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Copper–platinum catalysts prepared and characterized by electrochemical methods for the reduction of nitrate and nitrite

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Abstract

Platinized platinum catalysts were modified "in situ" by copper (sub)monolayers deposited under controlled conditions by electrochemical methods. They were characterized "in situ" by linear potential sweep cyclic voltammetry. Various Cu_{ads}/Pt catalysts with different copper coverages (θ_{Cu}) were obtained and tested for the reduction of nitrate and nitrite in aqueous solutions.

The intrinsic catalytic activity (at $t = 0$) and the selectivity in ammonia of Cu_{ads}/Pt depend on the platinum surface fraction occupied by copper adatoms (θ_{Cu}). The highest activities and selectivities in ammonia are obtained with $\theta_{Cu} \approx 0.4$–0.6. Moreover, higher activities were obtained in the reduction of nitrate than in the reduction of nitrite.

The change of catalysts potential, measured during the reaction, arises from the change of the solution pH, which is due to the generation of OH^- according to the global reduction reactions. The spontaneously established catalyst potential is a mixed potential corresponding to the different oxidoreduction reactions involved. © 2002 Published by Elsevier Science B.V.

Keywords: Copper–platinum catalyst; Underpotential deposition; Electrochemical characterization; Copper monolayer; Nitrate reduction; Nitrite reduction

1. Introduction

Nowadays, the increasing contamination of ground waters by nitrates, due to overfertilization and to waste waters, becomes an important problem for health and environment and their removal gains renewed attention.

One decontamination method, largely studied during the last decade, is the selective catalytic (or electrocatalytic) reduction of nitrate and nitrite into nitrogen [1–14].

Bimetallic catalysts composed generally of a noble metal (from the group VIII) and of a second less noble metal were widely investigated [1–7,9–11,13]. Most of these catalysts are quite active, the only problem, still existing, being the inadequate selectivity into nitrogen. Indeed, during this reaction ammonia is also obtained as an undesired by-product, which should not exceed 0.5 mg l^{-1} according to the European Community Directive (1980).

At present, the most efficient catalysts are some palladium-based bimetallic catalysts such as Pd–Cu, Pd–Sn and Pd–In [1–7,10,13].

However, very few works related to platinum-based catalysts (or electrocatalysts) are reported in the literature [1,8,9,11–14] although this metal displays an excellent stability and good reduction properties in aqueous solutions.

In electrocatalysis the reduction of nitrates and nitrites with platinum electrodes in acid and basic solutions was studied by different authors [8,9,12–14] and an inhibition of platinum activity in the presence of high hydrogen coverages (at about $0 < E < 0.1$ V/RHE) was found [8,9]. The effect of different adatoms (such as Cu, Ge, Pd) on Pt or Pd was also reported

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[9,10,13]. In most of works, concerning the electrocatalytic reduction of nitrate and nitrite, ammonia seems to be the principal product obtained although no a systematic study of reaction products was generally undertaken. Nevertheless, in some recent studies [10,12–14] the use of on line mass spectroscopy combined with cyclic voltammetry allowed to analyse the volatile products obtained during the electroreduction of nitrate and nitrite as a function of potential.

In catalysis the performance of supported Pt–Cu bimetallic catalysts prepared by controlled deposition of copper on platinum surface was recently studied in our laboratory [11].

However, the surface composition and the adsorption properties of bimetallic catalysts are generally difficult to characterize “in situ”, especially for reactions carried out in aqueous solutions. Yet, electrochemical methods can be easily used for the “in situ” characterization of metal catalysts [15].

In addition, it is possible to modify the surface of platinum (or other noble metals) by controlled deposition of (sub)monolayers of a second metal according to the property of “underpotential deposition” (u.p.d.) [18] and to characterize the obtained bimetallic catalyst (amount and coverage by the second metal, modification of the geometrical and electronic properties) by electrochemical methods [9,10,13,15,18]. This property was largely applied in aqueous phase catalytic hydrogenations in previous works in our laboratory (summarized in [15]) and allowed to explain the modification of the catalytic and adsorption properties of platinum induced by deposition of (sub)monolayers of different metals or additives.

