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Joudia Akil, Stéphane Siffert, Laurence Pirault-Roy, Sébastien Royer, Fengjiao Shen, et al.. Investigation of catalysts M/CeO<sub>2</sub> (M = Pt, Rh, or Pd) for purification of CO<sub>2</sub> 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-02982886v1>**

Submitted on 23 Mar 2023

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1 **Investigation of catalysts M/CeO<sub>2</sub> (M = Pt, Rh or Pd) for purification**  
2 **of CO<sub>2</sub> derived from oxycombustion in absence or presence of water**

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14 **Abstract:**

15 Oxyfuel combustion is a promising technology to produce a CO<sub>2</sub> rich flue gas ready suitable  
16 for sequestration or valorization. But its storage as well as its further valorization requires to  
17 increase the CO<sub>2</sub> purification as a small amount of CO and NO<sub>x</sub> are produced during  
18 combustion. Based on the technology developed for three-way converters, similar systems  
19 i.e M/CeO<sub>2</sub> where M is Pt, Pd or Rh were studied for NO-CO abatement in a gas stream  
20 similar to those obtained when an oxyfuel combustion is performed. The results evidenced  
21 that the role of the metal nature influences the performances obtained on NO-CO  
22 abatement, platinum supported on ceria being the most efficient catalyst. We also measured  
23 the impact of the presence of water in the reaction stream on the catalytic activity of these  
24 materials. It appears that the presence of water has a beneficial effect on the different  
25 reactions due to a water gas shift reaction that increases the reduction of the NO and favors  
26 the formation of N<sub>2</sub>. The study pointed out that platinum supported on ceria remained the

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

29

30 **Keywords:**

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

32 **1. Introduction**

33 The main part of energy production is coming from fossil fuels burning that leads to increase  
34 CO<sub>2</sub> concentration in the atmosphere and finally the average surface temperature of Earth. If  
35 energy production based on renewable sources can replace those obtained from fossil fuels  
36 power station, a large part of industrial activities as steel industries, cement production or  
37 domestic waste incinerator will still need combustion processes and require solutions to  
38 reduce CO<sub>2</sub> discharge. Capture and purification of CO<sub>2</sub> for storage or valorization is a key-  
39 parameter to reduce its concentration in the atmosphere and to limit global warming  
40 (Ademe et al. 2014; Dumergues et al. 2014; Ferrari et al. 2019). Among the proposed  
41 processes, oxyfuel combustion is a promising technology (Perrin et al. 2013; Iloeje et al.  
42 2015). This process consists of burning a fuel using pure oxygen instead of air to produce a  
43 CO<sub>2</sub> rich flue gas ready suitable for sequestration or valorization (for example CO<sub>2</sub>  
44 methanation). Although small amount of CO and NO<sub>x</sub> are produced in lesser extent than a  
45 classical combustion, they should be removed before CO<sub>2</sub> capture and storage. Indeed, these  
46 gases are not respectful of the environment; moreover they can lead to corrosion of the  
47 transfer lines and will be disruptive elements for a possible utilization of the stored CO<sub>2</sub>  
48 (Meunier et al. 2014; Iloeje et al. 2015). Based on the technology developed for three-way  
49 converters (TWC), similar systems can be proposed for the purification of CO<sub>2</sub> by reducing  
50 NO<sub>x</sub> using CO as a reducing agent. But we must note some important differences between a  
51 “classical” NO-CO reaction in TWC and a NO-CO reaction in oxyfuel combustion. Firstly, the  
52 gas composition is different with a noticeable higher amount of oxygen and water in oxyfuel  
53 condition (Table 1). Moreover, during our reaction, we are in presence of a significant  
54 amount of CO<sub>2</sub> which can be troublesome for the catalytic activity depending on the  
55 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; Almusaiter and Chuang 1998; Kolli et al. 2005a)
		With maximum 4% of O <sub>2</sub>	(Ogura et al. 2000; Shimokawabe and Umeda 2004; Zhu et al. 2009; Dasari et al. 2013)
		With maximum 5% of H <sub>2</sub> O	(Wen and He 2002; Dasari et al. 2013)
Oxyfuel combustion	<1	With minimum 5% of water and 4% of O <sub>2</sub>	(Andersson et al. 2008; Illoeje et al. 2015)

62 Secondly, the gas treatment temperature can be adjusted by placing the catalytic bed at a  
63 desired height in the industrial chimney, which is not possible for a vehicle which is  
64 dependent on the reaction and its exothermicity to ensure the temperature increase of the  
65 TWC. Thirdly, additional gas as water, ammonia or others, can be introduced easily in the gas  
66 flow on the contrary of TWC. Finally, the flow rate can be controlled during the oxyfuel for  
67 example by increasing the chimney diameter while the constraints in terms of flow and  
68 exhaust diameter are higher on the TWC. Despite of all these difference about gas  
69 composition, flow rate, temperature the process of car exhausts treatment can be a source  
70 of inspiration because the nature of the gases is similar (Meunier et al. 2014; Iloeje et al.  
71 2015; Kumar and Subramanian 2017; Sim and Sim 2017). For catalytic converters, supported  
72 noble metal catalysts have been widely used in the control of atmospheric pollution and  
73 have demonstrated high activity (Gandhi et al. 2003; Ivanova et al. 2010). The three precious  
74 metals used i.e platinum, palladium and rhodium, have been dispersed, stabilized,  
75 promoted, allied and separated in a progressively sophisticated way over the years to  
76 achieve exceptional progress in terms of performance and long term lifetime (Gandhi et al.  
77 2003). Platinum and palladium (higher availability and lower cost than Pt) are known for  
78 their oxidizing ability and have been chosen for the simultaneous oxidation of carbon  
79 monoxide and hydrocarbons in the very first two-way (or "oxidation") catalytic converters.  
80 Rhodium, meanwhile, was added to ensure the reduction of nitrogen oxides to dinitrogen  
81 leading to a third way and emerging three-way converters. The support targeted for three-  
82 way catalysts was ceria ( $\text{CeO}_2$ ). The application dates back to the late 1970s and since then  
83 has been continuously implemented to achieve a high level of efficiency (Aneggi et al. 2016).  
84 The importance of this oxide for these reactions is reflected in its high oxygen storage and  
85 release capacity thanks to its redox  $\text{Ce}^{4+}/\text{Ce}^{3+}$  pair (Yao and Yao 1984; Gandhi et al. 2003).

