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The Influence of Metal-Support Interaction and the Quantity of Formic Acid on the Activity and the Selectivity of Pd–In/Support Catalyst for Nitrate Reduction in Water

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Pierre Gerard TCHIETA*, Charles MELEA KEDE

Bio-organic, Analytical and Structural Chemistry Laboratory, Faculty of Science, University of Douala; BP 24157 Douala, Cameroon

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ABSTRACT

The objective of this study is to prepare, characterize and test in catalytic reduction of nitrates and nitrites in aqueous medium of metal catalysts supported based on a noble metal promoted selective out of molecular nitrogen. The effective catalyst for this reduction is a bimetallic catalyst comprising a noble metal as the palladium (Pd) which is associated a metal promoter such as indium (In). We used the catalytic reduction method to prepare our catalysts. This type of catalyst deposited on various supports ceria, titania, alumina and silicia (CeO_2, TiO_2, Al_2O_3, SiO_2) was studied in order to identify the best support. The titania (TiO_2) support led to the best catalytic performances. The catalysts prepared were characterized by Temperature Programmed Reduction (TPR) and by nitrogen physical absorption Brunauer-Emmet-Teller (BET). The thermograms obtained for these various catalysts show a consumption of hydrogen at the beginning of the reaction, indicating that the reduction of palladium oxides begins at room temperature. The smallest BET area and the most significant size of the pores are obtained on supports titania (TiO_2), the nature of oxide thus exploits a significant role the catalyst reaction of reduction of nitrates in the water.

1. INTRODUCTION

The concentration of nitrate in the soil, and subsequently in ground and surface water has become a severe problem throughout the world. Nitrate converted to nitrite by microbes can lead to harmful effects on the human body, such as liver damage, cancers and blue baby syndrome Huang *et al*., (1998); Gavagnin *et al*., (2002). The maximum level of nitrate, nitrite and ammonium species recommended in drinking water by the World Health Organization (WHO) Sheffer *et al*., (2008) is of 44, 0.1 and 0.5 mg L^{-1}, respectively. The US Environmental Protection Agency (USEPA) has proposed 10 mg/L of nitrate as a guide level for dinking USEPA (2008).

There are different commercial techniques for removing nitrates from water such as reverse osmosis and electrodialysis. They are effective but they generate a polluted waste that should be treated or disposed of Kapoor *et al*., (1997). Several studies have demonstrated that monometallic catalysts are practically inactive for nitrate reduction and that some bimetallic catalysts are effective for this reaction Epron *et al*., (2001); Vorlop *et al*., (1989); Soares *et al*., (2008); Prusse *et al*., (2001); Pintar *et al*., (2003); Epron *et al*., (2002). However, monometallic Pd catalysts supported on SnO_2 Sheffer *et al*., (2008), CeO_2 Sá *et al*., (2005) and TiO_2 Horold *et al*., (1993), were reported as showing some activity for nitrate reduction. Previous studies have shown that the best catalysts for nitrate reduction in water are bimetallic systems based on Pd modified by Cu, In and Sn Epron *et al*., (2002); Kima *et al*., (2013); D'Arino *et al*., (2004); Prusse *et al*., (2000). Many others investigations have shown that the activity and selectivity are strongly influenced by several factors such as the reaction conditions, the catalysts preparation, the way the noble metal is promoted, and the catalyst support Aksoylu *et al*., (2000); Gauthard *et al*., (2003); Prusse *et al*., (1997); Soares *et al*., (2009); Yoshinaga *et al*., (2002); Garron *et al*., (2005). Many supports have been studied, such as alumina Gasparovicova *et al*., (2005); Palomares *et al*., (2010); Strukul *et al*., (2000), zirconia, titania and alumina membranes Lemaignen *et al*., (2002), activated carbon Prusse *et al*., (2001); Aksoylu *et al*., (2000); Gasparovicova *et al*., (2005); Sá *et al*., (2008), SnO_2 Epron *et al*., (2002); Gao *et al*., (2003), TiO_2 Horold *et al*., (1993); Garron *et al*., (2005); Sá *et al*., (2008); Gao *et al*., (2003), ceria Gavagnin *et al*., (2002), SiO_2 Palomares *et al*., (2003), hydrotalcite Wan *et al*., (2009), and γ–Al_2O_3 Yun *et al*., (2016), and it has been demonstrated that the different supports significantly affect the activity and selectivity of the catalysts for the nitrate reduction.

The reduction of nitrate produced an important quantity of ammonium; this value is unacceptable for drinking water and induces a decrease of both the activity and the selectivity towards N_2 Calvo *et al.*, (2010); Garron *et al.*, (2005). Different strategies have been developed to control the pH, the most common being the addition of HCl, HCOOH or CO_2 in the reaction media Pintar *et al.*, (1998).

Our objective in this study is to investigate the influence of metal-support interaction and the quantity of formic acid on the activity and the selectivity of Pd–In/Support catalyst for nitrate reduction.

2. MATERIAL AND METHODS

2.1. Preparation of the catalysts

The $PdCl_2$ (Alfa Aesar), and In $(NO_3)_3$ (Aldrich) were used as received.

2.1.1. Preparation of the monometallic catalysts

The monometallic catalysts were prepared by impregnation using an aqueous solution of $PdCl_2$ in order to obtain a catalyst containing 5 wt.% of palladium (Pd5%/Support). The suspension of support in aqueous solution containing the palladium salt was stirred for 2 h at room temperature. Then water was evaporated and the catalyst was dried on a sand bath at 80 °C and in an oven at the same temperature overnight.

