

Catalytic Reduction of Nitrate and Nitrite on Pt–Cu/Al₂O₃ Catalysts in Aqueous Solution: Role of the Interaction between Copper and Platinum in the Reaction

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Bimetallic platinum copper catalysts were prepared by deposition of copper on a parent monometallic platinum catalyst. Two techniques were employed favoring the deposition of copper either on the parent metal or on the support. The activity and selectivity of copper and platinum monometallic catalysts are compared to those of their bimetallic counterparts. Copper reduces nitrates and nitrites according to a redox process but deactivates rapidly. Monometallic platinum catalysts are inactive for nitrate reduction, while nitrates are totally and rapidly reduced on Pt–Cu bimetallic catalyst when both metals are in close contact. In the bimetallic catalyst, the role of copper is to reduce nitrate to nitrite according to a redox process. In this step, the interaction between copper and platinum is of major importance to maintain copper in the metallic state by way of hydrogen adsorbed on platinum. However, copper has a negative influence on the selectivity toward nitrogen. © 2001

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Key Words: nitrate; nitrite; Pt–Cu catalysts; catalytic reduction.

1. INTRODUCTION

Intensive agricultural activities and especially overfertilization induce an increase of nitrate concentration in groundwater. Nitrates consumed with drinking water can be converted into nitrites in human body and may cause methaemoglobinaemia in newborns, as well as other side effects like hypertension. The European Community has set the maximum permitted level of nitrate in drinking water to 50 mg · l⁻¹. To comply with the legislation, a specific treatment of drinking water is necessary. Nowadays, two types of processes are developed: (i) physico-chemical processes using ion exchange, electro dialysis, or reversed osmosis and (ii) biological processes, consisting of nitrate reduction by microorganisms into gaseous nitrogen (1, 2).

The electrolytic reduction of nitrate anions has been under investigation for a long time (3–9) and constitutes an

important part of the electrochemistry of nitrogen compounds. Chemical reduction of nitrate in water has also been studied (10, 11) in the presence of ferrous ions and a copper catalyst, or in the presence of metallic iron as reducing agent. More recently, catalytic denitratation has been developed (12–26) to obtain the selective reduction of nitrate into nitrogen, with the undesired formation of ammonia.

It was demonstrated (12–16) that nitrites are reduced by hydrogen either to nitrogen or to ammonia on various hydrogenation catalysts like Pd/C, Pd/Al₂O₃, Pt/C, Ru/Al₂O₃, Ir/Al₂O₃, and Rh/Al₂O₃. Among these six catalysts, those based on palladium show the highest activity and selectivity. On alumina support, the activity ranking is 5% Pd > 5% Rh > 2% Ir > 2% Ru and the selectivity sequence is 5% Pd > 2% Ru > 2% Ir = 5% Rh (15). From these results, palladium-based catalysts were used in all subsequent studies reported in the literature. Nevertheless, the activity and selectivity of alumina-supported, platinum-based catalysts were no longer studied.

To reduce nitrates, it is necessary to activate the precious metal-based catalysts by addition of a second metal such as copper or silver. In the early studies, the best activity and selectivity obtained with palladium-based bimetallic catalysts were found with palladium–copper catalysts (12–16). The catalytic liquid-phase hydrogenation of aqueous nitrate solution on these bimetallic Pd–Cu catalysts was the subject of kinetical studies (17, 19). More recently, other promoting metals like Sn and In (22, 23, 25) and Zn (25, 26) were investigated. In terms of activity, palladium–tin and palladium–indium catalysts seem to be more suited for nitrate reduction than their palladium–copper equivalents, minimizing at the same time the formation of ammonia.

With the aim of gaining a deeper understanding of the mechanism of nitrate reduction on bimetallic platinum-based catalysts, we have studied in this work the behavior of the monometallic platinum and copper catalysts. Palladium-based catalysts are not active for the liquid phase nitrate reduction (14) and this was verified in the case of

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monometallic platinum catalysts. Then we tested the activity of platinum catalysts for the liquid-phase nitrite hydro- genation, whereas the activity of monometallic and bimetal- lic copper-based catalysts were evaluated for both nitrate and nitrite reduction. To determine the role of the copper- platinum interaction in the reaction, two different prepa- ration techniques were chosen to favor the deposition of copper on a parent platinum catalyst, either on the plat- inum particles or on the support. The influence of Pt/Cu atomic ratio was also studied.

2. EXPERIMENTAL

2.1. Catalysts

2.1.1. Support

The support was an γ -alumina (Procatalyse) with a spe- cific surface area (BET method) of 215 m²/g, a total pore volume of 0.55 cm³/g, and an isoelectric point at pH 7. The support was crushed and sieved in order to retain particles with sizes between 0.04 and 0.08 mm.

2.1.2. Catalysts

Monometallic platinum and copper catalysts were pre- pared by impregnation of the support with Pt(NH₃)₄(OH)₂ or Cu(NO₃)₂ · 3 H₂O in an aqueous solution brought to pH 11 by the addition of ammonia. This pH value was cho- sen to ensure the cationic exchange between the precur- sor salt and the alumina surface (27, 28), leading therefore to a well-dispersed catalyst after activation. The mixture was stirred for 12 h and then ammonia and water were evap- orated by heating on a sandbath. After drying overnight at 120°C, catalysts were calcined in flowing air for 4 h, at 450°C for platinum and at 300°C for copper catalysts (to avoid copper aluminate formation). Then the oxidized platinum catalyst was reduced in flowing pure hydrogen at 500°C for 8 h. For copper catalyst, this reduction step was carried out at 320°C, *in situ*, i.e., in the same reactor as that used for the nitrate or nitrite reduction test. This made it possible to avoid any contact with air, thereby maintaining copper species into their metallic form.