86 Although many reports have been published on the NO-CO reaction on precious metal  
87 catalysts, few studies have addressed this reaction in the presence of excess oxygen and  
88 water as the main application was the three-way converters working in rich conditions in a  
89 narrow window around stoichiometry (Nanba et al. 2010). Indeed, CO is a reducing agent for  
90 three-way catalysts to reduce NOx but under oxidizing conditions, it will preferentially be  
91 oxidized by oxygen instead of performing nitric oxide reduction (Nakamura and Fujitani  
92 2009) which leads to a drastic decrease of the selectivity towards the dinitrogen (Kolli et al.

93 2005b). Nowadays, more attention is being paid to these systems to be used to purify the  
94 gas exhaust in particular after an oxyfuel combustion for CO and NO<sub>x</sub> removal (Illoeje et al.  
95 2015) before CO<sub>2</sub> capture and storage. However, the main challenge remains to perform this  
96 reaction in presence of an excess of oxygen. Indeed, many authors have studied the  
97 reaction of NO reduction by CO with very promising results (Kobylinski and Taylor 1974;  
98 Granger et al. 1998; Pérez-Hernández et al. 2005b; Zhu et al. 2009). However other studies  
99 have shown that low oxygen content (max 4%) is harmful for the reaction, because of a  
100 preferential oxidation of the reducing agent (Nakamura and Fujitani 2009). Thus, many  
101 authors have studied the competition between the two reactions CO-NO and CO-O<sub>2</sub>. Shelef  
102 et al. found that this second reaction is predominant on a number of supported Pt catalysts  
103 and transition metal oxide (Shelef et al. 1968). On the other hand, Zhu et al (Zhu et al. 2009)  
104 showed on Pt-based catalysts, a strong inhibition of NO reduction in the presence of an  
105 excess of oxygen: 100% conversion between 300 and 400 ° C without O<sub>2</sub>, to a maximum of  
106 18% in the same temperature range in the presence of O<sub>2</sub>. This inhibition is due to the fact  
107 that CO reacts more easily with O<sub>2</sub> than with NO, which inhibits the conversion of the latter.  
108 Kolli et al (Kolli et al. 2005b) report similar results on Pd catalysts. These authors showed an  
109 increase towards the formation of N<sub>2</sub>O in the presence of oxygen with a disappearance of  
110 the formation of N<sub>2</sub> (Kolli et al. 2005b). They also noticed that at 100% oxidation of CO, the  
111 NO begins to oxidize to NO<sub>2</sub> (Kolli et al. 2005b). Wang et al. (Wang et al. 2008) also reported  
112 a decrease in activity with respect to NO reduction in the presence of O<sub>2</sub> on the NiO/CeO<sub>2</sub>  
113 catalyst. To summarize in the absence of oxygen, the NO can play the role of oxidant on the  
114 catalyst active sites thus allowing CO oxidation whereas in presence of oxygen the catalyst  
115 active sites will be blocked by adsorbed oxygen hindering thus the NO conversion (Mantri  
116 and Aghalayam 2007). Few studies take into account the role of water in the stream  
117 although it can be crucial for catalysts stability.

118 In this paper, we will therefore study the possibility of transposing the knowledge from the  
119 catalytic conversion of vehicle effluents to the problem of the purification of CO<sub>2</sub> from oxy-  
120 fuel combustion in a chimney. The authors want to purify the CO<sub>2</sub> only with the component  
121 present in the flue gas; that is why the CO will be used to reduce the NO. The oxidation of CO  
122 is not the main problem which is the NO<sub>x</sub> reduction in oxidizing medium. Thus, the target is  
123 50% NO<sub>x</sub> abatement (an already considerable but nevertheless reasonable objective). Thus,

124 the effect of the nature of the active phase (Pd, Pt and Rh) supported on CeO<sub>2</sub> in the  
125 simultaneous oxidation of carbon monoxide and reduction of nitric oxide in an oxidizing  
126 medium (10% O<sub>2</sub>) and in the presence of H<sub>2</sub>O will be investigated in order to purify the CO<sub>2</sub>  
127 from the oxycombustion. We will also determine the selectivity of the best catalyst  
128 regarding to the formation of N<sub>2</sub> from nitric oxide reduction.

## 129 **2. Experimental**

### 130 **2.1. Catalysts preparation**

131 Ceria (HAS 20 (Rhodia)) with a specific surface area of 65 m<sup>2</sup>.g<sup>-1</sup> was used as support. Before  
132 any impregnation, ceria was calcined in air at 500 °C for four hours with a ramp of 5°C/min.

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

137 Table 2. Metal precursors used for the impregnation

<b>Metal</b>	<b>Palladium</b>	<b>Platinum</b>	<b>Rhodium</b>
<b>precursor used</b>	Pd(acac) <sub>2</sub>	Pt(NO <sub>2</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	Rh(NO <sub>3</sub> ) <sub>3</sub>

138

139 The impregnated support was left overnight in an oven at 393 K. It was then calcined in dry  
140 air and reduced in H<sub>2</sub> flow during 4 h at 773 K for both thermal treatments.

### 141 **2.2. Characterization of the catalysts**

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

144 The obtained samples were subsequently characterized by H<sub>2</sub> chemisorption. Ceria is a  
145 reducible oxide and some authors evidenced that the ceria surface close to the noble metal  
146 particles can be reduced via the spillover of H<sub>2</sub> even at room temperature which can cause a  
147 considerable disturbance of the measurements. Thus a new protocol was proposed for  
148 carrying out the chemisorption of hydrogen based on limitation of the spillover effect by

149 performing the adsorption at low temperature near - 70°C to block the kinetics of the H<sub>2</sub>  
150 chemisorption on ceria (Gatica et al. 2001). This protocol was retained to determine the  
151 metal dispersion of catalyst by hydrogen chemisorption and a chromatographic micro-  
152 reactor was used to perform the measurements. After a reduction under H<sub>2</sub> (350 °C, 60 min)  
153 and degassing under argon (350 °C, 180 min), hydrogen pulses (0.26 mL) were injected in the  
154 reactor where the catalyst was introduced, at regular interval of time and at -70 °C until  
155 saturation. The calculation of the particle sizes is performed with the cubic model with 5  
156 faces exposed corresponding to the Hughes hypothesis [8], with an equal distribution  
157 between (1 1 1), (1 1 0) and (1 0 0) planes.

