



Investigation of catalysts M/CeO₂ (M = Pt, Rh, or Pd) for purification of CO₂ derived from oxycombustion in the absence or presence of water

Joudia Akil, Stéphane Siffert, Laurence Pirault-Roy, Sébastien Royer,
Fengjiao Shen, Weidong Chen, Renaud Cousin, Christophe Poupin

► To cite this version:

Joudia Akil, Stéphane Siffert, Laurence Pirault-Roy, Sébastien Royer, Fengjiao Shen, et al.. Investigation of catalysts M/CeO₂ (M = Pt, Rh, or Pd) for purification of CO₂ derived from oxycombustion in the absence or presence of water. Environmental Science and Pollution Research, 2021, 28 (10), pp.12521-12532. 10.1007/s11356-020-11252-7 . hal-02982886

HAL Id: hal-02982886

<https://hal.science/hal-02982886>

Submitted on 23 Mar 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Investigation of catalysts M/CeO₂ (M = Pt, Rh or Pd) for purification of CO₂ derived from oxycombustion in absence or presence of water

Joudia Akil¹, Stéphane Siffert¹, Laurence Pirault-Roy², Sebastien Royer³, Fengjiao Shen⁴, Weidong Chen⁴, Renaud Cousin¹, Christophe Poupin^{1*}

¹ Univ. Littoral Côte d'Opale, UR 4492, UCEIV, Unité de Chimie Environnementale et Interactions sur le Vivant, SFR Condorcet FR CNRS 3417, F-59140 Dunkerque, France

² Institut de chimie des milieux et matériaux de Poitiers (IC2MP), Université de Poitiers, UMR 7285 CNRS, 4, rue Michel Brunet, 86073 Poitiers cedex 9, France.

³ Université Lille-1, CNRS, ENSCL, Centrale Lille, University of Artois, UMR 8181 - UCCS - Unité de catalyse et de chimie du solide, 59000 Lille, France

⁴ Univ. Littoral Côte d'Opale, UR 4493, LPCA, Laboratoire de Physico-Chimie de l'Atmosphère, F-59140 Dunkerque, France

*Corresponding author: christophe.poupin@univ-littoral.fr

Abstract:

Oxyfuel combustion is a promising technology to produce a CO₂ rich flue gas ready suitable for sequestration or valorization. But its storage as well as its further valorization requires to increase the CO₂ purification as a small amount of CO and NO_x are produced during combustion. Based on the technology developed for three-way converters, similar systems i.e M/CeO₂ where M is Pt, Pd or Rh were studied for NO-CO abatement in a gas stream similar to those obtained when an oxyfuel combustion is performed. The results evidenced that the role of the metal nature influences the performances obtained on NO-CO abatement, platinum supported on ceria being the most efficient catalyst. We also measured the impact of the presence of water in the reaction stream on the catalytic activity of these materials. It appears that the presence of water has a beneficial effect on the different reactions due to a water gas shift reaction that increases the reduction of the NO and favors the formation of N₂. The study pointed out that platinum supported on ceria remained the

best catalyst, under these wet operating conditions close to industrial ones, for purification of oxyfuel combustion exhausts.

Keywords:

Environmental chemistry, Oxyfuel Combustion, NO-CO reaction, Heterogeneous catalysis.

1. Introduction

The main part of energy production is coming from fossil fuels burning that leads to increase CO₂ concentration in the atmosphere and finally the average surface temperature of Earth. If energy production based on renewable sources can replace those obtained from fossil fuels power station, a large part of industrial activities as steel industries, cement production or domestic waste incinerator will still need combustion processes and require solutions to reduce CO₂ discharge. Capture and purification of CO₂ for storage or valorization is a key-parameter to reduce its concentration in the atmosphere and to limit global warming (Ademe et al. 2014; Dumergues et al. 2014; Ferrari et al. 2019). Among the proposed processes, oxyfuel combustion is a promising technology (Perrin et al. 2013; Iloeje et al. 2015). This process consists of burning a fuel using pure oxygen instead of air to produce a CO₂ rich flue gas ready suitable for sequestration or valorization (for example CO₂ methanation). Although small amount of CO and NO_x are produced in lesser extent than a classical combustion, they should be removed before CO₂ capture and storage. Indeed, these gases are not respectful of the environment; moreover they can lead to corrosion of the transfer lines and will be disruptive elements for a possible utilization of the stored CO₂ (Meunier et al. 2014; Iloeje et al. 2015). Based on the technology developed for three-way converters (TWC), similar systems can be proposed for the purification of CO₂ by reducing NO_x using CO as a reducing agent. But we must note some important differences between a “classical” NO-CO reaction in TWC and a NO-CO reaction in oxyfuel combustion. Firstly, the gas composition is different with a noticeable higher amount of oxygen and water in oxyfuel condition (Table 1). Moreover, during our reaction, we are in presence of a significant amount of CO₂ which can be troublesome for the catalytic activity depending on the catalysts acid-base properties used and, on the other hand, the presence of a significant

56 amount of oxygen which could promote the oxidation of CO like NO thus blocking the
 57 reduction of NO by CO. Furthermore, the composition of the gas is expected to be more
 58 stable during oxyfuel combustion as no alternative periods of lean and rich conditions will
 59 occur like in car converters due to vehicle acceleration and deceleration.

60 Table 1 : Difference between NO-CO reaction and the oxyfuel combustion to treat

	NO/CO ratio	Extra gas	Reference
"classical NO/CO reaction"	1	None	(Pérez-Hernández et al. 2005a; Kolli et al. 2005a; Miller and Chuang 2009; Baidya et al. 2013; Desai et al. 2015)
	>1	None	(Uchiyama et al. 2015)
	<1	None	(Kobylinski and Taylor 1974; Almusaiteer and Chuang 1998; Kolli et al. 2005a)
		With maximum 4% of O ₂	(Ogura et al. 2000; Shimokawabe and Umeda 2004; Zhu et al. 2009; Dasari et al. 2013)
		With maximum 5% of H ₂ O	(Wen and He 2002; Dasari et al. 2013)
Oxyfuel combustion	<1	With minimum 5% of water and 4% of O ₂	(Andersson et al. 2008; Iløje et al. 2015)

Secondly, the gas treatment temperature can be adjusted by placing the catalytic bed at a desired height in the industrial chimney, which is not possible for a vehicle which is dependent on the reaction and its exothermicity to ensure the temperature increase of the TWC. Thirdly, additional gas as water, ammonia or others, can be introduced easily in the gas flow on the contrary of TWC. Finally, the flow rate can be controlled during the oxyfuel for example by increasing the chimney diameter while the constraints in terms of flow and exhaust diameter are higher on the TWC. Despite of all these difference about gas composition, flow rate, temperature the process of car exhausts treatment can be a source of inspiration because the nature of the gases is similar (Meunier et al. 2014; Iloeje et al. 2015; Kumar and Subramanian 2017; Sim and Sim 2017). For catalytic converters, supported noble metal catalysts have been widely used in the control of atmospheric pollution and have demonstrated high activity (Gandhi et al. 2003; Ivanova et al. 2010). The three precious metals used i.e platinum, palladium and rhodium, have been dispersed, stabilized, promoted, allied and separated in a progressively sophisticated way over the years to achieve exceptional progress in terms of performance and long term lifetime (Gandhi et al. 2003). Platinum and palladium (higher availability and lower cost than Pt) are known for their oxidizing ability and have been chosen for the simultaneous oxidation of carbon monoxide and hydrocarbons in the very first two-way (or “oxidation”) catalytic converters. Rhodium, meanwhile, was added to ensure the reduction of nitrogen oxides to dinitrogen leading to a third way and emerging three-way converters. The support targeted for three-way catalysts was ceria (CeO_2). The application dates back to the late 1970s and since then has been continuously implemented to achieve a high level of efficiency (Aneggi et al. 2016). The importance of this oxide for these reactions is reflected in its high oxygen storage and release capacity thanks to its redox $\text{Ce}^{4+}/\text{Ce}^{3+}$ pair (Yao and Yao 1984; Gandhi et al. 2003).

Although many reports have been published on the NO-CO reaction on precious metal catalysts, few studies have addressed this reaction in the presence of excess oxygen and water as the main application was the three-way converters working in rich conditions in a narrow window around stoichiometry (Nanba et al. 2010). Indeed, CO is a reducing agent for three-way catalysts to reduce NO_x but under oxidizing conditions, it will preferentially be oxidized by oxygen instead of performing nitric oxide reduction (Nakamura and Fujitani 2009) which leads to a drastic decrease of the selectivity towards the dinitrogen (Kolli et al.

