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1 **Investigation of catalysts M/CeO₂ (M = Pt, Rh or Pd) for purification**
2 **of CO₂ 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 CO₂ rich flue gas ready suitable
16 for sequestration or valorization. But its storage as well as its further valorization requires to
17 increase the CO₂ purification as a small amount of CO and NO_x are produced during
18 combustion. Based on the technology developed for three-way converters, similar systems
19 i.e M/CeO₂ 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 N₂. 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 CO₂ 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 CO₂ discharge. Capture and purification of CO₂ 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 CO₂ rich flue gas ready suitable for sequestration or valorization (for example CO₂
44 methanation). Although small amount of CO and NO_x are produced in lesser extent than a
45 classical combustion, they should be removed before CO₂ 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 CO₂
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 CO₂ by reducing
50 NO_x 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 CO₂ 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 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; 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 (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_x removal (Illoeje et al.
95 2015) before CO₂ 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-O₂. 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 O₂, to a maximum of
106 18% in the same temperature range in the presence of O₂. This inhibition is due to the fact
107 that CO reacts more easily with O₂ 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 N₂O in the presence of oxygen with a disappearance of
110 the formation of N₂ (Kolli et al. 2005b). They also noticed that at 100% oxidation of CO, the
111 NO begins to oxidize to NO₂ (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 O₂ on the NiO/CeO₂
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 CO₂ from oxy-
120 fuel combustion in a chimney. The authors want to purify the CO₂ 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_x reduction in oxidizing medium. Thus, the target is
123 50% NO_x 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 CeO₂ in the
125 simultaneous oxidation of carbon monoxide and reduction of nitric oxide in an oxidizing
126 medium (10% O₂) and in the presence of H₂O will be investigated in order to purify the CO₂
127 from the oxycombustion. We will also determine the selectivity of the best catalyst
128 regarding to the formation of N₂ from nitric oxide reduction.

129 **2. Experimental**

130 **2.1. Catalysts preparation**

131 Ceria (HAS 20 (Rhodia)) with a specific surface area of 65 m².g⁻¹ 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

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

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 H₂ 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 H₂ 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 H₂ 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 H₂
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 H₂ (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**

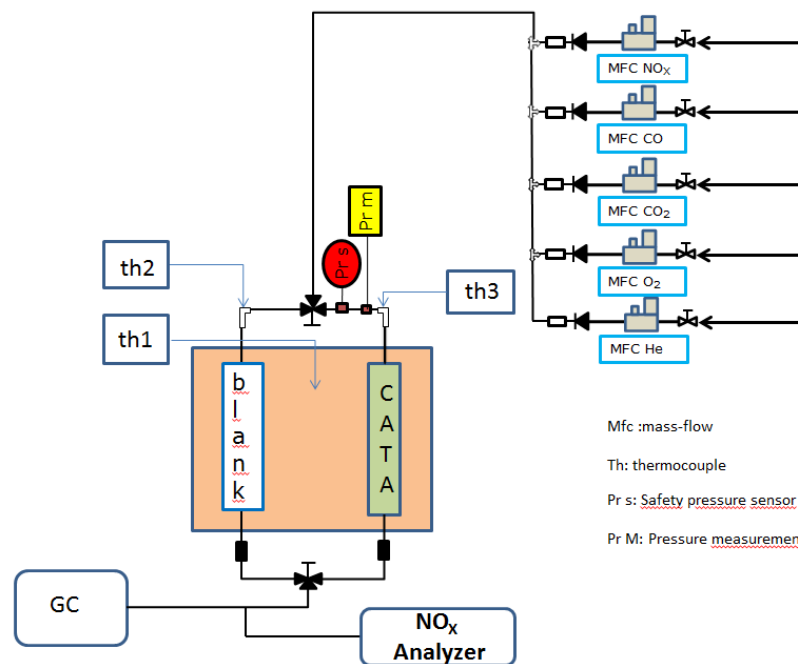
162 Before each test, the catalyst was treated in situ under He flow (40 mL.min⁻¹) at 473 K for 90
163 min. Then, CO₂ purification was carried out at atmospheric pressure in a fixed-bed flow
164 reactor containing 150 mg of catalyst. The catalysts were sieved in order to retain grains
165 with diameters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