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

### 161 **2.3. Catalytic tests**

162 Before each test, the catalyst was treated in situ under He flow (40 mL.min<sup>-1</sup>) at 473 K for 90  
163 min. Then, CO<sub>2</sub> purification was carried out at atmospheric pressure in a fixed-bed flow  
164 reactor containing 150 mg of catalyst. The catalysts were sieved in order to retain grains  
165 with diameters between 0.315 and 0.500 mm and diluted to a constant volume by SiC  
166 (which exhibited no activity in CO<sub>2</sub> purification from 50 to 500 °C) to ensure that all the  
167 experiments were carried out under the same conditions (GHSV = 2.24 10<sup>4</sup> h<sup>-1</sup>) and achieved  
168 in the mentioned experimental set up (Fig. 1).

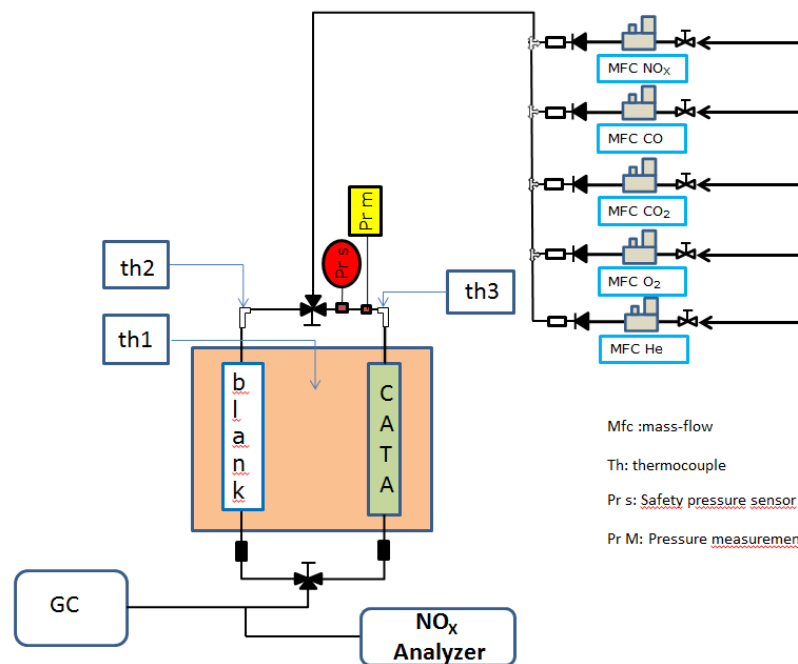
169 The flow of the reactant gases is composed of: 20 % CO<sub>2</sub>, 10 % O<sub>2</sub>, 0.5 % CO and 0.02 % NO  
170 (He as eluent gas) with a total flow of 200 mL.min<sup>-1</sup>, in the temperature range 50–500 °C. A  
171 normal oxyfuel combustion process is supposed to give a higher amount of CO<sub>2</sub>, but to be  
172 able to study the different reactions that can occur and to identify the species, a lower CO<sub>2</sub>  
173 concentration was chosen. Moreover, CO<sub>2</sub> is not expected to interfere in the CO-NO reaction  
174 except by covering the basic sites of the ceria and 20% of CO<sub>2</sub> will be enough to block all  
175 basic sites. So, a more important amount of carbon dioxide will not affect the NO-CO  
176 reaction in oxidizing medium and the data obtained in this work. The reaction products (CO<sub>2</sub>  
177 and N<sub>2</sub>) were analyzed on line by a gas chromatograph (Label GAS analyzer XXL1300), NO  
178 was analyzed with Xentra 4900C analyzer (Servomex). The measurement of NO<sub>2</sub> is done



179 indirectly using a NO<sub>2</sub> to NO converter BÜNOx (Bühler Technologies) by comparison. In  
 180 order to evaluate the selectivity of the catalysts, we used a room-temperature continuous-  
 181 wave (CW) external cavity quantum laser cascade (EC-QCL) -based optical sensor, with an  
 182 accuracy of 32.3ppbv. N<sub>2</sub>O sensor based on a continuous-wave (CW) external-cavity  
 183 quantum cascade laser (EC-QCL) operating at ~ 8 μm, coupled to a modified-Herriot multi-  
 184 pass cell is completely describe in the paper of Shen and al. (Shen et al. 2018).

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

- 186 - 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  
 187 the corresponding compounds “i” at the inlet and the outlet of the reactor.  
 188 - Selectivity:  $S_i (\%) = \frac{n_i}{\sum_i n_i} * 100$   
 189 - Yield:  $Y_i (\%) = X_i * S_i * 100$



190

191 **Figure 1:** Experimental setup for catalytic purification of CO<sub>2</sub> from oxyfuel combustion

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

196 **3. Results and discussion**

197 **3.1. Characterization**

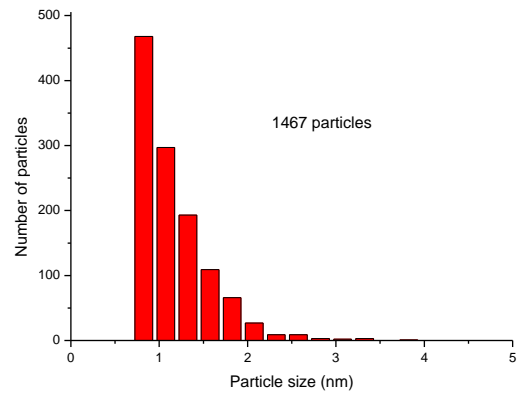
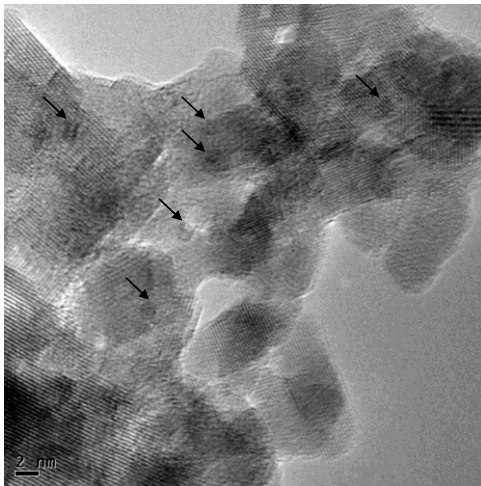
198 The catalysts prepared by impregnation of ceria targeting 1 wt-% of the noble metal were  
199 analyzed by ICP to determine the metallic content. The results are presented in Table 3. The  
200 catalysts were also characterized in order to determine their metal accessibility as well as  
201 their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

