area (S_{meso}) were calculated by the t-method

[b] A type IV deviation was noticed when the N_2 adsorption data was analysed by the Dubinin method; W_{01} and W_{02} are the micropore volumes associated to small and large micropores, respectively

[c] Average small micropores width (assuming split-shaped geometry)

No reduction of nitrate (Fig. 1) or nitrite (Fig. 2a) were achieved when the experiments were carried out using only the support or in the blank tests.

Figure 2a shows the results obtained for the reduction of nitrites over monometallic catalysts and Fig. 2b presents the corresponding evolution of ammonium concentration during the reaction. Contrary to the reduction of nitrate, nitrite is rapidly reduced in the presence of some of the monometallic catalysts (Fig. 2a). The conversions attained are quite different depending on the supported metal. The order of conversions in nitrite reduction is the following: Pd >> Ir > Pt >> Rh >> Cu > Zn ≈ Ru, corresponding to values after 5 h of 100%, 74%, 64%, 37%, 13%, 7% and 5%, respectively. On the other hand, Fe, Ni and Sn are practically inactive, at least under the experimental conditions studied. Copper presents some catalytic activity but the catalyst was completely deactivated after about 2 h. Significant concentrations of ammonium were measured only in the experiments with the three most active catalysts (Pd, Ir and Pt).

Figure 3 shows the evolution of nitrogen selectivities for the monometallic catalysts studied. As stated before, Pd is the most efficient metal for nitrite reduction; moreover, it is also more selective than Ir and Pt for the transformation of nitrite into nitrogen. These two catalysts give rise to a not very different nitrite conversion, but a lower ammonium formation is observed for the Pt catalyst (Fig. 2b). In fact, Ir is the less selective towards nitrogen among the catalysts studied. For example, for a nitrite conversion of 50%, the selectivities into nitrogen are the following: ~95% for Pd, ~40% for Pt and ~10% for Ir. Cu and Zn catalysts present 100% selectivity into nitrogen from the beginning of the reaction but, as mentioned before, these catalysts are only marginally active. Ru and Rh catalysts show a similar trend in the selectivities; however, the conversion reached is much lower for Ru.

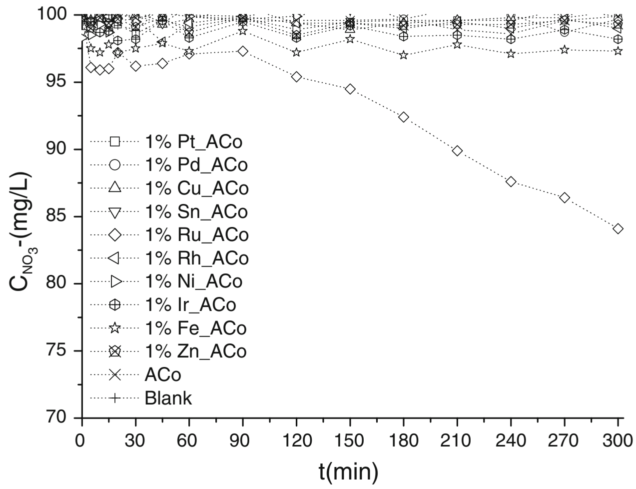

Fig. 1 NO_3^- concentration as a function of time during nitrate reduction in the presence of monometallic catalysts ($C_{NO_3^-{}_i}$ = 100 mg/L, catalyst = 0.5 g/L, pH 5.5, Q_{H_2} = 100 Ncm^3/min, Q_{CO_2} = 100 Ncm^3/min, T = 25 °C)

