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1 Surface effect of nano-sized cerium-zirconium oxides for the catalytic
2 conversion of methanol and CO₂ into dimethyl carbonate

3

4 **Cécile Daniel*, Yves Schuurman, David Farrusseng**

5 Université de Lyon, CNRS, IRCELYON, 2 Avenue Albert Einstein, Villeurbanne F-69626, France

6 **Abstract**

7 The direct synthesis of Dimethyl carbonate (DMC) from methanol and CO₂ is a green process which
8 allows CO₂ valorization. Among efficient catalysts, ceria, zirconia and cerium-zirconium mixed oxides
9 are often reported as the most active catalysts. In a recent report, we discovered that cerium-
10 zirconium mixed oxides prepared by Flame Spray Pyrolysis (FSP) show greater catalytic activities than
11 those prepared by precipitation, although both exhibit very similar surface area and bulk features.
12 The objective of this study was to find out the origins of the superior catalytic activities obtained by
13 flame spray pyrolysis synthesis method by a deeper analysis of bulk and surface properties. We have
14 opted to focus on mixed ceria-zirconia of equimolar composition (Ce_{0.5}Zr_{0.5}O₂) as it exhibits maximum
15 catalytic activity for both synthesis methods. Combining bulk and surface characterization as well as
16 surface adsorption measurements using probe molecules, we propose that flame spray pyrolysis
17 enables a surface enrichment in cerium oxide still in interaction with zirconium oxide that leads to a
18 high concentration of adsorbed methanol at the surface, which might explain the greater activity of
19 the catalysts prepared using this method. Beyond the application of DMC synthesis, we can
20 anticipate that Flame Spray Pyrolysis synthesis should generate relative high surface area mixed
21 oxides with different catalytic performances with respect to mixed oxides prepared at lower
22 temperature owing their metastable nature.

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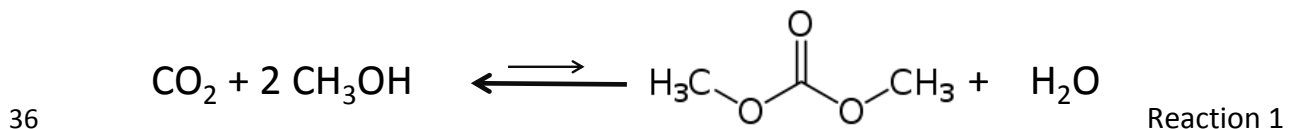
24 **Keywords:** methanol; CO₂; cerium; surface structure; flame spray pyrolysis; DMC

25

26

27 1. Introduction

28 Among organic carbonates, dimethyl carbonate (DMC) is a promising green chemical because of its
29 low toxicity and rapid biodegradability [1][2]. Its versatile chemical properties account for its
30 extensive use as an agent in carbonylation and methylation reactions, replacing DMSO, COCl₂ and
31 CH₃X [3][4]. It is also widely used as a precursor for the production of polycarbonates and
32 polyurethanes. DMC was historically synthesized by the harmful methanolysis of phosgene. Current
33 industrial processes include hazardous, corrosive oxidative carbonylation in the gas or liquid phase
34 [5]. Other possible routes are the transesterification of propylene carbonate and the methanolysis of
35 urea [6][7].



37 The direct synthesis of DMC from methanol and CO₂ (reaction 1) appears particularly attractive: it is a
38 greener alternative to the other routes that simultaneously allows CO₂ valorization [7]. However, the
39 methanol conversion in reaction 1, X_{MeOH} , is strongly limited by the thermodynamic equilibrium. DMC
40 yield, assuming 100% selectivity, can hardly exceed 2% even under favorable pressure and
41 temperature conditions [8].

42 Studies demonstrate that a direct synthesis process can technically enable a high DMC yield when an
43 efficient dehydration process is applied [9]. For example, in-situ reactive dehydration of reaction
44 system using 2-cyanopyridine as a dehydration agent led to remarkable enhancement of methanol
45 conversion and DMC yield [10]. Among non-reactive dehydration system, the application of catalytic
46 membrane reactors or ex-situ dehydration system [11][12] allowing continuous water withdrawal
47 during reaction has also been proposed. A successful proof of concept [13] was reported combining
48 both a continuous gas-phase reactor fed with a dehydrating agent.

49 A wide variety of catalysts have already been tested for the direct synthesis of DMC [14][15],
50 including organic metal-alkoxy compounds, metal oxides, metal-supported catalysts and ionic liquids.
51 Due to their relatively high activity, the majority of metal oxide studies deals with ceria, zirconia and

52 cerium-zirconium mixed oxides [16] [17][18][19] [20] [21] [22] [23] or “doped” versions thereof
53 [24][25] [26][27]. Current state of the art of DMC synthesis over ceria-based catalysts is detailed
54 elsewhere [28]. Among rare earth oxide elements, Y_2O_3 was also reported [29] to catalyze DMC
55 synthesis at 353 K, one of the lower temperature reported for this reaction.

56 It is acknowledged that “well-balanced acidic and basic” properties play a key role in DMC synthesis
57 for methanol activation [21] [24][16]. Thermal desorption (TPD) of NH_3 and CO_2 probe molecules is
58 often used to characterize acid and basic sites, respectively. In [30] Kumar et al. synthesized porous,
59 spherical cerium-zirconium oxide catalysts ($Ce_xZr_{1-x}O_2$) with different molar ratios. Within this serie,
60 the $Ce_{0.5}Zr_{0.5}O_2$ catalyst was found to present the highest concentration of basic and acid sites and
61 the highest DMC yield. Fu et al. [31] established a relationship between the initial rate of DMC
62 synthesis and the surface acidity/alkalinity of 1D CeO_2 nanowires as measured by TPD. Giram et al.
63 [32] investigated the synthesis of diethyl carbonate over metal-incorporated ceria catalysts and
64 reported an optimal dependence of the catalytic activity on the acidity/basicity ratio as measured by
65 NH_3 -TPD and CO_2 -TPD. Tomishige et al. [33] carried out propylene carbonate and ethylene
66 carbonate synthesis over CeO_2 - ZrO_2 solid solutions. They reported that the formation rate per acidic
67 and/or basic sites significantly increased on the catalysts calcined at higher temperature despite
68 lower surface area, and suggested that weak acidic/ basic site may promote activity.

69 On the other hand, the concentration of oxygen vacancies as measured by the oxygen storage
70 capacity (OSC) of mixed oxides has been reported to be a feature that can determine the degree of
71 acidity or basicity. It has been extensively reported that intermediate ceria-zirconia compositions
72 (i.e., $0.2 < x < 0.8$) are more active than are pure oxides for DMC synthesis, regardless of the synthesis
73 method (for example, sol-gel [21][23], coprecipitation [34] or templating [20]). It has been clearly
74 reported that the highest OSC of cerium-zirconium mixed oxides is also achieved for intermediate
75 compositions ($0.4 < x < 0.7$) [35][36]. Although some authors have identified a matching pattern
76 between the OSC and the DMC yield as a function of Ce-Zr composition, a direct link between oxygen
77 vacancies (i.e., the oxidation state of cerium) and the DMC yield has not been clearly established.
78 Wang et al. [37] synthesized CeO_{2-x} quantum dots, and measured a yield five times higher than for
79 commercial ceria nanoparticles. Marciniak [38] loaded CeO_2 with a small amount of Cu, reporting

80 that the highest catalytic activity and selectivity toward DMC were obtained with 0.02 wt.% Cu,
81 mostly due to basic sites associated with the presence of oxygen vacancies. In [39] Liu focused on
82 doping the ceria lattice with Zr atoms, producing a fluorite-like solid solution and promoting the
83 formation of oxygen vacancy sites. $Zr_{0.1}Ce$ nanorods, which exhibited the highest DMC synthesis
84 activity, also presented the highest concentration of oxygen vacancies. FTIR results demonstrated
85 that CO_2 can adsorb on the oxygen vacancy to form bidentate carbonate, which serves as an
86 intermediate in the reaction [33][30]. Katagiri [40] observed a correlation between the number of
87 surface bidentate species and the catalytic activity over ZrO_2 nanocrystals
88 [39][39][39][38][38][37][37][36][35][34]. Generally, the density of oxygen vacancies is associated
89 with the occurrence of defects and Ce^{3+} cations, which, however, have been reported not to be
90 active sites [41]. Indeed, Aresta established that Ce^{4+} is the active cation species, whereas Ce^{3+} is
91 inactive [27]. Also, Liu prepared $Ce_{0.5}Zr_{0.5}O_2$ by different methods, showing that the direct
92 carboxylation of methanol is mostly correlated with the proportion of Ce^{4+} in the catalyst surface
93 [22].