169 The flow of the reactant gases is composed of: 20 % CO₂, 10 % O₂, 0.5 % CO and 0.02 % NO
170 (He as eluent gas) with a total flow of 200 mL.min⁻¹, in the temperature range 50–500 °C. A
171 normal oxyfuel combustion process is supposed to give a higher amount of CO₂, but to be
172 able to study the different reactions that can occur and to identify the species, a lower CO₂
173 concentration was chosen. Moreover, CO₂ is not expected to interfere in the CO-NO reaction
174 except by covering the basic sites of the ceria and 20% of CO₂ 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 (CO₂
177 and N₂) were analyzed on line by a gas chromatograph (Label GAS analyzer XXL1300), NO
178 was analyzed with Xentra 4900C analyzer (Servomex). The measurement of NO₂ is done

179 indirectly using a NO₂ 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. N₂O 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 CO₂ from oxyfuel combustion

192 In order to compare the different materials, T₅₀ and T₉₀ 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**

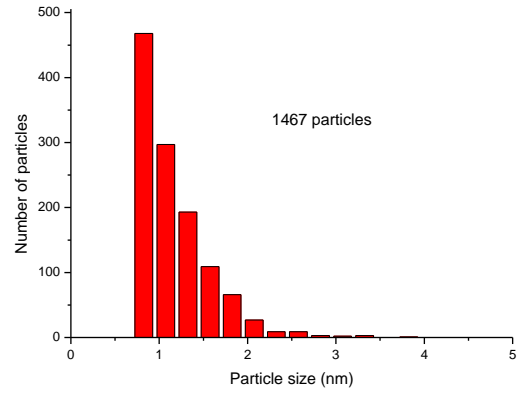
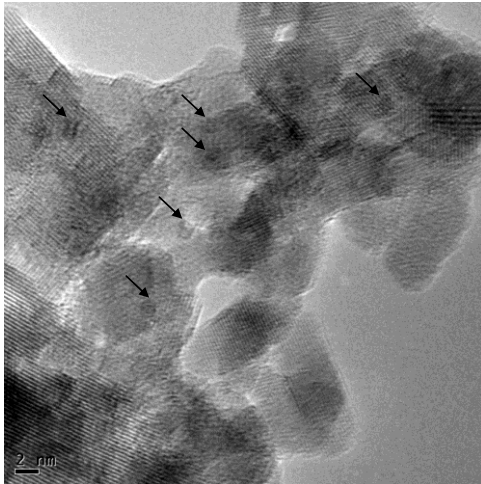
198 The catalysts prepared by impregnation of ceria targeting 1 wt-% of the noble metal were
199 analyzed by ICP to determine the metallic content. The results are presented in Table 3. The
200 catalysts were also characterized in order to determine their metal accessibility as well as
201 their particle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

