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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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Catalytic reduction of NO₃⁻ on Pt-Cu/Al₂O₃ catalysts

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Abstract :

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 towards nitrogen.

Key words : nitrate, nitrite, Pt-Cu catalysts, catalytic reduction

1. Introduction

Intensive agricultural activities and specially over-fertilization 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 new-borns, as well as other sides effects like hypertension. 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 in 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 presence of ferrous ions and a copper catalyst, or in 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 or Rh/Al₂O₃. Among these five 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 was no longer studied.

To reduce nitrates, it is necessary to activate the precious metal based catalysts by addition of a second metal 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), 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 monometallic platinum catalysts. Then, we tested the activity of platinum catalysts for the liquid-phase nitrite hydrogenation, whereas the activity of monometallic and bimetallic 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 preparation techniques were chosen to favor the deposition of copper on a parent platinum catalyst, either on the platinum particles or on the support. The influence of Pt/Cu atomic ratio was also studied.

2. Experimental

2.1. Catalysts

Support

The support was an γ -alumina (Procatalyse) with a specific surface area (BET method) of 215 m²/g, a total pore volume of 0.55 cm³/g and an isoelectric point at pH7. The support was crushed and sieved in order to retain particles with sizes between 0.04 and 0.08 mm.

Catalysts

Monometallic platinum and copper catalysts were prepared by impregnation of the support with $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ or $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ in an aqueous solution brought to pH 11 by addition of ammonia. This pH value was chosen to ensure the cationic exchange between the precursor salt and the alumina surface (27, 28), leading therefore to a well-dispersed catalyst after activation. The mixture was stirred for 12 hours and then ammonia and water were evaporated 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 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 than the one used for the nitrate or nitrite reduction test. This allowed 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 ‘parent’ platinum catalyst either on platinum particles or on the support :

- *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 prerduced 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 prerduced 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 ($\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$), containing a well-defined amount of copper, was then added and maintained in contact with the catalyst under hydrogen flow for 2 hours. 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’.

- *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 the one described above for the monometallic copper catalyst. This type of catalyst was called ‘SI catalysts’.

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

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 O_2/H_2 titration (33, 34). After reduction in H_2 at 500°C , the catalyst was flushed for 1 h 30 with helium at the same temperature to remove physically adsorbed hydrogen, and then cooled to room temperature. Pulses of oxygen were then introduced until full saturation of the catalyst. 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 temperature, 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 to determine 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 microscope 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 $\text{CuK}\alpha 1$ 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 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. 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. 90 mL 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 MΩ) 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, hydrogen flow rate ..., it was demonstrated that the kinetics of the overall process is not influenced by diffusion limitations. For example, Figure 1 demonstrates that the activity (in mol/min) 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.

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 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 towards 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 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 CR bimetallic catalyst, with an atomic ratio Cu/Pt of 1. Before 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 set-up 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. Hydrogen accounting for a majority of the gas phase, we chose this gas as a carrier to prevent its detection. Dinitrogen

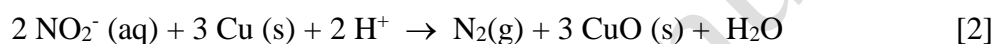
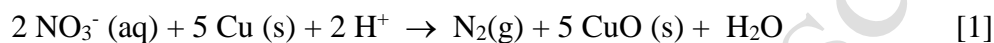
was the only gas detected by this method, although J. Daum and K-D. Vorlop (26) identified dinitrogen oxide as an intermediate product of nitrate reduction on Pd-Cu bimetallic catalysts. The absence of dinitrogen oxide in gas phase in the present case could be explained either by the change of bimetallic catalyst or by the high solubility of N₂O in water, which is 40 to 45 times higher than those of N₂ and H₂, or by amount of formed dinitrogen oxide below the detection limits of GC analysis.

2.4. Results and discussion

2.4.1. 1 wt.% Cu/Al₂O₃ catalysts

At first 1% Cu/Al₂O₃ catalysts were prepared as described in the experimental part but were reduced *ex-situ* and stocked several days under air before the reaction test in the presence of nitrate or nitrite and hydrogen. In 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 it is proved by the TPR profile presented Figure 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 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 on Figure 3. Although the amount of copper was sufficient, nitrate were not totally converted, copper being rapidly passivated by CuO or Cu₂O formation in water, occurring even in 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 following reactions :



2.4.2. 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 noticeably decreased to 26%. The same result is obtained after a “blank” reaction, in 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 the platinum accessibility modification during the reaction.