2005b). Nowadays, more attention is being paid to these systems to be used to purify the gas exhaust in particular after an oxyfuel combustion for CO and NO_x removal (Illoeje et al. 2015) before CO₂ capture and storage. However, the main challenge remains to perform this reaction in presence of an excess of oxygen. Indeed, many authors have studied the reaction of NO reduction by CO with very promising results (Kobylinski and Taylor 1974; Granger et al. 1998; Pérez-Hernández et al. 2005b; Zhu et al. 2009). However other studies have shown that low oxygen content (max 4%) is harmful for the reaction, because of a preferential oxidation of the reducing agent (Nakamura and Fujitani 2009). Thus, many authors have studied the competition between the two reactions CO-NO and CO-O₂. Shelef et al. found that this second reaction is predominant on a number of supported Pt catalysts and transition metal oxide (Shelef et al. 1968). On the other hand, Zhu et al (Zhu et al. 2009) showed on Pt-based catalysts, a strong inhibition of NO reduction in the presence of an excess of oxygen: 100% conversion between 300 and 400 ° C without O₂, to a maximum of 18% in the same temperature range in the presence of O₂. This inhibition is due to the fact that CO reacts more easily with O₂ than with NO, which inhibits the conversion of the latter. Kolli et al (Kolli et al. 2005b) report similar results on Pd catalysts. These authors showed an increase towards the formation of N₂O in the presence of oxygen with a disappearance of the formation of N₂ (Kolli et al. 2005b). They also noticed that at 100% oxidation of CO, the NO begins to oxidize to NO₂ (Kolli et al. 2005b). Wang et al. (Wang et al. 2008) also reported a decrease in activity with respect to NO reduction in the presence of O₂ on the NiO/CeO₂ catalyst. To summarize in the absence of oxygen, the NO can play the role of oxidant on the catalyst active sites thus allowing CO oxidation whereas in presence of oxygen the catalyst active sites will be blocked by adsorbed oxygen hindering thus the NO conversion (Mantri and Aghalayam 2007). Few studies take into account the role of water in the stream although it can be crucial for catalysts stability.

In this paper, we will therefore study the possibility of transposing the knowledge from the catalytic conversion of vehicle effluents to the problem of the purification of CO₂ from oxy-fuel combustion in a chimney. The authors want to purify the CO₂ only with the component present in the flue gas; that is why the CO will be used to reduce the NO. The oxidation of CO is not the main problem which is the NO_x reduction in oxidizing medium. Thus, the target is 50% NO_x abatement (an already considerable but nevertheless reasonable objective). Thus,

the effect of the nature of the active phase (Pd, Pt and Rh) supported on CeO₂ in the simultaneous oxidation of carbon monoxide and reduction of nitric oxide in an oxidizing medium (10% O₂) and in the presence of H₂O will be investigated in order to purify the CO₂ from the oxycombustion. We will also determine the selectivity of the best catalyst regarding to the formation of N₂ from nitric oxide reduction.

2. Experimental

2.1. Catalysts preparation

Ceria (HAS 20 (Rhodia)) with a specific surface area of 65 m².g⁻¹ was used as support. Before any impregnation, ceria was calcined in air at 500 °C for four hours with a ramp of 5°C/min.

Then, the catalysts were prepared by impregnation of ceria with the corresponding precursors mentioned in the following table (Table 2) using water as solvent for nitrous precursor and acetone for the organometallic compound. For all catalysts in powder form, the nominal contents targeted were of 1.0 wt%.

Table 2. Metal precursors used for the impregnation

Metal	Palladium	Platinum	Rhodium
precursor used	Pd(acac) ₂	Pt(NO ₂) ₂ (NO ₃) ₂	Rh(NO ₃) ₃

The impregnated support was left overnight in an oven at 393 K. It was then calcined in dry air and reduced in H₂ flow during 4 h at 773 K for both thermal treatments.

2.2. Characterization of the catalysts

The metal loadings of final catalysts were verified by inductively coupled plasma (ICP) analyses performed on an ICP/OES Perkin Elmer Optima 2000 DV apparatus.

The obtained samples were subsequently characterized by H₂ chemisorption. Ceria is a reducible oxide and some authors evidenced that the ceria surface close to the noble metal particles can be reduced via the spillover of H₂ even at room temperature which can cause a considerable disturbance of the measurements. Thus a new protocol was proposed for carrying out the chemisorption of hydrogen based on limitation of the spillover effect by

performing the adsorption at low temperature near - 70°C to block the kinetics of the H₂ chemisorption on ceria (Gatica et al. 2001). This protocol was retained to determine the metal dispersion of catalyst by hydrogen chemisorption and a chromatographic micro-reactor was used to perform the measurements. After a reduction under H₂ (350 °C, 60 min) and degassing under argon (350 °C, 180 min), hydrogen pulses (0.26 mL) were injected in the reactor where the catalyst was introduced, at regular interval of time and at -70 °C until saturation. The calculation of the particle sizes is performed with the cubic model with 5 faces exposed corresponding to the Hughes hypothesis [8], with an equal distribution between (1 1 1), (1 1 0) and (1 0 0) planes.

Transmission electron microscopy (TEM) was performed with a JEOL 2100 UHR microscope equipped with an energy dispersive X-ray (EDX). Reduced catalysts were suspended in ethanol under sonication for 5 min and loaded on holey carbon film Cu grid (300 mesh).

2.3. Catalytic tests

Before each test, the catalyst was treated in situ under He flow (40 mL.min⁻¹) at 473 K for 90 min. Then, CO₂ purification was carried out at atmospheric pressure in a fixed-bed flow reactor containing 150 mg of catalyst. The catalysts were sieved in order to retain grains with diameters between 0.315 and 0.500 mm and diluted to a constant volume by SiC (which exhibited no activity in CO₂ purification from 50 to 500 °C) to ensure that all the experiments were carried out under the same conditions (GHSV = 2.24 10⁴ h⁻¹) and achieved in the mentioned experimental set up (Fig. 1).

The flow of the reactant gases is composed of: 20 % CO₂, 10 % O₂, 0.5 % CO and 0.02 % NO (He as eluent gas) with a total flow of 200 mL.min⁻¹, in the temperature range 50–500 °C. A normal oxyfuel combustion process is supposed to give a higher amount of CO₂, but to be able to study the different reactions that can occur and to identify the species, a lower CO₂ concentration was chosen. Moreover, CO₂ is not expected to interfere in the CO-NO reaction except by covering the basic sites of the ceria and 20% of CO₂ will be enough to block all basic sites. So, a more important amount of carbon dioxide will not affect the NO-CO reaction in oxidizing medium and the data obtained in this work. The reaction products (CO₂ and N₂) were analyzed on line by a gas chromatograph (Label GAS analyzer XXL1300), NO was analyzed with Xentra 4900C analyzer (Servomex). The measurement of NO₂ is done

indirectly using a NO₂ to NO converter BÜNOx (Bühler Technologies) by comparison. In order to evaluate the selectivity of the catalysts, we used a room-temperature continuous-wave (CW) external cavity quantum laser cascade (EC-QCL) -based optical sensor, with an accuracy of 32.3ppbv. N₂O sensor based on a continuous-wave (CW) external-cavity quantum cascade laser (EC-QCL) operating at ~ 8 µm, coupled to a modified-Herriot multi-pass cell is completely describe in the paper of Shen and al. (Shen et al. 2018).