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

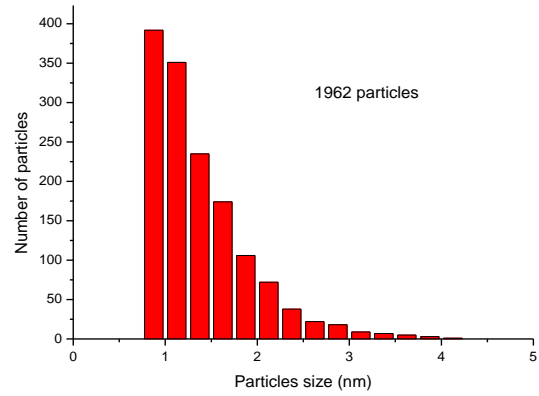
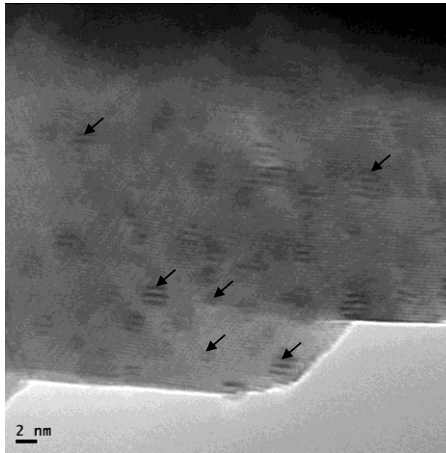
Catalysts	Reference	Measured metallic content (%)	Metallic accessibility (%)	< d > (nm) Before test H ₂ chemisorption / TEM	< d > (nm) After test deduced from H ₂ chemisorption
Pt/CeO₂	Pt/Ce	1.14	43	2.6 / 1.5	2.9
Rh/CeO₂	Rh/Ce	1.05	46	1.8 / 1.8	1.8
Pd/CeO₂	Pd/Ce	0.94	42	- / 1.5	--

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.

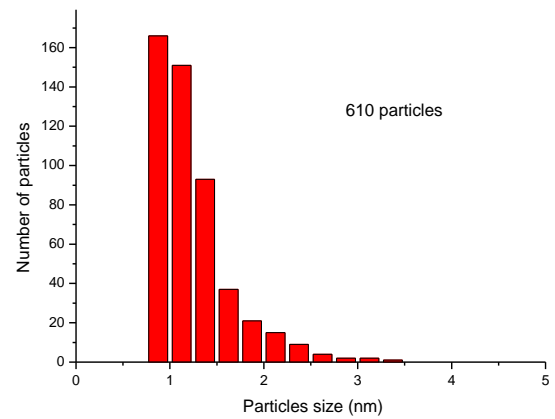
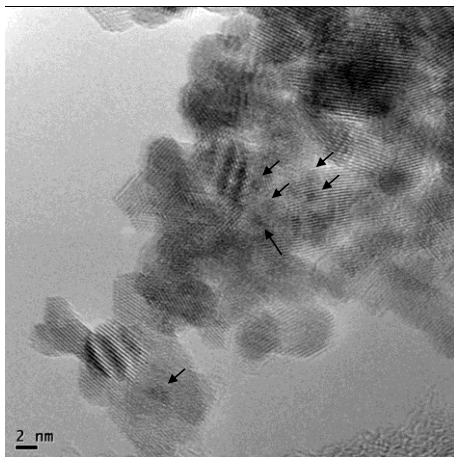
209 The morphology of the catalysts was evaluated by transmission electron microscopy (TEM)
210 coupled with energy dispersive X-ray spectroscopy (EDX), in order to observe the accurate
211 localization of the metallic particles, to analyze their chemical nature and to estimate their
212 average size 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/CeO₂



Rh/CeO₂



Pd/CeO₂

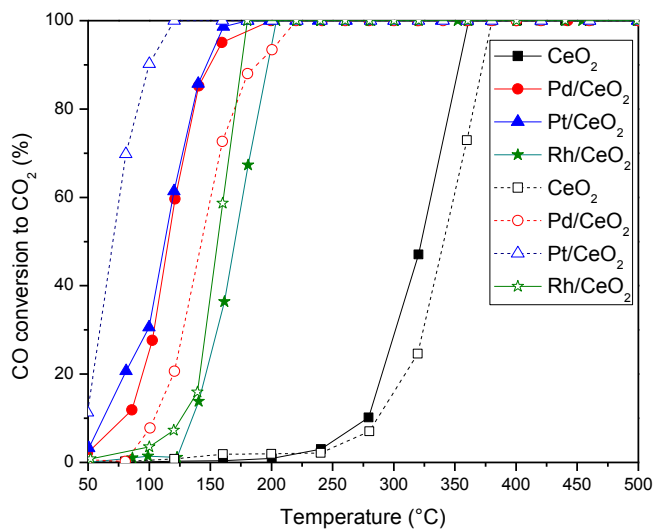
216 **Figure 2:** TEM images and particle size distributions of noble metal catalysts supported on
 217 ceria