2.1.2. Preparation of the bimetallic catalysts

A bimetallic Pd–In/Support catalyst was prepared either by catalytic reduction method. The palladium catalyst (Pd5%/Support) was flushed with N_2 during 20 min then was flushed with H_2 (250 $mL.min^{-1}$) for 1 h at room temperature. It was shown by TPR that the palladium catalyst is completely reduced at room temperature under hydrogen. After that, a second metal solution ($In(NO_3)_3$) was added on the reduced catalyst. This deposition was performed under the same H_2 flow for about 2 h. Then, the suspension was filtered and dried at 80 °C overnight.

2.3. Catalyst characterization

2.3.1. BET

The textural properties were measured by adsorption of nitrogen at −196 ˚C, in a Micromeritics TriStar-3000 apparatus. The S_{BET} was calculated by the BET equation, micropore specific surface area were obtained using the t-plot method, pore volume (Vp) and pore size distribution were determined using the BJH model.

2.3.2. Temperature-Programmed Reduction (TPR)

Samples of 200 mg were first heated in dry argon for 30 min at 150 ˚C to eliminate traces of adsorbed water. After cooling to room temperature, argon was replaced by the reducing gas (1% H_2/Ar, 10 cm3/min) and the linear temperature program was started (5 ˚C/min). The hydrogen consumption was measured by a thermal conductivity detector and recorded as a function of the temperature. It was verified that the TPR profiles were completely reproducible. TPR peaks were characterized by the temperature corresponding to the maximum hydrogen consumption rate. The amount of hydrogen consumed was calculated from the area under the TPR curves.

2.4. Catalytic test

The reaction was carried out in a semi-batch reactor, at atmospheric pressure and 25 ˚C. The catalyst (64 mg) was pretreated under hydrogen flow (250 mL min^{-1} at 25 ◦C for 0.5 h). Then, pure water (90 mL) was purged with nitrogen and added over the catalyst and then placed under hydrogen flow. Afterward, 10 mL of a degassed nitrate solution (1.6×10^{-2} mol L^{-1}) was introduced in the reactor to start the reaction. The catalyst dispersion in the aqueous medium was achieved by the hydrogen flow, introduced through a porous glass located at the bottom of the reactor with a flow rate of 250 mL min^{-1}. It was checked by using the criteria described in Garron *et al*., (2005) that the chosen reactions conditions avoid any limitation by interphase mass-transfer resistances. Representative aqueous samples were periodically withdrawn and analyzed by high performance liquid chromatography.

Nitrate and nitrite were determined after separation on a C18 column using an UV detector at = 210 nm. Ammonium ions were quantified using an Alltech Universal Cation column coupled with a conductivity detector. The acidic mobile phase (oxalic acid) used provided the complete conversion of the ammonia basic form into ammonium ions. Nitrogen was deduced by mass balance, taking into account the sum of all nitrogen-containing products Tchieta *et al*(2017).

3. RESULTS AND DISCUSSION

3.1. Characterisation

3.1.1. Specific surface area and porosity

The physisorption isotherms obtained by the discontinuous volumetric technique on the Pd-In catalysts supported on alumina, titanium dioxide, silica and cerine and the exploitations derived there from (BET and BJH transformation) give the specific surfaces as well as the size of Pores presented in the table below.

Table 1: B.E.T areas and pore size of catalyst 5% Pd-1.75% in on various supports.

Supports	B.E.T Area (m2 / g)	Pore size (Å)
Al_2O_3	190	91
SiO_2	130	188
TiO_2	32	301
CeO_2	50	92

The result of table 1 indicates that the catalyst on an alumina support has the largest BET area, but the smallest pore size; In view of these results and according to the literature, alumina should exhibit the best activity. The average pore size of the silica support should lead to better molecular nitrogen selectivity. Indeed, it has been demonstrated by Hörold *et al*. that the silica support leads to a lower catalyst activity, but a better selectivity than alumina and that on a charcoal support, the catalyst deactivates. Moreover, a correlation between the B.E.T area of the support and the activity and, on the other hand, between the size of the pores and the selectivity was demonstrated.

The results are different from those of the literature, because the support which exhibits the best activity and the best selectivity for nitrogen is the titanium dioxide support TiO_2. This leads us to conclude that a support which has a small surface area and a large pore size can lead to good catalytic performances and therefore that the nature of the oxide plays a more important role on the behavior of the catalyst in reduction of Nitrates than its structural properties.

3.1.2. Temperature Programmed Reduction (TPR)

TPR is used to determine the reducibility of a catalyst as well as the degree of oxidation of the active phase.

This experiment consists in monitoring the hydrogen consumption as a function of temperature. Due to its great sensitivity to the chemical modifications introduced by the promoter or the support, it is a particularly attractive method for studying the active phase-support or active dopant-phase interactions.

In addition, it is a means of determining the alloy phases in bimetallic catalysts. For this, it is necessary to first determine the reduction curves for each monometallic catalyst and then examine those of the bimetallic catalysts.

Metal-metal interactions have been shown to play a major role in the activity of the bimetallic Pt-Cu / γ Al_2O_3 catalyst for nitrate reduction Vorlop *et al*., (1999); Prusse *et al*., (1997). Indeed, a catalyst prepared by catalytic reduction where the interactions are promoted is much more active than a catalyst prepared by successive impregnations where the interactions are not controlled.

- Monometallic catalysts

Initially, we determined the reduction curves of the monometallic catalysts having the same metal percentage of the precursor salt (5%Pd). The three monometallic catalysts characterized are the following: 5% Pd / γ Al_2O_3, 5% Pd / TiO_2, 5% Pd / SiO_2, 5% Pd / CeO_2.

Before the characterization by RTP, the samples are subjected to oxidation under oxygen at 450°C. The thermograms(FIG$_1$, FIG$_2$, FIG$_3$, FIG$_4$) obtained for these various catalysts show a consumption of hydrogen at the beginning of the RTP, Indicating that the reduction of palladium oxides begins at room temperature. However, this low temperature consumption can also be related to the formation of hydrides Yoshinaga *et al*., (2002); Gao *et al*., (2003). For the catalyst supported on TiO_2, there is also a reduction peak which begins at about 450°C. and which can be attributed to the reduction of titanium dioxide in contact with palladium.