The conversion, selectivity and yields of the main products are defined in the following way:

- Conversion: $X_i (\%) = \frac{n_i^{int} - n_i^{out}}{n_i^{int}} * 100$ where n_i^{int} and n_i^{out} are number of moles of the corresponding compounds “i” at the inlet and the outlet of the reactor.
- Selectivity: $S_i (\%) = \frac{n_i}{\sum_i n_i} * 100$
- Yield: $Y_i(\%) = X_i * S_i * 100$

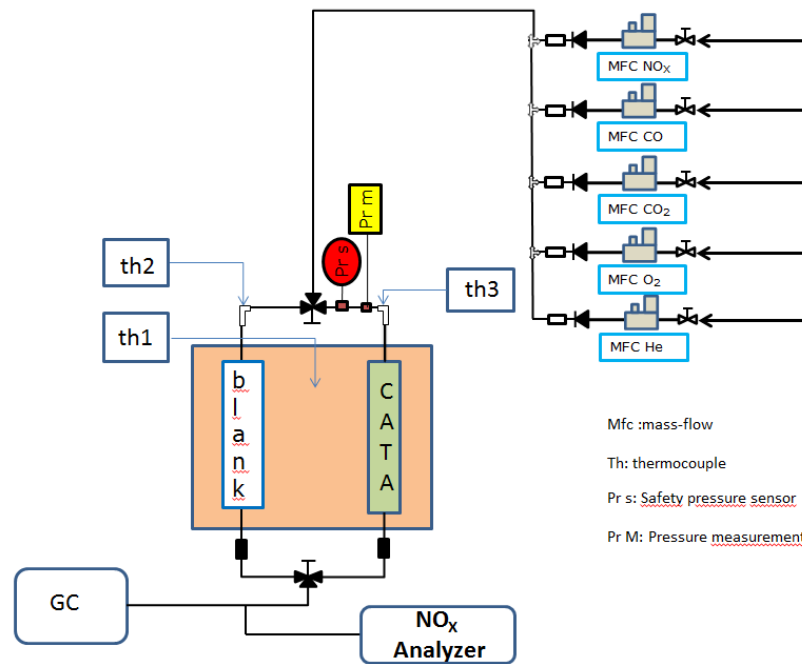


Figure 1: Experimental setup for catalytic purification of CO₂ from oxyfuel combustion

In order to compare the different materials, T₅₀ and T₉₀ values will be taken into account. These temperatures correspond respectively to the one at which 50% or 90 % of reagent is converted. For NO reduction, the catalysts will be compared according to their maximum efficiency (yield) at total conversion of CO.

3. Results and discussion

3.1. Characterization

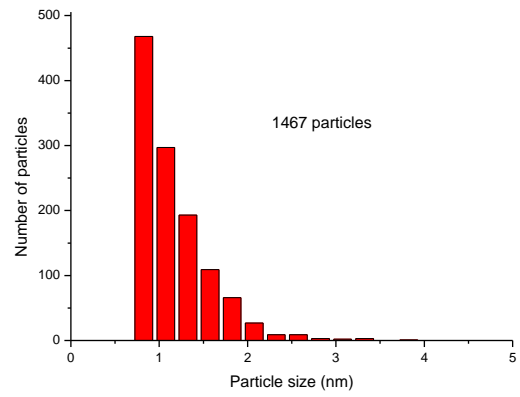
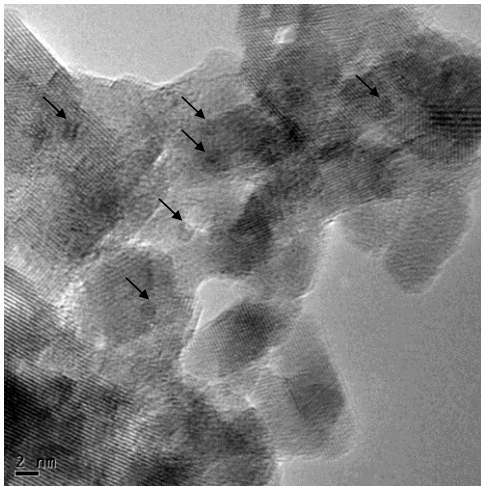
The catalysts prepared by impregnation of ceria targeting 1 wt-% of the noble metal were analyzed by ICP to determine the metallic content. The results are presented in Table 3. The catalysts were also characterized in order to determine their metal accessibility as well as their particle sizes by hydrogen chemisorption.

Table 3. Properties of catalysts: metallic content, particles size and metallic accessibility.

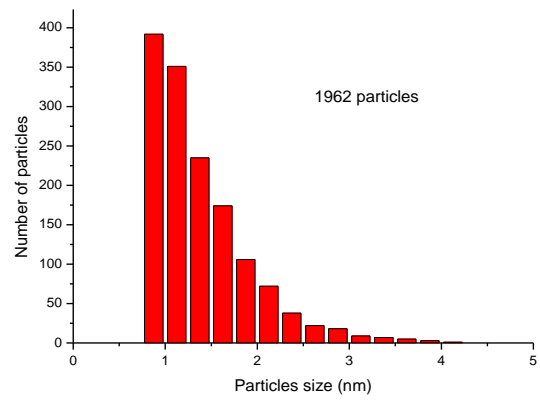
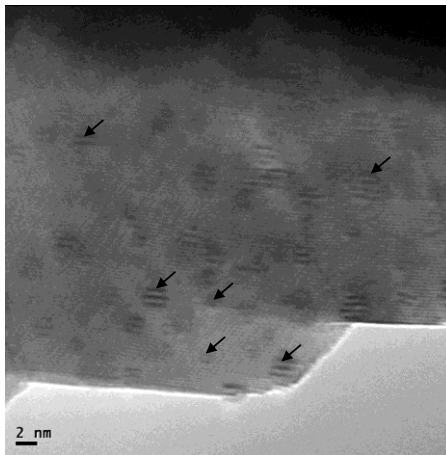
Catalysts	Reference	Measured metallic content (%)	Metallic accessibility (%)	< d > (nm) Before test H ₂ chemisorption / TEM	< d > (nm) After test deduced from H ₂ chemisorption
Pt/CeO₂	Pt/Ce	1.14	43	2.6 / 1.5	2.9
Rh/CeO₂	Rh/Ce	1.05	46	1.8 / 1.8	1.8
Pd/CeO₂	Pd/Ce	0.94	42	- / 1.5	--

The metallic contents are very close to the targeted ones. The metal accessibilities measured by hydrogen chemisorption and reported in Table 3, are similar for all the catalysts with a metal accessibility of about 40% corresponding to similar particle sizes also of about 2 nm, allowing us to carry out a relevant comparison of the catalytic activity of the different materials.

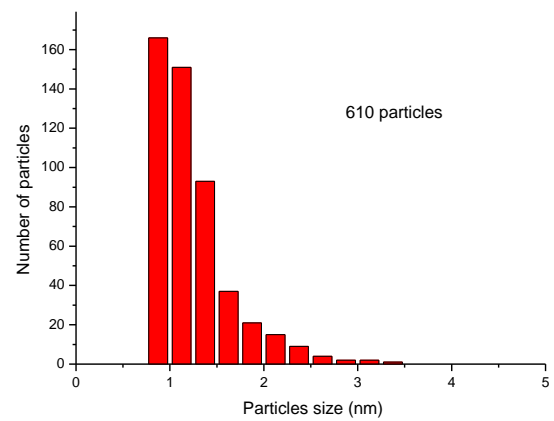
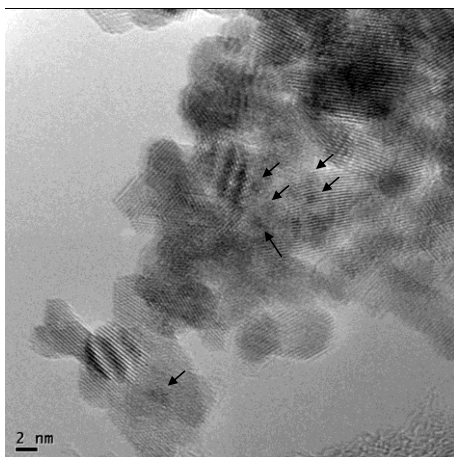
The morphology of the catalysts was evaluated by transmission electron microscopy (TEM) coupled with energy dispersive X-ray spectroscopy (EDX), in order to observe the accurate localization of the metallic particles, to analyze their chemical nature and to estimate their average size and dispersion. Figure 2 displays representative TEM images and particle size distributions. The mean particle diameters and metal dispersions are reported in Table 2. For all catalysts, the metallic phase is homogeneously dispersed on the support with particle sizes comprised mainly between 0.7 and 4.0 nm.



Pt/CeO₂



Rh/CeO₂



Pd/CeO₂

216 **Figure 2:** TEM images and particle size distributions of noble metal catalysts supported on
 217 ceria

3.2. Catalytic reaction

The catalytic activity test was carried out in the presence of 20% CO₂, 10% O₂, 0.5% CO, 0.02% NO in helium, with a total flow of 200 cm³.min⁻¹ in the presence of 150 mg of catalyst shaped and diluted with SiC. The experiments were performed in presence or not of water to check the influence of this parameter on activity, selectivity and stability. The 8.5% of water was added using passing the flow gas through a saturator whose temperature was set at 42 °C.