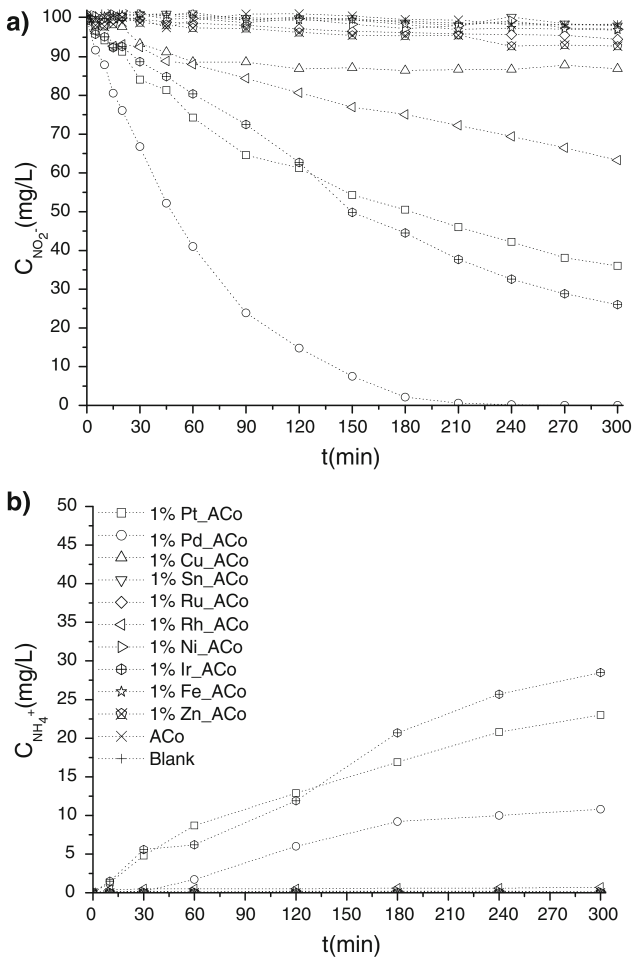

Fig. 2 (**a**) NO_2^- and (**b**) NH_4^+ concentrations as a function of time during nitrite reduction in the presence of monometallic catalysts ($C_{NO_2^-{}_i}$ = 100 mg/L, catalyst = 0.5 g/L, pH 5.5, Q_{H_2} = 100 Ncm^3/min, Q_{CO_2} = 100 Ncm^3/min, T = 25 °C)

The results obtained are not in total agreement with those obtained by Horold et al. [24] in the screening of several metal catalysts for nitrite reduction. They observed that platinum supported on carbon was more active than palladium supported on alumina; iridium and rhodium catalysts supported on alumina reduced completely nitrite into ammonia; and only palladium was suitable for a selective nitrite reduction towards nitrogen. In the present work, it was observed that palladium is the most active catalyst, platinum and iridium present intermediate activities, but iridium is the most selective into ammonium, and rhodium is highly selective into nitrogen. The other catalysts tested are not suitable for practical purposes.

Considering that the same amount of metal was used in all the catalysts, their different performances should be related to the chemical nature of the metal and/or metallic

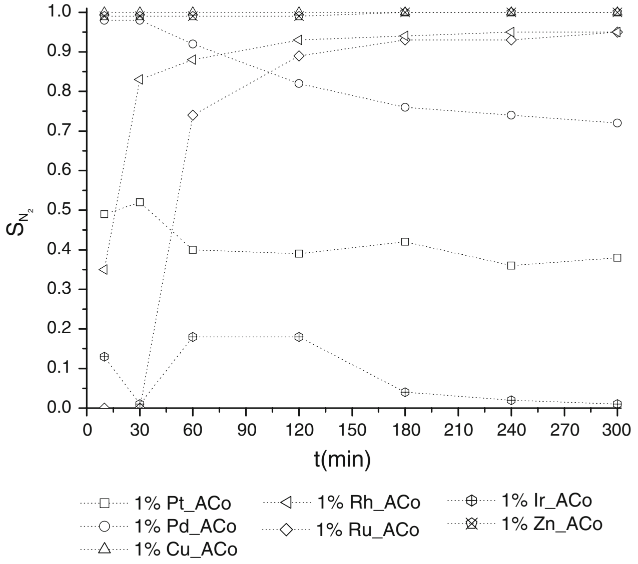

Fig. 3 N_2 selectivities as a function of time during nitrite reduction in the presence of monometallic catalysts ($C_{NO_2^-{}_i}$ = 100 mg/L, catalyst = 0.5 g/L, pH 5.5, Q_{H_2} = 100 Ncm^3/min, Q_{CO_2} = 100 Ncm^3/min, T = 25 °C)