94 In a recent study [42] we set up a reliable protocol to measure catalytic activity over a diverse library
95 of catalysts. The screening we carried out reveals the outstanding activity of ceria-zirconia flame-
96 sprayed catalysts. Surprisingly, although coprecipitated and flame-sprayed catalysts apparently show
97 similar surface areas and bulk composition, they perform very differently.

98 The aim of this work is to investigate the origin of different catalytic activities for two synthesis
99 methods: coprecipitation and flame spray pyrolysis. We have opted to focus on mixed ceria-zirconia
100 of equimolar composition ($Ce_{0.5}Zr_{0.5}O_2$) as it exhibits maximum catalytic activity for both synthesis
101 methods. Nevertheless, we have investigated a series of ceria-zirconia solids with compositions
102 spanning from pure ceria to pure zirconia in order to facilitate the identification of trends in their
103 properties. Combining bulk and surface characterization as well as surface adsorption measurements
104 using probe molecules, we propose that flame spray pyrolysis enables a surface enrichment in ceria
105 in close interaction with zirconium oxide that leads to a high concentration of adsorbed methanol at
106 the surface, which might explain the greater activity of the catalysts prepared using this method.

107 2. Materials and methods

108 2.1 *Synthesis of catalysts*

109 Two series of ceria–zirconia solids ranging from pure zirconia to pure ceria were prepared: one by
110 flame spray pyrolysis and the other by coprecipitation. The flame spray pyrolysis samples, hereafter
111 denoted FSP, were synthesized by Johnson Matthey following a protocol described in [43] [44]. The
112 general principle can be summarized as follow. Aqueous metal salt solutions were prepared with
113 desired concentration of metals. The solutions were sprayed as a fine mist into a flame (up to
114 2200°C). High space velocities and heat radiation loss lead to extremely short residence times
115 (milliseconds) with high temperature gradients up to 170 K.cm⁻¹ along the flame axis [45]. The metal
116 oxide atoms aggregated into nanoparticles, which were then collected on a filter.

117 Coprecipitated catalysts, denoted CP, were synthesized from the appropriate nitrate salts using
118 NaOH as the precipitating agent, as described in an earlier publication [42]. The coprecipitated solids
119 were heat-treated in air at 500°C (CP-500) and 850°C (CP-850) for 4 hours. The temperature of 850°C
120 was chosen to obtain catalysts with higher crystallinity and a relatively high surface area similar to
121 those of the catalysts prepared by flame spray pyrolysis.

122 The subscript x hereafter stands for the molar cerium content in Ce_xZr_{1-x}O₂ solids as determined by
123 elemental analysis. As indicated above, the results presented here focus on the mixed oxides
124 prepared by the two methods and presenting approximately equal cerium and zirconium contents,
125 because they are representative and relevant solids. The notations CZ-CP and CZ-FSP refer to solids
126 of composition Ce_{0.45}Zr_{0.55}O₂ for coprecipitation and Ce_{0.5}Zr_{0.5}O₂ for flame spray pyrolysis,
127 respectively.

128 2.2 *Catalytic activity measurements*

129 The evaluation of catalyst activities was carried out using a method detailed in [42]. In short, the
130 triphasic catalytic carboxylation of methanol was carried out in a high-pressure Parr Instrument
131 vessel of 50 mL volume equipped with a pressure indicator and used as a batch reactor. Typically, an
132 adjusted amount of dried catalyst in powder form (ranging from 20 mg to 500 mg) and 12 g of
133 methanol with 0.1 wt.% anhydrous toluene as internal standard were introduced into the vessel. The
134 amount of catalyst was adjusted so that the methanol conversion was always lower than 0.6% after a

135 4-hour reaction time. Then an 18-mL volume of liquid CO₂ kept at 4°C and 50 bar was fed into the
136 autoclave by an Isco 250D syringe pump. The vessel was heated under magnetic stirring in an oil bath
137 at 140°C for 4 hours. Finally, the vessel was cooled down in an ice bath.

138 Only DMC was detected as product (Shimadzu GCMS-QP2010 equipped with a ZB-WAX column). The
139 amount of DMC produced was quantified by a gas chromatograph (6850 GC Agilent) equipped with a
140 DB-WAXetr capillary column (30 m) and a flame ionization detector. Catalyst activity is expressed as
141 follows:

$$Activity = \frac{n_{DMC} (mol)}{m_{catalyst} (g) * time (s)}$$

142 2.3 Characterization of catalysts

143 Elemental analysis of the catalysts was carried out by inductively coupled plasma-optical emission
144 spectrometry (ICP-OES; ACTIVA instrument from HORIBA Jobin Yvon) equipped with a CCD detector
145 for the determination of metal loadings. Measurements were duplicated and the average was
146 calculated. The experimental error is estimated to be +/- 3%.

147 Catalyst morphology was analyzed by TEM (JEOL 2010 Lab 6) under 200 kV acceleration.

148 Crystalline phases were characterized by X-ray diffraction and Raman spectroscopy. Data were
149 collected for 2θ between 4° and 80° with a step of 0.02° using a Bruker D8 A25 Advance
150 diffractometer with Cu Kα radiation operated at 50 KV and 35 mA. Crystallite sizes were estimated by
151 the Scherrer equation over several diffractogram peaks. Raman spectra were recorded with a Lab
152 RAM HR (Horiba) equipped with an Ar laser (514.4 nm) and a CCD detector.

153 The surface area structure was measured by nitrogen adsorption at 77 K using the Brunauer-Emmett-
154 Teller (BET) method on a Belsorp MAX instrument (Bel Japan). Prior to measurements, the samples
155 were desorbed at 300°C for 3 hours using a Belprep vacuum instrument.

156 XPS measurements were performed using a Kratos Axis Ultra DLD spectrometer. The base pressure in
157 the analysis chamber was lower than 5 × 10⁻⁸ Pa. XPS spectra of O 1s, C 1s, Zr 3d, Zr 3p, Ce 4d and Ce
158 3d levels were measured at 90° (the normal angle with respect to the plane of the surface) using a
159 monochromated Al Kα X-ray source with a pass energy of 20 eV and a spot size aperture of 300 μm.

160 Binding energies were corrected relative to the C 1s signal at 284.6 eV. The atomic compositions in
161 cerium and zirconium were determined using the Ce3d and Zr3p signals by integrating the areas
162 under the corresponding peaks after subtracting the Shirley background. Same Ce/Zr ratio trends
163 were obtained by using Ce4d and Zr3d signals instead (results not shown).