The results presented in this work concern the performance of a model platinized platinum catalyst, modified by copper adatoms (or (submonolayers) and tested in the reduction of nitrate and nitrite in an aqueous solution. Electrochemical techniques were used “in situ” for the controlled surface modification (by u.p.d.) and characterization of platinized platinum catalysts.

2. Experimental

2.1. Experimental conditions

It should be underlined that the same cell was used for the electrochemical characterization and modification of the catalyst and also for the hydrogenation experiments. It is made of Pyrex and allows the passage of three electrodes, the introduction and the evacuation of solutions and the inlet and outlet of gases. In this way the preparation and the characterization of the bimetallic catalyst and also the catalytic hydrogenation experiments were carried out “in situ” [15,16]. The electronic equipment includes a potentiostat (Wenking LB 81 M), a function generator (Wenking LSG 72) and a XY recorder (ABB).

The hydrogenation of nitrate or nitrite salts (KNO_3, KNO_2 (Merck pro analysis)) was carried out in 60 ml of aqueous solutions ($C = 10^{-3}$ M) in the presence of gaseous hydrogen (Air Liquide I, purity: 99.95%) dissolved in the solution under controlled stirring (flow rate: 190 ml/min). Ultra pure water of a resistivity equal to 18 MΩ cm (produced by a Millipore Milli-Q device) was used for the preparation of solutions.

The evolution of concentrations of nitrate, nitrite and ammonia, during the reaction, was followed by HPLC analysis. The spontaneously established potential of the catalyst and the solution pH were measured during the reduction reactions.

The platinized platinum catalyst was prepared by electrolytic deposition of platinum on a Pt wire (Johnson Matthey, 99.95%) at a controlled potential equal to −0.05 V/SCE (versus a saturated calomel electrode) in a solution of 3% chloroplatinic acid in 1 M HCl. The roughness factor of the platinum surface, defined as the ratio of the real (or effective) area, obtained after the electrolytic deposition, to the geometric area, (calculated on the basis of the dimensions of the wire), $r = S_r/S_g$, was equal to 90.

2.2. Characterization and modification of platinum

Before each experiment the platinum surface was cleaned by electrochemical potential cycling between 0 and 1.5 V/RHE in a solution of 0.25 M $HClO_4$ (Merck, 70% suprapure). Then the effective surface area of platinum was evaluated “in situ” by linear potential sweep cyclic voltammetry (LPSCV) [15–17].

This method, first developed by Woods [17], is based on the measure of the quantity of electricity, Q_H^0, exchanged during the underpotential adsorption or desorption of a monolayer of hydrogen (between

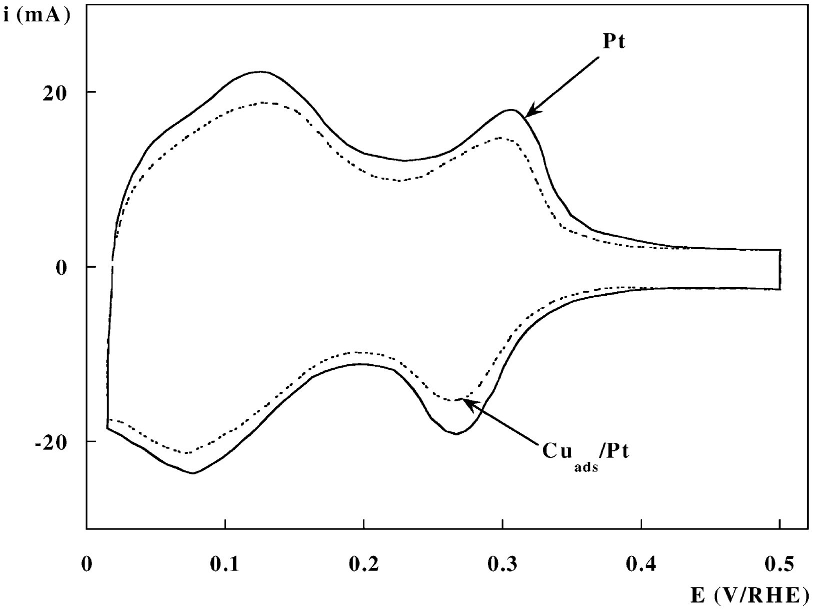

Fig. 1. Voltammogram of platinum (in the potential range of hydrogen adsorption and desorption) in the absence (full line) and in the presence (dotted line) of adsorbed copper previously deposited (0.25 M $HClO_4$, $v = 50$ mV/s).