218 **3.2. Catalytic reaction**

219 The catalytic activity test was carried out in the presence of 20% CO₂, 10% O₂, 0.5% CO,
220 0.02% NO in helium, with a total flow of 200 cm³.min⁻¹ 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 CO₂ purification, simultaneous reactions should be achieved: oxidation of CO and
227 reduction of NO_x 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/CeO₂
 237 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

238

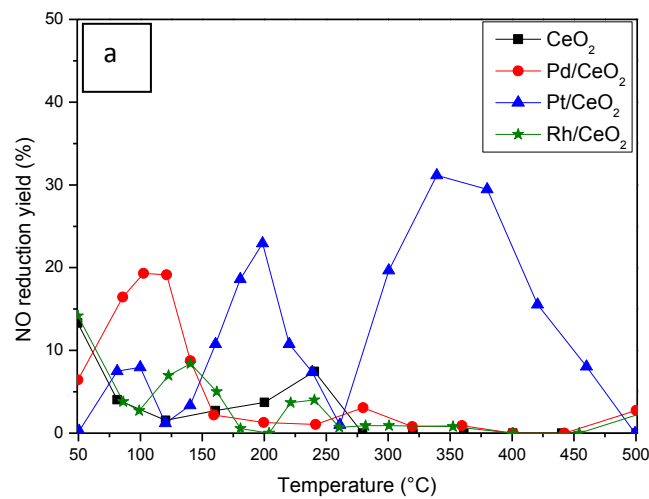
239 Addition of noble metal to ceria increases in the oxidation activity. Yao et al. have shown
 240 that the presence of a noble metal (Pt, Pd or Rh) on ceria favors its ability to store/exchange
 241 oxygen atoms, thus facilitating the oxidation of CO at lower temperatures than these same
 242 noble 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/CeO₂ and Pd/CeO₂ catalysts while Rh/CeO₂
 249 catalyst shows an oxidation of carbon monoxide at a higher temperature with a T₅₀ of 170°C.
 250 Both of Pd and Pt materials have near-similar T₅₀ and T₉₀ 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/CeO₂ catalyst (and
 253 Rh/CeO₂ too) whereas a detrimental effect was observed on Pd/CeO₂. According to Table 3,
 254 the addition of water to the reaction stream makes it possible to reduce the conversion
 255 temperatures T₅₀ and T₉₀ of the carbon monoxide on the Pt/CeO₂ and Rh/CeO₂ 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

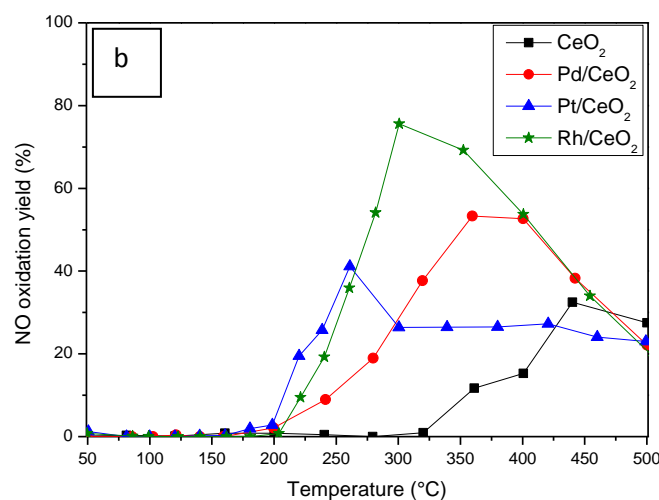
258 role of a second oxidant for carbon monoxide in addition to oxygen during the WGS
259 reaction. Rh and Pt metals are more active for the WGS reaction than Pd one leading to an
260 increase of CO conversion higher than that observed on Pd/CeO₂ (Panagiotopoulou and
261 Kondarides 2006). A ranking based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

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 CeO₂

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/CeO₂ 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 CeO₂ 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/CeO₂ catalyst in our experimental conditions.

