OXIDATION OF LEAN METHANE OVER COBALT CATALYSTS SUPPORTED ON CERIA/ALUMINA

A. Choya, B. de Rivas, J.R. González-Velasco, J.I. Gutiérrez-Ortiz, R. López-Fonseca

1 **OXIDATION OF LEAN METHANE OVER COBALT CATALYSTS**

2 **SUPPORTED ON CERIA/ALUMINA**

3

4 Andoni Choya, Beatriz de Rivas, Juan Ramón González-Velasco,

5 Jose Ignacio Gutiérrez-Ortiz, Rubén López-Fonseca*

6

7

8 Chemical Technologies for Environmental Sustainability Group,

9 Department of Chemical Engineering, Faculty of Science and Technology,

10 University of The Basque Country UPV/EHU, PO Box 644, E-48080 Bilbao, Spain

11

12

13 *Corresponding author:

14 Phone: +34-94-6015985

15 Fax: +34-94-6015963

16 E-mail address: ruben.lopez@ehu.eus

17

18 **ABSTRACT**

19 Cobalt (30%wt.) oxide catalysts supported over ceria-modified (3-18%wt.) alumina

20 supports were examined for the combustion of lean methane. The prepared samples

21 were characterised by wavelength dispersive X-ray fluorescence, N_2 physisorption, X-

22 ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, transmission

23 electron microscopy, temperature-programmed reduction with hydrogen and

24 temperature-programmed reaction with methane. A significant enhancement of the

25 activity was evidenced with respect to the catalyst supported over bare alumina, with an

26 optimal cerium loading of 12%wt. and a resultant T_{50} value of 480 °C. The ceria

27 modification was found to induce a dual positive effect on the performance of the cobalt

28 catalysts. On one hand, it acted as a physical barrier between deposited cobalt and

29 alumina, thus inhibiting the cobalt-alumina interaction and the subsequent cobalt

30 aluminate formation. On the other hand, the insertion of cerium ions in the spinel lattice

31 led to a distortion of the structure that in turn resulted in an enhanced mobility of the

32 oxygen species. The optimised catalyst exhibited a relatively good thermal stability for

33 prolonged reaction time intervals (150 h) under dry conditions. The presence of water

34 vapour markedly affected the catalytic performance although this negative effect was

35 partially reversible.

36

37 *Keywords: methane oxidation, cobalt oxide, modified alumina, ceria, lattice distortion*

38

1. Introduction

Cobalt-based catalysts have been largely used as oxidation catalysts in numerous environmental applications including VOC abatement and combustion of soot [1,2]. In this context, the control of emissions from natural gas vehicles (unburned methane) over this class of metal oxides has been also explored [3-5]. The use of cobalt catalysts with Co_3O_4 as the main active phase is frequently considered as a cheaper viable alternative to expensive noble-metal based catalysts with a proven higher specific activity [6]. The notable activity of this metal oxide is related to its good redox properties, and in particular, the easiness that the cobalt ions possess to switch between its two oxidation states (+3 and +2), which provides oxygen species in the lattice with a high mobility [7]. Since the oxidation of methane by these type of catalysts is deemed to occur via a Mars-van Krevelen mechanism, where the oxygen species from the spinel lattice are responsible for the oxidation reaction [8,9], these redox properties are crucial for the activity of Co_3O_4-based catalysts, to the point that even catalysts with poor textural and structural properties can exhibit a relatively good performance [10,11]. Consequently, when proposing an efficient strategy for designing highly active Co_3O_4 catalysts it is extremely important to maintain the structure and redox properties of the spinel as intact as possible.

The most commonly applied enhancing strategy is to support the cobalt oxide over the surface of a porous media, in order to disperse it and increase the amount of the available active surface area. Generally, this option produces catalysts with high specific surface areas and a small crystallite size of Co_3O_4, but it presents a major drawback in the form of a strong cobalt-support interaction that often negatively affects the redox properties of the cobalt oxide [12,13]. More specifically, when the support is alumina, this cobalt-support interaction usually provokes a partial reduction of Co^{3+} ions

64   to Co^{2+} and their subsequent fixation in the alumina lattice, which leads to the formation

65   of cobalt aluminate ($CoAl_2O_4$) [14]. The cobalt ions fixed in this phase lose almost all

66   their mobility and cannot revert to the +3 oxidation state at moderate temperatures

67   (< 600 °C), and therefore are rendered inactive for the oxidation reaction [15].

