

## RESEARCH NOTE

Catalytic Reduction of Nitrate in Water on a Monometallic Pd/CeO<sub>2</sub> CatalystFlorence Epron,<sup>1</sup> Florence Gauthard, and Jacques Barbier*Laboratoire de Catalyse en Chimie Organique (UMR6503), CNRS—Université de Poitiers, 40, Avenue du Recteur Pineau, 86022 Poitiers Cedex, France*

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Whereas monometallic palladium catalysts deposited on classical supports such as silica, alumina, or carbon are totally inactive for nitrate reduction, we have demonstrated that a reduced Pd/CeO<sub>2</sub> catalyst is active for this reaction (33 mmol/(min g<sub>met</sub>)). The promoting effect of the support, based on its redox properties, was clearly identified, nitrate reduction probably occurring through the interaction of oxygen atoms of nitrate with the oxygen vacancies created at the ceria surface upon the reduction treatment. Conversely, nitrite intermediates are converted through a classical catalytic reaction by hydrogen adsorbed on palladium sites. © 2002 Elsevier Science (USA)

**Key Words:** nitrate; nitrite; Pd/CeO<sub>2</sub> catalyst; catalytic reduction.

## 1. INTRODUCTION

Catalytic reduction was developed at the end of the 1980s to decrease excessive nitrate concentration in drinking water (1). It was demonstrated that nitrites are reduced by hydrogen on various hydrogenation catalysts, like palladium or platinum supported on alumina, whereas these catalysts are inactive for nitrate reduction. To reduce nitrates, it is necessary to activate the precious metal by addition of a promoter. Bimetallic palladium–copper catalysts were the most investigated active catalysts for nitrate reduction (1–13). Recently, we studied the activity of Pt–Cu/Al<sub>2</sub>O<sub>3</sub> bimetallic catalysts and determined the role of the interaction between copper and platinum in the reaction (14). These catalysts were prepared by depositing copper on a parent monometallic catalyst, using two different techniques favoring the deposition of copper either on the parent metal or on the support. We demonstrated that nitrates are totally and rapidly reduced when both metals, platinum and copper, 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. With regards to the nitrite intermediates, they can be reduced either by redox reaction on copper or by catalytic reduction on the precious metal (14). According to this model, any catalyst associating a noble metal able to chemisorb hydrogen and a component with a redox behavior could catalyze nitrate reduction.

Cerium based catalysts have been extensively studied for the catalytic control of automotive exhaust. Various promoting effects, mainly related to the Ce<sup>4+</sup>/Ce<sup>3+</sup> redox couple, were examined, such as (i) oxygen storage capacity (OSC) (15), (ii) stabilization of noble metal dispersion (16), or (iii) selective catalytic reduction (SCR) of NO (17, 18). In this article, we report the activity of monometallic catalysts toward nitrate reduction when CeO<sub>2</sub> is utilized as support.

## 2. EXPERIMENTAL

## 2.1. Catalysts

**2.1.1. Preparation.** The support was a Ceria (Rhodia) with a specific surface area (BET method) of 200 m<sup>2</sup>/g, an isoelectric point at pH 6, and a particle size between 10 and 40 μm. This size is sufficiently low to work in the chemical regime (10). Palladium was deposited by impregnation of the ceria support with a Tetraammine Palladium (II) Nitrate solution (Pd(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>). Samples were dried at 393 K for 12 h and calcined in flowing air (60 cm<sup>3</sup> min<sup>-1</sup>) at 673 K for 4 h. A Pd/γ-Al<sub>2</sub>O<sub>3</sub> catalyst was prepared in the same way. Characteristics of the alumina support are reported in Ref. (14).