164 The total acidity and basicity of the oxides were quantified by the temperature-programmed
165 desorption (TPD) of probe molecules (ammonia and CO₂, respectively). The TPD of ammonia and CO₂
166 (NH₃-TPD, CO₂-TPD) were carried out on a homemade device. Typically, 100 mg of powdered sample
167 were dried and desorbed for 1 hour at 300°C under helium flow. Adsorption of CO₂ was carried out at
168 30°C under a flow of 20 vol.% CO₂ in He, whereas adsorption of NH₃ was carried out at 100°C in a 5
169 vol.% NH₃ stream. Then the sample was purged under He flow for one hour to remove weakly
170 adsorbed probe molecules. Programmed desorption was carried out under He with a heating rate of
171 10°C.min⁻¹ and a flow rate of 25 mL.min⁻¹. Desorption of probe molecules was measured with a mass
172 spectrometer (Transpector II Inficon) during the heating step. The total number of basic sites was
173 calculated by integrating the flow of CO₂ desorbed by TPD between 50 and 700°C, while the total
174 number of acid sites was calculated by integrating the flow of NH₃ desorbed between 80 and 400°C.

175 The nature of surface hydroxyl species and the coordination number of oxides were investigated by
176 diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), as the nature of the hydroxyl
177 groups can vary considerably depending on the exposed (111) or (100) surface or on the degree of
178 reduction [46]. Catalyst spectra were recorded on a Magna 550 Nicolet spectrometer with a
179 resolution of 4 cm⁻¹ and 32 scans.

180 The surface was characterized upon methanol adsorption using a DRIFTS cell (Harrick Scientific).
181 Methanol is a relevant probe molecule since it is a reactant in DMC synthesis. Prior to adsorption, the
182 catalysts were dried in situ under Ar flow at 250°C.

183

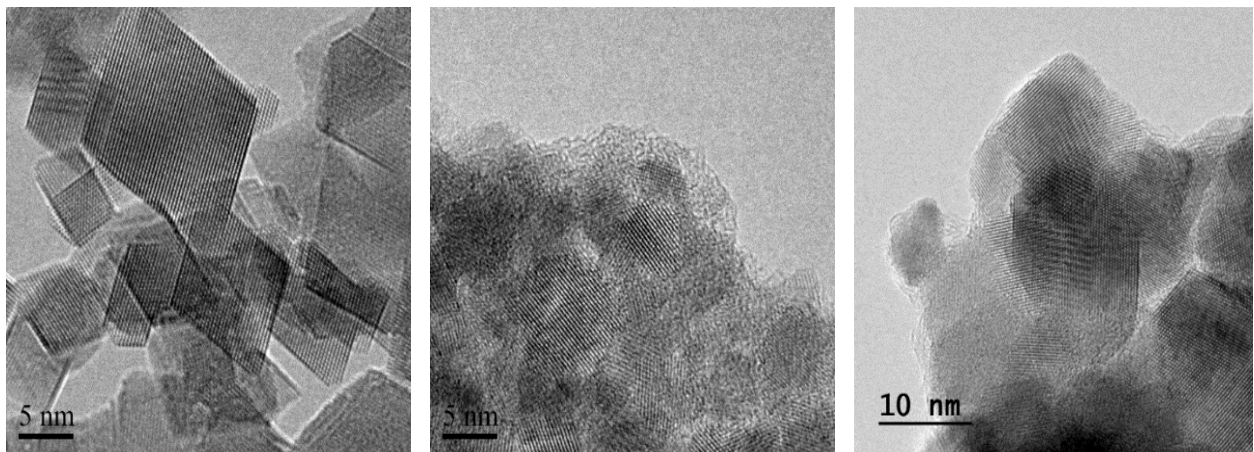
184 3. Results

185

186 3.1 Structural characterization

187

188 Fig. 1 (left) shows a transmission electron micrograph of flame-sprayed CZ-FSP featuring free, highly
189 crystalline octahedral particles between 5 and 10 nm in size. No sintering or agglomeration is visible.
190 The morphology dominated by {111}-enclosed octahedral particles was also found in other flame-
191 sprayed ceria-zirconia samples described in [44][47] . On the other hand, coprecipitated CZ-CP-500
192 (Fig. 1, centre) exhibits rough agglomerated particles of irregular shape that are much less crystalline
193 but of similar size (5-10 nm) compared to the FSP sample. The level of crystallinity of the
194 coprecipitated CP-500 set of samples increases with thermal treatment at 850°C, as indicated by
195 larger fringe domains and the clearly visible sintering of particles. (CZ-CP-850, Fig. 1, right).
196 Nevertheless, the surface of the coprecipitated solid even treated at 850°C CZ-CP-850, remains less



197 organized than for CZ-FSP solid.

CZ-FSP

CZ-CP-500

CZ-CP-850

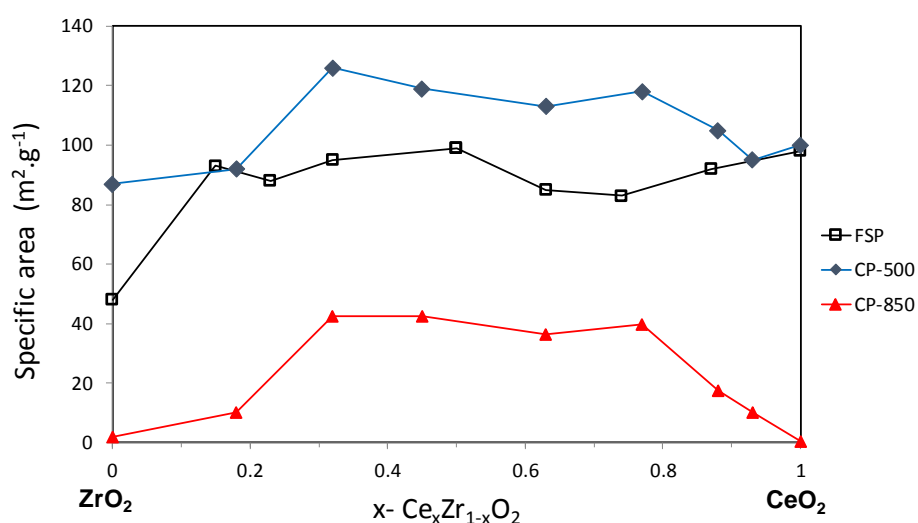
198

199 Fig. 1: TEM images of CZ-FSP ($x=0.5$, left), CZ-CP-500 ($x=0.45$, center) and CZ-CP-850
200 ($x=0.45$, right)

201

202 The specific surface areas of the FSP and coprecipitated ceria-zirconia catalysts are reported in Figure
 203 2. Except when the solid compositions approach those of pure ceria or zirconia, the surface area of
 204 mixed oxides is relatively insensitive to composition, as can be seen by the plateau at compositions
 205 $0.3 < x < 0.8$. While FSP oxides exhibit surface areas in the range of $90 (\pm 10) \text{ m}^2 \cdot \text{g}^{-1}$, the CP-500
 206 samples have slightly higher surface areas in the range of $120 (\pm 10) \text{ m}^2 \cdot \text{g}^{-1}$, in good agreement with
 207 earlier reports for these two synthesis methods [44][47]. The thermal treatment at 850°C applied on
 208 coprecipitated oxides yields lower surface areas in line with the sintering observed on the TEM
 209 images. As reported elsewhere in the literature [48] [49], an addition of zirconia to ceria limits
 210 sintering during thermal treatments. Importantly, we can see a plateau at compositions $0.3 < x < 0.8$
 211 for CP-850, with specific surface areas in the range of $40 (\pm 3) \text{ m}^2 \cdot \text{g}^{-1}$. For the equimolar ceria-
 212 zirconia samples (denoted CZ), the surface areas are 99, 119 and $42 \text{ m}^2 \cdot \text{g}^{-1}$, for CZ-FSP, CZ-CP-500 and
 213 CZ-CP-850, respectively.