surface area. It is assumed that the nitrite reduction involves the H_2 chemisorption on the metal in one of its mechanism steps [3, 25]. Therefore, the results can be rationalized according to the Sabatier principle, which states that metals that form a medium-strength bond with hydrogen are expected to be particularly catalytically active. A qualitative assessment based on the classification of Bond [26] for the H_2 chemisorption on metals (nil for Sn and Zn, weak for Cu, moderate for the noble metals Rh, Pd, Pt and Ir, and strong for Ni, Ru and Fe), already points out for the expected good performance of the noble metals tested. The metallic dispersion obtained (see Table 1) can be explained by the calcinations and reduction temperatures used. In spite of the different TPR profiles obtained for the catalysts tested (results not shown), for comparative purposes, all of them were calcined and reduced at the same temperature (400 °C). This temperature may be too high to guarantee a good metal dispersion in some of the catalysts. Therefore, the low dispersions obtained seem to be caused by the high temperatures used in the preparation stage, and a trend in the increasing of the dispersion with the increasing of the melting point of the metal was observed. In order to have a quantitative justification for the nitrite reduction, the average activity obtained considering the first 4 h of reaction (expressed as mol of nitrite converted per hour and per mol of accessible metal atoms) as a function of the hydrogen chemisorption energy per atom, obtained from Norskov et al. [27] was calculated. These results (Table 3) shows that the maximum catalytic activity is achieved, as expected, at intermediate strength of chemisorptions (Pd, Pt, Ir and Rh); if the reactant is strongly adsorbed (e.g. Ni), the metal is inactive; and if it is weakly adsorbed (e.g. Cu) the catalytic activity is minimal.

Table 3 Activity for nitrite reduction over monometallic catalysts as a function of the hydrogen chemisorption energy per atom of metal

Metal	ΔE_H (eV)	Activity mol NO_2^- converted/(mol accessible metal) * h))
Ni	−0.51	0
Pd	−0.38	441
Rh	−0.34	27
Pt	−0.33	76
Ir	−0.21	35
Cu	−0.05	≈0

3.2 Bimetallic Catalysts

The monometallic Pd, Pt, Rh and Ir catalysts are not able to reduce nitrates; the presence of a second metal is mandatory to attain significant conversions. Most of the work in the area of catalytic nitrate reduction has been done using Pd–Cu bimetallic catalysts; also Pd–Sn and Pt–Cu on different supports, mainly alumina, have been considered [1–4, 6–8, 17–19]. A few investigations have been reported for other metallic pairs [15, 20, 22, 28–31]. Therefore, we decided to study systematically the nitrate reduction in the presence of a larger set of bimetallic catalysts (Pd–Cu, Pt–Cu, Rh–Cu, Ru–Cu, Pd–Ir, Pd–Sn, Pd–Fe, Pd–Ni, Pd–Zn, Ir–Cu, Rh–Sn, Pt–Sn and Pt–Fe) supported on activated carbon, with 1 wt% of each metal, in order to select the most promising systems. The nitrate conversions attained were used to characterize the catalysts efficiencies (Fig. 4a). Figure 4b and c show, respectively, the nitrite and ammonium formed during the reaction.

The reduction of nitrate proceeds by a pathway involving consecutive and competitive reactions. Actually, the concentration of ammonium increases gradually with nitrate conversion for all the catalysts (Fig. 4c). A similar trend is observed for the evolution of nitrogen. On the contrary, nitrite acts as an intermediate, since the respective concentration goes through a maximum (Fig. 4b).