**2.1.2. Characterization.** Palladium dispersion was determined by hydrogen chemisorption, in a pulsed chromatographic reactor. Samples of about 200 mg were reduced at 400°C under flowing hydrogen (30 ml min<sup>-1</sup>) for 1 h and outgased under flowing argon (30 ml min<sup>-1</sup>) at the same temperature for 3 h. Samples were finally cooled

<sup>1</sup> To whom correspondence should be addressed. E-mail: [florence.epron.cognet@univ-poitiers.fr](mailto:florence.epron.cognet@univ-poitiers.fr).

under argon to the adsorption temperature. To prevent hydrogen spillover on ceria-containing supports, measurements were carried out at  $-85^{\circ}\text{C}$ . This optimized method was first described by Madier (19). Pulses of hydrogen are injected until full saturation of the sample. The amount of hydrogen consumed in this way corresponds to the total hydrogen (reversibly and irreversibly 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.

## 2.2. Reaction

The reactions were carried out in a 250-ml batch reactor at  $25^{\circ}\text{C}$ . In a typical experiment, the catalyst (200 mg) was introduced in the reactor and reduced at  $300^{\circ}\text{C}$  for 1 h under pure hydrogen, flowing at a rate of  $250\text{ ml min}^{-1}$ . Ninety milliliters of ultrapure water with predissolved hydrogen was then added. Ultrapure water ( $18.2\text{ M}\Omega$ ) was obtained by a Millipore purifying system. The catalyst dispersion in the aqueous medium was achieved by the hydrogen flow ( $p_{\text{H}_2} = 1\text{ bar}$ , flowrate =  $250\text{ ml min}^{-1}$ ) or by a flowing  $\text{H}_2/\text{CO}_2$  mixture ( $p_{\text{H}_2} = 0.5\text{ bar}$ ,  $p_{\text{CO}_2} = 0.5\text{ bar}$ , total flowrate =  $250\text{ ml min}^{-1}$ ) through a porous glass located at the bottom of the reactor. This hydrogen flow and the resulting stirring were sufficient to ensure that a complete saturation of the gases was achieved in the liquid and that the reaction was not rate-limited by reactant diffusion (14). Afterward, 10 ml of a degassed aqueous solution of nitrate ( $\text{KNO}_3$ ) or nitrite ( $\text{KNO}_2$ ) ( $1.6 \cdot 10^{-2}\text{ mol/l}$ ) were introduced in the reactor to start the reaction. At appropriate time intervals, samples of the reaction mixture were withdrawn and filtered.

The amount of metal ions present in solution during nitrate and nitrite reduction was below the detection limit of the atomic absorption spectroscopy.

Nitrate and nitrite concentrations were determined by HPLC analysis, according to the experimental procedure described in Ref. (14). Ammonium ions were also determined by HPLC analysis on an Alltech Universal Cation column coupled with a conductimeter (Alltech 550). The mobile phase (oxalic acid  $2\text{ mmol l}^{-1}$ ) was sufficiently acidic to totally convert the ammonia basic form into ammonium ions.

## 3. RESULTS

### 3.1. Nitrate and Nitrite Reduction under Flowing Pure Hydrogen

Figure 1 shows that nitrate are totally reduced within 20 min on a 1.6 wt% Pd/CeO<sub>2</sub> catalyst, without any nitrite

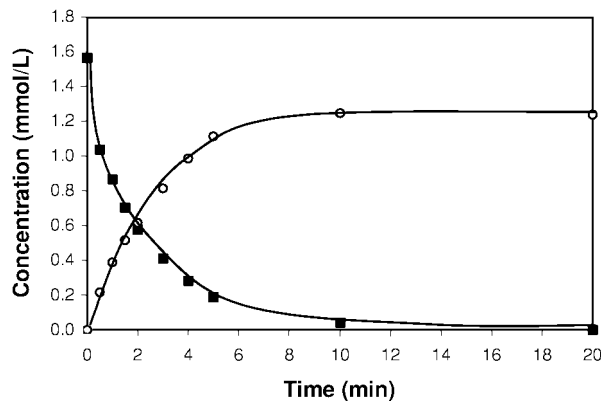


FIG. 1. (■) Nitrate and (○) ammonia concentration vs time in the presence of 1.6 wt% Pd/CeO<sub>2</sub> catalyst under pure hydrogen flowing.