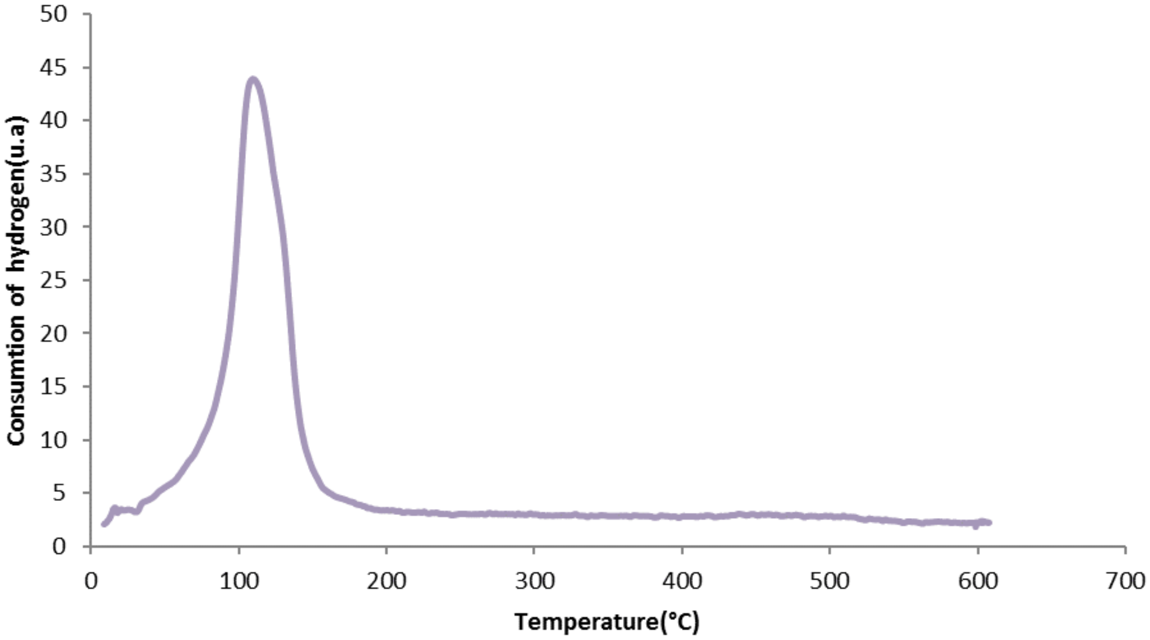

FIG.1: Thermogram of monometallic catalyst 5% Pd / Al_2O_3 (mcat = 50mg, rise in temperature = 5°C / min)

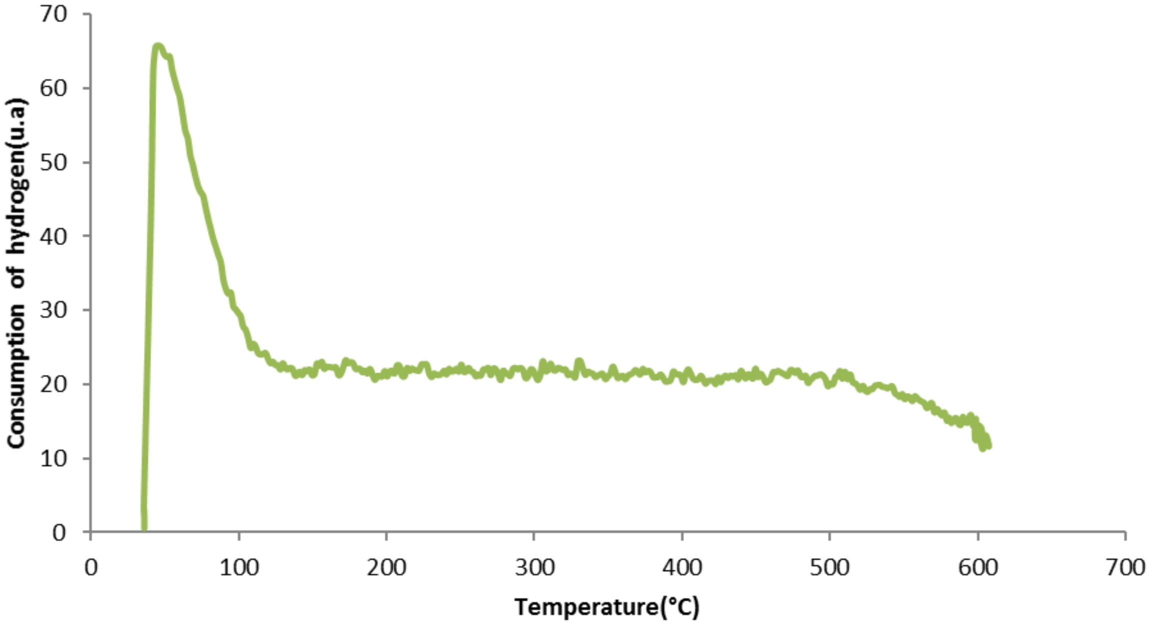

FIG. 2: Thermogram of the monometallic catalyst 5% Pd / SiO_2 (m_{cat} = 50 mg, rise in temperature = 5 °C/min)