3.2.1. CO oxidation with or without water in the gas stream

For CO₂ purification, simultaneous reactions should be achieved: oxidation of CO and reduction of NO_x in an oxidizing atmosphere and generally with water. Our catalysts were tested to investigate the influence of the metal nature and the presence of water (8.2%) for these simultaneous reactions focusing first on CO oxidation. The figure 3 presents the light-off curves of CO oxidation according the metal deposited on ceria with and without water in the gas stream.

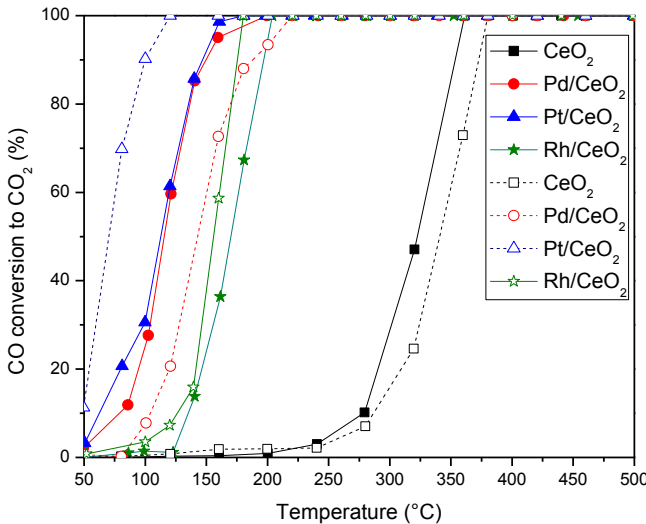


Figure 3: CO oxidation over Pt, Rh or Pd supported on ceria catalysts in the absence (closed symbols) and presence (open symbols) of water

Table 4. Half conversion (T₅₀) and 90% conversion (T₉₀) temperatures of CO on M/CeO₂ catalysts (M = Pd, Pt or Rh) in presence or not of water

Catalysts	Without water		With water	
	T ₅₀ (°C)	T ₉₀ (°C)	T ₅₀ (°C)	T ₉₀ (°C)
CeO₂	323	351	342	370
Pd/CeO₂	116	147	143	183
Pt/CeO₂	112	145	70	100
Rh/CeO₂	170	196	156	172

Addition of noble metal to ceria increases in the oxidation activity. Yao et al. have shown that the presence of a noble metal (Pt, Pd or Rh) on ceria favors its ability to store/exchange oxygen atoms, thus facilitating the oxidation of CO at lower temperatures than these same noble metals supported on alumina (Yao and Yao 1984). This has been confirmed by Vayssilov et al. during theoretical calculations on transfers between noble metal and ceria. Their modeling carried out with Pt demonstrated that there were two types of transfer during the reaction, on the one hand there is an electronic transfer between Pt and ceria, and on the other hand ceria provides Pt with activated oxygen favoring thus the oxidation reactions (Vayssilov et al. 2011).

The best performances were obtained on Pt/CeO₂ and Pd/CeO₂ catalysts while Rh/CeO₂ catalyst shows an oxidation of carbon monoxide at a higher temperature with a T₅₀ of 170°C. Both of Pd and Pt materials have near-similar T₅₀ and T₉₀ values when the experiments were carried out in absence of water. On the contrary, in the presence of water, their activities became different. The results evidenced a beneficial effect of water for Pt/CeO₂ catalyst (and Rh/CeO₂ too) whereas a detrimental effect was observed on Pd/CeO₂. According to Table 3, the addition of water to the reaction stream makes it possible to reduce the conversion temperatures T₅₀ and T₉₀ of the carbon monoxide on the Pt/CeO₂ and Rh/CeO₂ catalysts by approximately 45°C and 20°C respectively. This improvement is due to the reaction of water gas shift ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) (Grenoble et al. 1981). Indeed, the added water plays the

role of a second oxidant for carbon monoxide in addition to oxygen during the WGS reaction. Rh and Pt metals are more active for the WGS reaction than Pd one leading to an increase of CO conversion higher than that observed on Pd/CeO₂ (Panagiotopoulou and Kondarides 2006). A ranking based T₅₀ as well as T₉₀ shows the following order: CeO₂ < Rh/CeO₂ < Pd/CeO₂ < Pt/CeO₂.

3.2.2. NO conversion with or without water in the gas stream

In order to compare the catalytic performances of our materials with respect to the conversion of nitric oxide, the reduction (a) and oxidation (b) yields of the latter in absence of water are presented in Figure 4.

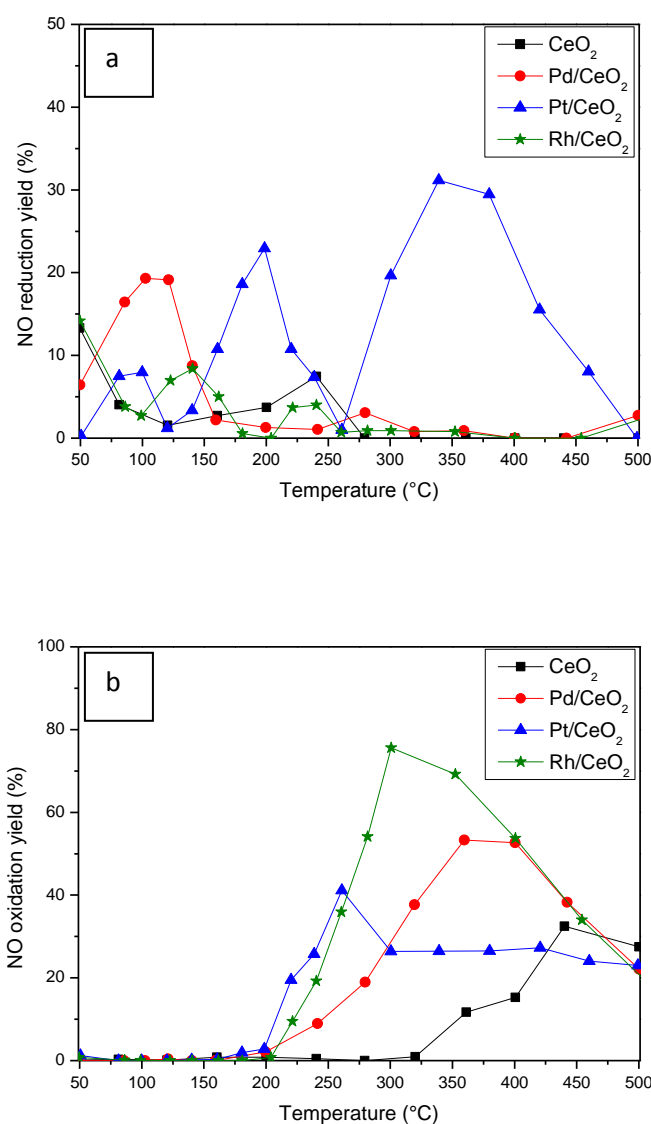


Figure 4: Reduction (a) and oxidation (b) yields of NO on noble metals (Pd, Pt and Rh) supported on CeO₂

It clearly appears that the choice of the metal has a predominant effect on the NO reduction and that of its oxidation, which must be avoided. The reduction profiles appear different depending on the impregnated active phase.

The NO reduction starts at lower temperature on the Pd/CeO₂ catalyst than other catalysts and reaches a 19% maximum reduction at 100 °C. Indeed, several authors have shown an influence of the Pd-Ce interaction on the adsorption of NO (Cordatos and Gorte 1996; Ciuparu et al. 2000). According to Holles et al., ceria affects the NO-CO reaction by facilitating the dissociation of NO at the Pd/support interface, thus promoting its reduction (Holles et al. 2000).

Rhodium has the smallest reduction performance with a maximum of conversion around 8% at 140°C. On this catalyst, at low temperature [50-100°C], the NO reduction profile corresponds perfectly to that obtained on the CeO₂ support alone. Holles et al. also pointed out a beneficial effect of ceria on rhodium-based catalysts for the dissociation of NO (Holles et al. 2000). However, this effect was less pronounced than on the palladium catalysts according to these same authors (Holles et al. 2000). In addition, it has been evidenced in the literature that although rhodium is well-known for NO reduction, it is sensitive to the presence of oxygen and deactivates in oxidizing environments (Panayotov et al. 1996). This explains the low activity of the Rh/CeO₂ catalyst in our experimental conditions.