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

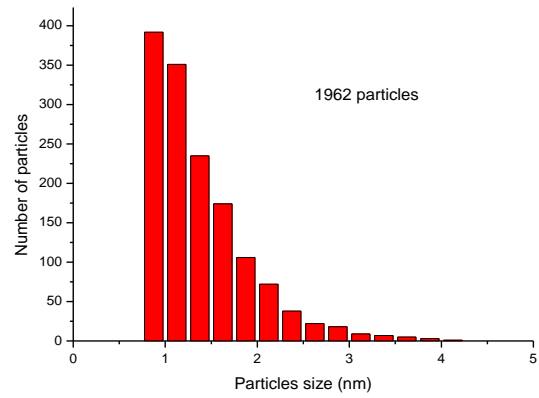
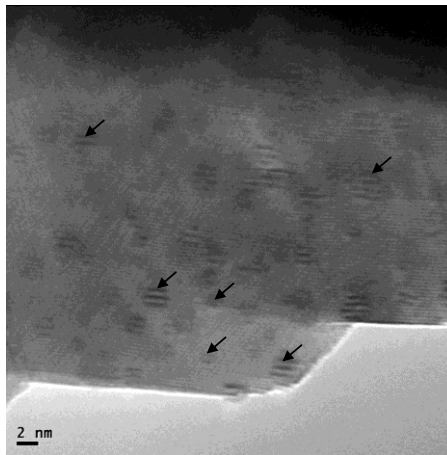
Catalysts	Reference	Measured metallic content (%)	Metallic accessibility (%)	< d > (nm) Before test H <sub>2</sub> chemisorption / TEM	< d > (nm) After test deduced from H <sub>2</sub> chemisorption
<b>Pt/CeO<sub>2</sub></b>	Pt/Ce	1.14	43	2.6 / 1.5	2.9
<b>Rh/CeO<sub>2</sub></b>	Rh/Ce	1.05	46	1.8 / 1.8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

203  
204 The metallic contents are very close to the targeted ones. The metal accessibilities measured  
205 by hydrogen chemisorption and reported in Table 3, are similar for all the catalysts with a  
206 metal accessibility of about 40% corresponding to similar particle sizes also of about 2 nm,  
207 allowing us to carry out a relevant comparison of the catalytic activity of the different  
208 materials.

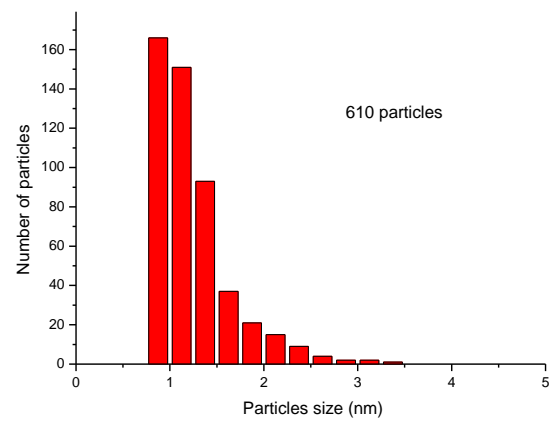
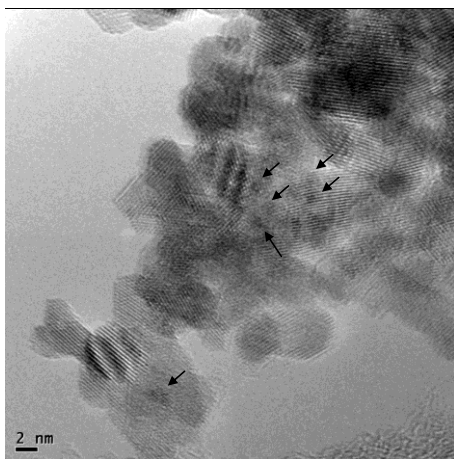
209 The morphology of the catalysts was evaluated by transmission electron microscopy (TEM)  
210 coupled with energy dispersive X-ray spectroscopy (EDX), in order to observe the accurate  
211 localization of the metallic particles, to analyze their chemical nature and to estimate their  
212 average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



Pt/CeO<sub>2</sub>



Rh/CeO<sub>2</sub>



Pd/CeO<sub>2</sub>

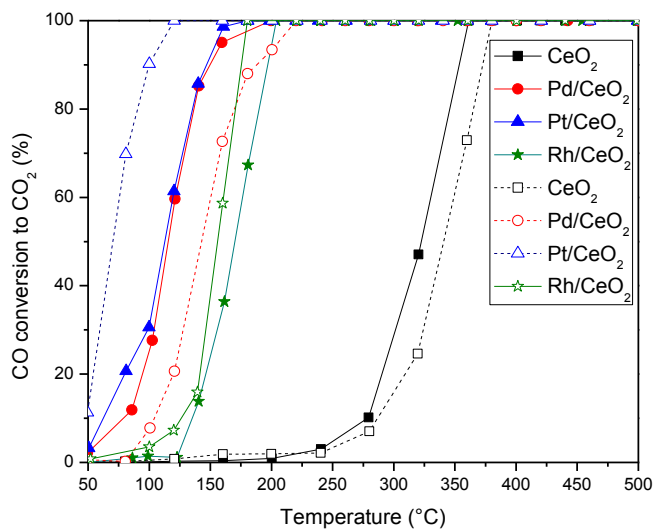
216 **Figure 2:** TEM images and particle size distributions of noble metal catalysts supported on  
 217 ceria

218 **3.2. Catalytic reaction**

219 The catalytic activity test was carried out in the presence of 20% CO<sub>2</sub>, 10% O<sub>2</sub>, 0.5% CO,  
220 0.02% NO in helium, with a total flow of 200 cm<sup>3</sup>.min<sup>-1</sup> in the presence of 150 mg of catalyst  
221 shaped and diluted with SiC. The experiments were performed in presence or not of water  
222 to check the influence of this parameter on activity, selectivity and stability. The 8.5% of  
223 water was added using passing the flow gas through a saturator whose temperature was set  
224 at 42 °C.