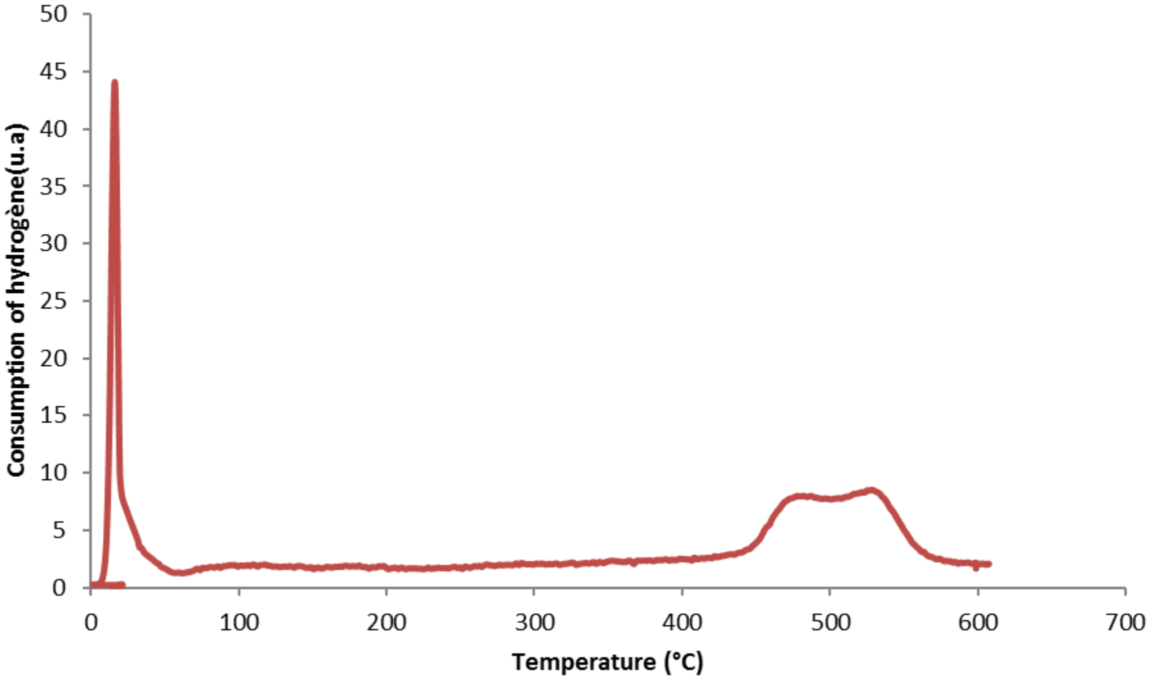

FIG. 3: Thermogram of the monometallic catalyst of 5% Pd / TiO_2 (m_{cat} = 50 mg, rise in temperature = 5°C./min)

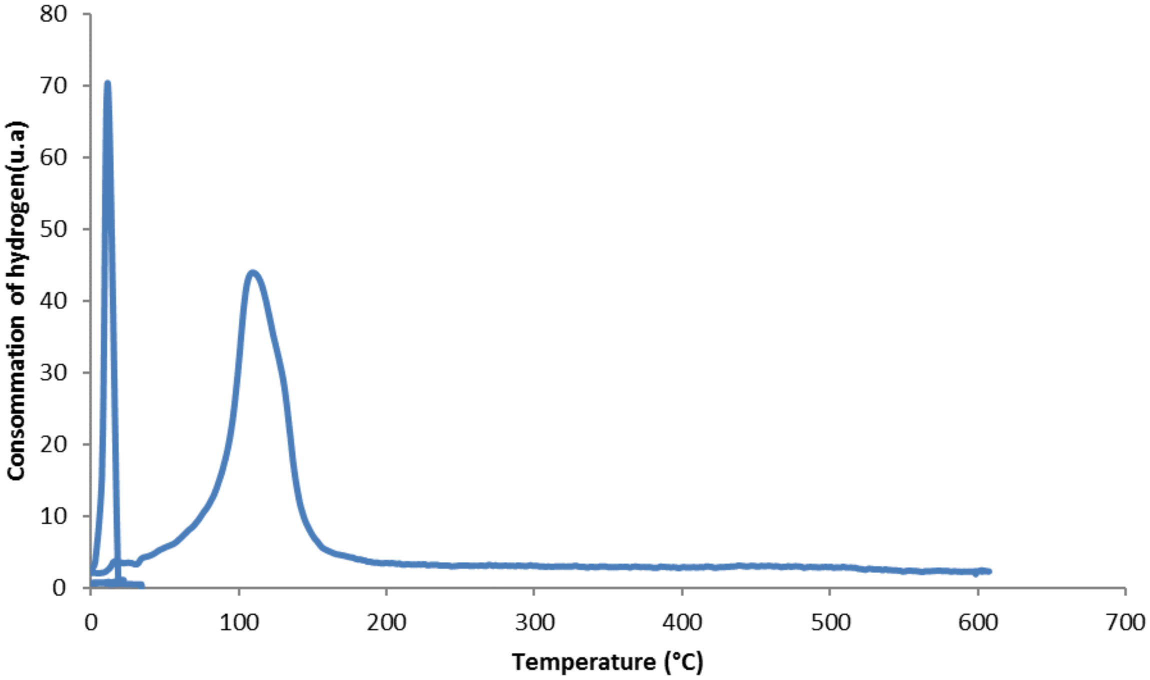

FIG. 4: Thermogram of the monometallic catalyst 5% Pd / CeO_2 (m_{cat} = 50 mg, rise in temperature = 5 ° C./min)

The following table shows the amount of hydrogen consumed by each monometallic catalyst; it gives the amount of hydrogen consumed in moles per gram of catalyst, in moles per gram of palladium and in moles per mole of palladium.

Table 2 : Amount of hydrogen consumed in mole per gram of catalyst, in moles per gram of palladium and in moles per mole of palladium as a function of the support.

Amount of H_2 Support	**Amount of hydrogen en µmol /g_{cat}**	**Amount of hydrogen** In **mol /g_{Pd}**	**Amount of hydrogen** In **mol /mol_{Pd}**
TiO_2	763	0,08	13,7
SiO_2	946	2,00	11,9
Al_2O_3	991	2,10	1,3
CeO2	1123	2,40	6,9

Table 2, it can be seen that the hydrogen consumption per gram of catalyst is higher on ceria support, as is the hydrogen consumption per gram of palladium. These results seem to justify the low activity of the catalyst obtained on the supports ceria and alumina for an initial concentration of weak formic acid.