The nitrite evolution during the reaction is presented on Figure 4.

The initial reaction rate is approximately equal to 6.10^{-6} mol/min.gcat, which corresponds to a turnover frequency of $7.5.10^{-3}$ s⁻¹, calculated from the observed specific reaction rate and the fraction of exposed platinum atoms (26%). The selectivity towards NH₄⁺ is 2%. The apparent activation energy of this reaction, calculated from the Arrhenius plot (Figure 5) between 10 and 26°C, is equal to 45 ± 2.5 kJ.mol⁻¹, which is higher than the value found for 5 wt.% Pd/ γ -Al₂O₃ by Tacke and Vorlop (14).

2.4.3. 1 wt.% Pt-Cu/Al₂O₃ bimetallic catalysts

a- Characterization of CR and SI catalysts (atomic ratio $\frac{\text{Cu}}{\text{Pt}}$ of 1)

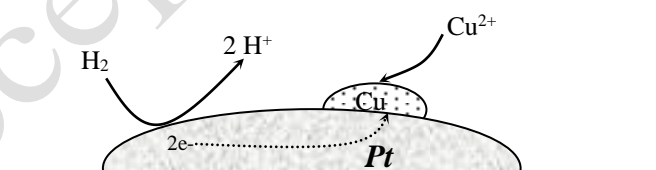
Temperature programmed reduction (TPR) profiles of fresh CR and SI are presented on Figure 2 and compared to those of corresponding monometallic catalysts. They were established after preparation and exposition to air at ambient temperature. In the case of CR catalyst, one can observe an important hydrogen uptake between 50 and 250 °C, with two maxima at about 115°C and 205°C followed by a lower hydrogen uptake, between 270 and 400°C. For SI catalyst, two hydrogen uptakes can be identified with maxima at 100°C 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 CR catalyst is significantly different and the first domain, with maxima at 115°C 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 on Figure 6, for a global $\frac{\text{Cu}}{\text{Pt}}$ atomic ratio equal to 1, corresponding to 50 at.% of copper. TEM pictures of these catalysts are shown on Figure 7.

- *CR catalyst*

The particle size of CR catalyst was determined from TEM pictures (Figure 7a) by means of histogram as illustrated on Figure 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 $25 \pm 2.5 \text{ \AA}$.

According to the preparation method, catalytic reduction favors the deposition of copper onto platinum particles. 80% 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 ($\frac{\text{Cu}}{\text{Pt}} = 1$), this indicates that the amount of deposited copper 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 bulk copper deposition on platinum under 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 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 compound (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 $\frac{\text{Cu}}{\text{Pt}}$ atomic ratio equal to 1 were recorded after adsorption of CO at a pressure of 10 torr following by an evacuation for 1 h at room temperature (Figure 9). The band at about 2055 cm^{-1} can be attributed to CO bonded to surface platinum atoms in the linear form (45), that proves that platinum surface remains accessible to gases in the bimetallic catalyst.

- *SI catalyst*

Contrary to CR catalyst, the particle composition of SI catalyst is very heterogeneous, the analyzed sample (Figure 6) being composed of copper or platinum monometallic particles and of either platinum-rich or copper-rich bimetallic particles. TEM analysis on this type of catalyst confirmed that samples are constituted 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.

b- 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

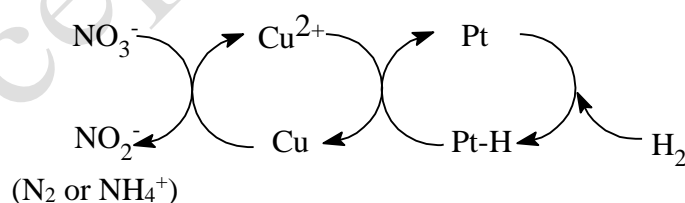
($\frac{\text{Cu}}{\text{Pt}} = 1$) is presented on Figure 10 a and b. Nitrite evolution is expressed as a function of nitrate conversion. The initial activities of CR and SI catalysts are reported in Table 2.