To prepare Pt–Cu bimetallic catalysts, two techniques were chosen to deposit copper onto the monometallic “par- ent” platinum catalyst either on platinum particles or on the support:

a. Catalytic reduction. This technique, widely used in our laboratory (29–32), was developed in order to favor the deposition of the second metal on the prereduced parent metal. A platinum monometallic catalyst was modified by the surface reaction between chemisorbed hydrogen and the second metal, according to the overall reaction



A given amount of the prereduced parent platinum catalyst was introduced in an aqueous solution previously degassed by bubbling nitrogen and continuously stirred by a counter- current hydrogen flow (1 h). The solution of the copper salt (Cu(NO₃)₂ · 3 H₂O), containing a well-defined amount of copper, was then added and maintained in contact with the catalyst under hydrogen flow for 2 h. We verified, by atomic absorption spectroscopy (Perkin–Elmer 3300), that copper was totally absent in solution after the deposition reaction. Bimetallic catalysts were then filtered, washed with water, and dried at 120°C overnight. In the following, this type of catalysts is referred to as “CR catalysts.”

b. Successive impregnation by cationic exchange. This technique was used to favor the copper deposition on the support and therefore to minimize interactions between platinum and copper. The experimental procedure was the same as that described above for the monometallic copper catalyst. This type of catalyst is called “SI catalysts.”

Both types of bimetallic catalysts were activated by direct reduction at 380°C under flowing pure hydrogen for 2 h.

The monometallic and bimetallic catalysts contained 1 wt.% of metal (platinum and/or copper on alumina).

2.2. Characterization Methods

2.2.1. Determination of Platinum Dispersion

Platinum accessibility was determined by O₂/H₂ titration (33, 34). After reduction in H₂ at 500°C, the catalyst was flushed for 1 h 30 min with helium at the same temperature to remove physically adsorbed hydrogen, and then cooled to room temperature. Pulses of oxygen were then intro- duced until full saturation of the catalyst was achieved. The chemisorbed oxygen was titrated by hydrogen. The amount of hydrogen consumed in this way corresponds to the total hydrogen (reversibly and unreversibly bound) HT1. The catalyst was then degassed for 20 min at room tempera- ture, and a second hydrogen chemisorption was carried out corresponding to the reversibly bound and/or physisorbed hydrogen HT2. The amount of adsorbed hydrogen on the metal surface (HT) is simply the difference between HT1 and HT2.

The gases used in this study were of ultra-high-purity grade.

This method was effective in determining the platinum accessibility in the monometallic catalyst, but unsuitable for the bimetallic catalysts.

2.2.2. Electron Microscopy

Electron microscopy was mostly used to characterize bimetallic catalysts.

Transmission electron microscopy (TEM) in a bright field mode was carried out in a Philips CM120 electron micro- scope operating at 120 kV with a theoretical resolution of 0.35 nm. The sample was embedded in a polymeric resin

(spurr) and cut into a section as small as 40 nm with an ultramicrotome equipped with a diamond knife. Cuts were then deposited on an Al grid previously covered with a thin layer of carbon. EDX analysis of elements was carried out in the STEM mode of the microscope using a Si (Li) Super UTW detector.

2.2.3. X-Ray Diffraction

XRD analysis were carried out in a Siemens D500 powder diffractometer using CuK α ₁ radiation, but only peaks due to support phases were detected, which can be explained on the one hand by the small amount of metal loading and, on the other hand, by the high dispersion of metallic phases.

2.2.4. Fourier Transform Infrared Spectroscopy

Carbon monoxide adsorption on bimetallic catalysts was followed by a Fourier-transform infrared (FTIR) experiment using a Nicolet Magna-750 spectrometer, on a sample of about 20 mg compressed into a disk and placed into a glass cell. After reduction *in situ* in flowing pure hydrogen at 400°C for 2 h, the pellet was outgassed for 1 h at the same temperature and then cooled. CO was admitted in the cell by injecting pulses at room temperature until a pressure of 10 Torr (1 Torr = 133.3 N · m⁻²), corresponding to the apparent saturation of the platinum surface, was achieved. Then the samples were evacuated at room temperature for 1 h.

2.3. Nitrate and Nitrite Reduction Reactions

The reactions were carried out in a 250-mL batch reactor. In a typical experiment, the catalyst was introduced in the reactor and degassed under N₂ upflowing. Ninety milliliters of ultrapure water with predissolved hydrogen was then added and the temperature was lowered to 10°C. Then 10 mL of a concentrated aqueous solution of nitrate (10⁻² mol/L) were introduced in the reactor to start the reaction. Ultrapure water (18.2 M Ω) was obtained by a Millipore purifying system. Operating conditions are reported in Table 1. The catalyst dispersion in the aqueous medium was operated by the hydrogen bubbling flow through a porous glass located at the bottom of the reactor. It was checked that the hydrogen flow and the resulting stirring were sufficient to ensure that the reaction was not rate-limited by reactant diffusion. By varying experimental parameters, like reaction temperature, catalyst amount, metal or catalyst loading, and hydrogen flow rate, it was demonstrated that the kinetics of the overall process is not influenced by diffusion limitations. For example, Fig. 1 demonstrates that the activity (in moles per minute) for nitrate reduction is proportional to the catalyst loading up to 2 g/100 mL of catalyst. This confirms that the nitrate disappearance rate was not influenced by diffusion phenomena with the catalyst loading of 0.8 g/100 mL applied in the present study.