214



215

216 Fig. 2: Specific surface area of flame spray pyrolysis (FSP) (□) and coprecipitated oxide
 217 catalysts fired at 500°C (CP-500) (◆) and 850°C (CP-850) (▲)

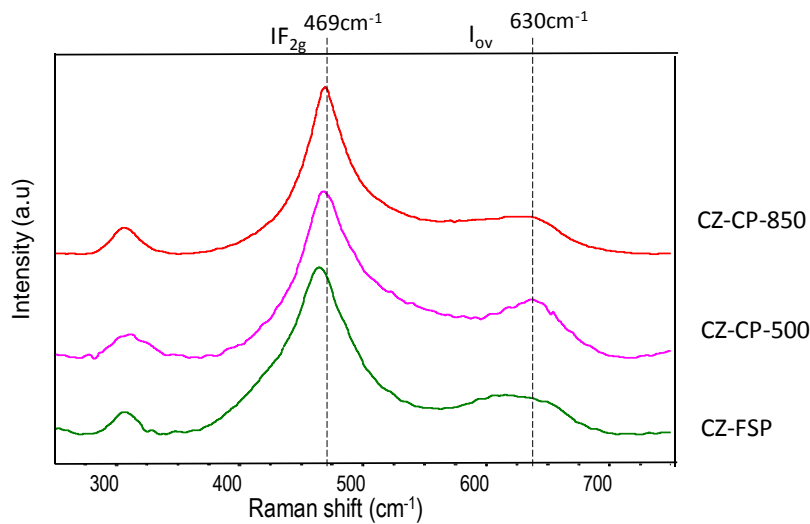
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219 The mean sizes of the crystallized domains were estimated by applying the Scherrer method to
 220 several peaks of the diffraction pattern (SI). The 850°C heat treatment conducted on the
 221 coprecipitated oxides led to significantly sharpened diffraction peaks. Similarly to surface area,

222 crystallite sizes are insensitive to oxide composition for $0.3 < x < 0.8$. In this region, the CP-500 and
223 FSP mixed oxides show crystallite sizes ranging between 5 and 10 nm which is coherent with TEM
224 pictures. The crystallized domain sizes of the CP-850 samples are systematically higher than those of
225 the corresponding CP-500 samples, in agreement with the sintering phenomena observed.
226 Crystalline domain sizes increase when compositions approach pure oxides (either CeO_2 or ZrO_2),
227 especially for CP-850. For ceria-zirconia of equivalent ($x=0.5$) content (CZ samples), the mean
228 crystalline domain sizes are 5 (+/-1) for CZ-FSP, CZ-CP-500 and CZ-CP-850, respectively.

229 The X-ray diffraction patterns of the coprecipitated series heat-treated at 500°C or 850°C (CP-500,
230 CP-850) exhibit a continuous shift in peak reflection as the Zr content increases attesting to the
231 synthesis of solid solutions [50] (SI). Only pure zirconia exhibits a different pattern featuring both
232 monoclinic and tetragonal phases. The X-ray patterns of the FSP samples also reflect the mixing of
233 ceria and zirconia over the whole range of compositions ($0.15 < x < 0.87$), indicating the existence of
234 a set of solid solutions.

235 The XRD peak broadening caused by the nano-size of the particles does not allow clear identification
236 of phases, even by Rietveld refinement. We referred to the existing literature to conduct a tentative
237 assignment of crystalline phases by crossing information with the Raman spectra [49] [51] [52] (see
238 SI). By crossing the Raman spectra and the X-ray diffraction patterns, we can confirm the formation
239 of ceria-zirconia solid solutions as in [53]. We have noticed that, irrespective of the synthesis
240 method, cerium-zirconium oxides crystallize in the same phase for a given composition x . For
241 example, for CZ oxides ($x=0.5$), very similar ceria-zirconia spectra featuring a t' tetragonal phase are
242 observed.



243

244 Fig. 3: Raman spectra of CZ-CP-500 (violet), CZ-CP-850 (red) and CZ-FSP (green)

245

246 The band at 630 cm^{-1} is commonly assigned to oxygen vacancies caused by Ce^{3+} in the CeO_2 lattice
 247 [54][55]. The ratio of the intensity of the band at 630 cm^{-1} (oxygen vacancies / I_{ov}) to that of $I_{F_{2g}}$ (464
 248 cm^{-1}) reflects the concentration of defects in the oxide [56] (Table 1). We can see that the ratio of
 249 oxygen vacancies is similar for the CP-850 and FSP series for compositions ranging from $x=0.45$ to
 250 $x=1$. In contrast, we can see a significant oxygen vacancy decrease after the heat treatment of CP-500
 251 leading to CP-850, for the composition $x=0.45$.

252

253 Table 1 : Defect concentration in oxides estimated by Raman spectroscopy

CeO ₂ content (x)	Synthesis method	$I_{ov}/I_{F_{2g}}$
1	FSP	0.02
1	CP-850	0.01
0.74	FSP	0.10
0.77	CP-850	0.09
0.63	FSP	0.10

0.63	CP-850	0.11
0.5	FSP	0.23
0.45	CP-850	0.22
0.45	CP-500	0.37

254

255

256 3.2 Surface characterization

257

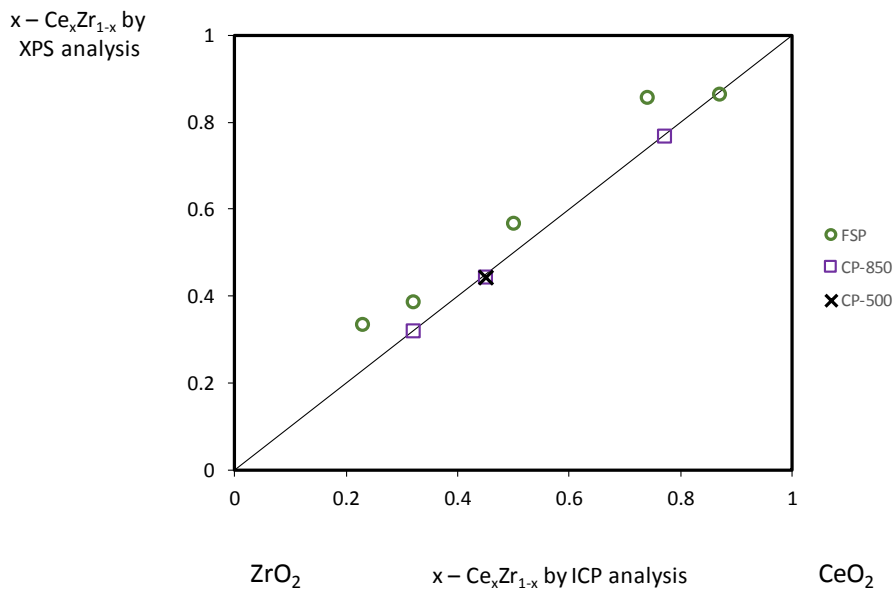
258 Surface compositions in cerium and zirconium were determined by peak integration of Ce_{3d} and Zr_{3p}
 259 for the each mixed-oxide FSP series and four CP solids (SI). We found that for all solids, the estimated
 260 binding energies (181.85 +/-0.05 for Zr_{3d} and 882.2 +/-0.2 for Ce_{3d}) are similar to values reported in
 261 the literature [57][58]. We remind here that XPS results probe a depth ranging between 3nm and
 262 10nm depending on samples and that the first layer would impact for about 10% of the signal
 263 intensity. Hence XPS is sensitive to metal segregation at the surface even if a few atomic layers are
 264 probed. Interestingly, two characteristic signals of Ce^{3+} at 884 eV (v') and the shoulder 903 eV (u')
 265 are more pronounced in the case of CP-500 which is in good line with defect concentrations
 266 estimated by Raman results (Table 1).