Higher activities being obtained with 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 converted into nitrites, these intermediates could be reduced either on the bimetallic particles or on platinum monometallic particles. Nitrite evolution vs. nitrate conversion is presented on Figure 5b. Whereas the curves are nearly similar, the maximum amount of nitrite present in solution is higher for SI catalyst ($0.53 \cdot 10^{-3}$ mol/L) than for CR catalyst ($0.43 \cdot 10^{-3}$ mol/L). This maximum is reached at about 80 percent nitrates 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 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 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. SI catalyst being constituted of mostly small monometallic platinum or copper particles, together with large bimetallic particles (see § 2-4-3), we can conclude that

the nitrite reduction occur principally on monometallic platinum sites on 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 J. 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 catalyst is 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 intermediate 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 regard to the nitrite intermediates, they can be reduced either on copper, according to the same redox process than the one 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

GeO₂ in solution as promoter. It was suggested that, in the presence of the noble metal and hydrogen, GeO₂ rapidly disappears from the solution and an intermetallic compound, Pd₂Ge, was identified by X-ray diffraction. The metallic state of germanium was very surprising since it is a non-precious-metal, which is thermodynamically unstable in the presence of water. However it was verified later by XPS that germanium, present in sub-monolayer 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.

c- Effect of $\frac{\text{Cu}}{\text{Pt}}$ atomic ratio

We varied the copper and the platinum amount in the catalyst to obtain an $\frac{\text{Cu}}{\text{Pt}}$ 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 on Figure 6. Irrespective of the preparation method, the best initial activity is obtained for $\frac{\text{Cu}}{\text{Pt}} = 1$ atomic ratio corresponding to 50 percent of copper in the metallic phase. This result is different from the one obtained by Hörold et al. (15) on palladium based catalysts who presented the better activity for $\frac{\text{Cu}}{\text{Pd}} = 0.42$ atomic ratio. 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 hypothesis, we prepared and tested different palladium-copper catalysts according to the experimental conditions described in the present study. Results are presented on Table 3 and compared with those obtained with Pt-Cu/Al₂O₃

catalysts containing the same molar amount of noble metal (about $1.5 \cdot 10^{-4}$ mole per 100 g of alumina). As we obtained the same optimal composition as Hörold 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 on 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 type of platinum-based catalysts (CR and SI), when $\frac{\text{Cu}}{\text{Pt}} > 1$, the activity decreases as copper content increases, to reach the activity of monometallic copper catalyst when 90 percent of copper is present in the metal phase. This can be explained by the low accessibility of platinum sites when copper amount is too important. The selectivity towards ammonium is increasing 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.

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 catalyst when both metals are in close contact. The catalytic reduction preparation method, consisting in 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 towards nitrogen.

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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 μm
Initial nitrate or nitrite concentration in the reactor	10^{-3} mol/L
Nitrate source	$\text{Mg}(\text{NO}_3)_2$
Nitrite source	$\text{Ba}(\text{NO}_2)_2$
Gas flow rate	180 mL/mn

Table 2 : Activity of CR and SI bimetallic and platinum monometallic catalysts for nitrate and nitrite reduction

Catalyst	Cu (wt.%)	Pt (wt.%)	$\frac{\text{Cu}}{\text{Pt}}$ (atomic ratio)	Activity* for nitrate reduction, (mol/min.g _{cat})	Selectivity (% of NH ₄ ⁺) for nitrate reduction
CR Pt-Cu/Al ₂ O ₃	0.25	0.75	1	11.10 ⁻⁶	5
SI Pt-Cu/Al ₂ O ₃	0.25	0.75	1	4.10 ⁻⁶	7
Pt/Al ₂ O ₃	0	0.75	0	0	-
Pt/Al ₂ O ₃	0	1	0	0	-

*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.....)

Table 3 : Activity for nitrate reduction of Pd-Cu/Al₂O₃ and Pt-Cu/Al₂O 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.%)	$\frac{\text{Cu}}{\text{Pd or Pt}}$ (atomic ratio)	Activity* 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

*absolute error $\pm 0.5.10^{-6}$ 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.....)

Figure captions

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

Figure 2 : TPR profile 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 (d) 1% Cu/Al₂O₃ (atomic ratio Cu/Pt of 1 in bimetallic catalysts)

Figure 3 : Nitrate evolution vs. time during nitrate reduction in the presence of 1 wt.% Cu/Al₂O₃ in the presence of hydrogen (●) or nitrogen (v) (p_{H₂ or N₂} = 1, gas flowrate = 180 mL/min, T = 10°C).