0 and 0.35 V/RHE) (see Fig. 1), following the reaction:

$$H^+ + e^- \rightleftarrows H_{ads} \quad (1)$$

Indeed, through integration of the anodic or cathodic part relative to the hydrogen region of the voltammogram (after correction of the current of the double layer) (Fig. 1, full line) it is possible to obtain the quantity of electricity, Q_H^0, associated with the hydrogen monolayer [15–17] and to calculate the initial number, N_H^0, of surface platinum atoms (Fig. 1, full line), with the general accepted assumption: $H/Pt = 1$ and with $N_H^0 = Q_H^0(\mu C)/1.6 \times 10^{-13}$ (assuming that one platinum atom occupies an average area close to 7.6 Å^2, i.e. 1.31×10^{15} atoms/cm^2).

The platinum surface, after the measurement of its initial area, was modified by adsorption of copper.

The copper adatoms deposition was carried out by electrolysis of a $Cu(ClO_4)_2{\cdot}6H_2O$ solution at a potential ($E = 0.5$ V/RHE) fixed in the double layer region where no undesirable electrochemical reaction occurs. Furthermore, in this region of potential it is possible to cover only a fraction of the surface by copper adatoms without any bulk deposition, the potential being more positive than the thermodynamic potential of bulk deposition, following the property of u.p.d. [15,18].

The copper adatoms deposited on platinized platinum modify the cyclic voltammetry curves characteristic of this metal (Fig. 1, dotted line).

In the adsorption region of hydrogen, the observed decrease of the height of the corresponding adsorption and desorption peaks indicates that a fraction of the surface area has been occupied by copper adatoms, which are not able to adsorb hydrogen, thus decreasing the quantity of initial adsorbed hydrogen on platinum (Fig. 1).

The difference between the curves corresponding to the desorption or the adsorption of hydrogen in the absence (full line) and in the presence (dotted line) of copper adatoms, allows to measure the fraction, θ_{Cu}, of platinum surface which is occupied by copper (or “coverage degree”):

$$\theta_{Cu} = \frac{Q_H^0 - Q_H^{Cu}}{Q_H^0}$$

with Q_H^0 and Q_H^{Cu} the quantities of electricity associated with the oxidation of adsorbed hydrogen in the absence and in the presence of copper adatoms, respectively. Taking into account the atomic radii of Pt (1.38 Å) and of Cu (1.28 Å) one copper atom is adsorbed on one platinum atom, as it has been found in previous works [15] and in the literature [18].

By varying the concentration of $Cu(ClO_4)_2{\cdot}6H_2O$ in the solution different quantities of copper were deposited leading to various θ_{Cu}.

After the preparation and characterization of each Pt–Cu_{ads} catalyst the copper containing acid solution was evacuated under nitrogen flow, in order to avoid the oxidation and dissolution of copper adatoms. Then, the cell was washed several times with ultrapure water, previously deoxygenated by nitrogen bubbling, until a neutral pH was obtained.

The bimetallic Pt–Cu_{ads} catalysts prepared were tested in the reduction of nitrate and nitrite.

It should be underlined that the deposited copper remained adsorbed on the platinum surface as it was checked by LPSCV at the end of the reduction experiments.

3. Results and discussion

3.1. Reduction of nitrate

The evolution of the reduction of nitrate as a function of reaction time, over a Pt–Cu_{ads} catalyst with a copper coverage $\theta_{Cu} = 0.3$, is shown, as an example, in Fig. 2 (with $C_{nitrate} = 10^{-3}$ M, $P(H_2) = 1$ atm, $T = 298$ K). The evolution of nitrite formed as a reaction intermediate, and of ammonia, a final reaction product, is also presented in this figure.

The intrinsic initial catalytic activity (at $t = 0$), expressed in mol/min cm^2 (reported to the total platinum surface), was measured by tracing the tangent on the $C = f(t)$ graph at $t = 0$. This parameter was determined for various copper coverages, θ_{Cu}.