TABLE 1

Experimental Conditions of the Catalytic Reduction of Nitrate

Temperature	10°C
Initial pH value	5.5
Total pressure	1 bar
Hydrogen partial pressure	1 bar
Reaction volume	100 mL
Catalyst weight	0.8 g
Catalyst particle diameter	40–80 μ m
Initial nitrate or nitrite concentration in the reactor	10 ⁻³ mol/L
Nitrate source	Mg(NO ₃) ₂
Nitrite source	Ba(NO ₂) ₂
Gas flow rate	180 mL/min

At appropriate time intervals, an aliquot of the reaction mixture was sampled and filtered. Nitrate and nitrite intermediate concentrations were determined by HPLC analysis, on an Interchrom Inertsil ODS2 column coupled with a UV-VIS spectrophotometer (Thermo Separation Products, Spectra SERIES UV100). The mobile phase was a mixture of acetonitrile, diamminohydrogenophosphate, *N*-Octylamine (high-purity grades), and ultrapure water. The pH was kept between 6 and 6.5 using 86% H₃PO₄ (35). The use of *N*-octylamine in the eluent allows the separation of inorganic anions. Operating conditions consisted of a flow rate of 1.2 mL/min and a detection wavelength of 210 nm.

The pH of the initial and final solutions were determined by means of a digital pH meter (Consort).

The amount of ammonium ions was measured at the end of the reaction using a selective electrode (Mettler Toledo). In this study, the selectivity toward ammonium ions was always lower than 30%, except for nitrate reduction on monometallic copper catalyst. However, considering both the pH value at the end of the reaction (near 9) and the further possibility of cationic adsorption on alumina at this pH value, the amount of total ammonia (basic and acidic

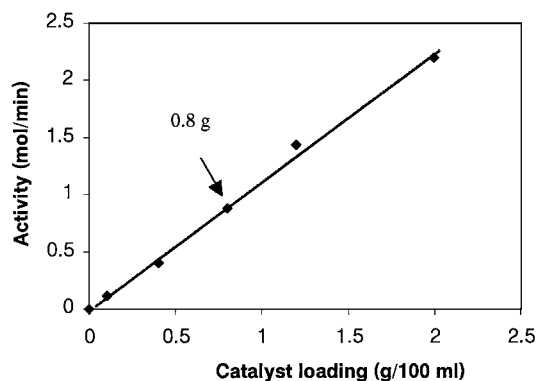


FIG. 1. Activity of CR catalyst (with Cu/Pt = 1) for nitrate reduction (in mol/min) vs catalyst loading.

forms) was probably much higher. Still, by comparing the amount of the ammonium ions produced, it was possible to assess the performance of various catalysts in this work, since the pH value of the solution at the end of the reaction was nearly the same.

To identify gaseous products during nitrate reduction, a separate experiment was conducted in a batch reactor in the presence of a CR bimetallic catalyst, with an atomic ratio Cu/Pt of 1. Before the addition of nitrate, the solution and the reactor volume were saturated with hydrogen and the gas was recirculated from the top to the bottom of the reactor to create mixing conditions equivalent to a semi-batch setup with hydrogen bubbling. We checked that the nitrate disappearance rate was unchanged compared to typical experimental conditions. Gases were analyzed by gas chromatography equipped with a catharometer, after separation on a molecular sieve 5A column coupled with a Porapak Q column. With hydrogen accounting for a majority of the gas phase, we chose this gas as a carrier to prevent its detection. Dinitrogen was the only gas detected by this method, although Daum and Vorlop (26) identified dinitrogen oxide as an intermediate product of nitrate reduction on Pd–Cu bimetallic catalysts. The absence of dinitrogen oxide in gas phase in the present case could be explained either by the change of bimetallic catalyst or by the high solubility of N_2O in water, which is 40 to 45 times higher than those of N_2 and H_2 , or by the amount of dinitrogen oxide formed below the detection limits of GC analysis.

3. RESULTS AND DISCUSSION

3.1. 1 wt.% Cu/Al₂O₃ Catalysts

At first 1% Cu/Al₂O₃ catalysts were prepared as described under Experimental but were reduced *ex situ* and stocked several days under air before the reaction test in the presence of nitrate or nitrite and hydrogen. Under the same conditions, Pintar and Kajiuchi (18) observed that the catalyst is totally inactive for nitrate reduction. If we consider the redox potential of the principal species involved in this reaction (36, 37), nitrate or nitrite should be reduced by metallic copper. This inactivity can be explained by a surface oxidation of copper in contact with air, leading to CuO, Cu₂O, or CuCO₃·Cu(OH)₂ basic copper carbonate species (38), giving a green color to this catalyst. To avoid this phenomenon, the catalyst was reduced *in situ*, i.e., in the reactor, at 320°C for 150 min. This temperature is sufficient to reduce copper, as is proved by the TPR profile presented in Fig. 2d, where the peaks at 260 and 320°C could be respectively assigned to superficial Cu₂O and CuO reduction to metallic copper, respectively (39). After copper reduction nitrate or nitrite solution was added. As expected, nitrate and nitrite were reduced, principally to ammonia, under both hydrogen and nitrogen atmospheres, confirming a redox mechanism between