Figure 4 : Nitrite concentration vs. time during nitrite reduction in the presence of 1 wt.% Pt/Al₂O₃ (p_{H₂} = 1, gas flowrate = 180 mL/min, T = 10°C).

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

Figure 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)

Figure 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.

Figure 8 : Metal particle size distribution for CR catalyst (number of analyzed particles 665)

Figure 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.

Figure 10 : Nitrate concentration vs. time (a) and nitrite concentration vs. nitrate conversion X(NO₃⁻) (b) in the presence of 1 wt.% Pt-Cu/ Al₂O₃ (▲) CR catalyst (■) SI catalyst.

Figure 11 : Initial activity (—) and selectivity towards ammonium ions formation (-----) for nitrate reduction as a function of copper content in the metal phase (Cu/(Cu+Pt) at.%) for CR (▲) and SI (■) catalysts.

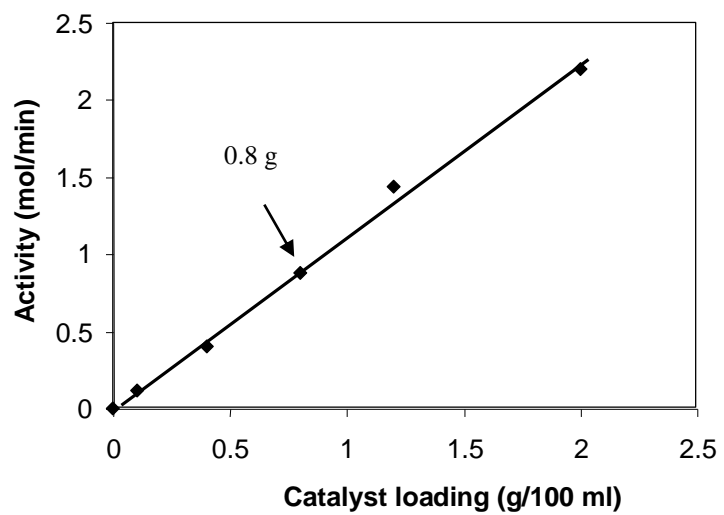


Figure 1

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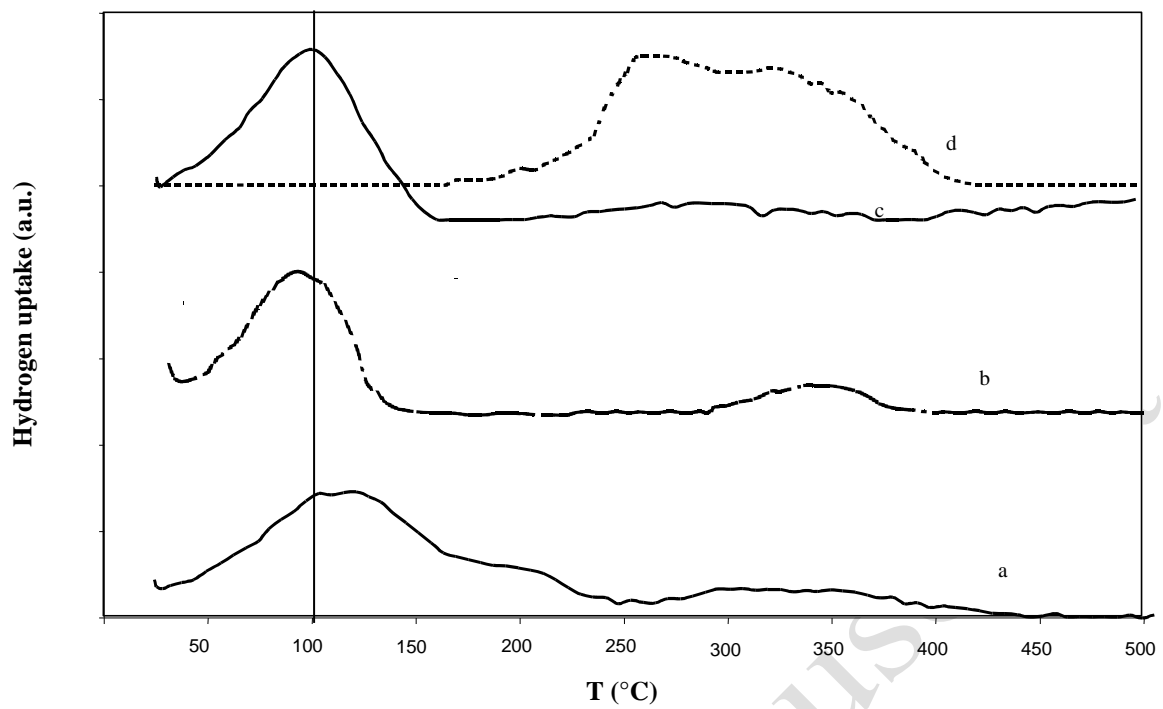