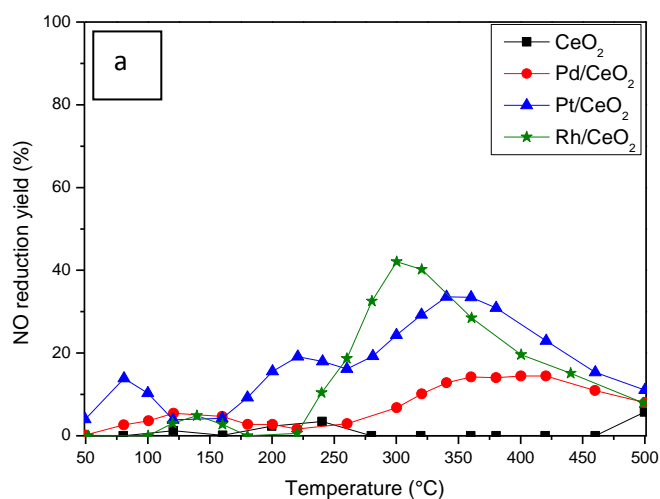
289 Platinum has an even more different behavior for reducing NO than other catalysts. This
290 metal exhibits three reduction zones 50-120, 120-260 and 260-500 °C with a maximum
291 reduction in the third zone of 31% at 340 °C. Despite its somewhat surprising profile, our
292 catalyst is more efficient (31% reduction) compared to 7% reported in the literature on a
293 similar 1% Pt/CeO₂ 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:

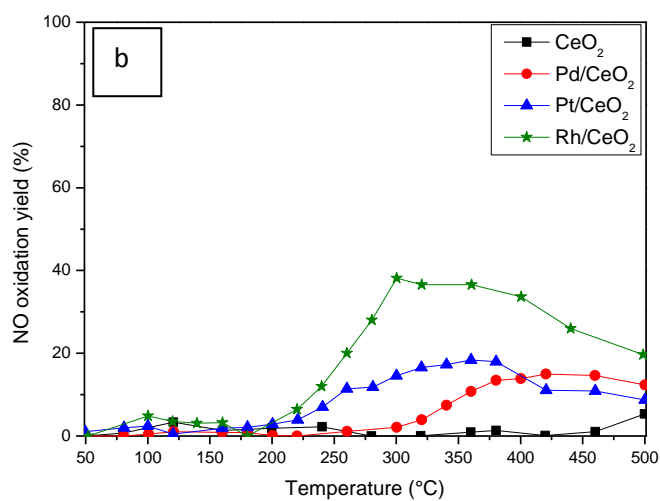
299 $\text{CeO}_2 < \text{Rh/CeO}_2 < \text{Pd/CeO}_2 < \text{Pt/CeO}_2$. This ranking corresponds perfectly to that achieved for
300 the oxidation of CO.

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 .



309



310

311 **Figure 5:** Reduction (a) and oxidation (b) yields of NO on noble metals Pd, Pt and Rh
312 deposited on CeO₂ 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/CeO₂ catalyst with 42% reduction at 300°C,
316 followed by the Pt/CeO₂ catalyst with 34% reduction at 340°C and finally the Pd/CeO₂
317 catalyst with 14% reduction at 360°C.