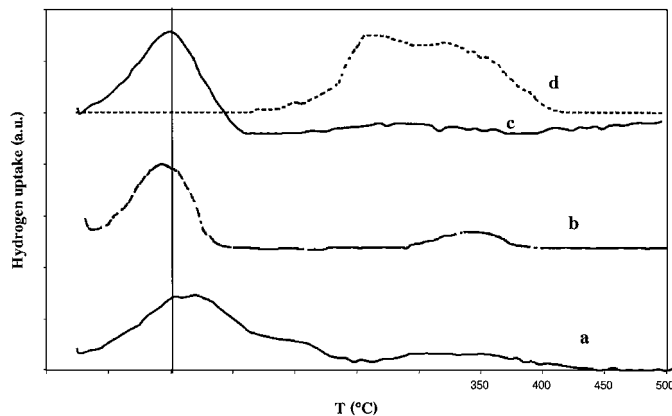


FIG. 2. TPR profiles obtained after catalyst preparation and exposition to ambient air. Operating conditions: sample weight = 300 mg, 5°C/min, 1% H₂ in Ar, gas-flow rate = 14 mL/min. (a) CR catalyst, (b) SI catalyst, (c) 1% Pt/Al₂O₃, and (d) 1% Cu/Al₂O₃ (atomic ratio Cu/Pt of 1 in bimetallic catalysts).

metallic copper and nitrate or nitrite. The evolution of nitrate concentration in presence of 1 wt.% Cu/Al₂O₃ is plotted as a function of time in Fig. 3. Although the amount of copper was sufficient, nitrate was not totally converted, copper being rapidly passivated by CuO or Cu₂O formation in water, occurring even in the presence of hydrogen (36, 39). The same result was obtained during nitrite reduction. At the end of the reaction, the concentration of copper ions in aqueous solution was below the detection limit of atomic absorption spectroscopy. According to the pH value at the beginning of the reaction (pH 5.5) the thermodynamically favored reactions lead to NO(g), N₂O(g), N₂(g), NO₂⁻(aq), and NH₄⁺(aq). For example, the nitrate and nitrite reduction leading to nitrogen could be written according to the reactions

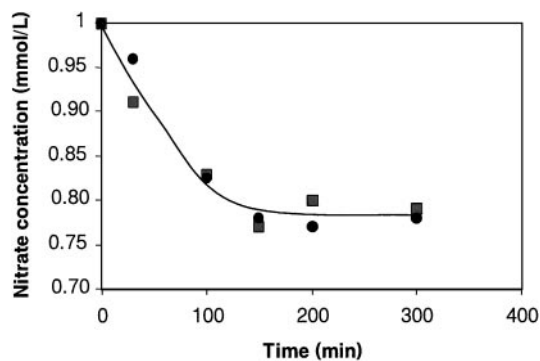
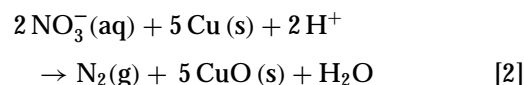


FIG. 3. Nitrate evolution vs time during nitrate reduction in the presence of 1 wt.% Cu/Al₂O₃ in the presence of hydrogen (●) or nitrogen (■) ($p_{H_2 \text{ or } N_2} = 1$, gas-flow rate = 180 mL/min, $T = 10^\circ\text{C}$).

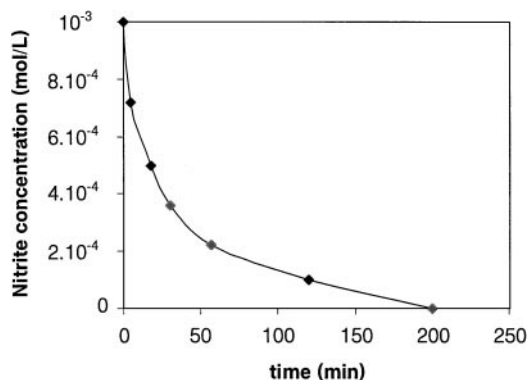
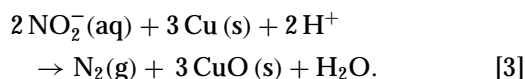


FIG. 4. Nitrite concentration vs time during nitrite reduction in the presence of 1 wt.% Pt/Al₂O₃ ($p_{\text{H}_2} = 1$, gas-flow rate = 180 mL/min, $T = 10^\circ\text{C}$).



3.2. 1 wt.% Pt/Al₂O₃ Catalyst

After preparation (fresh catalyst) the metallic accessibility of 1 wt.% Pt/Al₂O₃ catalyst is 46%, which corresponds to a particle diameter of approximately 18 Å. After reaction in the presence of nitrites and hydrogen (Pt/Al₂O₃ is inactive for nitrate reduction), the accessibility of platinum is notably decreased to 26%. The same result is obtained after a "blank" reaction, in the presence of hydrogen only. This sintering phenomenon, occurring in water under hydrogen, has already been observed for precious metal-based catalysts (29, 40). Consequently, catalysts were aged by hydrogen bubbling in water before nitrite introduction to avoid platinum accessibility modification during the reaction.

The nitrite evolution during the reaction is presented in Fig. 4.

The initial reaction rate is approximately equal to $6 \times 10^{-6} \text{ mol/min} \cdot \text{g}_{\text{cat}}$, which corresponds to a turnover frequency of $7.5 \times 10^{-3} \text{ s}^{-1}$, calculated from the observed specific reaction rate and the fraction of exposed platinum atoms (26%). The selectivity toward NH₄⁺ is 2%. The apparent activation energy of this reaction, calculated from the Arrhenius plot (Fig. 5) between 10 and 26°C, is equal to $45 \pm 2.5 \text{ kJ} \cdot \text{mol}^{-1}$, which is higher than the value found for 5 wt.% Pd/ γ -Al₂O₃ by Tacke and Vorlop (14).