Figure 2

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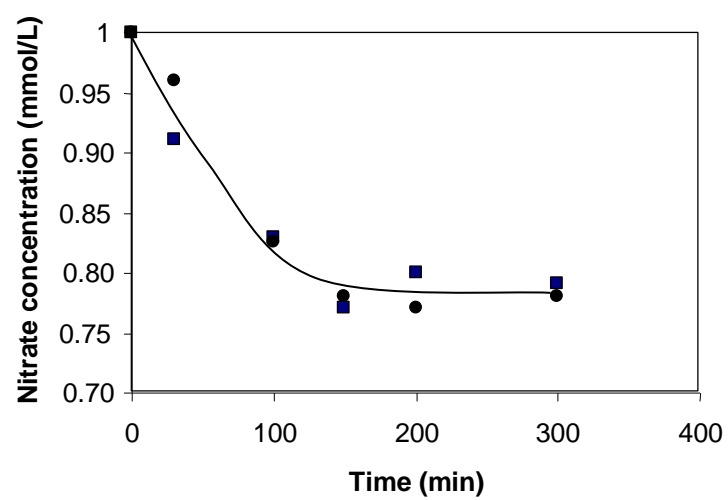


Figure 3

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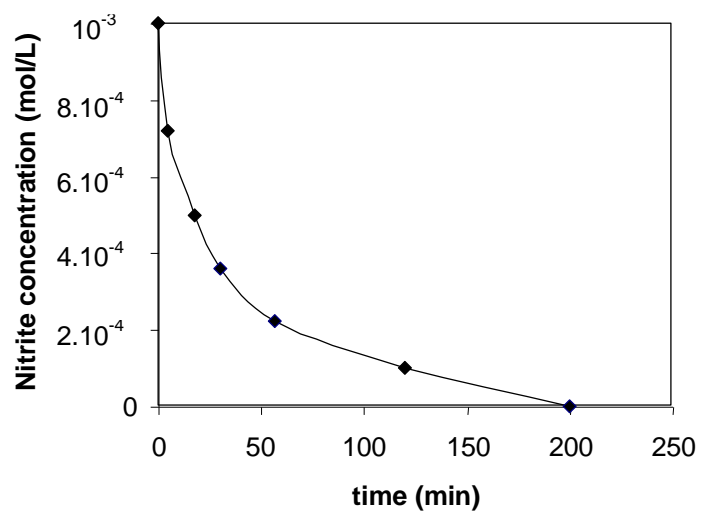


Figure 4

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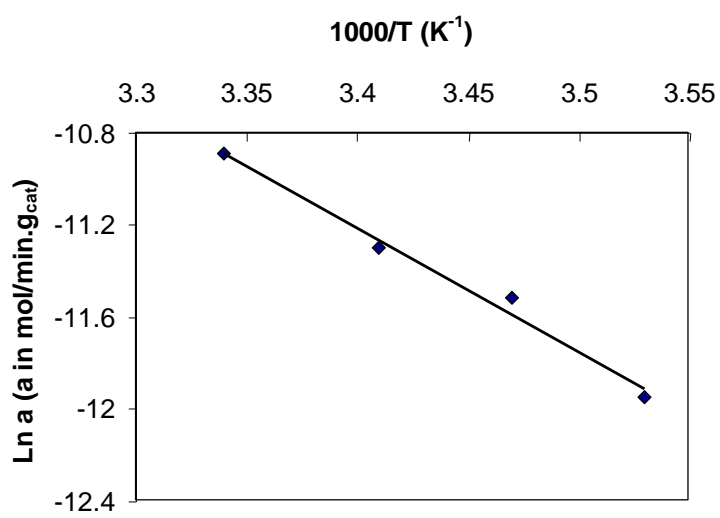