Platinum has an even more different behavior for reducing NO than other catalysts. This metal exhibits three reduction zones 50-120, 120-260 and 260-500 °C with a maximum reduction in the third zone of 31% at 340 °C. Despite its somewhat surprising profile, our catalyst is more efficient (31% reduction) compared to 7% reported in the literature on a similar 1% Pt/CeO₂ catalyst with only 2% oxygen in their reaction stream (Zhu et al. 2009). This difference could be due to the fact that their catalyst was in the oxidized state at the beginning of the reaction and not reduced contrary to our conditions.

The oxidation of NO also seems to vary with the metal (Figure 3b). The catalyst with the best reduction performance for nitric oxide is the one with the lowest oxidation of the latter and vice versa. Indeed, a ranking of the best catalyst for the conversion of NO can be established:

299 $\text{CeO}_2 < \text{Rh/CeO}_2 < \text{Pd/CeO}_2 < \text{Pt/CeO}_2$. This ranking corresponds perfectly to that achieved for
 300 the oxidation of CO.

301 The higher activity of the Pt/CeO_2 catalyst could be correlated, according to the literature,
 302 with the interaction between platinum and the CeO_2 support which can inhibit the sintering
 303 of platinum (Nagai et al. 2006; Suzuki et al. 2009), unlike the $\text{Pt/Al}_2\text{O}_3$ catalyst (Nagai et al.
 304 2006). Indeed, the CeO_2 support plays an interesting role in the stabilization of platinum
 305 species by maintaining them strongly dispersed.

306 Figure 5 presents the results obtained for the reduction of nitric oxide and the oxidation of
 307 the latter in the presence of 8.2% of H_2O on palladium, platinum and rhodium catalysts
 308 supported on CeO_2 .

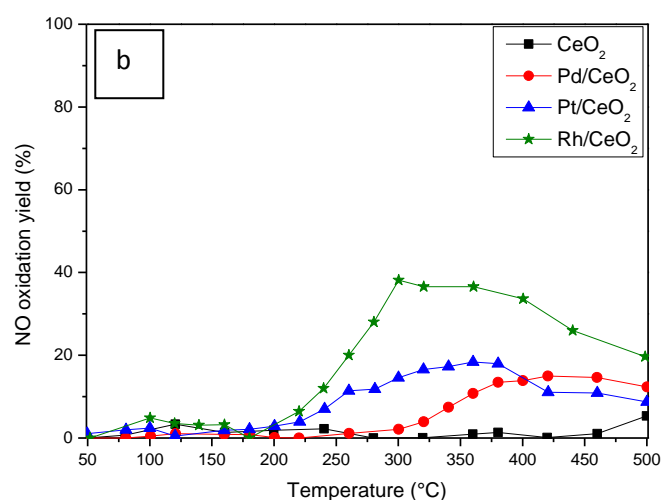
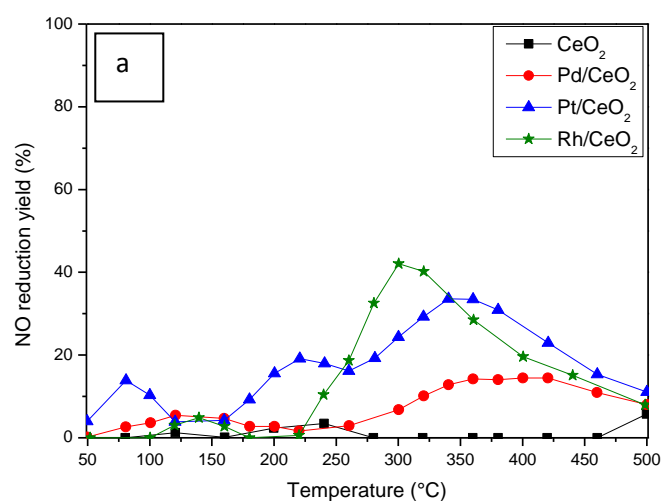


Figure 5: Reduction (a) and oxidation (b) yields of NO on noble metals Pd, Pt and Rh deposited on CeO₂ in the presence of 8.2 % of water

The addition of the metal to ceria increases the NO reduction efficiency and reduces the NO oxidation yield in the presence of water as expected.

The best reduction yield was obtained on the Rh/CeO₂ catalyst with 42% reduction at 300°C, followed by the Pt/CeO₂ catalyst with 34% reduction at 340°C and finally the Pd/CeO₂ catalyst with 14% reduction at 360°C.

The oxidation of the NO follows the same order of ranking of the catalysts as for the reduction of NO.

Indeed, this improvement of activity in the presence of water is due to the reaction of water gas shift. Indeed, it turns out that ceria is a promoter for these noble metals in the "water gas shift" reaction [21]. Studies have shown a significant metal support interaction in the case of noble metal catalysts supported on ceria (Courtois et al.; Shelef and Graham 1994; Bunluesin et al. 1998; Daturi et al. 2001; Wang et al. 2017; Koga et al. 2018). They showed that this metal support interaction creates active oxygen species facilitating oxidation of CO. In addition, it creates oxygen vacancies that make it the NO dissociation easier. Ceria will be re-oxidized by the presence of water thus forming H₂ by the reaction of water gas shift ($\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$) at temperatures above 200 °C. Finally, this H₂ formed can react with NO to form NH₃. H₂ and NH₃ formed within the reaction, are more powerful reductants than CO and then lead to a more effective catalytic reduction of NO. In addition, Koga et al showed that there was a greater electron transfer in Rh/CeO₂ thus allowing for a better catalytic activity of NO conversion (Koga et al. 2018). Meanwhile, Pt is 15–20 times more active than Rh and 50 times more active than Pd, at 250°C (Panagiotopoulou and Kondarides 2006).

3.2.3. Selectivity

It has been shown in the previous paragraphs that the Pt/CeO₂ catalyst maintains its activity with respect to the reduction of nitric oxide in the absence and in the presence of water. Indeed, this catalyst is known for its activity in the gas-to-water reaction or "water gas shift" reaction which generates hydrogen, a second reducing agent for nitric oxide, to produce either directly N₂ or N₂O either NH₃ which is also a more powerful reductant than CO.

However, it has been proven in the literature that selectivity towards N_2 depends on the nature of the reductant (Liu and Anderson 2004; Pérez-Hernández et al. 2005b; Abdulhamid et al. 2006). It is therefore necessary to study the selectivity in the absence and in the presence of the water of this catalyst, especially since the latter is the only catalyst to have three distinct reduction zones shown in Figure 6. These three areas have already been observed and explained by Wuchen Ding et al. and D.M.F. Alves et al. (Alves et al. 2013; Ding and Li 2014). They showed that the formation of N_2 on a Pt/CeO₂ took place in 3 steps: gaseous N_2O formation, subsequent N_2O re-adsorption, and formation of N_2 . Table 4 shows the selectivity for N_2 and N_2O obtained on the Pt/CeO₂ catalyst in the presence and absence of H_2O . The measurements were performed at the maximum reduction yield of the three peaks.

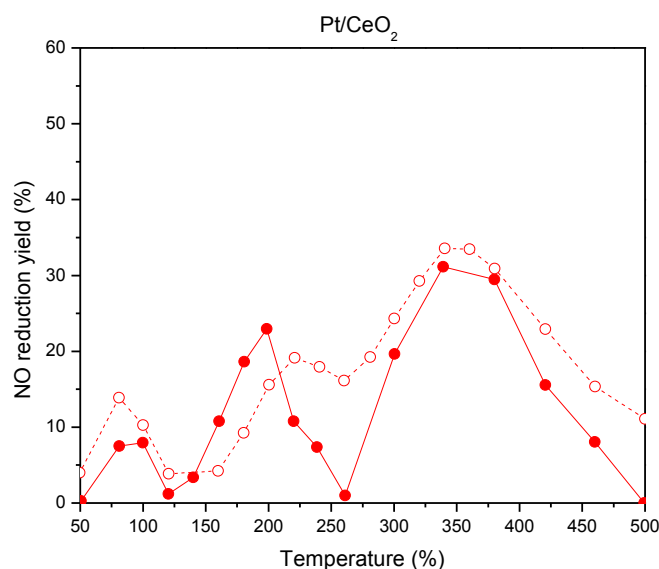


Figure 6: Reduction yields of NO on Pt/CeO₂ catalyst in the absence (closed symbols) and presence of water (open symbols)

Table 5. Selectivity of NO reduction on CeO₂-supported Pt catalyst in the presence and absence of H_2O