225 **3.2.1. CO oxidation with or without water in the gas stream**

226 For CO<sub>2</sub> purification, simultaneous reactions should be achieved: oxidation of CO and  
227 reduction of NO<sub>x</sub> in an oxidizing atmosphere and generally with water. Our catalysts were  
228 tested to investigate the influence of the metal nature and the presence of water (8.2%) for  
229 these simultaneous reactions focusing first on CO oxidation. The figure 3 presents the light-  
230 off curves of CO oxidation according the metal deposited on ceria with and without water in  
231 the gas stream.



232  
233 **Figure 3:** CO oxidation over Pt, Rh or Pd supported on ceria catalysts in the absence (closed  
234 symbols) and presence (open symbols) of water

235

236 Table 4. Half conversion (T50) and 90% conversion (T90) temperatures of CO on M/CeO<sub>2</sub>  
 237 catalysts (M = Pd, Pt or Rh) in presence or not of water

Catalysts	Without water		With water	
	T <sub>50</sub> (°C)	T <sub>90</sub> (°C)	T <sub>50</sub> (°C)	T <sub>90</sub> (°C)
<b>CeO<sub>2</sub></b>	323	351	342	370
<b>Pd/CeO<sub>2</sub></b>	116	147	143	183
<b>Pt/CeO<sub>2</sub></b>	112	145	70	100
<b>Rh/CeO<sub>2</sub></b>	170	196	156	172

238

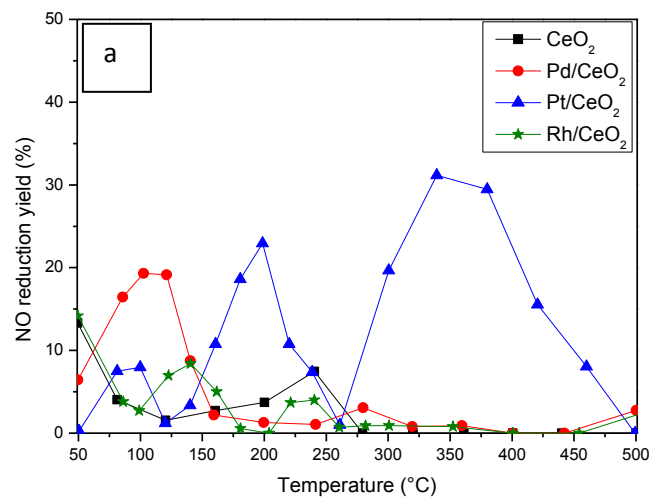
239 Addition of noble metal to ceria increases in the oxidation activity. Yao et al. have shown  
 240 that the presence of a noble metal (Pt, Pd or Rh) on ceria favors its ability to store/exchange  
 241 oxygen atoms, thus facilitating the oxidation of CO at lower temperatures than these same  
 242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

248 The best performances were obtained on Pt/CeO<sub>2</sub> and Pd/CeO<sub>2</sub> catalysts while Rh/CeO<sub>2</sub>  
 249 catalyst shows an oxidation of carbon monoxide at a higher temperature with a T<sub>50</sub> of 170°C.  
 250 Both of Pd and Pt materials have near-similar T<sub>50</sub> and T<sub>90</sub> values when the experiments were  
 251 carried out in absence of water. On the contrary, in the presence of water, their activities  
 252 became different. The results evidenced a beneficial effect of water for Pt/CeO<sub>2</sub> catalyst (and  
 253 Rh/CeO<sub>2</sub> too) whereas a detrimental effect was observed on Pd/CeO<sub>2</sub>. According to Table 3,  
 254 the addition of water to the reaction stream makes it possible to reduce the conversion  
 255 temperatures T<sub>50</sub> and T<sub>90</sub> of the carbon monoxide on the Pt/CeO<sub>2</sub> and Rh/CeO<sub>2</sub> catalysts by  
 256 approximately 45°C and 20°C respectively. This improvement is due to the reaction of water  
 257 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

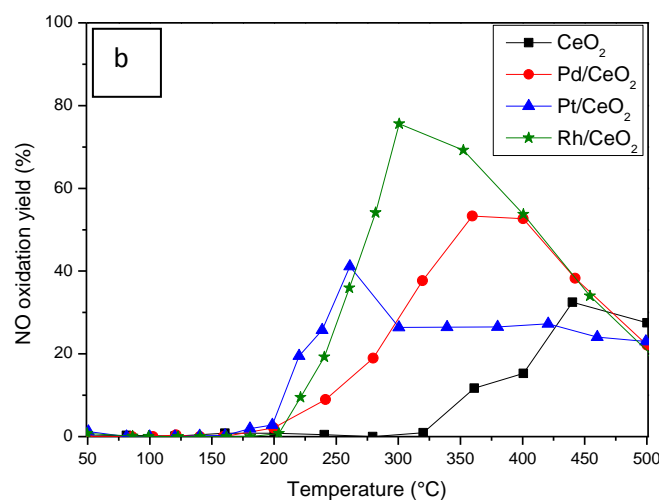
258 role of a second oxidant for carbon monoxide in addition to oxygen during the WGS  
259 reaction. Rh and Pt metals are more active for the WGS reaction than Pd one leading to an  
260 increase of CO conversion higher than that observed on Pd/CeO<sub>2</sub> (Panagiotopoulou and  
261 Kondarides 2006). A ranking based T<sub>50</sub> as well as T<sub>90</sub> shows the following order: CeO<sub>2</sub>  
262 <Rh/CeO<sub>2</sub> <Pd/CeO<sub>2</sub> <Pt/CeO<sub>2</sub>.