Figure 4a shows that the order of efficiencies for the nitrate reduction after 5 h of reaction in the presence of bimetallic catalysts is the following: Rh–Cu >> Pd–Cu >> Ir–Cu ≥ Pt–Cu ≈ Rh–Sn >> Pd–Ni > Ru–Cu ≥ Pt–Sn. Additionally, it is observed that the bimetallic catalysts Pd–Ir, Pd–Sn, Pd–Fe, Pd–Zn and Pt–Fe are inactive under the conditions used in this work, and they will not be further discussed. Several investigations have reported that Pd–Sn may be effective for this reaction [8, 16, 17, 19]; this was not verified in our study, probably because higher contents and/or dispersions of the active phases would be necessary.

Figure 5a and b show respectively the calculated ammonium and nitrogen selectivities as a function of time for the bimetallic catalysts studied.

The highest conversion of nitrate was obtained with the Rh–Cu catalyst, although for short reaction times (less than 2.5 h) the Pd–Cu catalyst was the most efficient. However, the Rh–Cu catalyst has the disadvantage of being only moderately selective towards nitrogen; additionally, significant amounts of ammonium are obtained. As mentioned before, the Pd–Cu catalyst is more efficient than the Pt–Cu catalyst, but ammonium and nitrogen selectivities are similar for both, at least for reaction times >1 h (Fig. 5a, b. A similar behaviour in the reduction of nitrate was observed for Pt–Cu and Rh–Sn catalysts, being the corresponding efficiencies slightly lower than that associated to the Ir–Cu catalyst. However, Pt–Cu catalyst is much more selective towards nitrogen than Ir–Cu and Rh–Sn. The Ir–