3.3. 1 wt.% Pt-Cu/Al₂O₃ Bimetallic Catalysts

3.3.1. Characterization of CR and SI Catalysts (Atomic Ratio Cu/Pt of 1)

Temperature-programmed reduction (TPR) profiles of fresh CR and SI are presented in Fig. 2 and compared to those of corresponding monometallic catalysts. They were established after preparation and exposition to air at ambient temperature. In the case of the CR catalyst, one can

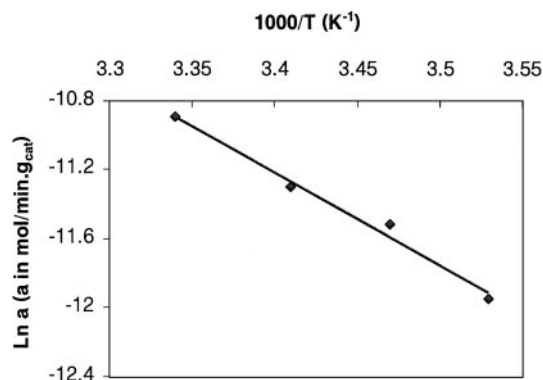


FIG. 5. Arrhenius plot used to obtain the activation energy relative to the nitrite reduction on 1 wt.% Pt/Al₂O₃.

observe an important hydrogen uptake between 50 and 250°C, with two maxima at about 115 and 205°C followed by a lower hydrogen uptake between 270 and 400°C. For the SI catalyst, two hydrogen uptakes can be identified with maxima at 100 and 345°C approximately. In this case, the TPR profile is essentially the overlap of the individual contributions of monometallic platinum and copper catalysts. The profile of the CR catalyst is significantly different, and the first domain, with maxima at 115 and 205°C, could be attributed to the reduction of mixed Pt-Cu oxidized species where both metals are mutually interacting (41). From the TPR profiles, one can deduce that a temperature of 380°C is sufficient to reduce all species present in the SI and CR catalysts.

The average composition of bimetallic particles in CR and SI catalysts is presented in Fig. 6, for a global Cu/Pt atomic ratio equal to 1, corresponding to 50 at.% of copper. TEM pictures of these catalysts are shown in Fig. 7.

a. CR catalyst. The particle size of the CR catalyst was determined from TEM pictures (Fig. 7a) by means of a histogram as illustrated in Fig. 8. The particle diameter, calculated as $d_p = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$, where d_p is the average diameter of the particles and n_i the number of particles having diameter in the range ($d_i \pm 2.5 \text{ \AA}$), is equal to $25 \pm 2.5 \text{ \AA}$.

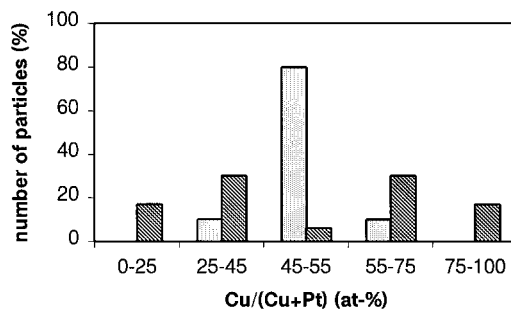


FIG. 6. Number of particles vs copper percentage in metallic particles on SI (▨) and CR (▤) catalysts for an atomic ratio Cu/Pt = 1 (number of analyzed particles: 15).

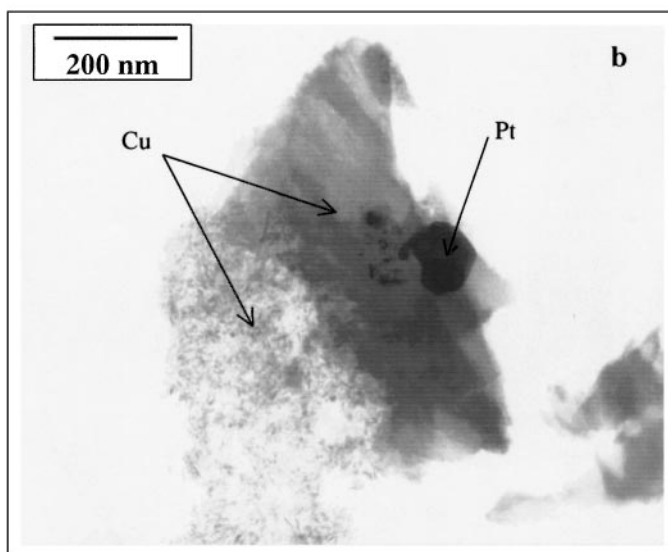
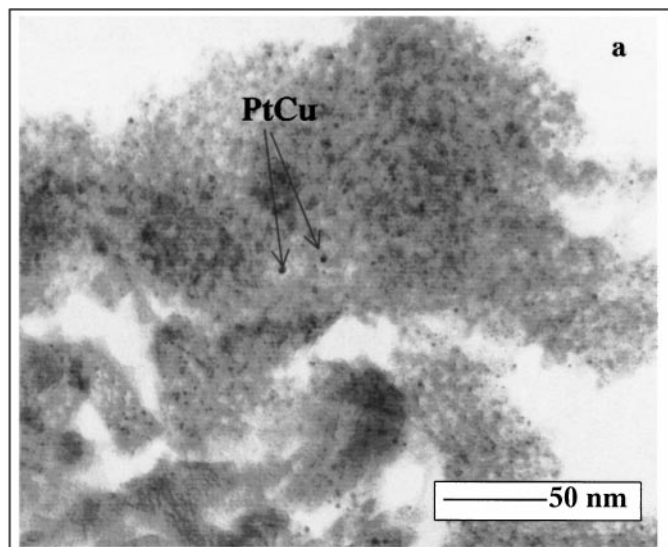
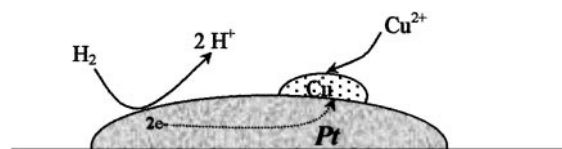


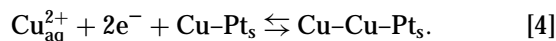
FIG. 7. Transmission electron microscopy of 1 wt.% Pt-Cu/Al₂O₃ with an atomic ratio Cu/Pt = 1. (a) CR catalyst shows small bimetallic particles, (b) SI catalyst shows large agglomerates of copper and platinum on the alumina surface.