3.2. Influence of the support

3.2.1. Catalytic reduction of nitrates under standard conditions

Bimetallic catalysts 5% Pd-1.75% In / support (support = Al_2O_3, SiO_2, TiO_2, CeO_2) were prepared by the catalytic reduction method. These catalysts were then tested under the standard nitrate reduction conditions in the presence of formic acid.

The following curves represent the results obtained during the reduction of the nitrates on these various supports

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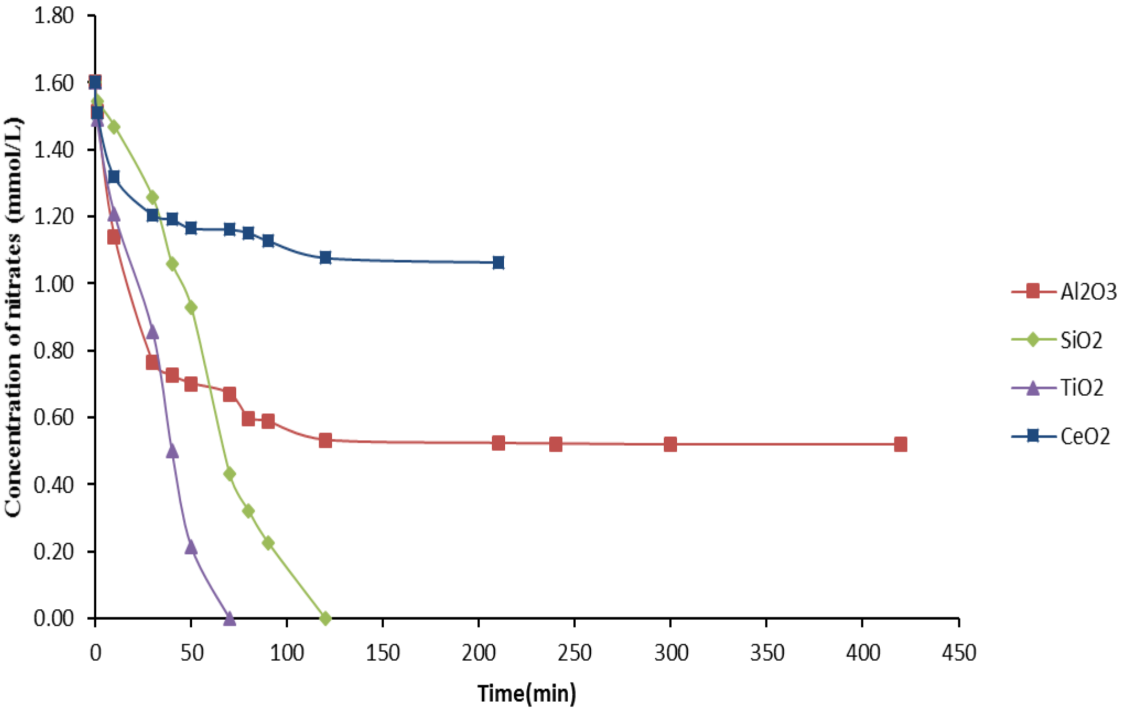

FIG. 5: Reduction of the nitrates for the catalysts 5% Pd-1.75% In according to the nature of the support used.

FIG. 5 shows that the total conversion of the nitrates is possible only for the supports TiO_2 and SiO_2. For the other two carriers, a maximum conversion is reached rapidly, after about 120 minutes. This maximum conversion is 67% on the alumina support and 32% on the cerium support.

During the reduction of the nitrates not only nitrates are formed but also intermediate nitrite ions and undesirable ammonium ions; Moreover, the level of nitrite ions formed is very negligible for the supports TiO_2 and SiO_2; This is explained by the speed of reduction of the nitrites probably very fast for these supports.

FIGS. 6 and 7 show the experimental curves of formation of nitrite ions and ammonium ions for these different supports.

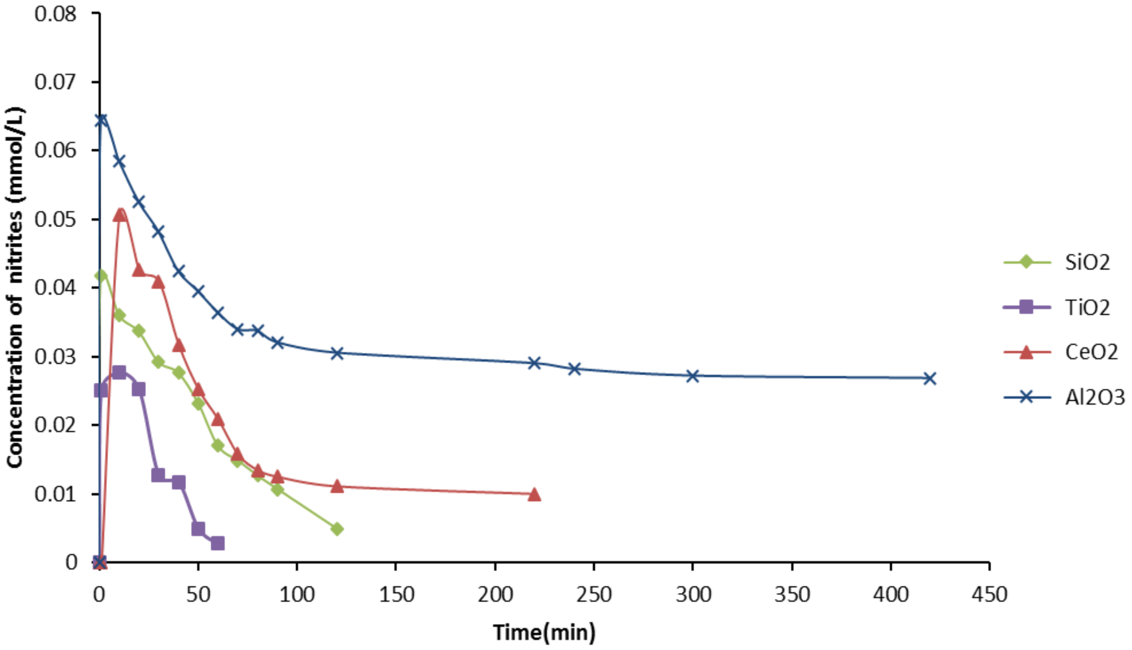

FIG. 6: Experimental curves of formation of nitrite ions during the reduction of the nitrates for the catalysts 5% Pd-1.75% In according to the nature of the support used.