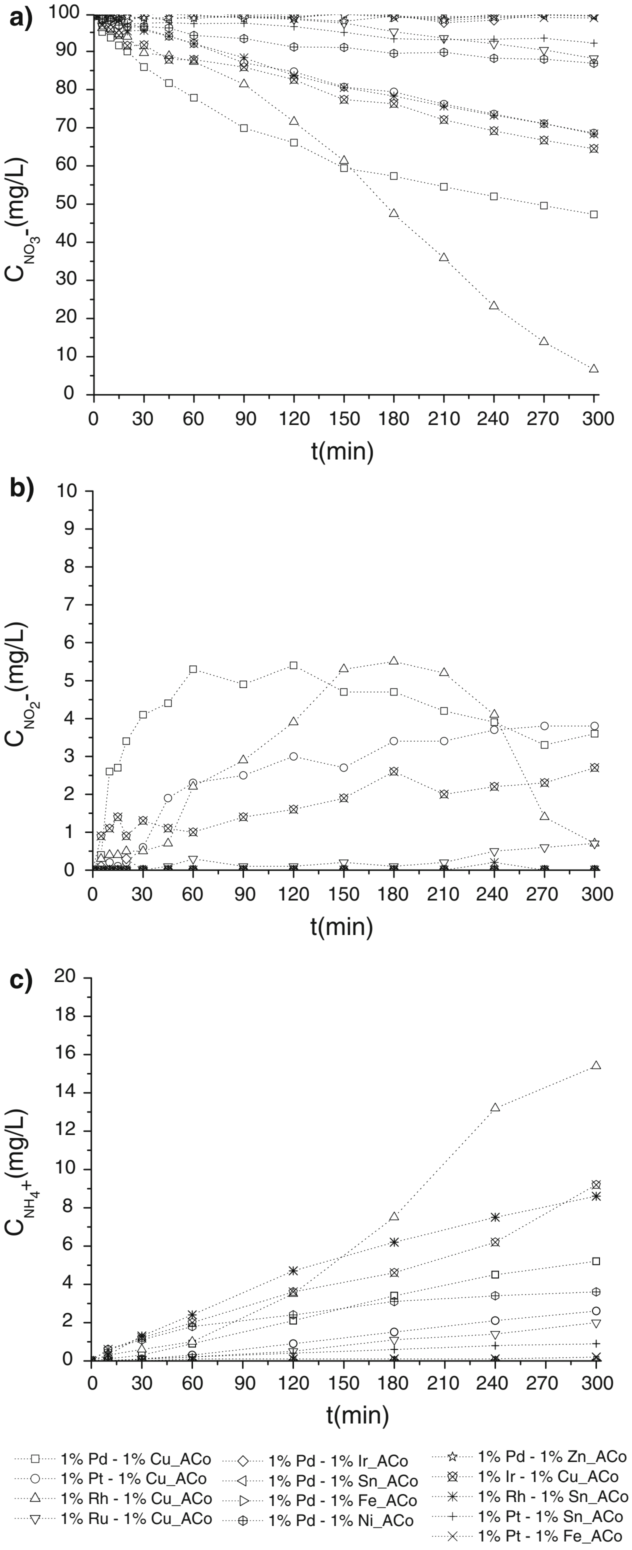

Fig. 4 (**a**) NO_3^-, (**b**) NO_2^- and (**c**) NH_4^+ concentrations as a function of time during nitrate reduction in the presence of bimetallic catalysts ($C_{NO_{3\,i}^-}$ = 100 mg/L, catalyst = 0.5 g/L, pH 5.5, Q_{H_2} = 100 Ncm^3/min, Q_{CO_2} = 100 Ncm^3/min, T = 25 °C)

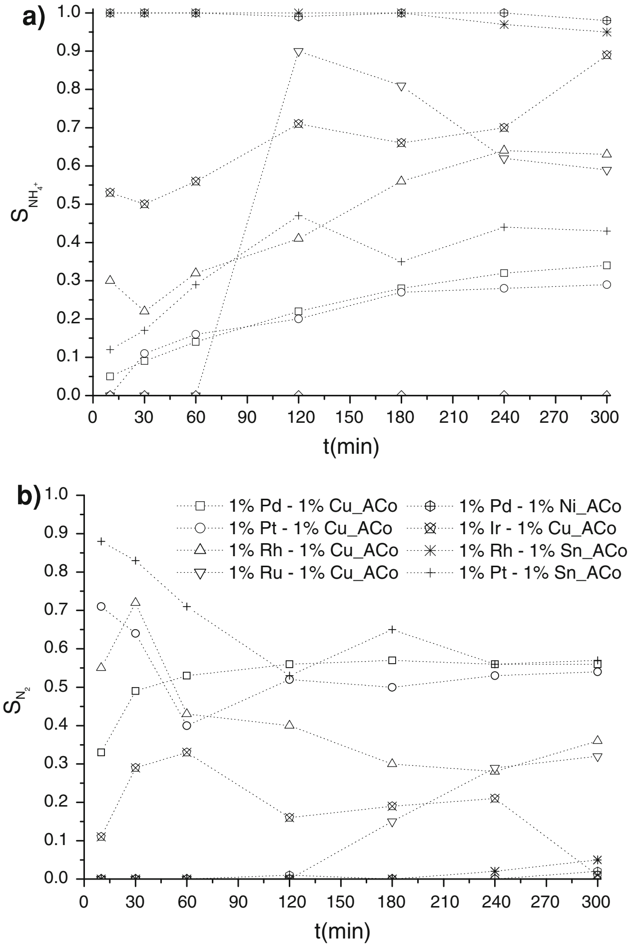

Fig. 5 (**a**) NH_4^+ and (**b**) N_2 selectivities as a function of time during nitrate conversion in the presence of bimetallic catalysts ($C_{NO_{3\,i}^-}$ = 100 mg/L, catalyst = 0.5 g/L, pH 5.5, Q_{H_2} = 100 Ncm^3/min, Q_{CO_2} = 100 Ncm^3/min, T = 25 °C)