According to the preparation method, catalytic reduction favors the deposition of copper onto platinum particles. Eighty percent of individual particles analyzed by EDX have the average composition of the whole catalyst, which proves the strong interaction between copper and platinum. Given the platinum dispersion in the parent catalyst (26%) and the particle composition (Cu/Pt = 1), this indicates that the amount of copper deposited is approximately four times higher than the amount of accessible platinum surface Pt_s. Assuming that each adsorbed copper atom may occupy one adsorption site of hydrogen on platinum (42), and recalling the similar size of platinum and copper atoms, this corresponds to a bulk copper deposition

on platinum under a hydrogen atmosphere. This type of deposition on platinum can occur via the electrons generating by the hydrogen ionization on the noble metal, according to the following scheme:



This mechanism implies that platinum surface is not totally covered by copper, even for such an amount of second metal added, and that some sites of platinum remain accessible to hydrogen. Using electrochemical methods, Furuya and Motoo (43) studied copper deposition on a platinum electrode in an acidic medium. They demonstrated that close to the reversible hydrogen potential, the following reaction take place before all platinum sites are occupied by copper adatoms:



For larger amounts of copper, we can assume that copper deposition on copper leads to tridimensional structure sufficiently organized to be stable.

Another possibility involves the diffusion of copper atoms into the platinum particles during copper layer formation, since copper and platinum form series of stable intermetallic compounds (44).

To verify the accessibility of platinum in the bimetallic CR catalyst, we studied the adsorption of CO by FTIR spectroscopy. The spectra of CO adsorbed onto the bimetallic CR catalyst with a global Cu/Pt atomic ratio equal to 1 were recorded after adsorption of CO at a pressure of 10 Torr followed by an evacuation for 1 h at room temperature (Fig. 9). The band at about 2055 cm⁻¹ can be attributed to

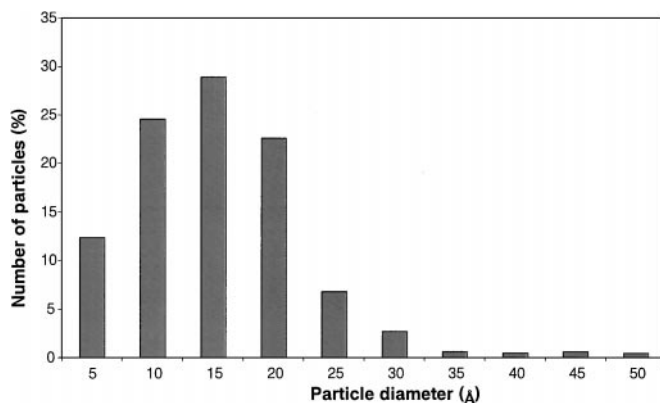


FIG. 8. Metal particle size distribution for CR catalyst (number of analyzed particles, 665).

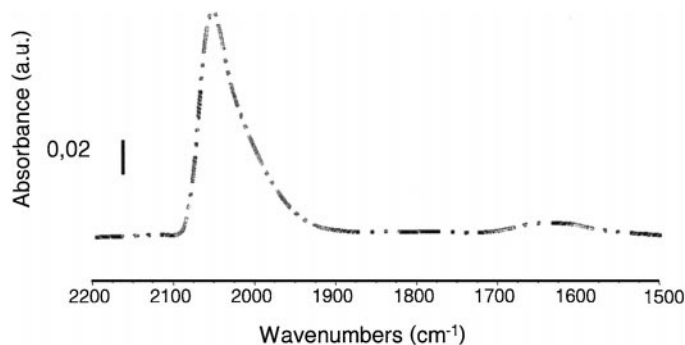


FIG. 9. FTIR spectra of CO adsorbed at room temperature onto CR catalyst with an atomic ratio Cu/Pt = 1 after exposition to 10 Torr of CO following by an evacuation for 1 h at room temperature.

CO bonded to surface platinum atoms in linear form (45), which proves that platinum surface remains accessible to gases in the bimetallic catalyst.

b. SI catalyst. In contrast to the CR catalyst, the particle composition of the SI catalyst is very heterogeneous, the analyzed sample (Fig. 6) being composed of copper or platinum monometallic particles and of either platinum-rich or copper-rich bimetallic particles. TEM analysis of this type of catalyst confirmed that samples are composed of small particles (average size 30 Å) of pure platinum or copper, favored by the ion exchange preparation, but larger particles were found, with a bimetallic composition. Figure 7b shows an example of this type of bimetallic particle where copper agglomerates surround platinum. This could be explained by the broad distribution of platinum and copper particle size, preferred interactions taking place between the largest particles of each metal.

3.3.2. Effect of the Preparation Method on the Nitrate and Nitrite Reduction Reaction

Nitrate and nitrite evolution during the reaction in the presence of CR or SI catalysts (Cu/Pt = 1) is presented in Figs. 10a and 10b. Nitrite evolution is expressed as a function of nitrate conversion. The initial activities of CR and SI catalysts are reported in Table 2.