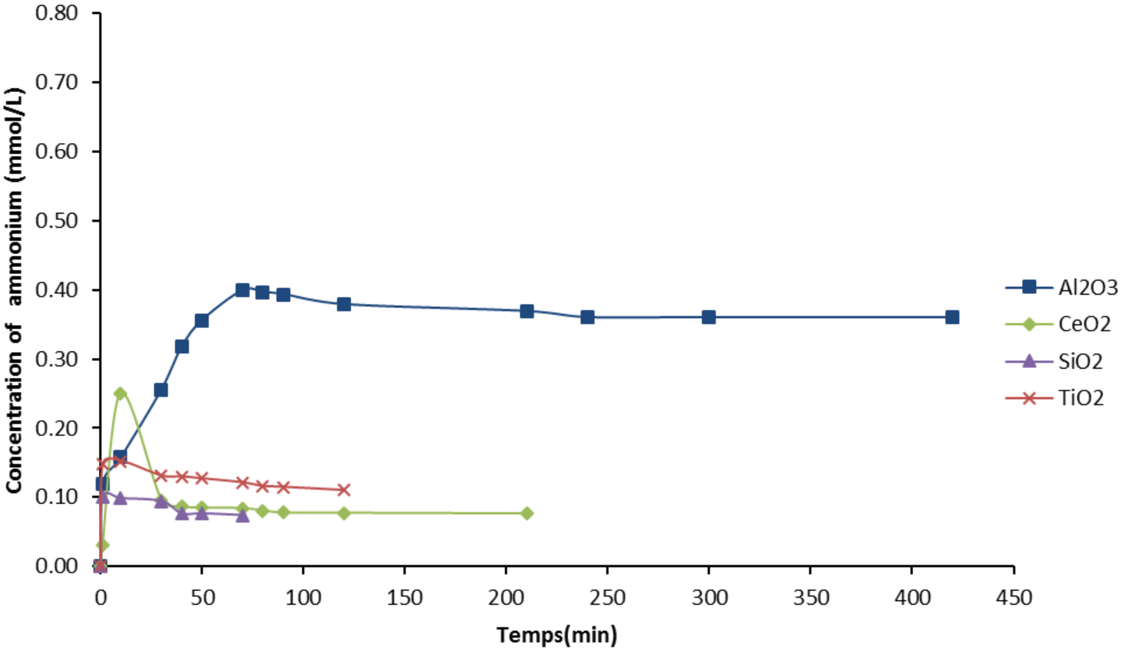

FIG. 7: Experimental curves of formation of ammonium ions during the reduction of the nitrates for the catalysts 5% Pd-1.75% In according to the nature of the support used.

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The results reported in the table below group nitrate reduction activities, ammonium ion selectivity and conversion rate.

Table 3: Properties of the Pd-In bimetallic catalysts with respect to the reduction of the nitrates according to the nature of the support.

Name of catalyst	**Global Activity A(mmol.min^{-1}.g$_{cat}$$^{-1}$)**	**Selectivity to ammonium ions (%)**	**Duration of reaction(min)**	**Conversion rate (%)**
5%Pd-1,75%In/SiO_2	0,0211	6	120	100
5%Pd-1,75%In/TiO_2	0,0422	5	60	100
5%Pd-1,75%In/Al_2O_3	0,0040	29*	420	67
5%Pd-1,75%In/CeO_2	0,0029	12*	220	32

* Selectivity determined at maximum conversion reached

According to the table 3 above, the activity and the selectivity according to the support can be classified in the following order:

Activity: $TiO_2 > SiO_2 > Al_2O_3 > CeO_2$

Selectivity to ammonium ions: $Al_2O_3 > CeO_2 > SiO_2 > TiO_2$

The support which gives the best results in terms of activity and nitrogen selectivity for the reduction of nitrates is the TiO_2 support. This could be explained by the reducibility of this support which intervenes in the reaction. However, the ceria support is also reducible and yet leads to much less performance.

In addition, the most important selectivity of ammonium ions is obtained on Al_2O_3 support; those linked to the SiO_2 and TiO_2 supports are close.

For the ceria and alumina supports, the total conversion was not achieved. This phenomenon could be explained by deactivation of the catalyst during the reaction. However, no deactivation was observed by Garron et *al*(2005) for bimetallic catalysts supported on alumina and tested under similar conditions. The low conversion achieved could also be due to an insufficient amount of formic acid in the medium, and thus of a reducing agent, so that the conversion is complete. This is why we carried out the same experiments with an initial quantity of formic acid 4 times greater. The results are reported in the next paragraph.

3.2.2. Catalytic reduction of nitrates in the presence of a large amount of formic acid

Pd-In catalysts on different supports were compared when reducing nitrates in the presence of a large amount of formic acid, ie 32 mmol/L, instead of 8 mmol / L under standard conditions.

The table below summarizes the different concentrations of the nitrate ions obtained during the reaction and the concentrations of the nitrite ions and the ammonium ions formed over time as a function of the support and of the high concentration of formic acid.