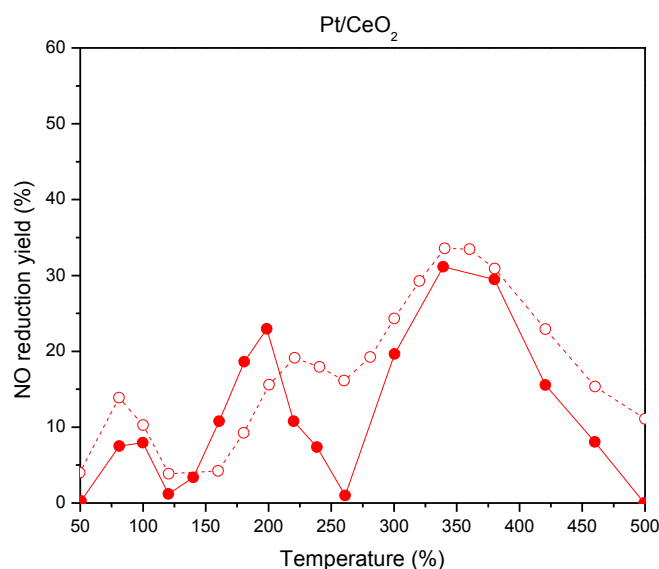
318 The oxidation of the NO follows the same order of ranking of the catalysts as for the
319 reduction of NO.

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 H₂ by the reaction of water gas shift (CO +
328 H₂O = H₂ + CO₂) at temperatures above 200 °C. Finally, this H₂ formed can react with NO to
329 form NH₃. H₂ and NH₃ 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/CeO₂ 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/CeO₂ 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 N₂ or N₂O either NH₃ which is also a more powerful reductant than CO.

340 However, it has been proven in the literature that selectivity towards N₂ 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 N₂ on a Pt/CeO₂ took place in 3 steps:
 347 gaseous N₂O formation, subsequent N₂O re-adsorption, and formation of N₂. Table 4 shows
 348 the selectivity for N₂ and N₂O obtained on the Pt/CeO₂ catalyst in the presence and absence
 349 of H₂O. The measurements were performed at the maximum reduction yield of the three
 350 peaks.



351
 352 **Figure 6:** Reduction yields of NO on Pt/CeO₂ catalyst in the absence (closed symbols) and
 353 presence of water (open symbols)

354 Table 5. Selectivity of NO reduction on CeO₂-supported Pt catalyst in the presence and
 355 absence of H₂O

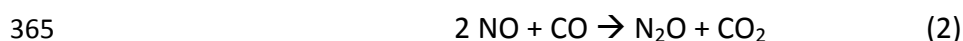
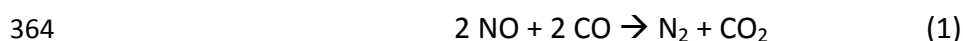
Temperature (°C)	without H ₂ O		with H ₂ O	
	N ₂ O (%)	N ₂ (%)	N ₂ O (%)	N ₂ (%)
80-100 (1st reduction zone)	1,9	98,1	2,8	97,2

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

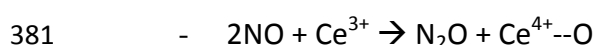
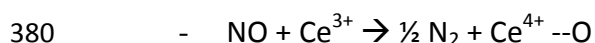
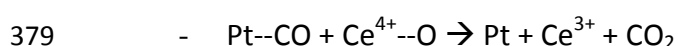
357 It therefore seems that in our reaction conditions, the Pt/CeO₂ catalyst is very selective
 358 towards dinitrogen production with at least 98% in the absence of water and 97% in
 359 presence of water. Very low selectivity (<3%) in N₂O was observed at low conversion
 360 temperatures. As the temperature 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:

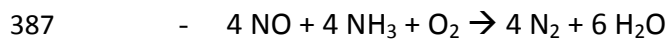
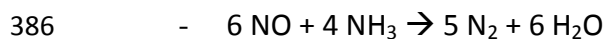
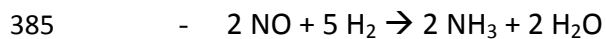