Figure 5

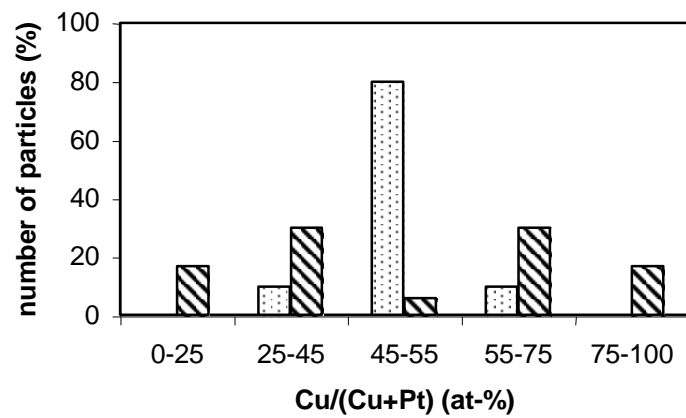


Figure 6

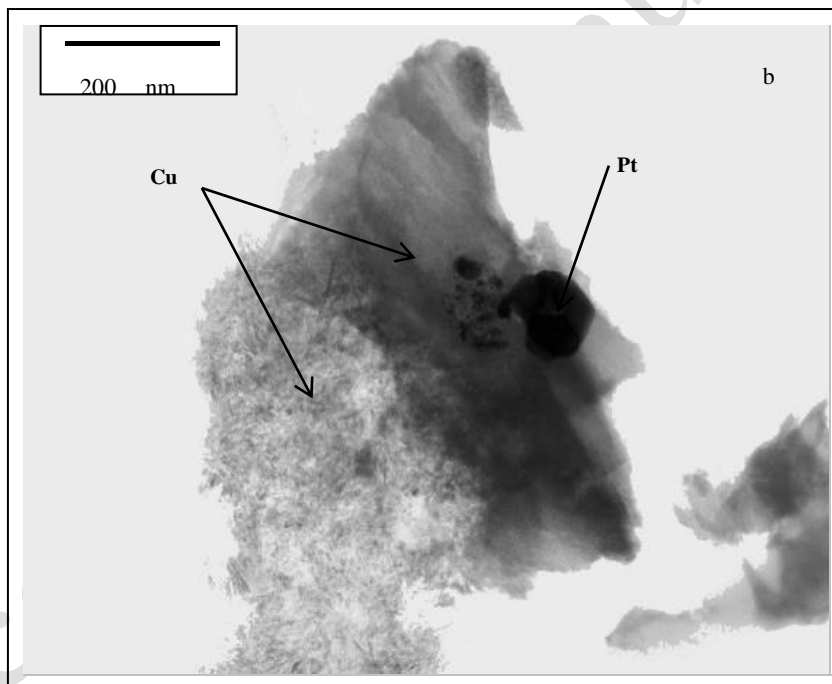
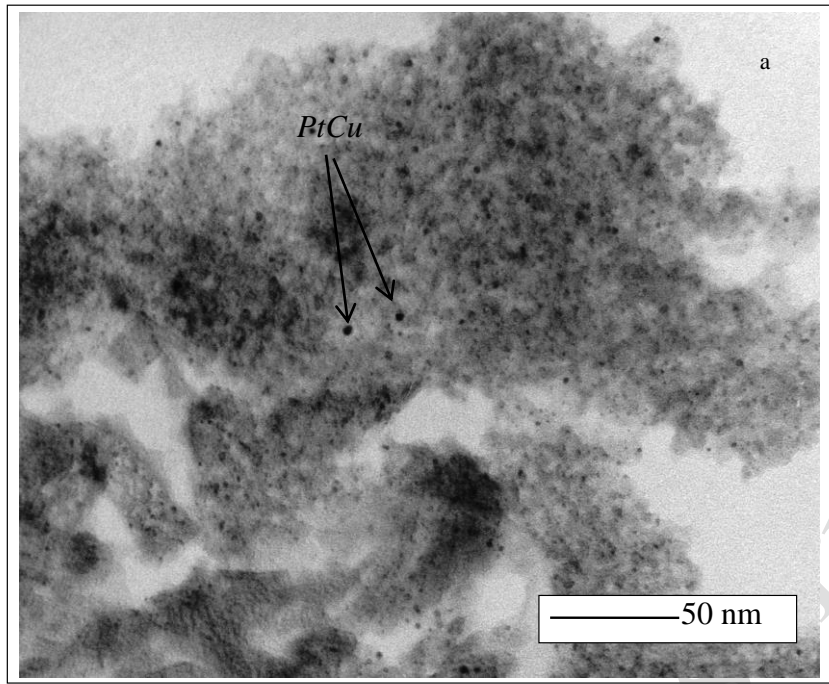