The results obtained during the reduction of the nitrates in the presence of the Pd-In catalysts on the various supports are shown in FIG. 8.

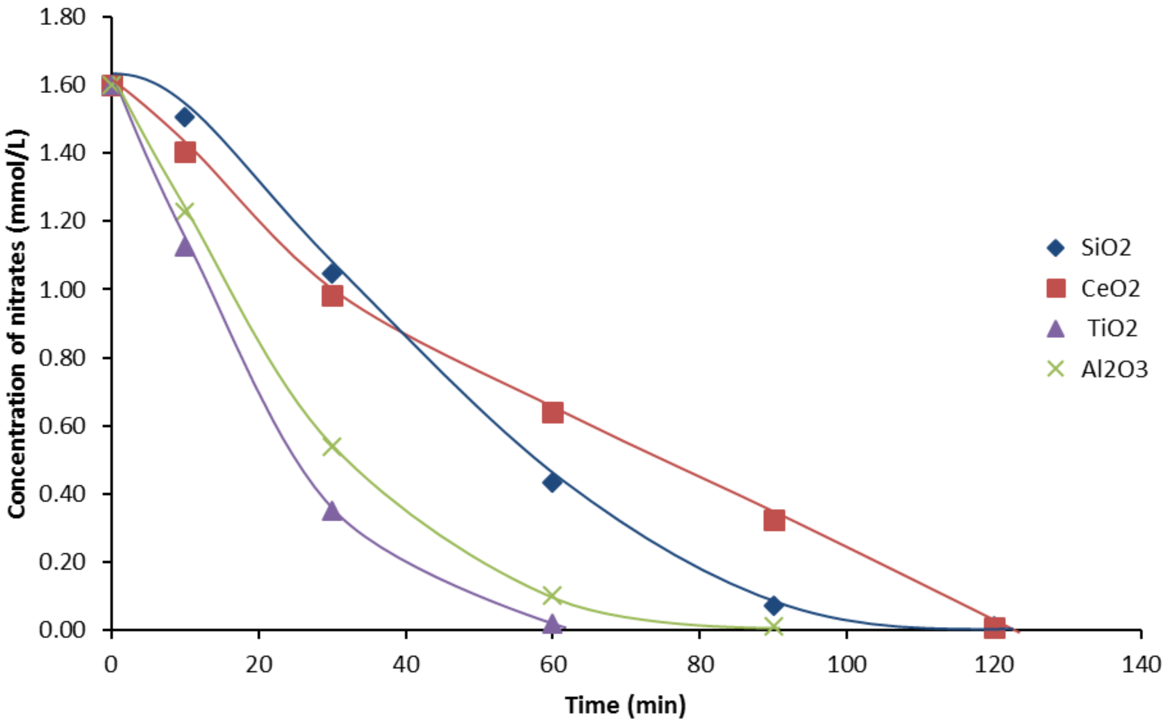

FIG. 8: Experimental nitrate reduction curves for catalysts 5% Pd-1.75% In depending on the different supports ([HCOOH] = 32 mmol / L)

Each catalyst used to carry out this nitrate reduction reaction produces intermediate nitrites whose maximum amount observed in solution depends on the support (FIG. 9).

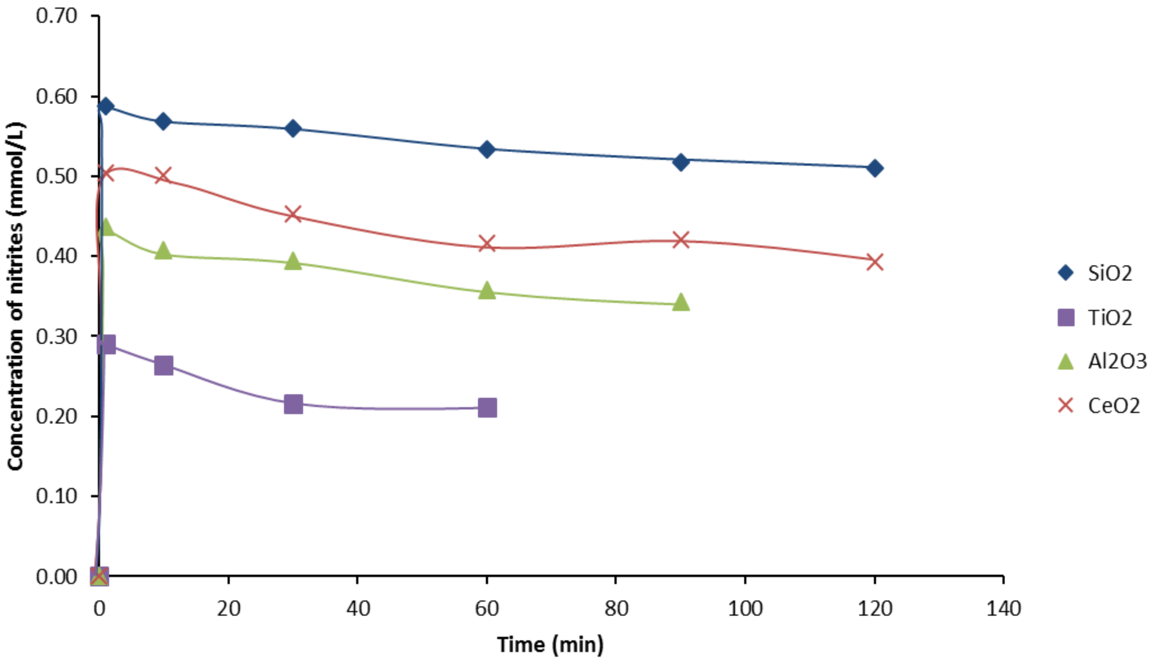

FIG. 9: Curves of formation of the nitrite ions for the bimetallic catalysts 5% Pd-1.75% In on various supports.