### 263 3.2.2. NO conversion with or without water in the gas stream

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



267



268

269 **Figure 4:** Reduction (a) and oxidation (b) yields of NO on noble metals (Pd, Pt and Rh)  
270 supported on CeO<sub>2</sub>

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

274 The NO reduction starts at lower temperature on the Pd/CeO<sub>2</sub> catalyst than other catalysts  
275 and reaches a 19% maximum reduction at 100 °C. Indeed, several authors have shown an  
276 influence of the Pd-Ce interaction on the adsorption of NO (Cordatos and Gorte 1996;  
277 Ciuparu et al. 2000). According to Holles et al., ceria affects the NO-CO reaction by  
278 facilitating the dissociation of NO at the Pd/support interface, thus promoting its reduction  
279 (Holles et al. 2000).

280 Rhodium has the smallest reduction performance with a maximum of conversion around 8%  
281 at 140°C. On this catalyst, at low temperature [50-100°C], the NO reduction profile  
282 corresponds perfectly to that obtained on the CeO<sub>2</sub> support alone. Holles et al. also pointed  
283 out a beneficial effect of ceria on rhodium-based catalysts for the dissociation of NO (Holles  
284 et al. 2000). However, this effect was less pronounced than on the palladium catalysts  
285 according to these same authors (Holles et al. 2000). In addition, it has been evidenced in  
286 the literature that although rhodium is well-known for NO reduction, it is sensitive to the  
287 presence of oxygen and deactivates in oxidizing environments (Panayotov et al. 1996). This  
288 explains the low activity of the Rh/CeO<sub>2</sub> catalyst in our experimental conditions.

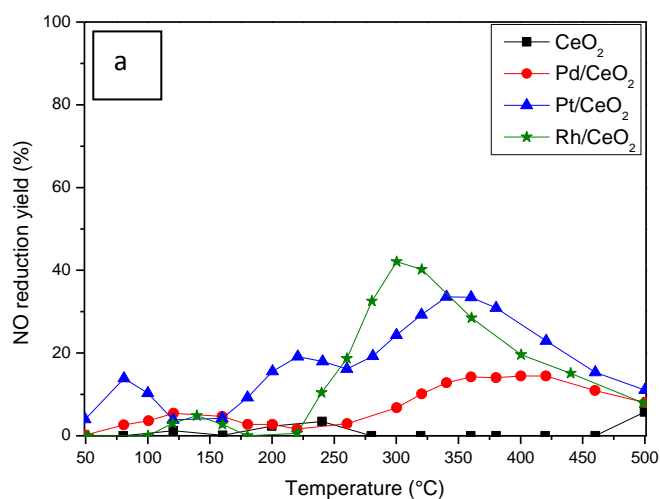
289 Platinum has an even more different behavior for reducing NO than other catalysts. This  
290 metal exhibits three reduction zones 50-120, 120-260 and 260-500 °C with a maximum  
291 reduction in the third zone of 31% at 340 °C. Despite its somewhat surprising profile, our  
292 catalyst is more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

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

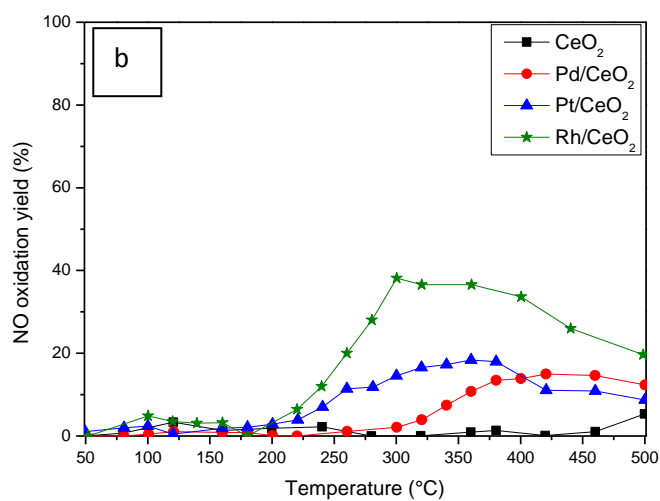
299  $\text{CeO}_2 < \text{Rh}/\text{CeO}_2 < \text{Pd}/\text{CeO}_2 < \text{Pt}/\text{CeO}_2$ . This ranking corresponds perfectly to that achieved for  
300 the oxidation of CO.

301 The higher activity of the  $\text{Pt}/\text{CeO}_2$  catalyst could be correlated, according to the literature,  
302 with the interaction between platinum and the  $\text{CeO}_2$  support which can inhibit the sintering  
303 of platinum (Nagai et al. 2006; Suzuki et al. 2009), unlike the  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst (Nagai et al.  
304 2006). Indeed, the  $\text{CeO}_2$  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  $\text{H}_2\text{O}$  on palladium, platinum and rhodium catalysts  
308 supported on  $\text{CeO}_2$ .



309



310



311 **Figure 5:** Reduction (a) and oxidation (b) yields of NO on noble metals Pd, Pt and Rh  
312 deposited on CeO<sub>2</sub> in the presence of 8.2 % of water

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

315 The best reduction yield was obtained on the Rh/CeO<sub>2</sub> catalyst with 42% reduction at 300°C,  
316 followed by the Pt/CeO<sub>2</sub> catalyst with 34% reduction at 340°C and finally the Pd/CeO<sub>2</sub>  
317 catalyst with 14% reduction at 360°C.

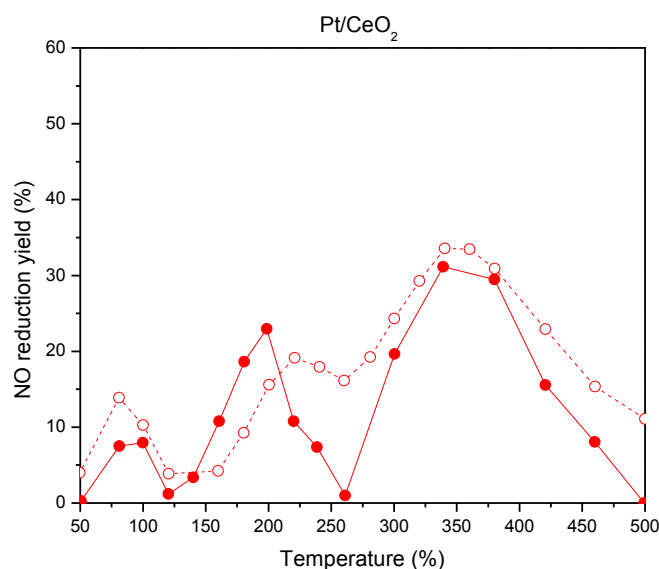
318 The oxidation of the NO follows the same order of ranking of the catalysts as for the  
319 reduction of NO.