367 CO₂ formation occurs directly (reaction 1) and sequentially (reactions 2 and 3). Since the
 368 selectivity of N₂ was almost 100%, we assume that reaction 1 (NO-CO direct reaction)
 369 occurred as a main reaction pathway. Indeed, it has been generally accepted that the
 370 formation of N₂O is an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



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

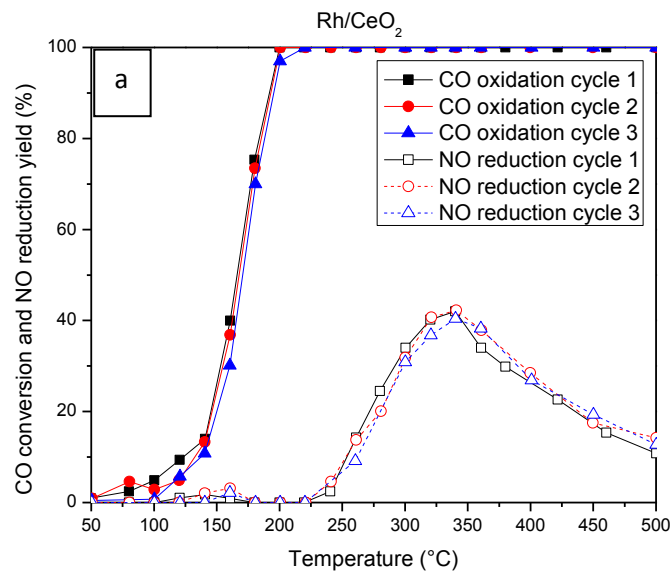


388 Despite the small amount of N₂O produced, it should be noted that this catalyst produces
389 more N₂O at low temperature than at high temperature. Panayotov & al. have observed on
390 Pt and/or Rh supported on ceria catalysts that N₂O is the dominant product at low
391 temperature whereas N₂ is almost 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.

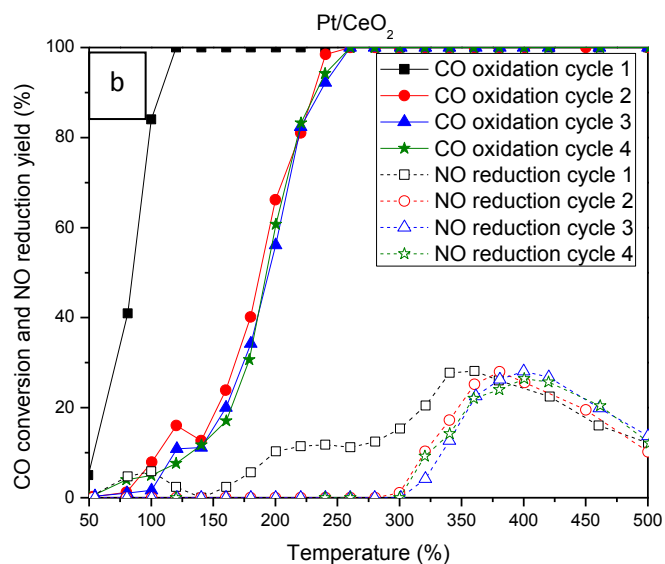
393 **3.2.4. Stability test**

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/CeO₂ and
396 Pt/CeO₂.

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/CeO₂ and Pt/CeO₂ 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/CeO₂ (a) and
 407 Pt/CeO₂ (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/CeO₂ (a) and Pt/CeO₂ (b) catalysts. The
 411 Rh/CeO₂ catalyst proved to be stable and resistant towards deactivation during three
 412 successive cycles. Structural analysis of the aged catalyst by H₂-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/CeO₂ catalysts for the same reasons (Hou et al.
417 2015; Zhao et al. 2018).

418 In contrast to the Rh-based catalyst, the Pt/CeO₂ 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 CO₂ 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/CeO₂ 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 H₂O in addition to NO and O₂. 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 H₂ increased the reduction of the NO and favored the formation of N₂. 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

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