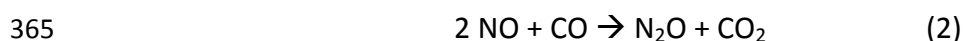
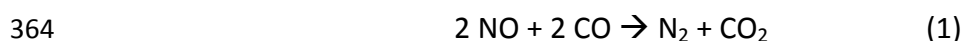
Temperature (°C)	without H ₂ O		with H ₂ O	
	N ₂ O (%)	N ₂ (%)	N ₂ O (%)	N ₂ (%)
80-100 (1st reduction zone)	1,9	98,1	2,8	97,2

200-220 (2nd reduction zone)	1,1	98,9	0,8	99,2
340-350 (3rd reduction zone)	0,2	99,8	0,3	99,7

356

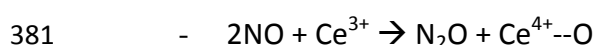
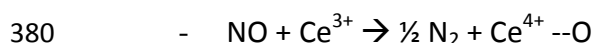
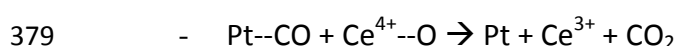
357 It therefore seems that in our reaction conditions, the Pt/CeO₂ catalyst is very selective
 358 towards dinitrogen production with at least 98% in the absence of water and 97% in
 359 presence of water. Very low selectivity (<3%) in N₂O was observed at low conversion
 360 temperatures. As the temperature raises up, the selectivity in N₂ increases to approach
 361 100% with or without water in the gas stream.

362 In the absence of water, the reduction of the NO is ensured by the CO according to the
 363 following steps:

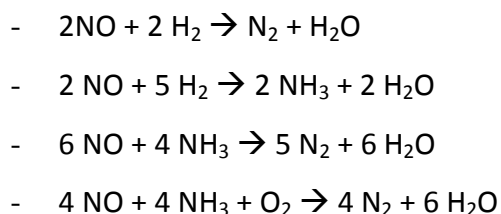


367 CO₂ formation occurs directly (reaction 1) and sequentially (reactions 2 and 3). Since the
 368 selectivity of N₂ was almost 100%, we assume that reaction 1 (NO-CO direct reaction)
 369 occurred as a main reaction pathway. Indeed, it has been generally accepted that the
 370 formation of N₂O is an intermediate in the overall reaction of NO-CO in the low temperature
 371 region (Panayotov et al. 1996).

372 In presence of water, another mechanism occurs as proposed by Alves et al (Alves et al.
 373 2013) for temperatures below 300 °C. It was supplemented by Wang et al (Wang et al. 2017)
 374 for temperatures above 300 °C. Below 300 °C, the conversion of the NO is obtained by a
 375 redox exchange of the Ce⁴⁺/Ce³⁺ pair with the supported noble metal, thus creating an
 376 oxygen vacancy. Thus NO promotes the oxidation of the reduced cerium that explains the
 377 formation of N₂O and N₂, according to the following mechanism (Alves et al. 2013):



While above 300 °C, the production of H₂ by WGS, thus promoting the formation of N₂, according to the following reactions:



Despite the small amount of N₂O produced, it should be noted that this catalyst produces more N₂O at low temperature than at high temperature. Panayotov & al. have observed on Pt and/or Rh supported on ceria catalysts that N₂O is the dominant product at low temperature whereas N₂ is almost exclusively produced at high temperature (Panayotov et al. 1996). This has not been the case on our catalysts; however the trend is the same.

3.2.4. Stability test

In order to study the stability of these materials as a function of time, we chose to carry out tests combining several cycles on the two most active materials, namely Rh/CeO₂ and Pt/CeO₂.

These catalysts were pretreated under helium for 90 min at 200 °C, before being submitted to the reaction mixture under the same conditions of tests previously carried out in the presence of water. The data are collected and interpreted in the same way than for activity tests. Several successive cycles have been carried out and each cycle involves a rise in temperature ranging from 50 to 500 °C under the reaction flow up to see the same curves meaning a stabilization phase. The stability of Rh/CeO₂ and Pt/CeO₂ catalysts during successive cycles are presented in Figure 7.

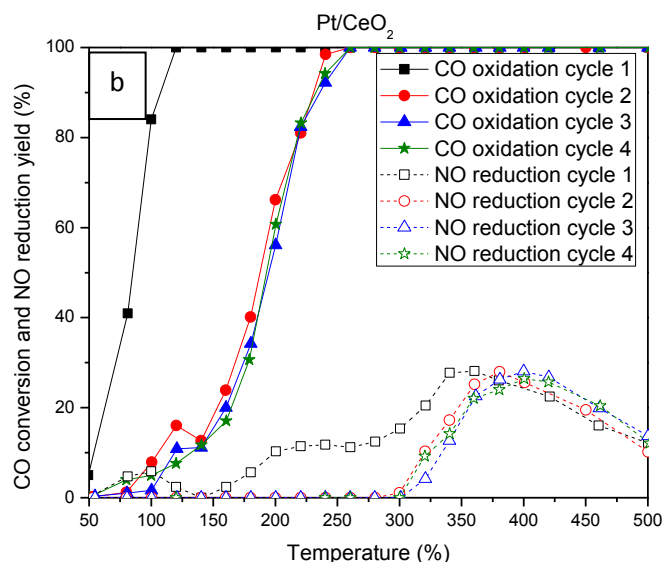
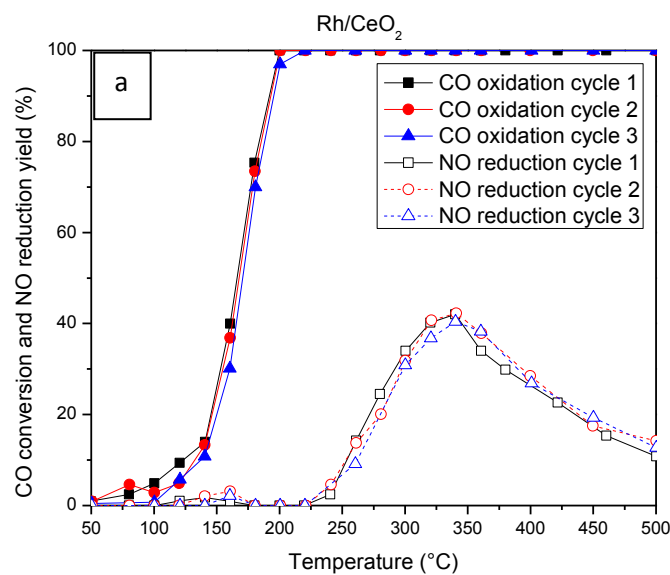


Figure 7: Stability test for several successive cycles in the presence of Rh/CeO₂ (a) and Pt/CeO₂ (b) focusing on the carbon monoxide conversion rate (closed symbols) and NO reduction yield (open symbols) as a function of temperature

Fig. 7 illustrates the temperature dependence of CO oxidation and NO reduction yield in oxidative conditions and presence of water over Rh/CeO₂ (a) and Pt/CeO₂ (b) catalysts. The Rh/CeO₂ catalyst proved to be stable and resistant towards deactivation during three successive cycles. Structural analysis of the aged catalyst by H₂-chemisorption proved that no sintering of Rh particles occurred in the presence of water during 3 cycles test (stable at around 2 nm) thus guaranteeing stability of this catalyst, probably because the strong

interaction between Rh and ceria support efficiently inhibited Rh particles sintering. several authors have reported a good stability of Rh/CeO₂ catalysts for the same reasons (Hou et al. 2015; Zhao et al. 2018).

In contrast to the Rh-based catalyst, the Pt/CeO₂ catalyst, beyond the first cycle, presents a decrease in the CO conversion rate and NO reduction yields at low temperature. This observation can be explained either by the particles size increase in the presence of water (sintering) or the adsorption of the water molecules on the catalysts surface blocking the active sites, either by changing the degree of oxidation of the active metal. The latter type is often encountered in an oxidizing medium, leading to a superficial oxidation of the particles which are less active than in the metallic state. No significant change can be observed after the first cycle as the 2, 3 and 4 cycles show similar selectivities and activities.

4. Conclusion

In this work, we studied the catalytic performance of palladium, platinum and rhodium based material supported on ceria for purification of CO₂ derived from oxycombustion in absence or presence of water. The ceria impregnation with 1 wt.% of platinum, palladium or rhodium led to a good improvement of CO oxidation and NO reduction. The same activity order was obtained concerning the two reactions studied (simultaneous CO oxidation and NO reduction): Rh < Pd < Pt. The most efficient catalyst Pt/CeO₂ exhibited the most important NO reduction (31% at 340°C) with total CO oxidation at low temperature (around 150°C). In addition, the oxidation of NO, to be avoided, was less important than on the other metals.