intermediate production. The initial activity of this catalyst is equal to  $33\text{ mmol/min g}_{\text{met}}$ . By comparison, precious metal monometallic catalysts such as palladium deposited on alumina, silica, or carbon supports are totally inactive for nitrate reduction (1, 4–6). The selectivity toward ammonia is equal to 80% at the end of the reaction. Whereas nitrite is an intermediate product that appears in solution during nitrate reduction on a classical bimetallic catalyst under pure hydrogen atmosphere, nitrite is not detected during nitrate reduction on the monometallic palladium catalyst supported on ceria. This result could be explained by the high activity of the Pd/CeO<sub>2</sub> with respect to the nitrite reduction. Then, the monometallic catalyst was tested for nitrite removal. Results are shown in Fig. 2. With this catalyst, nitrite are totally converted within 2 min, with a selectivity toward ammonia of approximately 80%. The activity of the Pd/CeO<sub>2</sub> catalyst ( $250\text{ mmol/min g}_{\text{Pd}}$ ) for nitrite reduction is 7.5 times higher than its activity for nitrate reduction, which explains the absence of nitrite intermediate during nitrate reduction. This activity value is also much higher than the activity of monometallic catalyst on

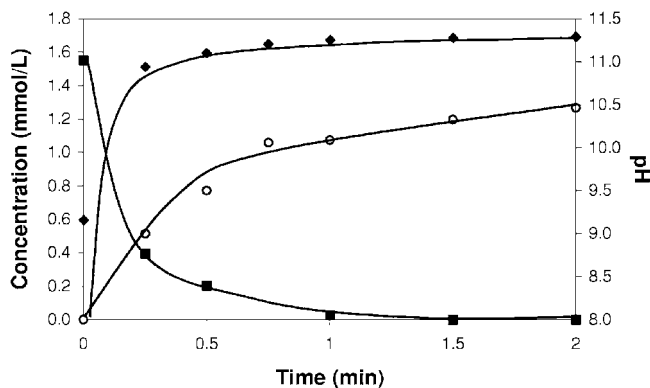


FIG. 2. (■) Nitrite, (○) ammonia concentration, and (◆) pH vs time in the presence of 1.6 wt% Pd/CeO<sub>2</sub> catalyst under pure hydrogen flowing.

TABLE 1

Activity and Dispersion of 1.6 wt% Pd Supported on Ceria or on Alumina

Catalyst	a <sub>0</sub> (mmol min <sup>-1</sup> g <sub>Pd</sub> <sup>-1</sup> )	Pd dispersion (%)	TOF (s <sup>-1</sup> )
Pd/CeO <sub>2</sub>	250	70	0.63
Pd/Al <sub>2</sub> O <sub>3</sub>	2	13	0.027

classical supports (4, 6). We compared the activity for nitrite reduction of the 1.6 wt% Pd/CeO<sub>2</sub> catalyst to the one of a 1.6 wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, prepared and tested according to the same experimental procedure (Table 1). The activity of the ceria-supported catalyst is much higher than the activity of monometallic catalyst on a classical support such as alumina. The influence of the support on activity could be rationalized by the difference of the metallic surface. For comparison, dispersions of the noble metal and turnover frequencies (TOF) are also listed in Table 1.

The palladium dispersion is much higher on ceria than on alumina, thereby confirming the promoting effect of this support on the metal dispersion. The TOF is also 23 times higher on ceria than on alumina support. The different dispersion of the two catalysts supported either on ceria or on alumina could account for the difference in turnover frequency, the dispersion strongly affecting the metal reducibility and therefore the catalytic properties.