320 Indeed, this improvement of activity in the presence of water is due to the reaction of water  
321 gas shift. Indeed, it turns out that ceria is a promoter for these noble metals in the "water  
322 gas shift" reaction [21]. Studies have shown a significant metal support interaction in the  
323 case of noble metal catalysts supported on ceria (Courtois et al.; Shelef and Graham 1994;  
324 Bunluesin et al. 1998; Daturi et al. 2001; Wang et al. 2017; Koga et al. 2018). They showed  
325 that this metal support interaction creates active oxygen species facilitating oxidation of CO.  
326 In addition, it creates oxygen vacancies that make it the NO dissociation easier. Ceria will be  
327 re-oxidized by the presence of water thus forming H<sub>2</sub> by the reaction of water gas shift (CO +  
328 H<sub>2</sub>O = H<sub>2</sub> + CO<sub>2</sub>) at temperatures above 200 °C. Finally, this H<sub>2</sub> formed can react with NO to  
329 form NH<sub>3</sub>. H<sub>2</sub> and NH<sub>3</sub> formed within the reaction, are more powerful reductants than CO  
330 and then lead to a more effective catalytic reduction of NO. In addition, Koga et al showed  
331 that there was a greater electron transfer in Rh/CeO<sub>2</sub> thus allowing for a better catalytic  
332 activity of NO conversion (Koga et al. 2018). Meanwhile, Pt is 15–20 times more active than  
333 Rh and 50 times more active than Pd, at 250°C (Panagiotopoulou and Kondarides 2006).

### 334 **3.2.3. Selectivity**

335 It has been shown in the previous paragraphs that the Pt/CeO<sub>2</sub> catalyst maintains its activity  
336 with respect to the reduction of nitric oxide in the absence and in the presence of water.  
337 Indeed, this catalyst is known for its activity in the gas-to-water reaction or "water gas shift"  
338 reaction which generates hydrogen, a second reducing agent for nitric oxide, to produce  
339 either directly N<sub>2</sub> or N<sub>2</sub>O either NH<sub>3</sub> which is also a more powerful reductant than CO.

340 However, it has been proven in the literature that selectivity towards N<sub>2</sub> depends on the  
 341 nature of the reductant (Liu and Anderson 2004; Pérez-Hernández et al. 2005b; Abdulhamid  
 342 et al. 2006). It is therefore necessary to study the selectivity in the absence and in the  
 343 presence of the water of this catalyst, especially since the latter is the only catalyst to have  
 344 three distinct reduction zones shown in Figure 6. These three areas have already been  
 345 observed and explained by Wuchen Ding et al. and D.M.F. Alves et al. (Alves et al. 2013; Ding  
 346 and Li 2014). They showed that the formation of N<sub>2</sub> on a Pt/CeO<sub>2</sub> took place in 3 steps:  
 347 gaseous N<sub>2</sub>O formation, subsequent N<sub>2</sub>O re-adsorption, and formation of N<sub>2</sub>. Table 4 shows  
 348 the selectivity for N<sub>2</sub> and N<sub>2</sub>O obtained on the Pt/CeO<sub>2</sub> catalyst in the presence and absence  
 349 of H<sub>2</sub>O. The measurements were performed at the maximum reduction yield of the three  
 350 peaks.



351  
 352 **Figure 6:** Reduction yields of NO on Pt/CeO<sub>2</sub> catalyst in the absence (closed symbols) and  
 353 presence of water (open symbols)

354 Table 5. Selectivity of NO reduction on CeO<sub>2</sub>-supported Pt catalyst in the presence and  
 355 absence of H<sub>2</sub>O

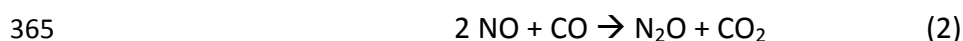
Temperature (°C)	without H <sub>2</sub> O		with H <sub>2</sub> O	
	N <sub>2</sub> O (%)	N <sub>2</sub> (%)	N <sub>2</sub> O (%)	N <sub>2</sub> (%)
<b>80-100 (1<sup>st</sup> reduction zone)</b>	1,9	98,1	2,8	97,2

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

356

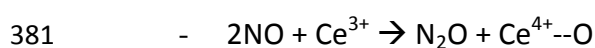
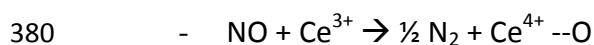
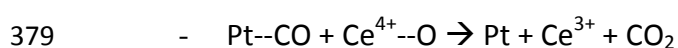
357 It therefore seems that in our reaction conditions, the Pt/CeO<sub>2</sub> catalyst is very selective  
 358 towards dinitrogen production with at least 98% in the absence of water and 97% in  
 359 presence of water. Very low selectivity (<3%) in N<sub>2</sub>O was observed at low conversion  
 360 temperatures. As the temperature raises up, the selectivity in N<sub>2</sub> 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:

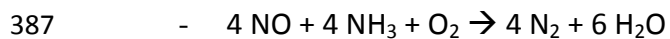
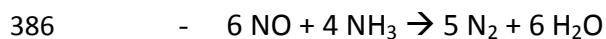
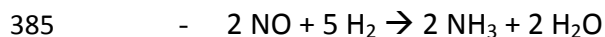


367 CO<sub>2</sub> formation occurs directly (reaction 1) and sequentially (reactions 2 and 3). Since the  
 368 selectivity of N<sub>2</sub> was almost 100%, we assume that reaction 1 (NO-CO direct reaction)  
 369 occurred as a main reaction pathway. Indeed, it has been generally accepted that the  
 370 formation of N<sub>2</sub>O 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 Ce<sup>4+</sup>/Ce<sup>3+</sup> 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 N<sub>2</sub>O and N<sub>2</sub>, according to the following mechanism (Alves et al. 2013):