267 We have plotted a parity diagram of surface molar composition estimated by XPS as a function of
 268 the bulk composition analyzed by ICP-OES (Fig. 4). Importantly, we can observe that the surface
 269 composition is the same as the bulk composition for the three CP-850 oxides analyzed here. In
 270 addition, we can note the very good matching of bulk and surface compositions for the
 271 coprecipitated oxides with a molecular cerium composition of $x=0.45$. As expected, the bulk
 272 compositions of CZ-CP 500 and CZ-CP 850 are identical, since the CZ-CP 850 is obtained by the heat
 273 treatment of CZ-CP 500.

274 By contrast, the FSP oxide series systematically shows a discrepancy between the compositions
 275 analyzed by XPS and those analyzed by ICP-OES. Indeed, the XPS results indicate an enrichment of
 276 cerium at the surface. The exact location and depth of this cerium surface enrichment can hardly be

277 estimated, however. For the CZ-FSP sample of bulk composition $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$, the surface composition
278 estimated by XPS would be $\text{Ce}_{0.57}\text{Zr}_{0.43}\text{O}_2$. To our knowledge, surface composition analyses of cerium-
279 zirconium mixed oxides synthesized by flame spray pyrolysis have not been reported elsewhere.

280



281

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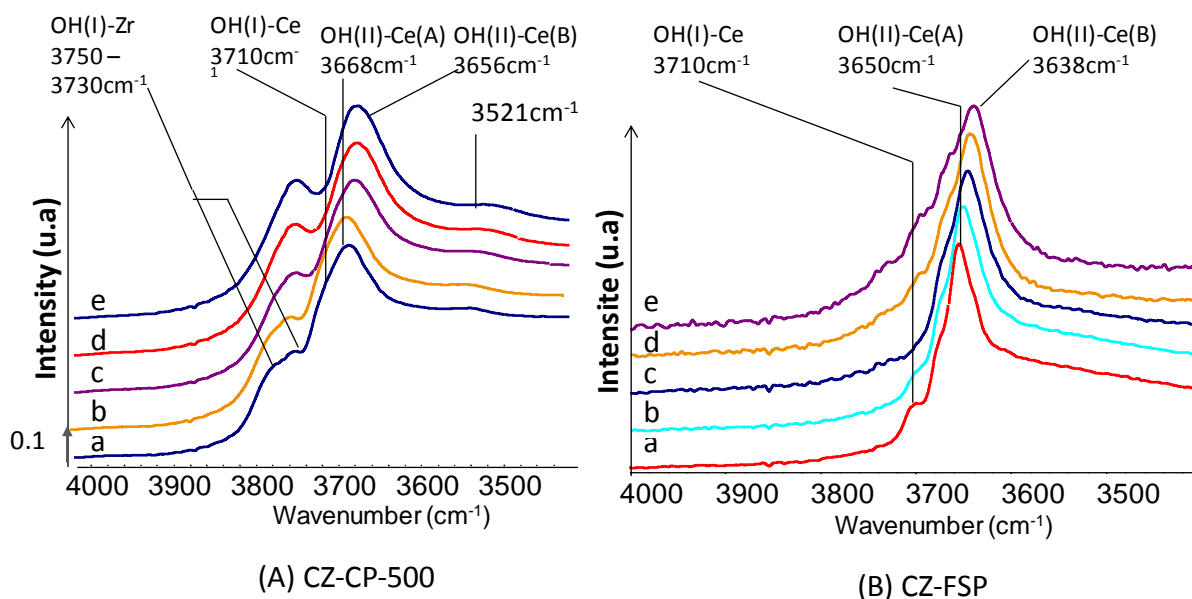
283 Fig. 4: Parity diagram of molar composition x measured by XPS versus molar composition x
284 measured by ICP-OES for (o) FSP, (□) CP-850 and (x) CP-500 solids

285

286

287 The structure of the hydroxyl groups on ceria and zirconia has been characterized by FTIR as a
288 function of temperature. It is recognized that the wavelength of the OH species associated with the
289 temperature originates from the nature of the hydroxyls and their local reorganization [67] [60][61].

290



291

292 Fig. 5: DRIFTS in the OH region of CZ oxides with $x \approx 0.5$ as a function of temperature at (a)
 293 100°C; (b) 200°C; (c) 300°C; (d) 400°C; and (e) 500°C; sample CZ-CP-500 (left), sample CZ-FSP
 294 (right).

295

296 The CZ CP-500 solid exhibits both hydroxyls OH(I)-Zr at 3750 cm^{-1} and CeOH(I)-Ce at 3710 cm^{-1} at
 297 100°C (Fig. 5A). Upon thermal treatment, the OH(I)-Zr signal remains, while the OH(II)-Ce(A) hydroxyl
 298 signal at 3668 cm^{-1} shifts to OH(II)-Ce(B) at 3656 cm^{-1} , a phenomenon usually associated with the
 299 creation of oxygen vacancies next to cerium.

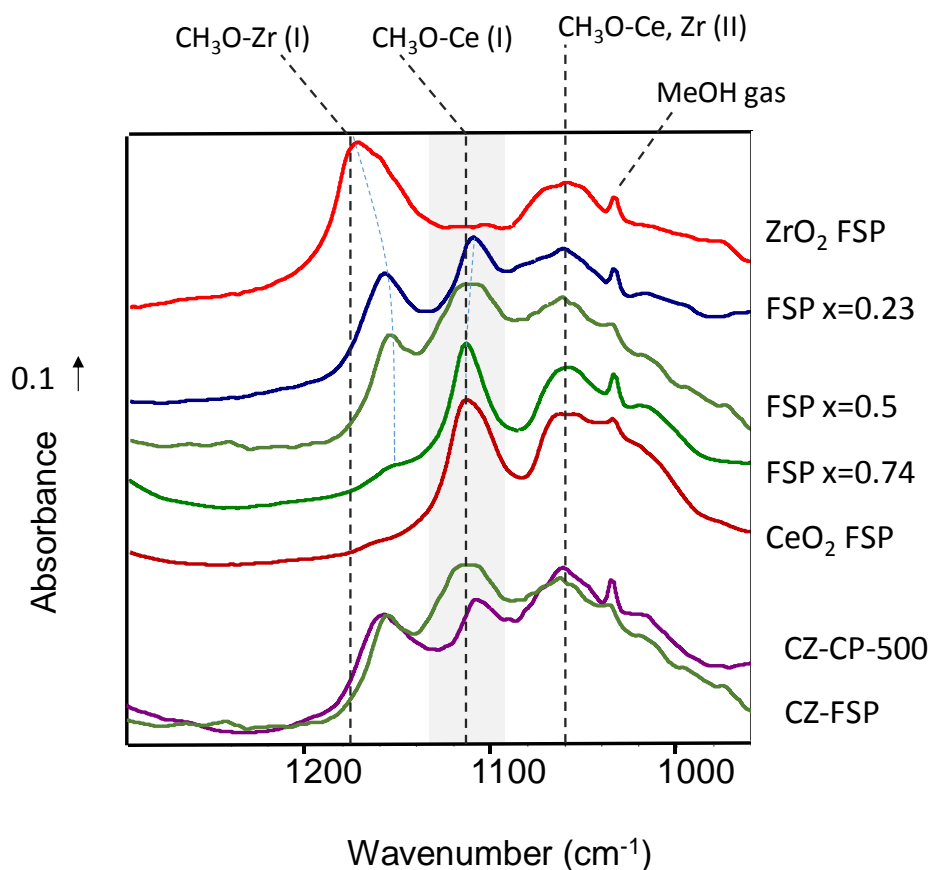
300 We can note that the DRIFT spectra of the CZ-FSP solid are significantly different from those of CZ-
 301 CP-500 despite similar bulk composition (Fig 5B). Interestingly, the OH(I)-Zr hydroxyl signal is not
 302 visible. The band corresponding to OH(I)-Ce is clearly identified at 3710 cm^{-1} but vanishes at
 303 temperatures higher than 300°C, while the OH(II)-Ce signals shift progressively from (A) to (B). In
 304 summary, DRIFTS also reveals the dominance of ceria hydroxyls at the surface of the FSP oxides,
 305 whereas both ceria and zirconia hydroxides are present in the CP oxides.