### 3.2. Nitrate and Nitrite Reduction under Flowing H<sub>2</sub>/CO<sub>2</sub> Mixture

We have established that ceria support has an important promoting effect on the activity of monometallic palladium catalyst for nitrite reduction, and it allows nitrate reduction without adding a second metal. However, the reaction is too selective toward ammonia, which is an undesired product. This high ammonia production could be due to the high pH value of the nitrate and nitrite solution during the reaction. Indeed, the pH is an important parameter that affects

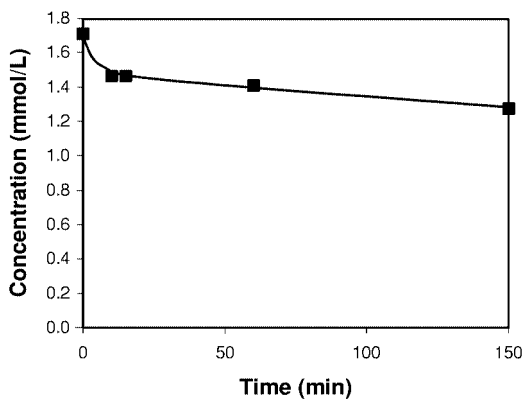


FIG. 3. Nitrate concentration vs time in the presence of 1.6 wt% Pd/CeO<sub>2</sub> catalyst under 50% H<sub>2</sub>/50% CO<sub>2</sub> flow.

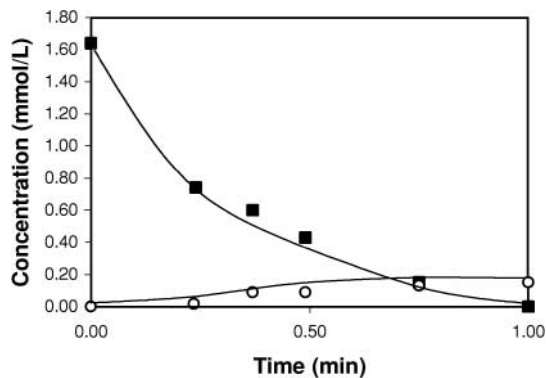


FIG. 4. (■) Nitrite, (○) ammonia concentration vs time in the presence of 1.6 wt% Pd/CeO<sub>2</sub> catalyst under 50% H<sub>2</sub>/50% CO<sub>2</sub> flow.

the activity and selectivity of catalysts for nitrate and nitrite reduction (1, 2, 4, 8, 9). When pH is buffered at an acidic value, the activity is increased and the production of ammonium ions is decreased. A common route to neutralize the hydroxide ions generated during the reaction consists of saturating the solution with carbon dioxide. Pintar *et al.* (8) demonstrated that the selectivity with respect to ammonium ions production amounts to 70% for nitrite reduction on 5 wt% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> under pure hydrogen flow, whereas this value is only 15% in the presence of 60% of carbon dioxide. Therefore, the nitrate and nitrite reduction was carried out in the presence of 1.6 wt% Pd/CeO<sub>2</sub> under a H<sub>2</sub>/CO<sub>2</sub> mixture (50% of carbon dioxide). The evolution of nitrate and nitrite under mixed flow is presented in Figs. 3 and 4, respectively. Under H<sub>2</sub>/CO<sub>2</sub> mixture, only 25% of nitrate are converted after 150 min and the catalyst seems to be completely deactivated. Moreover, the ammonia concentration, after 150 min of reaction, is equal to 0.2 mmol/l that corresponds to a selectivity toward ammonia formation higher than 50%. In contrast, the activity for nitrite reduction is not modified by the presence of carbon dioxide in the gas mixture, whereas the selectivity is reduced to 10%. This is consistent with the results reported on nitrite reduction in the presence of palladium supported on alumina (8).