Figure 7 a and b

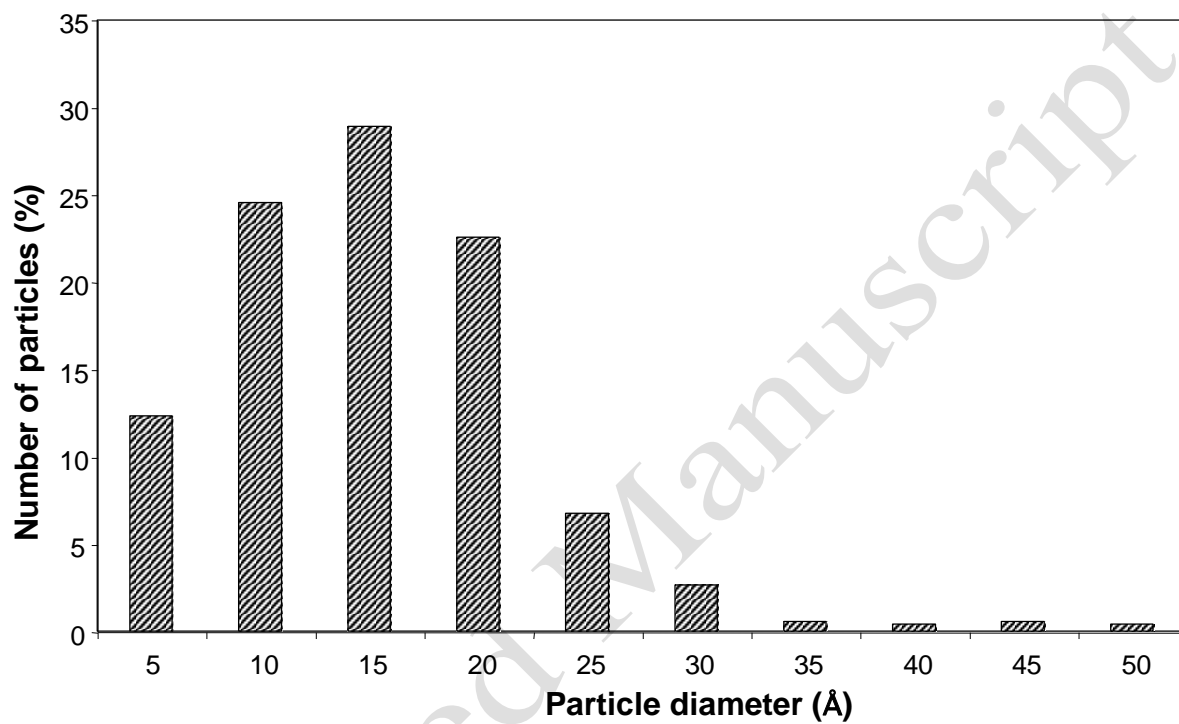


Figure 8

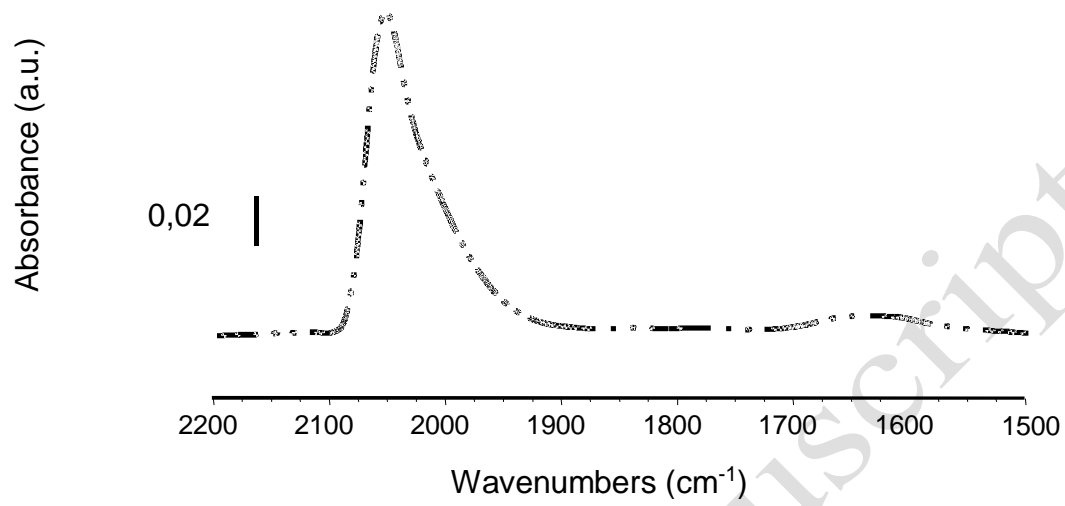


Figure 9