306 3.3 Surface reactivity characterization by probe molecules

307

308 Inspired by the clear differences observed in the OH region through the use of DRIFTS, we have
 309 further investigated the characteristics of the surface by using methanol as a probe molecule, as this

310 process can reveal information on the surface composition and heterogeneity of cerium-zirconium
 311 oxides [62]. It is important to stress that methanol is a reactant in DMC synthesis and that
 312 information on how methanol compensates for the coordinative unsaturation of surface cations is
 313 relevant for the kinetics. Methanol dissociation occurs on a Lewis acid/base pair (Zr^{4+} or Ce^{4+} , and O^{2-}
 314), yielding different methoxide species that are associated with specific wavelengths [63][64] (see SI).
 315 Though the DRIFTS method does not allow the quantitative measurement of surface species, the
 316 mean apparent absorption coefficients of $CH_3O-Ce(I)$ and $CH_3O-Zr(I)$ were nevertheless reported to
 317 be equal at $\epsilon = 6.9 \text{ mol}^{-1}$, a situation that permits semi-quantitative analysis [65].



318
 319 Fig. 6: DRIFTS results under 5 vol.% CH₃OH in Ar flow at 100°C
 320

321 DRIFT spectra under methanol adsorption equilibrium for the FSP series (top), along with a
 322 comparison with CZ-FSP and CZ-CP-500 (bottom), are plotted in Fig. 6. A small peak near 1050 cm⁻¹ is
 323 attributed to the contribution of gaseous methanol present in the cell. On the spectrum of pure ceria
 324 ($x=1$), the vibration of $CH_3O-Ce(I)$ methoxide at 1115 cm⁻¹ is dominant, but it vanishes as the

325 concentration of cerium decreases. Inversely, the $\text{CH}_3\text{O-Zr(I)}$ methoxide band at 1171 cm^{-1} , which is
326 intense for the pure zirconium oxide ($x=0$), vanishes as the cerium content increases. In accordance
327 with earlier publications, a large band at $1060\text{-}1080\text{ cm}^{-1}$ can be assigned to $\text{CH}_3\text{O-Zr(II)}$ and $\text{CH}_3\text{O-}$
328 Ce(II) methoxides [63][64]. For the FSP mixed oxides ($x=0.23, 0.5, 0.74$), the four methoxide species
329 described here coexist.

330 The spectra corresponding to the CZ-FSP and CZ-CP-500 samples of similar composition are
331 compared at the bottom of Fig 6. The two spectra look relatively similar and feature the presence of
332 the four methoxide species. Yet the band assigned to $\text{CH}_3\text{O-Ce(I)}$ is more intense for FSP and for the
333 CP-500 mixed oxides, unlike the $\text{CH}_3\text{O-Zr(I)}$ bands, which are of similar intensity. This reveals a higher
334 concentration of unsaturated Ce^{4+} cations on the FSP with respect to the CP-500 oxide.

335 The surface concentrations of acid and basic sites were quantified by NH_3 and CO_2 temperature-
336 programmed desorption for the whole FSP series and selected CP-850 samples (see SI). TPD results
337 do not reveal significant differences between CZ-FSP and CZ-CP-850 in terms of acid site
338 concentrations (0.15 versus $0.10\text{ }\mu\text{mol.m}^{-2}$) or basic site concentrations (1.10 versus $1.19\text{ }\mu\text{mol.m}^{-2}$).
339 In addition, the concentration of basic sites does not vary significantly over the entire range of
340 compositions for the FSP series, in contrast to catalytic activity, which is composition-sensitive as
341 shown below (see SI). Also, the catalytic activity trend cannot be linked to the concentration of acid
342 sites, which does not vary between $x=0.5$ and $x=1.0$ (see SI).

343

344 3.4 Catalytic activity in DMC synthesis

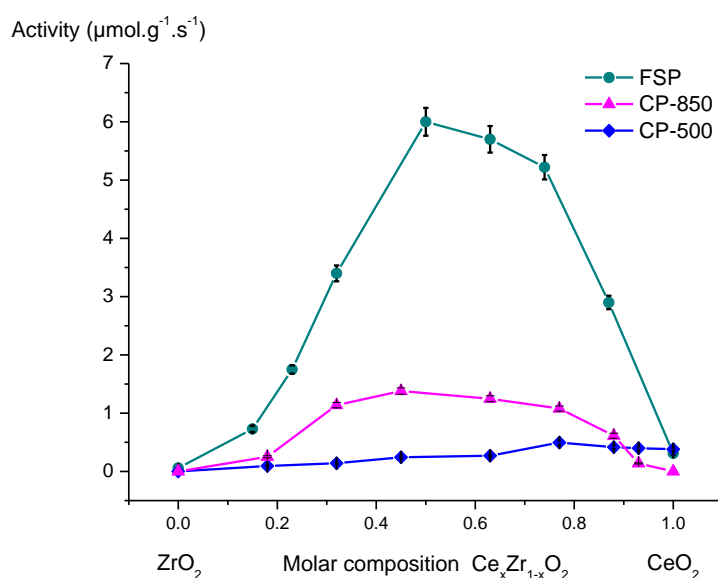
345

346 The catalytic activity per mass unit of the three series of ceria-zirconia solids (CP-500, CP-850 and
347 FSP) is reported as a function of cerium composition (Fig. 7). Mixed oxides prepared by FSP are much
348 more active catalysts compared to the coprecipitated oxides at iso-composition. The FSP series
349 exhibits, on average, a five-fold increase in activity compared to CP-800. Irrespective of the synthesis
350 methods, all mixed oxides are more active than pure ceria and zirconia, attesting to a synergistic
351 effect of ceria and zirconia mixing, which is well in line with previous reports [16][23][21]. For each

352 set of catalysts, the activity versus composition curve resembles a volcano plot. The highest activities
 353 are obtained for molar compositions x ranging between 0.4 and 0.8. For mixed oxides with equal Ce-
 354 Zr content ($x=0.5$), CZ-FSP activity is $6.0 \mu\text{mol.g}^{-1}.\text{s}^{-1}$ compared to $1.37 \mu\text{mol.g}^{-1}.\text{s}^{-1}$ and $0.24 \mu\text{mol.g}^{-1}.\text{s}^{-1}$
 355 $^{-1}$ for CZ-CP-850 and CZ-CP-500, respectively. Interestingly, the catalytic activities of pure ceria and
 356 pure zirconia do not depend on the synthesis method. In particular, the activity gain of FSP mixed
 357 oxides is not observed in the cases of CeO_2 or ZrO_2 . This suggests that the higher catalytic activities of
 358 the FSP samples could not arise from the particular particle morphology provided by the flame spray
 359 synthesis, otherwise higher catalytic activities for ceria and zirconia would also have been seen.
 360 Furthermore, we note that the catalytic activity of mixed oxides is not correlated with their surface
 361 area (Fig. 8). Although the CP-500 series shows a higher surface area than FSP, these catalysts
 362 perform very poorly per surface unit. For mixed oxides with equal Ce-Zr content ($x=0.5$), the activity
 363 of CZ-FSP is $0.06 \mu\text{mol.m}^{-2}.\text{s}^{-1}$, versus $0.03 \mu\text{mol.m}^{-2}.\text{s}^{-1}$ and $0.002 \mu\text{mol.m}^{-2}.\text{s}^{-1}$ for CZ-CP-850 and CZ-
 364 CP-500, respectively.