It can be remarked that the nitrite is more slowly reduced than the nitrate even after the complete conversion of nitrate (Fig. 2).

The presence of copper adatoms induces a promotion of the catalytic activity and a maximum of activity at about $\theta_{Cu} \approx 0.5$ can be remarked on the graph $a = f(\theta_{Cu})$ (Fig. 3). This result suggests that a kind of synergetic effect between copper and platinum is

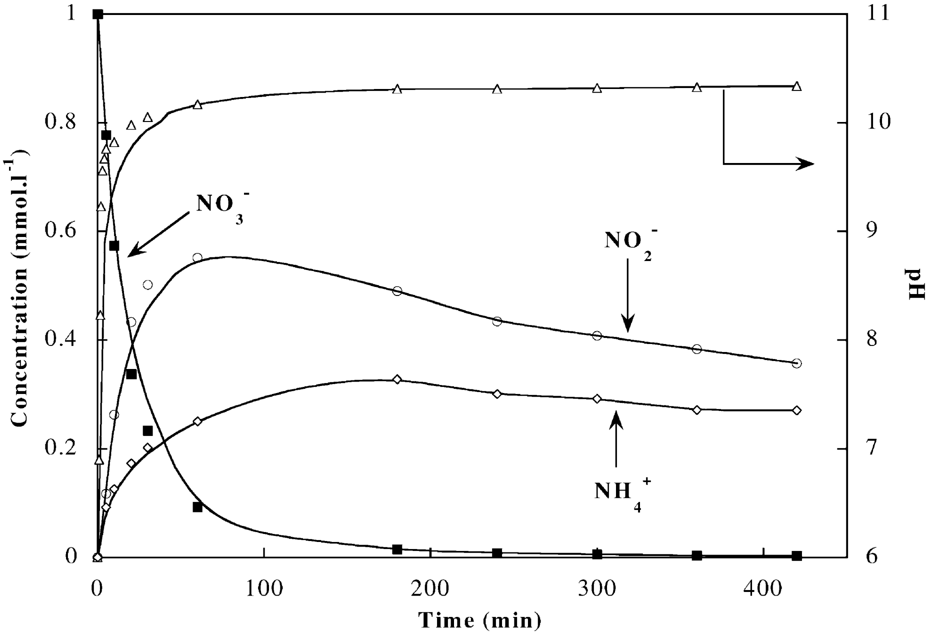

Fig. 2. Evolution of concentrations of nitrate, nitrite, ammonia and of pH as a function of reaction time during the reduction of nitrate (catalyst: Cu_{ads}/Pt with $\theta_{Cu} = 0.3$, $C_{nitrate} = 10^{-3}$ M, $P(H_2) = 1$ atm, $T = 298$ K).

involved in the reaction mechanism. A volcano-type dependence of the specific activity versus the overall Cu atomic weight percentage was also observed in the case of Pt–Cu/alumina [11]. Furthermore, a similar evolution of the intrinsic activity (TOF) of Pd–Cu/pumice catalysts was found [5]. However, in the case of the electrocatalytic reduction of nitrate (in solutions of pH 13.7) with Pd/Cu electrodes a different evolution of the current density versus copper coverage was reported [10].

Moreover, a pure platinized platinum catalyst is not active for this reaction (Fig. 3) in agreement with the literature concerning supported catalysts [1,11]. In the electrocatalytic reduction of nitrate also very low current densities are obtained with platinum electrodes [8–10].

The selectivity in ammonia (dissolved in the solution), expressed in percentage (%) as the ratio of the quantity of ammonia produced to the quantity of nitrate converted: $((\text{ammonia}/\text{nitrate}) \times 100)$, was also determined (at a conversion of 40%) for various copper coverages (Fig. 3). This parameter also depends on the coverage degree of copper and becomes maximum for about $\theta_{\text{Cu}} \approx 0.4$–$0.6$ (Fig. 3) and minimum with a low copper coverage ($\theta_{\text{Cu}} \approx 0.11$). These remarks indicate that the promotion effect induced by copper, found previously, is beneficial for the reaction pathway leading to the formation of ammonia (see farther on the global reactions 2, 3, 6, 7 and 10).