382 While above 300 °C, the production of H<sub>2</sub> by WGS, thus promoting the formation of N<sub>2</sub>,  
383 according to the following reactions:

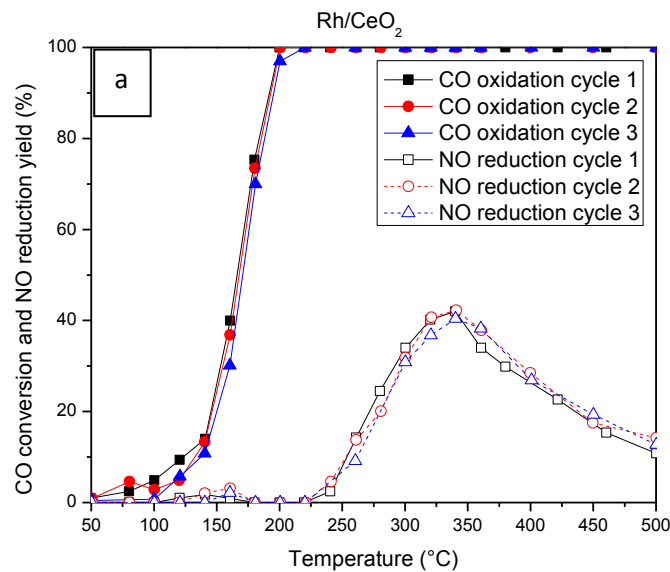


388 Despite the small amount of N<sub>2</sub>O produced, it should be noted that this catalyst produces  
389 more N<sub>2</sub>O at low temperature than at high temperature. Panayotov & al. have observed on  
390 Pt and/or Rh supported on ceria catalysts that N<sub>2</sub>O is the dominant product at low  
391 temperature whereas N<sub>2</sub> is almost exclusively produced at high temperature (Panayotov et  
392 al. 1996). This has not been the case on our catalysts; however the trend is the same.

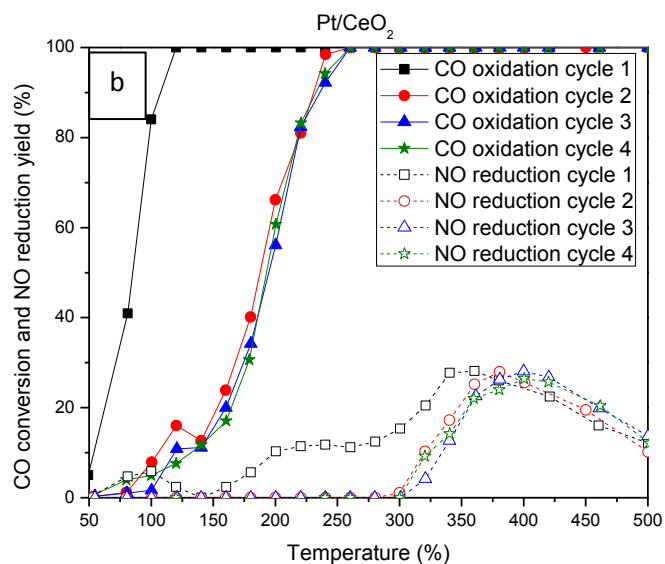
#### 393 **3.2.4. Stability test**

394 In order to study the stability of these materials as a function of time, we chose to carry out  
395 tests combining several cycles on the two most active materials, namely Rh/CeO<sub>2</sub> and  
396 Pt/CeO<sub>2</sub>.

397 These catalysts were pretreated under helium for 90 min at 200 °C, before being submitted  
398 to the reaction mixture under the same conditions of tests previously carried out in the  
399 presence of water. The data are collected and interpreted in the same way than for activity  
400 tests. Several successive cycles have been carried out and each cycle involves a rise in  
401 temperature ranging from 50 to 500 °C under the reaction flow up to see the same curves  
402 meaning a stabilization phase. The stability of Rh/CeO<sub>2</sub> and Pt/CeO<sub>2</sub> catalysts during  
403 successive cycles are presented in Figure 7.



404



405

406 **Figure 7:** Stability test for several successive cycles in the presence of Rh/CeO<sub>2</sub> (a) and  
 407 Pt/CeO<sub>2</sub> (b) focusing on the carbon monoxide conversion rate (closed symbols) and NO  
 408 reduction yield (open symbols) as a function of temperature

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

415 interaction between Rh and ceria support efficiently inhibited Rh particles sintering. several  
416 authors have reported a good stability of Rh/CeO<sub>2</sub> catalysts for the same reasons (Hou et al.  
417 2015; Zhao et al. 2018).

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

426  
427

#### 428 **4. Conclusion**

429 In this work, we studied the catalytic performance of palladium, platinum and rhodium  
430 based material supported on ceria for purification of CO<sub>2</sub> derived from oxycombustion in  
431 absence or presence of water. The ceria impregnation with 1 wt.% of platinum, palladium or  
432 rhodium led to a good improvement of CO oxidation and NO reduction. The same activity  
433 order was obtained concerning the two reactions studied (simultaneous CO oxidation and  
434 NO reduction): Rh < Pd < Pt. The most efficient catalyst Pt/CeO<sub>2</sub> exhibited the most  
435 important NO reduction (31% at 340°C) with total CO oxidation at low temperature (around  
436 150°C). In addition, the oxidation of NO, to be avoided, was less important than on the other  
437 metals.

438 We also investigated the impact of the presence of 8.2% water in the reaction stream on the  
439 catalytic activity of these materials. It appeared that the presence of water had a beneficial  
440 effect on the different reactions. Indeed, the addition of water decreased the temperature  
441 of CO oxidation following the addition of a third oxidant H<sub>2</sub>O in addition to NO and O<sub>2</sub>. This  
442 reaction ( $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ ) called WGS also influenced the NO reduction. Indeed, the  
443 production of H<sub>2</sub> increased the reduction of the NO and favored the formation of N<sub>2</sub>. This  
444 was verified on all the catalysts with the exception of the palladium catalyst. The stability

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

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

455

#### 456 **Acknowledgements**

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

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