365

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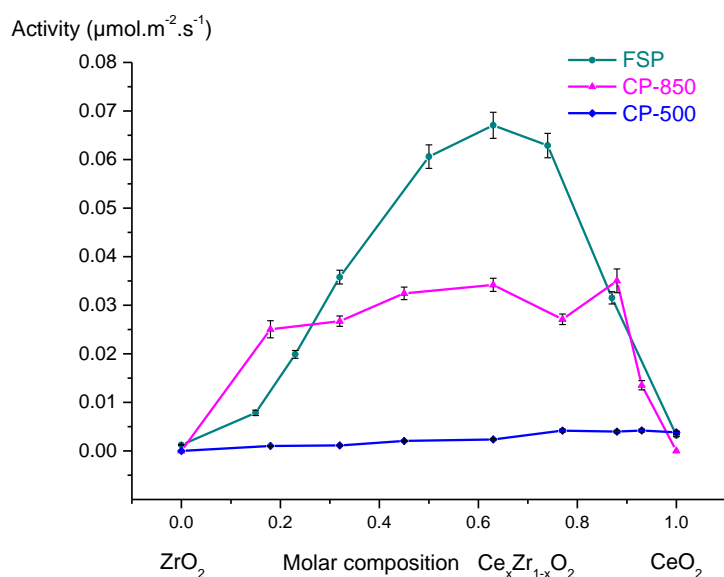
368

369

370 Fig. 7: Catalytic activity per unit of mass vs. molar composition x for FSP (●), CP-500 (◇) and CP-
 371 850 (Δ) solids. Conditions: 140°C, 4 h, 120 bar, 12 g methanol.

372

373



374

375 Fig. 8: Catalytic activity per unit of surface vs. molar composition x for FSP (●), CP-500 (◇) and CP-
376 850 (Δ) solids. Conditions: 140°C, 4 h, 120 bar, 12 g methanol.

377

378

379 4. Discussion

380

381 Mixed cerium-zirconium oxides at intermediate compositions ($0.2 < x < 0.8$) are more active than the
382 pure oxides, irrespective of the synthesis method, in line with other reports using sol-gel [21] [23],
383 coprecipitation [34] and templating [30] methods. That said, the FSP synthesis makes it possible to
384 achieve record activity when compared to results found in the literature, i.e., about 10 times higher
385 than most of active catalysts listed in this review [28]. To the best of our knowledge, the highest
386 activity ($3\mu\text{mol.g}^{-1}.\text{s}^{-1}$) of ceria was reported by optimization of calcination temperature at 873K [66]
387 which further confirms the beneficial effect of elevated firing temperature despite lower surface
388 area.

389

390 At equimolar composition ($\text{Ce}_{0.5}\text{Zr}_{0.5}$), the activity obtained with the FSP sample is fivefold higher than
391 for CP-850, which is the most active oxide prepared by coprecipitation. We want to stress that the
392 synthesis of mixed oxides by precipitation, and especially the thermal treatments, have been
393 adjusted to achieve solids whose high surface area and crystallinity are “comparable” to those of the
394 FSP samples. For this purpose, different firing temperatures were investigated (500 and 850°C). It
395 was nonetheless impossible to achieve both high crystallinity and high surface area for the
396 coprecipitated oxides due to the sintering of the nano-oxides. Here, we have presented
397 characterization results obtained for coprecipitated catalysts fired at 500°C and 850°C, a situation
398 presenting the best compromise between these two criteria with the objective of establishing
399 structure-activity relationships with FSP catalysts.

400 Bulk characterization techniques (X-ray diffraction and Raman spectroscopy) do not reveal any
401 differences that could be at the origin of the large difference in activities between the FSP and CP
402 catalysts. At equimolar composition ($\text{Ce}_{0.5}\text{Zr}_{0.5}$), the same tetragonal phase has been identified
403 irrespective of the synthesis process. Also, the slight differences in surface area between the CP-500
404 and FSP solids ($120\text{ m}^2\cdot\text{g}^{-1}$ and $99\text{ m}^2\cdot\text{g}^{-1}$, respectively), and hence a possibly higher number of
405 catalytic sites, cannot account for such a large activity difference between the two catalysts. We did
406 not observe any obvious correlations of catalytic activities with the concentration of acid or basic
407 sites similar to those found in the literature for nanorods, nanocubes and octahedrons of cerium-
408 zirconium oxides [67] [68][69] and for polyoxometallates [70]. In this study, the concentration of acid
409 and basic sites for CZ-FSP and CZ-CP-850 are very similar, although the catalytic activity of the former
410 is five-fold higher. We could hypothesize that the characterization of the acidity and basicity by the
411 TPD of NH_3 and CO_2 may discriminate oxides that are poorly active or inactive from those that are
412 active. In this study, the challenge was to determine the origin of the greatly enhanced activity of FSP
413 mixed oxides as compared to coprecipitated mixed oxides which are already active.

414 As described above, neither bulk characterization nor morphological aspects can explain the superior
415 activity of the FSP catalysts. Instead, all other analysis points toward surface aspects as an
416 explanation. First, we have shown by XPS that the surface is enriched in cerium as compared to the
417 bulk. This surface enrichment is very specific to flame spray pyrolysis, as it is not found for

418 coprecipitated catalysts. We can propose that the cerium enrichment at the surface may originate
419 from the very high temperature which permits the surface composition to be at equilibrium. This
420 hypothesis is supported by theoretical study which shows by a combination of density functional
421 theory calculations and statistical mechanics that a wide range of intermediate compositions of
422 ceria–zirconia solid solutions are thermodynamically metastable with respect to phase separation
423 into Ce-rich and Zr-rich phases [64]. Kinetic barriers for cation diffusion normally prevent the
424 decomposition/segregation of ceria–zirconia solid solutions in typical “calcination” treatment or
425 catalytic applications where low to moderate temperature are applied. But for thermal treatment at
426 high temperature applied in ceramic materials or for catalytic converters where temperature well
427 above 900°C, a rearrangement of the cations in the solid solution can occur leading to phase
428 separation. More importantly, the same study estimates that the cation rearrangement in the top
429 (111) layer of an initial 50 : 50 solid solution leads to equilibrium Ce content of the surface of 90%
430 while the second layer contains 70% of Zr. This theoretical study supports that (i) the top layer of CZ-
431 CP catalysts is composed of a Ce and Zr in equivalent concentrations as indicated by XPS
432 measurements and (ii) the composition of top layer of CZ-FSP is very Ce-rich. The high degree of
433 surface organization of the FSP particles observed by TEM may indicate that the surface has even
434 reached thermodynamic equilibrium with respect to composition.

435 Beyond the tentative explanation of the origin of the higher catalytic activities of FSP catalysts, the
436 assumption of surface induced Ce enrichment triggered by high temperature treatment also explains
437 the higher activities of CP catalysts which are heat-treated at 850°C. We can propose that the heat
438 treatment at 850°C was high enough to trigger some Ce segregation at the surface while its
439 concentration shall remain below those obtained by FSP.