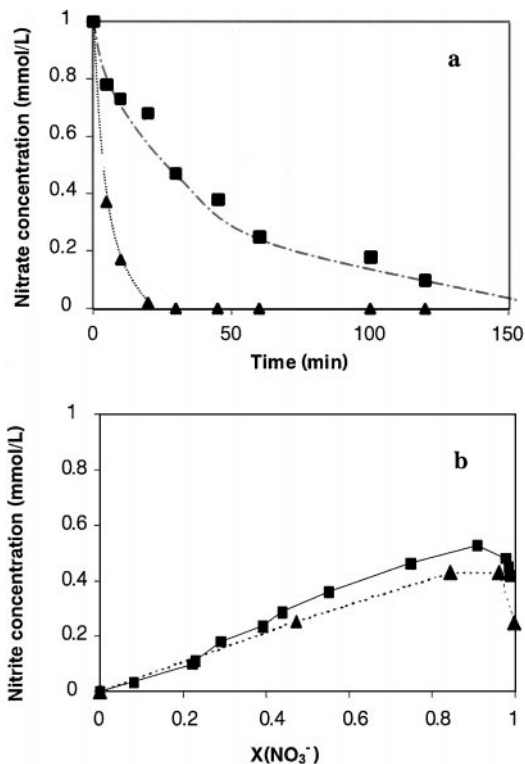


FIG. 10. Nitrate concentration vs time (a) and nitrite concentration vs nitrate conversion $X(\text{NO}_3^-)$ (b) in the presence of 1 wt.% Pt-Cu/Al₂O₃: (▲) CR catalyst, (■) SI catalyst.

Since higher activities are obtained with the CR catalyst, these results demonstrate that the preparation method of the bimetallic catalyst is of major importance when using the same impregnation sequence (platinum deposited first). If the catalyst activity for the nitrate reduction can be directly related to the interactions between the noble metal and copper, the difference of activity between SI and CR catalysts may be explained only by the number of bimetallic active sites, which are optimum on the CR catalyst. Once nitrates are converted into nitrites, these intermediates could be reduced either on the bimetallic particles or on platinum monometallic particles. Nitrite evolution vs nitrate

TABLE 2

Activity of CR and SI Bimetallic and Platinum Monometallic Catalysts for Nitrate and Nitrite Reduction

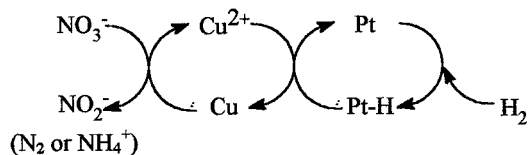
Catalyst	Cu (wt.%)	Pt (wt.%)	Cu/Pt (atomic ratio)	Activity ^a for nitrate reduction (mol/min · g _{cat})	Selectivity (% of NH ₄ ⁺) for nitrate reduction	Activity ^a for nitrite reduction (mol/min · g _{cat})	Selectivity (% of NH ₄ ⁺) for nitrite reduction
CR Pt-Cu/Al ₂ O ₃	0.25	0.75	1	11 · 10 ⁻⁶	5	7 × 10 ⁻⁶	5
SI Pt-Cu/Al ₂ O ₃	0.25	0.75	1	4 · 10 ⁻⁶	7	4 × 10 ⁻⁶	5
Pt/Al ₂ O ₃	0	0.75	0	0	—	4 × 10 ⁻⁶	—
Pt/Al ₂ O ₃	0	1	0	0	—	6 × 10 ⁻⁶	2

^a Absolute error ± 0.5 × 10⁻⁶ mol/min · g_{cat} (by taking into account the error on sample weighing during preparation procedure, and reaction test, on solution volumes, on HPLC analysis, etc.).

conversion is presented in Fig. 5b. Whereas the curves are nearly similar, the maximum amount of nitrite present in solution is higher for the SI catalyst (0.53×10^{-3} mol/L) than for the CR catalyst (0.43×10^{-3} mol/L). This maximum is reached at about 80% nitrate conversion for both catalysts. Considering the catalyst activity for nitrite reduction (Table 2), we can deduce that the higher amount of nitrite in solution during nitrate reduction on the SI catalyst may be partly explained by the lower activity of this catalyst for nitrite reduction. Alternatively, another explanation could be the favored nitrite desorption on the SI catalyst. If we now compare the activity of SI bimetallic and monometallic catalysts at similar platinum content (0.75 wt.%) (Table 2), we observe that they are quite similar. Since the SI catalyst is composed of mostly small monometallic platinum or copper particles, together with large bimetallic particles (see above), we can conclude that the nitrite reduction occurs principally on monometallic platinum sites on the SI catalyst. The CR catalyst activity being much higher, this indicates that bimetallic sites are more active for nitrite reduction.

These results are quite different from those obtained for palladium-based catalysts by Batista *et al.* (46), who found that the relative location of palladium and copper in the catalyst has no influence on the observed activity for the nitrate reduction. This different behavior could be attributed to the precious metal change or by the different preparation procedure.

In the present study, it was shown that monometallic platinum catalysts are inactive for nitrate reduction, while metallic state copper is able to reduce nitrate according to a redox reaction, although it is rapidly deactivated. Therefore, we can deduce that the first step in the nitrate reduction is probably a redox reaction between Cu^0 and NO_3^- , leading to nitrite intermediates or directly to N_2 or NH_4^+ , and to an oxidized form of copper. Subsequently, the role of the precious metal is to activate hydrogen, allowing the reduction of copper according to the following scheme:



With regards to the nitrite intermediates, they can be reduced either on copper, according to the same redox process as that described above, or on the precious metal by catalytic reduction.