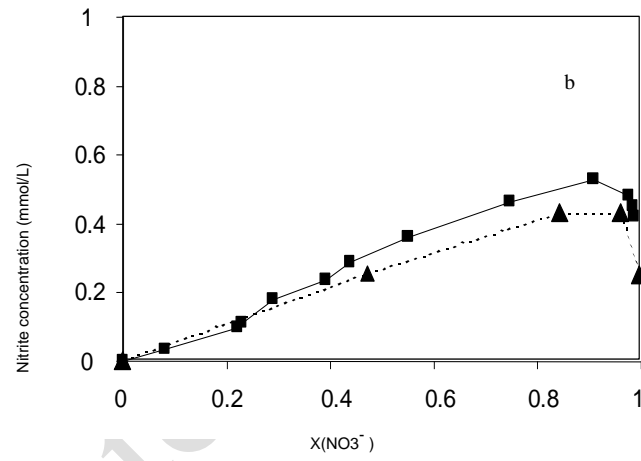
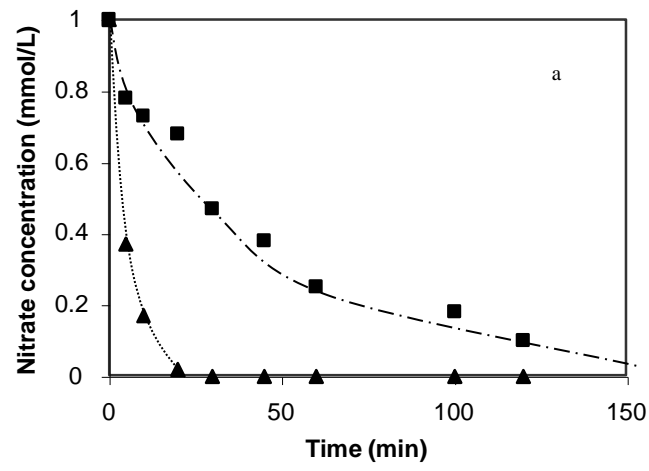


Figure 10a and b

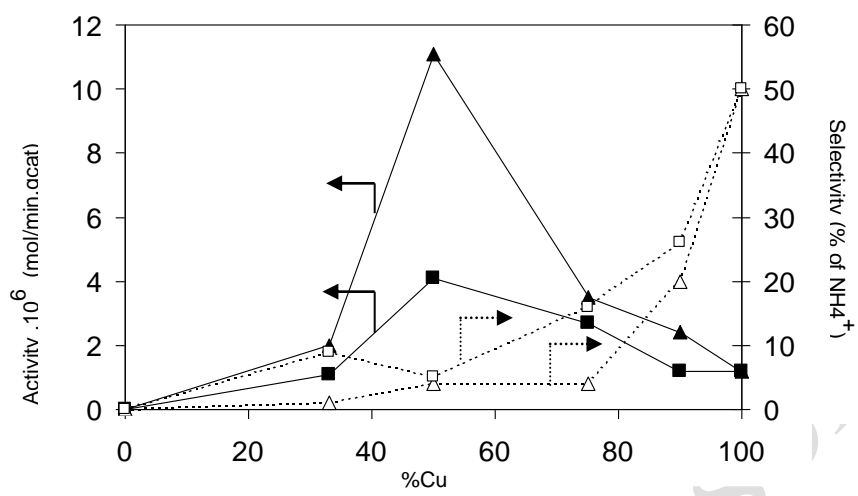


Figure 11