3.2. Reduction of nitrite

The catalytic reduction of nitrite was also investigated with Pt–Cu_{ads} catalysts of a similar surface composition and in the same experimental conditions as those used for the reduction of nitrate in order to compare the reduction rates of these two compounds.

The evolution of $C_{\text{nitrite}} = f(t)$ and of $C_{\text{ammonia}} = f(t)$ graphs allowed to calculated the intrinsic initial catalytic activity and the selectivity in ammonia of different Pt–Cu_{ads} catalysts studied, corresponding to various θ_{Cu} (as explained previously).

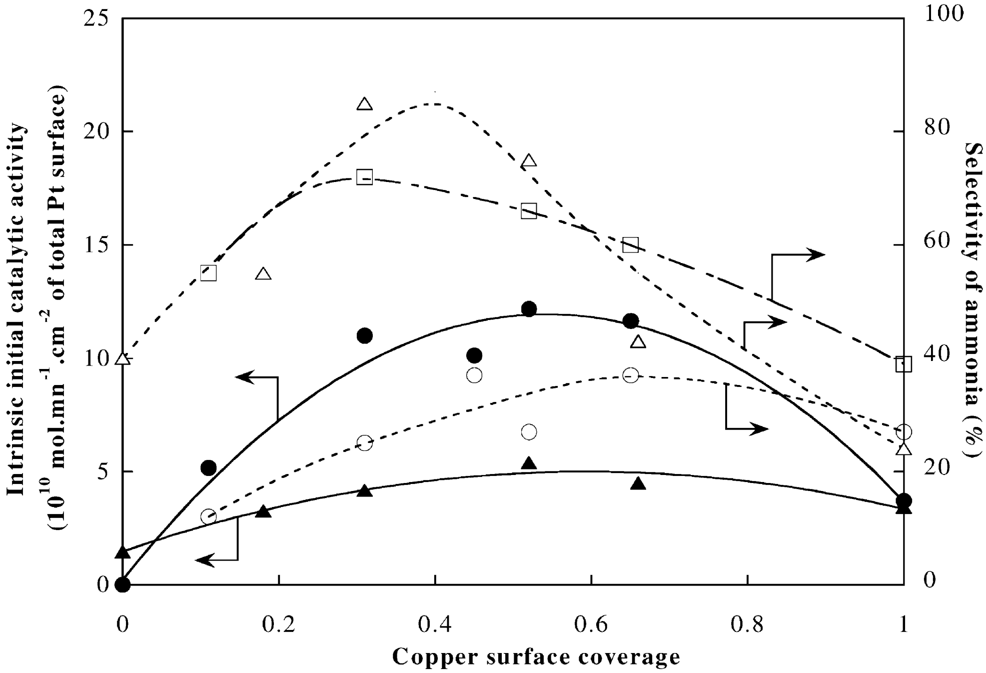

Fig. 3. Evolution of the intrinsic catalytic activity and of ammonia selectivity (for a 40% initial conversion) of Cu_{ads}/Pt catalysts as a function of copper surface coverage for the reduction of nitrate (circle) and for the reduction of nitrite (triangle). Solid symbol: catalytic activity, open symbol: selectivity of ammonia. Open squares: ammonia selectivity of nitrate reduction after correction for the presence of nitrite.

The obtained evolution of the intrinsic activity and that of ammonia selectivity as a function of θ_{Cu}, presented in Fig. 3, is qualitatively similar to that obtained in the case of nitrate.

Nevertheless, the quantitative comparison of each of these two parameters (activity and selectivity) with those obtained in the case of nitrate reduction allows to point out some important remarks (Fig. 3):

- Pure platinum is active for the reduction of nitrite whereas it is inactive for the reduction of nitrate. This result confirms those found in the literature [1,11].
- Equal activities for the reduction of nitrate and the reduction of nitrite are obtained with a platinum surface completely covered by copper.
- The activity of Pt–Cu$_{ads}$ catalysts, for $0.05 < \theta_{Cu} < 1$, is higher in the reduction of nitrate than in the reduction of nitrite (by a parameter of 2–3 for $\theta_{Cu} \approx$ 0.5–0.6).
- At first sight the selectivity in ammonia of Pt–Cu$_{ads}$ catalysts, for $0.1 < \theta_{Cu} < 0.9$, seems to be higher (by a parameter of 2–3) in the reduction of nitrite than in the reduction of nitrate.