We also investigated the impact of the presence of 8.2% water in the reaction stream on the catalytic activity of these materials. It appeared that the presence of water had a beneficial effect on the different reactions. Indeed, the addition of water decreased the temperature of CO oxidation following the addition of a third oxidant H₂O in addition to NO and O₂. This reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) called WGS also influenced the NO reduction. Indeed, the production of H₂ increased the reduction of the NO and favored the formation of N₂. This was verified on all the catalysts with the exception of the palladium catalyst. The stability

was tested for the Pt and Rh catalysts. The results evidenced that the Rh catalyst is very stable during at least four cycles. For the Pt catalyst, a decrease of activity and selectivity is pointed out after the first cycle but no changes are observed for the subsequent cycles.

To conclude, we evidenced that the metal nature influences the performances obtained on NO-CO abatement, and that platinum supported on ceria is the best catalysts under these operating conditions close to industrial ones for purification of oxyfuel combustion exhausts and in particular in presence of water. This technology could be integrated in a two-level technology: level 1 should remove the presence of sulfur compounds able to deactivate catalysts by using well-known processes as water spray curtain trapping followed by soda neutralization and level 2 to remove NO and CO via a catalytic way.

Acknowledgements

The authors would like to thank the partners: Innocold, Dunkerque LNG, Greater Dunkirk Council, and ULCO for their financial supports. S. R. acknowledges Chevreul institute (FR 2638), Ministère de l'Enseignement Supérieur, de la Recherche, et de l'Innovation, Région Nord – Pas de Calais and FEDER for supporting and funding partially this work.

References

- Abdulhamid H, Fridell E, Skoglundh M (2006) The reduction phase in NO_x storage catalysis: Effect of type of precious metal and reducing agent. *Appl Catal B Environ* 62:319–328. <https://doi.org/10.1016/j.apcatb.2005.08.014>
- El Khamlichi A, Thybaud N (2014) Valorisation Chimique du CO. Ademe report
- Almusaiteer K, Chuang SSC (1998) Isolation of Active Adsorbates for the NO – CO Reaction on Pd / Al₂O₃ by Selective Enhancement and Selective Poisoning. 170:161–170
- Alves DMF, Alves FS, Ribeiro DG, et al (2013) Study of the activity and selectivity of PtCZ and PtCZBa model catalysts in the reduction of NO by CO. *Chem Eng J* 223:239–245. <https://doi.org/10.1016/j.cej.2013.02.120>
- Andersson K, Normann F, Johnsson F, Leckner B (2008) NO emission during oxy-fuel combustion of lignite. *Ind Eng Chem Res* 47:1835–1845. <https://doi.org/10.1021/ie0711832>
- Aneggi E, Boaro M, Colussi S, et al (2016) Ceria-Based Materials in Catalysis: Historical Perspective and Future Trends. *Handb Phys Chem Rare Earths* 50:209–242. <https://doi.org/10.1016/BS.HPCRE.2016.05.002>
- Baidya T, Bera P, Mukri BD, et al (2013) DRIFTS studies on CO and NO adsorption and NO+CO reaction over Pd²⁺-substituted CeO₂ and Ce_{0.75}Sn_{0.25}O₂ catalysts. *J Catal* 303:117–129. <https://doi.org/10.1016/j.jcat.2013.03.020>
- Bunluesin T, Gorte RJ, Graham GW (1998) Studies of the water-gas-shift reaction on ceria-supported Pt, Pd, and Rh: Implications for oxygen-storage properties. *Appl Catal B Environ* 15:107–114. [https://doi.org/10.1016/S0926-3373\(97\)00040-4](https://doi.org/10.1016/S0926-3373(97)00040-4)
- Ciuparu D, Bensalem A, Pfefferle L (2000) Pd–Ce interactions and adsorption properties of palladium: CO and NO TPD studies over Pd–Ce/Al₂O₃ catalysts. *Appl Catal B* 26:241–255
- Cordatos H, Gorte RJ (1996) CO , NO , and H₂ Adsorption on Ceria-Supported Pd. *J Catal* 159:112–118
- Courtois X, B N, Marrcot P, Duprez D Chapter 8 THE ROLE OF CERIUM-BASED OXIDES USED AS OXYGEN STORAGE MATERIALS IN DeNO_x CATALYSIS

488 Dasari P, Muncrief R, Harold MP (2013) Cyclic lean reduction of NO by CO in Excess H₂O on
 489 Pt-Rh/Ba/Al₂O₃: Elucidating mechanistic features and catalyst performance. *Top Catal*
 490 56:1922–1936. <https://doi.org/10.1007/s11244-013-0129-8>

491 Daturi M, Bion N, Saussey J, et al (2001) Evidence of a lacunar mechanism for deNO activity
 492 in ceria-based x catalysts. 30:28–31

493 Desai MSF, Kunkalekar RK, Salker A V (2015) Preparation , Characterization and NO-CO
 494 Redox Reaction Studies over Palladium and Rhodium Oxides Supported on Manganese
 495 Dioxide. 10:98–103. <https://doi.org/10.9767/bcrec.10.1.7802.98-103>

496 Ding W, Li W (2014) First-principles study of NO reduction by CO on transition metal atoms-
 497 doped CeO₂ (111). *Chinese J Catal* 35:1937–1943. [https://doi.org/10.1016/S1872-](https://doi.org/10.1016/S1872-2067(14)60169-8)
 498 2067(14)60169-8

499 Dumergues L, Favier B, Claver RA (2014) CO₂ Reuse . State of the Art and Expert Opinion
 500 Case of waste treatment activities

501 Ferrari N, Mancuso L, Burnard K, Consonni F (2019) Effects of plant location on cost of CO₂
 502 capture. 90:. <https://doi.org/10.1016/j.ijggc.2019.102783>

503 Gandhi HS, Graham GW, McCabe RW (2003) Automotive exhaust catalysis. *J Catal* 216:433–
 504 442. [https://doi.org/10.1016/S0021-9517\(02\)00067-2](https://doi.org/10.1016/S0021-9517(02)00067-2)

505 Gatica M, Baker RT, Fornasiero P, Kas J (2001) Characterization of the Metal Phase in NM /
 506 Ce_{0.68}Zr_{0.32}O₂ (NM : Pt and Pd) Catalysts by Hydrogen Chemisorption and HRTEM
 507 Microscopy : A Comparative Study. 2:1191–1199

508 Granger P, Dathy C, Lecomte JJ, et al (1998) Kinetics of the NO and CO reaction over
 509 platinum catalysts: I. Influence of the support. *J Catal* 173:304–314

510 Grenoble D, Estadt MM, Ollis DF (1981) The chemistry and catalysis of the water gas shift
 511 reaction 1. The kinetics over supported metal catalysts. *J Catal* 67:90–102.
 512 [https://doi.org/10.1016/0021-9517\(81\)90263-3](https://doi.org/10.1016/0021-9517(81)90263-3)

513 Holles JH, Switzer M a., Davis RJ (2000) Influence of Ceria and Lanthana Promoters on the
 514 Kinetics of NO and N₂O Reduction by CO over Alumina-Supported Palladium and Rhodium. *J*

515 Catal 190:247–260. <https://doi.org/10.1006/jcat.1999.2780>

516 Hou T, Yu B, Zhang S, et al (2015) Hydrogen production from ethanol steam reforming over
517 Rh/CeO₂ catalyst. Catal Commun 58:137–140.
518 <https://doi.org/10.1016/J.CATCOM.2014.09.020>

519 Iløeje C, Field R, Ghoniem AF (2015) Modeling and parametric analysis of nitrogen and sulfur
520 oxide removal from oxy-combustion flue gas using a single column absorber. Fuel 160:178–
521 188. <https://doi.org/10.1016/j.fuel.2015.07.057>

522 Ivanova AS, Slavinskaya EM, Gulyaev RV, et al (2010) Metal–support interactions in Pt/Al₂O₃
523 and Pd/Al₂O₃ catalysts for CO oxidation. Appl Catal B Environ 97:57–71.
524 <https://doi.org/10.1016/J.APCATB.2010.03.024>

525 Kobylinski TP, Taylor BW (1974) The catalytic chemistry of nitric oxide. II. Réduction of nitric
526 oxide over noble metal catalysis. J Catal 33:376–384