Cu and, principally, the Rh–Sn catalysts are highly selective into ammonium (an undesired by-product) in all the conversion range. For example, for a nitrate conversion of 30%, the selectivities into nitrogen of the Pd–Cu, Pt–Cu, Rh–Cu, Ir–Cu and Rh–Sn catalysts are, approximately, 55%, 55%, 40% 20% and 5%, respectively. The bimetallic Pd–Ni catalyst can promote the reduction of nitrate but the degradation rate is very slow; moreover, it presents an ammonium selectivity of almost 100%. Some activity was observed for the Ru–Cu catalyst, but the conversion only starts 90 min after the beginning of the reaction, which is a behaviour similar to the monometallic Ru catalyst (cf. Fig. 1a). Finally, no nitrite was measured and a high selectivity towards nitrogen was determined for the Pt–Sn catalyst, but unfortunately the conversion of nitrate is not significant for practical application.

Once again, the results obtained are not in total agreement with those obtained by Horold et al. [24], where alumina was used as support and only Pd was tested as noble metal. They observed a low nitrate removal and high ammonium formation when iron, cobalt or platinum were used as promoter metal; the Pd–Ni catalyst presented a high activity but reduced the nitrate quantitatively to ammonium; the Pd–Ag catalyst showed a comparable activity and considerable formation of ammonium; and the Pd–Cu catalyst had the highest activity and the lowest formation of ammonium. In the present study, it was observed that the Pd–Fe catalyst is inactive, the Pd–Ni catalyst reduces nitrate very slowly but also presents high ammonium selectivity, and Pd–Cu also presents a high selectivity into nitrogen.

An important feature is that among the Pd catalysts the combination with copper is the best, which is in line with the literature, followed by the catalyst with nickel, but in this case with a much lower activity. The Pd based bimetallic catalysts containing iridium, tin, iron or zinc are inactive, under the tested conditions. According to Gauthard et al. [15], the promoting effect of the second metal is related to their ability to reduce nitrate according to a redox reaction. Among the Pt catalysts tested, the combination with copper is the most efficient, followed by the Pt–Sn, which has only a residual activity. Considering the performance of the promoter metal, copper seems to be the most effective, which is in agreement with the literature [1, 3, 11, 13], followed by tin. In addition, for the catalysts with tin, the highest conversion is obtained for that containing Rh.

4 Conclusions

To the best of our knowledge, this was the first time that an extensive evaluation of the most effective metallic catalysts supported on activated carbon for the reduction of nitrite and nitrate was carried out. According to the experimental results, the following main conclusions can be drawn:

1. The monometallic catalysts tested are inactive or practically inactive (Ru) for nitrate reduction.
2. Nitrite was shown to be reduced in the presence of monometallic catalysts, preferably Pd, although other noble metals such as Ir, Pt and Rh also presented significant activities, but they are generally less selective into nitrogen (the exception is Rh). A relationship between the activity for nitrite reduction over monometallic catalysts and the hydrogen chemisorption energy per atom was found.
3. Considering the bimetallic catalysts, the Rh–Cu catalyst shows the highest efficiency for nitrate reduction; however, a large amount of ammonium is produced. The Pd–Cu catalyst gives rise to higher conversions than Pt–Cu catalyst, although both catalysts present similar selectivities into nitrogen. The systems Pd–Ir, Pd–Sn, Pd–Fe, Pd–Zn and Pt–Fe are inactive for the reduction of nitrate, under the conditions studied.
4. Among the catalyst tested, activated carbon supported Pd–Cu catalyst is the most promising when both conversion and selectivity towards nitrogen are considered. However, considering that catalysts composition was not optimised, also the pairs Rh–Cu, Pt–Cu and Ir–Cu supported on activated carbon are under further investigation.

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