## 4. DISCUSSION

### 4.1. Nitrate and Nitrite Reduction under Pure Hydrogen Flowing

Until now, it was admitted that the reduction of nitrate requires the promotion of the noble metal by adding a second metal such as copper or tin, the monometallic catalyst being totally inactive. However, the present results prove that a monometallic catalyst can be active for nitrate reduction by using ceria as support, which suggests that the support may be directly involved in the reaction over Pd/CeO<sub>2</sub> catalyst. In a previous study (14) using a bimetallic Pt-Cu/Al<sub>2</sub>O<sub>3</sub> catalyst, we have evidenced that nitrate may be reduced

into nitrite on metallic copper according to a redox reaction leading to the oxidation of copper species. Subsequently, the role of the precious metal is to activate hydrogen, enabling the reduction of copper. We may suggest that the same type of mechanism is involved in the reduction of nitrate on monometallic Pd/CeO<sub>2</sub> catalyst. This assumes that ceria is in a reduced state in the reaction conditions. In the literature, the reduction of ceria was the object of numerous studies (15, 20–22). The temperature programmed reduction of the cerium oxide is characterized by two reduction peaks at approximately 520 and 830°C, indicative of the reduction of CeO<sub>2</sub> to Ce<sub>2</sub>O<sub>3</sub>. The first peak is attributed to the reduction of the ceria surface while the second peak corresponds to the removal of bulk oxygen. The Ce<sup>4+</sup> to Ce<sup>3+</sup> reduction is accompanied by the formation of oxygen vacancies. This process occurs first on the surface and then progressively affects the bulk. The addition of only a few percent of noble metals promotes the reduction of surface oxygen only, which corresponds to a shift of the first peak to lower temperatures (20, 23). The TPR profile for the removal of oxygen anions from the Pd/CeO<sub>2</sub> sample is displayed in Fig. 5 and compared with the profile obtained with a Pd/Al<sub>2</sub>O<sub>3</sub> with the same metal loading. During the reduction of the 1.6 wt% Pd/CeO<sub>2</sub> sample, the peak appearing between ambient temperature and 200°C is associated with the reduction of the supported palladium oxides; in particular, the most reducible surface oxygen on the ceria support adjacent to the metal. In this case, the amount of hydrogen consumed is much higher than with the Pd/Al<sub>2</sub>O<sub>3</sub> sample. In addition, one can note two reduction peaks in the temperature region between 200 and 600°C. Thus we can expect that the surface oxygen atoms of the ceria are reduced after the catalyst pretreatment at 300°C under hydrogen flowing.

Nevertheless, whereas noble metals promote the low temperature reduction of ceria by hydrogen, they also enhance the rate of ceria oxidation by water to yield hydro-

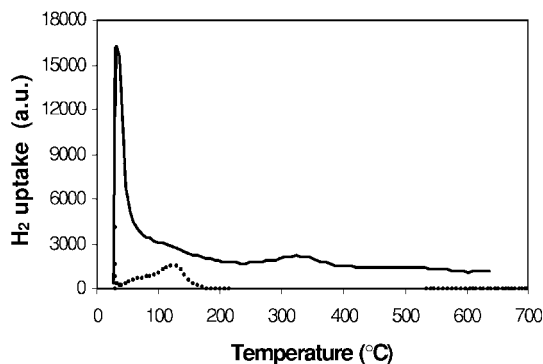


FIG. 5. TPR profile obtained after catalyst preparation and exposition to ambient air. Operating conditions: 5°C/min, 1% H<sub>2</sub> in Ar, gas flow rate: 14 ml/min. (—) 1.6 wt% Pd/CeO<sub>2</sub> sample weight = 50 mg, (···) 1.6 wt% Pd/Al<sub>2</sub>O<sub>3</sub> sample weight = 200 mg.