Ammonium ions are also formed during the reaction; the results are shown in FIG. 10.

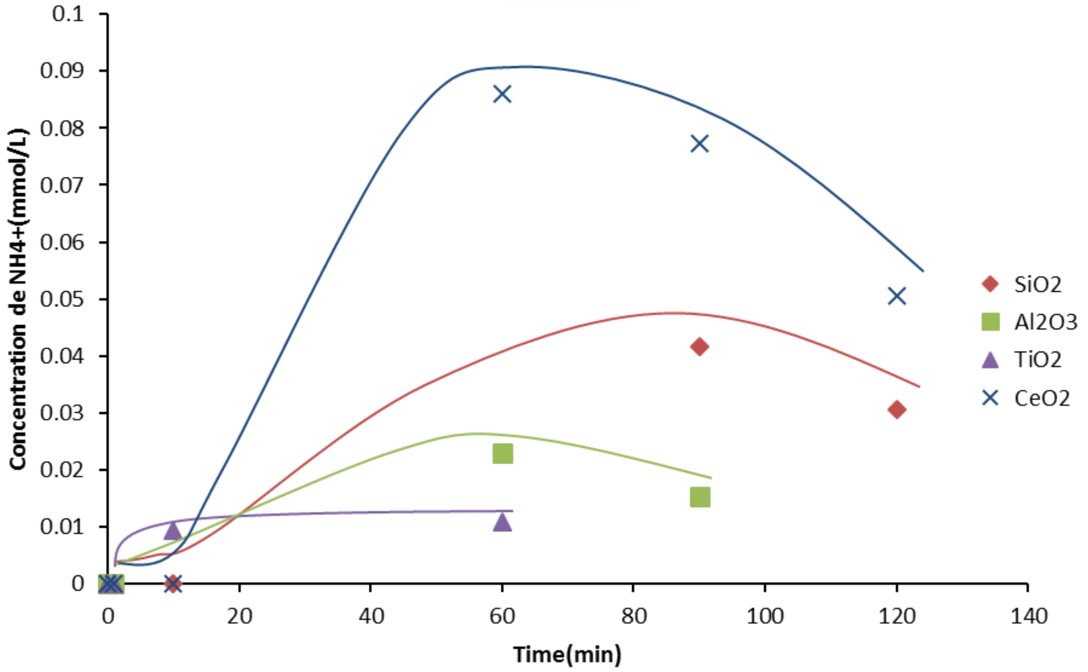

FIG. 10: Ammonium ion formation curves for bimetallic catalysts 5% Pd-1.75% In on various supports.

The results reported in the table 4 together the activity and the selectivity for ammonium ions.

Table 4: Catalytic properties of bimetallic catalysts with respect to the reduction of nitrates as a function of the support

Name of catalyst	Global activity A (mmol.min^{-1}.g$_{cat}$$^{-1}$)	Selectivities in ammonium ions (%)	Duration of reaction (min)	Conversion rate	Final pH
5%Pd-1,75%In/SiO_2	0,0211	2,62	120	(>99%)	2,73
5%Pd-1,75%In/TiO_2	0,0422	0,48	60	(>99%)	2,73
5%Pd-1,75%In/Al_2O_3	0,0277	1,69	90	(>99%)	3,05
5%Pd-1,75%In/CeO_2	0,0207	5,59	120	(>99%)	3,51

Contrary to what has been observed previously (table 3) in the presence of four times less amount of formic acid, a total conversion is reached this time regardless of the support used. The low conversion previously achieved with the alumina and ceria supports was due to a lack of reducing agent in the medium so that the reduction of the nitrates is total. On the other hand, it is found that the overall activity of the catalysts on silica supports and titanium dioxide has not been modified with respect to the previous experiment.

The activity of the catalyst on an alumina support has increased considerably, a conversion is observed above 99%, for an ammonium ion selectivity of 1.69%. The exaltation of the activity of the catalyst on support Ceria is the most important. We note a considerable decrease in the selectivity of ammonium ions for this support.

We also notice the large formation of intermediate nitrites at the beginning of the reaction. On the other hand, in all cases, the selectivity to ammonium is considerably lower, and consequently, the selectivity to nitrogen is markedly improved in the presence of a large amount of formic acid, whatever the support. This can be explained by the formation of greater amounts of carbon dioxide during the decomposition of the formic acid, which makes it possible to buffer the medium at a pH of the order of 3. It is known that values of pH of the order of 3-4 make it possible to limit the formation of ammonium ions.

These results are in agreement with the results of Prüss *et al.*(2000) who found that for the Pd-Sn / Al_2O_3 catalyst system the same pH influence was observed as for the Pd-Cu system, that is to say that A decrease in activity and an increase in selectivity towards $NH_4{}^+$ are always related to the increase in pH, and vice versa. The use of hydrogen as a reducing agent without pH control, i.e. without addition of acid to the medium, results in the formation of hydroxide ions which strongly absorb and block the active sites. To this problem, formic acid would be the solution.

Under these experimental conditions, that is to say for an initial concentration of formic acid equal to 32 mmol/L, the effectiveness of the support in terms of activity follows the following order: $TiO_2 > Al_2O_3 > SiO_2 > CeO_2$

The selectivity for ammonium ions is as follows: $TiO_2 < Al_2O_3 < SiO_2 < CeO_2$

The TiO_2 support, as in the preceding conditions, exhibits the best activity and the best selectivity to nitrogen, with selectivity close to 0% in ammonium ions. The SiO_2 support also leads to good results.

These results confirm that the activity and the selectivity depend strongly on the amount of formic acid in solution.

4. CONCLUSION

At the end of this work, we can conclude that the metal-carrier interactions as well as the quantity of the reducing agent (HCOOH) play an essential role in the reduction of nitrates and nitrites in an aqueous medium. The nitrogen selectivity is also influenced by these parameters.

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