However, taking into account the presence of nitrite intermediate and the high selectivity in ammonia obtained by reduction of this compound (Fig. 3), the actual selectivity in ammonia for the nitrate reduction (calculated with the assumption that, in the reduction of nitrite, equal selectivities in ammonia are obtained with or without a competitive reduction of nitrate) becomes approximately as high as that of nitrite (see corrected curve in Fig. 3).

These results suggest that, in the case of nitrate reduction, the rate determining step should not be the first reduction step of nitrate to nitrite (otherwise lower reaction rates than in the reduction of nitrite would be obtained) but rather the consecutive reduction of nitrite, which is a common step in the two reduction reactions studied.

3.3. Evolution of solution pH and of catalyst potential

During the reduction experiments the solution pH and the spontaneously established potential of the catalyst were measured. The pH of the solution increases steeply in the beginning of the reaction (during the first 20–40 min) and then it increases very slowly and tends to a value equal to about 9–10.5 (Fig. 2).

This evolution of pH is due to the global reactions involved in these reduction processes leading to the formation of OH$^-$:

$$NO_3{}^- + 4Cu + 2H_2O \rightarrow NH_3 + 4CuO + OH^- \quad (2)$$

and/or

$$NO_3{}^- + 8Cu + 2H_2O \rightarrow NH_3 + 4Cu_2O + OH^- \quad (3)$$

$$2NO_3{}^- + 5Cu + H_2O \rightarrow N_2 + 5CuO + 2OH^- \quad (4)$$

and/or

$$2NO_3{}^- + 10Cu + H_2O \rightarrow N_2 + 5Cu_2O + 2OH^- \quad (5)$$

$$NO_2{}^- + 3Cu + 2H_2O \rightarrow NH_3 + 3CuO + OH^- \quad (6)$$

and/or

$$NO_2{}^- + 6Cu + 2H_2O \rightarrow NH_3 + 3Cu_2O + OH^- \quad (7)$$

$$2NO_2{}^- + 3Cu + H_2O \rightarrow N_2 + 3CuO + 2OH^- \quad (8)$$

and/or

$$2NO_2{}^- + 6Cu + H_2O \rightarrow N_2 + 3Cu_2O + 2OH^- \quad (9)$$

$$2NO_2{}^- + 6H_2 \xrightarrow{Pt} 2NH_3 + 2H_2O + 2OH^- \quad (10)$$

and/or

$$2NO_2{}^- + 3H_2 \xrightarrow{Pt} 2N_2 + 2H_2O + 2OH^- \quad (11)$$

$$2CuO + H_2 \xrightarrow{Pt} Cu_2O + H_2O \quad (12)$$

and/or

$$Cu_2O + H_2 \xrightarrow{Pt} 2Cu + H_2O \quad (13)$$

Simultaneously the catalyst potential decreases in consequence of this change of pH as it is shown in Fig. 4. Indeed, the catalyst potential decreases proportionally to the pH increase yielding a straight line with a slope of −60 mV for one pH unit (Fig. 4). This straight line is located at potential values more positive (by about +100 mV) than the straight line corresponding to the hydrogen reaction (Fig. 4)

$$H_2 + 2OH^- \rightleftarrows 2H_2O + 2e^- \quad (14)$$

Generally, during hydrogenation reactions in aqueous acid solutions the spontaneously set potential is determined mainly by the fast hydrogen reaction [19,20]:

$$H_2 \rightleftarrows 2H^+ + 2e^- \quad (15)$$

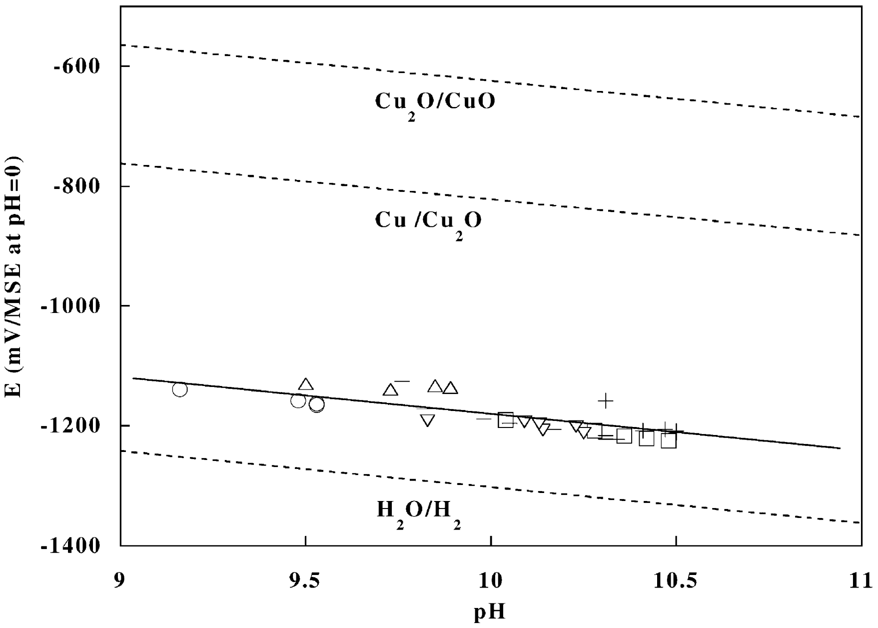

Fig. 4. Evolution of catalyst potential as a function of solution pH during the reduction of nitrate in the presence of Cu_{ads}/Pt catalysts with various θ_{Cu} ((○) 0.11; (–) 0.3; (□) 0.45; (△) 0.52; (+) 0.65; (▽) 1).

However, in the case of the reduction of nitrate and nitrite in neutral and slightly alkaline solutions, the catalyst potential is much more positive than that associated to reaction 14. In this case, a mixed potential, determined by the different oxidoreduction reactions involved (as e.g., those concerning the reduction of copper oxides (reactions 12 and 13) by hydrogen adsorbed on adjacent platinum sites (Pt–H_{ads}), produced as an intermediate during the oxidation of hydrogen (reaction 14), should be established. Indeed, the copper adatoms, after their oxidation by nitrate or nitrite, are supposed to be again reduced by the hydrogen adsorbed on platinum neighbouring sites.

Furthermore, the values of mixed potentials, measured in reaction conditions used in this work and their evolution as a function of pH (Fig. 4), suggest that copper adatoms should be on average in the metallic state and, in addition, the oxidoreduction reactions 12–14 should be in equilibrium [21].

However, in the case of supported Pd–Cu catalysts, investigated by “in situ” X-ray absorption spectroscopy, copper was found to be partially oxidized [22].

4. Conclusion

The obtained results allow to conclude that:

- Platinized platinum catalysts modified by electrochemical deposition of (sub)monolayers of copper (Pt–Cu_{ads}) are active catalysts for the reduction of nitrate and nitrite whereas pure platinized platinum is active only for the reduction of nitrite but not of nitrate.
- Copper reduces nitrate and nitrite by a direct oxidoreduction reaction.
- The catalytic activity of Pt–Cu_{ads} for the reduction of both nitrate and nitrite depends on the surface composition of the catalyst and becomes maximum when about 50% of platinum surface is occupied by copper ($\theta_{Cu} \approx 0.5$).
- Higher activities are obtained for the reduction of nitrate than for the reduction of nitrite at $0.05 < \theta_{Cu} < 1$ (by a parameter of 2–3 at $\theta_{Cu} \approx 0.5$).
- The selectivity in ammonia of Pt–Cu_{ads} depends also on the surface composition of the catalyst and

a maximum is obtained at $0.35 < \theta_{Cu} < 0.65$ for the reduction of nitrate and of nitrite.
- The promotion effect induced by copper for the reduction of nitrate and nitrite, found in this work, can be ascribed to an oxidoreduction mechanism induced by metallic copper adatoms which, after being oxidized by nitrates and nitrites, are again regenerated by the hydrogen adsorbed on neighbouring platinum atoms.
- The change of the spontaneously established potential of the catalyst during the reaction arises from the change of the solution pH which, itself, results from the reaction pathway generating OH^-.
- The catalyst potential can be considered as a mixed potential associated to the different oxidoreduction reactions involved (Cu^0/Cu^I, Cu^I/Cu^{II}, H_2O/H_2).

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