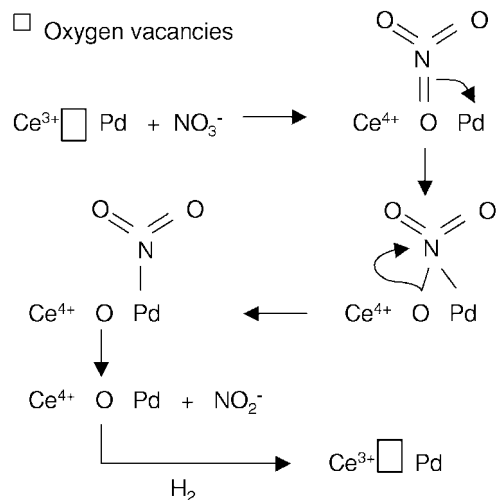


FIG. 6. Schematic representation of nitrate reduction on a reduced Pd/CeO<sub>2</sub> catalyst.

gen (23). This property is implied in the water–gas shift reaction on ceria-supported precious metal (21). However, Kundakovic *et al.* (25) found that adsorption of water on reduced ceria surfaces at low temperature does not lead to oxidation of ceria, nor does the formation of hydroxyls. Clear reoxidation of ceria was observed after exposure to water at elevated temperature. In the present study, at 25°C under pure hydrogen flowing, we can therefore assume that ceria surface is mainly in a reduced state, in spite of the presence of water. Within this assumption, nitrate reduction may occur through the interaction of oxygen atoms of nitrate with the oxygen vacancies created at the ceria surface upon the reduction treatment. This adsorption phenomena was verified by performing a “blank” test in the presence of ceria alone, reduced in the same conditions as those used for the Pd/CeO<sub>2</sub> catalyst, that means at 300°C for 1 h. In that case, only 8% of nitrate disappeared from the solution, but neither nitrite nor ammonia was detected. In this way, this nitrate disappearance probably corresponds to an adsorption phenomena. Thus, nitrate reduction into nitrite would probably involve both vacancies located at the metal–support interface and the noble metal. Figure 6 shows a schematic representation of this type of mechanism. As far as nitrite is concerned, it could be reduced either on the ceria sites, according to a redox reaction, or by hydrogen on the metallic sites, according to a classical catalytic reaction.

#### 4.2. Nitrate and Nitrite Reduction under Flowing H<sub>2</sub>/CO<sub>2</sub> Mixture

In the presence of carbon dioxide in the gas phase, nitrate reduction is inhibited (Fig. 3). This indicates that the active sites for nitrate reduction are poisoned by CO<sub>2</sub>. Conversely, nitrite reduction is not affected, implying different

active sites for nitrate and nitrite reduction. As CO<sub>2</sub> is strongly adsorbed on cerium oxides at room temperature, giving rise to carbonates and carboxylates (26–28), these species may affect the adsorption of N-species on ceria sites and then prevent the nitrate and nitrite reduction on the support. This result underlines the low potential of the Pd/CeO<sub>2</sub> catalyst for the nitrate removal from drinking water, which contains bicarbonate and carbonate species. Since the nitrate reduction is poisoned by the presence of CO<sub>2</sub> in the reaction medium, this reaction is likely to occur on ceria sites in accordance with the mechanism presented in Fig. 6, whereas the metal surface is the preferential site of nitrite reduction.

## 5. CONCLUSION

Whereas monometallic palladium catalysts deposited on classical supports such as silica, alumina, or carbon are totally inactive for nitrate reduction, we have demonstrated that a reduced Pd/CeO<sub>2</sub> catalyst is active for this reaction (33 mmol/(min g<sub>met</sub>)). The promoting effect of the support, based on its redox properties, was clearly identified, with nitrate reduction probably occurring through the interaction of oxygen atoms of nitrate with the oxygen vacancies created at the ceria surface upon the reduction treatment. Conversely, nitrite intermediates are converted through a classical catalytic reaction by hydrogen adsorbed on palladium sites. However, the Pd/CeO<sub>2</sub> catalyst is not suitable for drinking water treatment in comparison to traditional bimetallic catalysts, due to its poisoning by bicarbonates and carbonates and to its high selectivity toward ammonia formation.

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