527 Koga H, Hayashi A, Ato Y, et al (2018) Effect of ceria and zirconia supports on NO reduction
528 over platinum-group metal catalysts: A DFT study with comparative experiments. Catal
529 Today. <https://doi.org/10.1016/J.CATTOD.2018.07.023>

530 Kolli T, Rahkamaa-Tolonen K, Lassi U, et al (2005a) Comparison of catalytic activity and
531 selectivity of Pd/(OSC + Al₂O₃) and (Pd + OSC)/Al₂O₃ catalysts. Catal Today 100:297–
532 302. <https://doi.org/10.1016/J.CATTOD.2004.09.064>

533 Kolli T, Rahkamaa-Tolonen K, Lassi U, et al (2005b) Comparison of catalytic activity and
534 selectivity of Pd/(OSC + Al₂O₃) and (Pd + OSC)/Al₂O₃ catalysts. Catal Today 100:297–302.
535 <https://doi.org/10.1016/j.cattod.2004.09.064>

536 Kumar A, Subramanian KA (2017) Control of greenhouse gas emissions (CO₂ , CH₄ and N₂
537 O) of a biodiesel (B100) fueled automotive diesel engine using increased compression
538 ratio. Appl Therm Eng 127:95–105. <https://doi.org/10.1016/j.applthermaleng.2017.08.015>

539 Liu Z, Anderson JA (2004) Influence of reductant on the thermal stability of stored NO_x in
540 Pt/Ba/Al₂O₃ NO_x storage and reduction traps. J Catal 224:18–27.
541 <https://doi.org/10.1016/j.jcat.2004.01.020>

542 Mantri D, Aghalayam P (2007) Detailed surface reaction mechanism for reduction of NO by
543 CO. 119:88–93. <https://doi.org/10.1016/j.cattod.2006.08.002>

544 Meunier N, Laribi S, Dubois L, et al (2014) CO₂ capture in cement production and re-use :
545 first step for the optimization of the overall process. Energy Procedia 63:6492–6503.
546 <https://doi.org/10.1016/j.egypro.2014.11.685>

547 Miller DD, Chuang SSC (2009) The effect of O₂ on the NO-CO reaction over Ag-Pd/Al₂O₃: An
548 in situ infrared study. Catal Commun 10:1313–1318.
549 <https://doi.org/10.1016/j.catcom.2009.02.011>

550 Nagai Y, Hirabayashi T, Dohmae K, et al (2006) Sintering inhibition mechanism of platinum
551 supported on ceria-based oxide and Pt-oxide-support interaction. J Catal 242:103–109.
552 <https://doi.org/10.1016/j.jcat.2006.06.002>

553 Nakamura I, Fujitani T (2009) Adsorption behavior and reaction properties of NO and CO on
554 Rh(111). Catal Surv from Asia 13:22–29. <https://doi.org/10.1007/s10563-009-9064-x>

555 Nanba T, Wada K, Masukawa S, et al (2010) Enhancement of activity of Ir catalysts for
556 selective catalytic reduction of NO with CO by physical mixing with SiO₂. Appl Catal A Gen
557 380:66–71. <https://doi.org/10.1016/J.APCATA.2010.03.028>

558 Ogura M, Kawamura A, Matsukata M, Kikuchi E (2000) Catalytic Activity of Ir for NO-CO
559 Reaction in the Presence of SO₂ and Excess Oxygen. Chem Lett 146–147.
560 <https://doi.org/10.1246/cl.2000.146>

561 Panagiotopoulou P, Kondarides DI (2006) Effect of the nature of the support on the catalytic
562 performance of noble metal catalysts for the water-gas shift reaction. Catal Today 112:49–
563 52. <https://doi.org/10.1016/j.cattod.2005.11.026>

564 Panayotov D, Khristova M, Velikova M (1996) Interactions NO-CO and O₂-NO-CO on and on
565 γ -Al₂O₃- and CuCo₂O₄/ γ -Al₂O₃-supported Pt, Rh and Pt-Rh catalysts, a transient response
566 study. Appl Catal B Environ 9:107–132

567 Pérez-Hernández R, Aguilar F, Gómez-Cortés A, Díaz G (2005a) NO reduction with CH₄ or CO
568 on Pt/ZrO₂-CeO₂ catalysts. Catal Today 107–108:175–180.
569 <https://doi.org/10.1016/j.cattod.2005.07.086>

570 Pérez-Hernández R, Aguilar F, Gómez-Cortés A, Díaz G (2005b) NO reduction with CH₄ or CO
571 on Pt/ZrO₂-CeO₂ catalysts. *Catal Today* 107–108:175–180.
572 <https://doi.org/10.1016/j.cattod.2005.07.086>

573 Perrin N, Dubettier R, Lockwood F, et al (2013) Oxycombustion for carbon capture on coal
574 power plants and industrial processes : advantages , innovative solutions and key projects.
575 *Energy Procedia* 37:1389–1404. <https://doi.org/10.1016/j.egypro.2013.06.015>

576 Shelef M, Graham GW (1994) Why Rhodium in Automotive Three-Way Catalysts? *Catal Rev*
577 36:433–457. <https://doi.org/10.1080/01614949408009468>

578 Shelef M, Otto K, Ghandy H (1968) The oxidation of CO by O₂ and by NO on supported
579 chromium oxide and other metal oxide catalysts. 375:361–375

580 Shen F, Akil J, Wang G, et al (2018) Real-time monitoring of N₂O production in a catalytic
581 reaction process using mid-infrared quantum cascade laser. *J Quant Spectrosc Radiat Transf*
582 221:1–7. <https://doi.org/10.1016/J.JQSRT.2018.09.022>

583 Shimokawabe M, Umeda N (2004) Selective Catalytic Reduction of NO by CO over Supported
584 Iridium and Rhodium Catalysts. *Chem Lett* 33:534–535. <https://doi.org/10.1246/cl.2004.534>

585 Sim J, Sim J (2017) Air emission and environmental impact assessment of Korean automotive
586 logistics. *J Clean Prod* 159:130–140. <https://doi.org/10.1016/j.jclepro.2017.05.058>

587 Suzuki A, Nakamura K, Sato R, et al (2009) Development and Application of Sintering
588 Dynamics Simulation for Automotive Catalyst. *Top Catal* 52:1852–1855.
589 <https://doi.org/10.1007/s11244-009-9352-8>

590 Uchiyama T, Karita R, Nishibori M, et al (2015) Preparation and characterization of Pd loaded
591 Sr-deficient K₂NiF₄-type (La, Sr)₂MnO₄ catalysts for NO-CO reaction. *Catal Today* 251:7–13.
592 <https://doi.org/10.1016/j.cattod.2014.09.033>

593 Vayssilov GN, Lykhach Y, Migani A, et al (2011) Support nanostructure boosts oxygen
594 transfer to catalytically active platinum nanoparticles. *Nat Mater* 10:310–315.
595 <https://doi.org/10.1038/nmat2976>

596 Wang C, Zheng T, Lu J, et al (2017) Three-way catalytic reactions on Rh-based catalyst: Effect

597 of Rh/ceria interfaces. Appl Catal 544:30–39

598 Wang Y, Zhu A, Zhang Y, et al (2008) Catalytic reduction of NO by CO over NiO/CeO₂ catalyst
599 in stoichiometric NO/CO and NO/CO/O₂ reaction. Appl Catal B Environ 81:141–149.
600 <https://doi.org/10.1016/j.apcatb.2007.12.005>

601 Wen B, He M (2002) Study of the Cu-Ce synergism for NO reduction with CO in the presence
602 of O₂, H₂O and SO₂ in FCC operation. Appl. Catal. B Environ. 37:75–82

603 Yao HC, Yao YFY (1984) Ceria in automotive exhaust catalysts: I. Oxygen storage. J Catal
604 86:254–265. [https://doi.org/10.1016/0021-9517\(84\)90371-3](https://doi.org/10.1016/0021-9517(84)90371-3)

605 Zhao S, Cai W, Li Y, et al (2018) Syngas production from ethanol dry reforming over Rh/CeO₂
606 catalyst. J Saudi Chem Soc 22:58–65. <https://doi.org/10.1016/J.JSCS.2017.07.003>

607 Zhu H ou, Kim JR, Ihm SK (2009) Characteristics of Pt/WO₃/CeO₂/ZrO₂ catalysts for catalytic
608 reduction of NO by CO. Appl Catal B Environ 86:87–92.
609 <https://doi.org/10.1016/j.apcatb.2008.07.024>

610