Van de Moesdijk (47) proposed the same type of redox mechanism between the promoter and nitrate for the reduction of nitrate in water in the presence of Pd/C and/or Pt/C

catalysts and GeO_2 in solution as promoter. It was suggested that in the presence of the noble metal and hydrogen, GeO_2 rapidly disappears from the solution and an intermetallic compound, Pd_2Ge , was identified by X-ray diffraction. The metallic state of germanium was very surprising since it is a nonprecious metal, which is thermodynamically unstable in the presence of water. However it was verified later by XPS that germanium, present in submonolayer concentration on palladium, is completely reduced to the metallic state under hydrogen atmosphere (48), validating this type of mechanism.

Concerning the catalyst stability, the amount of metal ions present in solution after nitrate reduction in the presence of CR and SI catalysts was below the detection limit of the atomic absorption spectroscopy.

3.3.3. Effect of Cu/Pt Atomic Ratio

We varied the copper and the platinum amount in the catalyst to obtain an Cu/Pt atomic ratio between 0.5 and 9, with a constant metal loading equal to 1 wt.%. The influence of copper loading on the initial activity of CR and SI catalysts is presented in Fig. 6. Irrespective of the preparation method, the best initial activity is obtained for the atomic ratio $\text{Cu/Pt} = 1$, corresponding to 50% of copper in the metallic phase. This result is different from that obtained by Hörold *et al.* (15) on palladium-based catalysts, who presented the better activity for the atomic ratio $\text{Cu/Pd} = 0.42$. This different behavior can be explained either by the noble metal change or by the different experimental conditions (preparation method and/or reaction test conditions). To verify one of these hypotheses, we prepared and tested different palladium-copper catalysts according to the experimental conditions described in the present study. Results are presented in Table 3 and compared with those obtained with Pt-Cu/ Al_2O_3 catalysts containing the same molar amount of noble metal (about 1.5×10^{-4} mole per 100 g of alumina). As we obtained the same optimal composition as Hörold

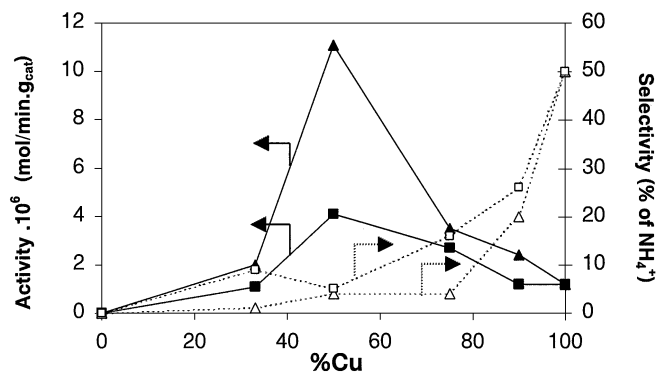


FIG. 11. Initial activity (—) and selectivity toward ammonium ions formation (· · ·) for nitrate reduction as a function of copper content in the metal phase ($\text{Cu}/(\text{Cu} + \text{Pt})$ at.%) for CR (\blacktriangle) and SI (\blacksquare) catalysts.

TABLE 3

Activity for Nitrate Reduction of Pd-Cu/Al₂O₃ and Pt-Cu/Al₂O₃ Prepared by Catalytic Reduction (CR) with the Same Molar Amount of Noble Metal (about 1.5×10^{-4} mole per 100 g of Alumina)

Cu (wt.%)	Pd or Pt (wt.%)	Cu Pd or Pt (atomic ratio)	Activity ^a for nitrate reduction, (mol/min · g _{cat})	Selectivity (% of NH ₄ ⁺) for nitrate reduction
● Pd-based catalysts				
3.9	1.7	4	2×10^{-5}	—
1	1.7	1	4×10^{-5}	4
0.7	1.7	0.71	5×10^{-5}	2
0.5	1.7	0.5	8×10^{-5}	1
0.4	1.7	0.4	7×10^{-5}	1
● Pt-based catalysts				
1	3	1	9×10^{-5}	4
0.5	3	0.5	3×10^{-5}	1

^a Absolute error $\pm 0.5 \cdot 10^{-6}$ mol/min · g_{cat} (by taking into account the error on sample weighing during preparation procedure, and reaction test, on solution volumes, on HPLC analysis, etc.).

et al. for palladium-based catalysts, we can conclude that this value depends mainly on the nature of metals present in the bimetallic phase. The comparison with the results obtained with platinum-based catalysts demonstrates that the performance of different bimetallic catalysts should be compared at the optimal composition rather than at a given composition.

For both types of platinum-based catalysts (CR and SI), when Cu/Pt > 1, the activity decreases as copper content increases, to reach the activity of monometallic copper catalyst when 90% of copper is present in the metal phase. This can be explained by the low accessibility of platinum sites when the copper amount is too important. The selectivity toward ammonium increases with the increase of copper content. Then, although copper is essential in the bimetallic catalyst to reduce nitrate to nitrite, it has a negative influence on selectivity.

4. CONCLUSION

Copper can reduce nitrates and nitrites according to a redox process but deactivates rapidly, copper being passivated by CuO or Cu₂O formation in water. Monometallic platinum catalysts are inactive for nitrate reduction.

Nitrates are totally and rapidly reduced on Pt-Cu bimetallic catalysts when both metals are in close contact. The catalytic reduction preparation method, consisting of Cu²⁺ reduction by hydrogen adsorbed on platinum, is particularly adapted to favor this interaction.

In the bimetallic catalyst, the role of copper is to reduce nitrate to nitrite according to a redox process. In this step,

the interaction between copper and platinum is of major importance, in order to maintain copper in the metallic state by way of hydrogen adsorbed on platinum. Although copper is essential in the bimetallic catalyst to reduce nitrate to nitrite, it has a negative influence on the selectivity toward nitrogen.

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