440 We cannot rule out that face exposures could also account for a difference in catalytic activities.
441 While the face exposure of FSP oxide is largely {111}, which is most classical exposed surface of
442 Cerium Zirconium mixed oxides, the surface of CP oxides does not show preferential orientations.
443 Therefore, it appears the surface exposure is not the main parameter, which governs the activity
444 although it could contribute.

445 Our hypothesis of cerium enrichment at the surface triggered by the high temperature of the FPS
446 process and its linked to enhanced catalytic performances are also supported by other experimental
447 data.

448 The CZ-FSP oxide does not present the Zr-OH(I) hydroxyl band at 3730-3750 cm^{-1} , which could
449 support the argument that the first surface layer consists mainly of cerium. Here, we want to stress
450 that the analysis is not quantitative, as the extension coefficients are likely not the same for the
451 different surface hydroxyls. Indeed, the presence of zirconium cations at the surface is confirmed by
452 the methoxy band at 1153 cm^{-1} upon methanol adsorption. Finally, for the $\text{CH}_3\text{O-Ce(I)}$ band at 1111
453 cm^{-1} , we can clearly observe a much more intense signal for FSP than for the CP mixed oxide, which
454 further confirms a higher concentration of cerium at the first layer of the surface. This feature is
455 particularly relevant given that the dissociative adsorption of methanol is the first step in the
456 catalytic mechanism, and the concentration of surface methoxide is a decisive kinetic input [39] [65]
457 [67][68]. Daturi et al. used FTIR to quantify the adsorption of methanol on a ceria-zirconia series
458 prepared by coprecipitation [69]. The density of methoxide (I) showed a maximum for intermediate
459 molar composition at $x=0.5$. They concluded that $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ mixed oxides prepared by
460 coprecipitation present at their surface an optimum number of Zr^{4+} and Ce^{4+} cations of similar Lewis
461 acid strength.

462 In order to further support our hypothesis on the key role of a high concentration of Ce methoxide,
463 we quantified the density of methoxide adsorbed at the surface by measuring adsorption isotherms
464 of methanol at 20°C (Fig. 9). The methanol pressure was limited to 0.1 kPa, assuming a monolayer
465 covering of the surface below this pressure. The amount of methanol adsorbed on CZ-FSP was 8
466 $\mu\text{mol.m}^{-2}$ at 0.1 kPa, but reached only 6 $\mu\text{mol.m}^{-2}$ and 4.2 $\mu\text{mol.m}^{-2}$ for CZ-CP-850 and CZ-CP-500,
467 respectively. These values are consistent with the densities of 6 $\mu\text{mol.m}^{-2}$ and 11 mol.m^{-2} for oxidized
468 ceria {111} and reduced ceria {111}, respectively [70]. Taking the surface occupied by an adsorbed
469 methanol molecule to be 0.22 nm^2 [71], we estimated a surface of 105 $\text{m}^2.\text{g}^{-1}$ for CZ-FSP using the
470 methanol isotherm, a value close to the one determined by the BET method (99 $\text{m}^2.\text{g}^{-1}$).

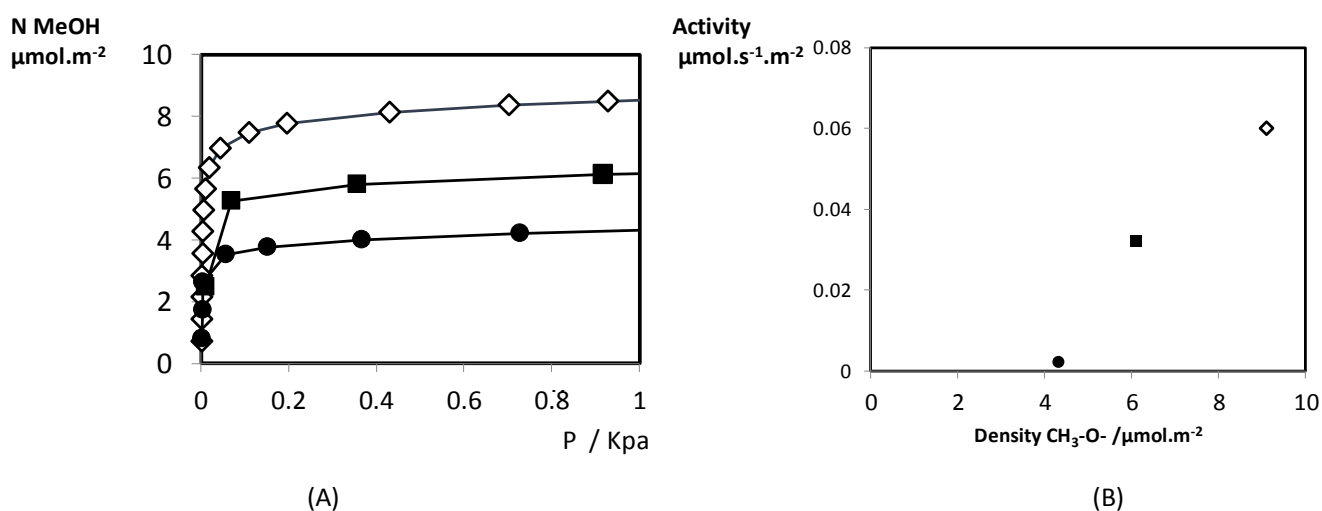
471 Catalytic activity is plotted as a function of the density of adsorbed methoxide for CZ-FSP, CZ-CP-500
472 and CZ-CP-850 in Fig. 9 . We can clearly see that the activity increases with the methoxide density,

473 which could be a clue to the origin of the superior activity of the FSP catalysts. We acknowledge that
474 the use of adsorption isotherms does not make it possible to differentiate between monodentate
475 methoxide species and bidentate methoxide species that have been identified as active and
476 spectator species, respectively. The higher activity of the FSP catalyst and also of CZ-CP-850 to a
477 lower extent can be explained by a higher density of Ce^{4+} surface cations that are able to activate large
478 amounts of methanol as monodentate species that are active in DMC synthesis.

479

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481



482

483 Fig. 9 (A) Isotherms of methanol at 20°C; (B) Activity versus adsorbed methoxide surface
484 density - CZ-CP-500 (●), CZ-CP-850 (■) and CZ-FSP (◇)

485

486

487 5. Conclusions

488 We discovered that cerium-zirconium mixed oxides prepared by flame spray pyrolysis show greater
489 catalytic activities in DMC synthesis than those prepared by precipitation. The objective of this study
490 was to find out the origins of the superior catalytic activities obtained by flame spray pyrolysis
491 synthesis method. Based on surface characterization by XPS as well as surface adsorption

492 measurements using probe molecules, we propose that flame spray pyrolysis enables a surface
493 enrichment in cerium oxide of the top layer that leads to a high concentration of adsorbed methanol
494 at the surface, which might explain the greater activity of the catalysts prepared using this method.
495 As pure cerium oxide is a poor catalyst, the composition of the sole top surface cannot be the only
496 parameter, which drives the high catalytic activity. In agreement with surface composition at
497 thermodynamic equilibrium, we propose that the most active catalysts are made with a top layer
498 mainly consisting of cerium oxides accompanied with a second layer consisting in majority of
499 zirconium oxide. The assumption of cerium surface enrichment triggered by thermal treatment also
500 holds for the explanation of the high catalytic activity of coprecipitated mixed oxides, which have
501 been treated at relative high temperature (850°C)

502 Beyond the application of DMC synthesis, we can anticipate that Flame Spray Pyrolysis synthesis shall
503 generate relative high surface area mixed oxides with different catalytic performances with respect
504 to mixed oxides prepared at lower temperature owing their metastable surface.

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