68   A possible solution to this problem is to modify the alumina support with a metallic

69   promoter, prior to the deposition of cobalt species, in order to increase its stability and

70   reduce its propensity to interact with the cobalt oxide deposited over it. This promoter

71   can be added during the synthesis of the alumina support itself. Thus, Liotta et al. [16]

72   found that adding Ba during the synthesis of Al_2O_3 by a sol-gel method inhibited solid

73   state diffusion of the Co^{2+} ions into the alumina after Co deposition. On the other hand,

74   Cheng et al. [17] reported that the incorporation of a fourth element during the synthesis

75   of an alumina supported copper-cobalt catalyst improved the reducibility of both metal

76   cations, especially when that fourth element was either Mn or Fe. Alternatively, the

77   promoter can be deposited over the surface of a as-synthesised alumina before the

78   deposition of cobalt. In this sense, Park et al. [18] and Park et al. [19], on different

79   studies, observed that the addition of P to Al_2O_3 resulted in the partial formation of

80    $AlPO_4$, which suppressed the formation of $CoAl_2O_4$. This inhibition effect was also

81   found for other metallic promoters such as Mg or Zr [20,21]. In all cases, the deposition

82   of the promoter over the alumina favoured a cobalt-promoter interaction at the cost of a

83   cobalt-alumina interaction. However, this interaction does not always work in favour of

84   the redox properties of the cobalt oxide. In this sense, previous investigations on the

85   effect of surface protection of Al_2O_3 with Mg revealed that the resulting Co-Mg

86   interaction led to the formation of a low reducibility CoO-MgO solid solution, as

87   reported by Ulla et al. [22] and Ji et al. [23].

88   Considering all the above-mentioned background, and based on our previous results on

89   the beneficial effect of cerium doping of Co_3O_4 bulk catalysts [24], this work proposes

90   the design of highly active Co/Al_2O_3 catalysts obtained by a previous incorporation of

91   ceria onto the support prior to cobalt precipitation. The premise supporting this

92   hypothesis is that the deposited CeO_2 could have a twofold function as a physical

93   barrier between cobalt and alumina, thus inhibiting the formation of $CoAl_2O_4$, and as a

94   redox promoter for Co_3O_4, thereby enhancing the intrinsic activity of the resulting

95   catalyst. The specific objective of the study will be to determine the amount of cerium

96   (5-30%wt.) to be loaded on the alumina support for the optimal performance of a

97   catalyst with a 30%wt.Co loading in the oxidation of methane in trace amounts ($< 1\%$)

98   under both dry and humid conditions.

99

100   **2.   Experimental**

101   *2.1.   Synthesis of the ceria-alumina supports and cobalt supported catalysts*

102   The ceria-modified alumina supports were prepared by a basic precipitation route of

103   cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, Sigma Aldrich) on a commercial γ-

104   Al_2O_3 (Saint Gobain) thermally stabilized at 850 °C for 8 hours. For each support, 5 g

105   of γ-Al_2O_3 were mixed with 100 mL of the cerium precursor with adjusted

106   concentrations of Ce and then a solution of Na_2CO_3 1.2M was added dropwise until the

107   pH reached 9.5. The temperature was kept constant at 80 °C. The selected cerium

108   loadings were 5, 10, 15, 20 and 30%wt. After an ageing step of 30 minutes at constant

109   temperature (80 °C) and pH (9.5), the obtained precipitates were filtered and thoroughly

110   washed with at least 5 litres of deionised water to remove all residual sodium ions that

111   could remain in the precursor, which have been proven to inhibit the activity of cobalt

112   oxide catalysts [25]. These modified supports were denoted as xCe-Al where x stands

113   for the nominal cerium loading. A support of pure ceria (CeO_2) was also synthesised by

114   the same route starting from a cerium (III) nitrate solution.

115   Cobalt catalysts supported on xCe-Al, CeO_2 and Al_2O_3 were prepared by following the

116   same synthesis route as for the supports but starting from a mixture of 5 g of each

117   support (modified alumina, bare ceria and bare alumina, respectively) and 100 mL of a

118   cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, Fluka) solution. All catalysts were

119   prepared with a cobalt loading of 30%wt. and denoted as Co/xCe-Al, Co/CeO_2 and

120   Co/Al_2O_3, respectively. A reference sample of bulk Co_3O_4 was also prepared as well by

121   precipitation of a solution of cobalt (II) nitrate.

122   All supports and catalytic precursors were dried at 110 °C for 16 hours and then

123   subjected to calcination in static air to produce the final supports and catalysts. The

124   calcination protocol was designed on the basis of previous thermogravimetric analysis

125   (Figure S1, Supplementary Material) and consisted of three heating ramps separated by

126   30-minute isothermal steps: an initial ramp from room temperature to 125 °C at

127   5 °C min^{-1}, a second ramp up to 300 °C at 1 °C min^{-1}, and a final ramp at 5 °C min^{-1} up

128   to 600 °C, temperature that was then maintained for 4 hours.

129

130   *2.2.   Characterisation techniques*

131   Textural properties were determined from the nitrogen-adsorption isotherms at -196 °C

132   obtained with a Micromeritics TriStar II apparatus. The specific surface of the samples

133   was obtained by the BET method, while the pore volume and the pore size distributions

134   were estimated using the BJH method. All samples were degassed prior to analysis on a

135   Micromeritics SmartPrep apparatus at 300 ºC for 10 hours with a N_2 flow.

136   The composition was determined by Wavelength Dispersive X-Ray Fluorescence

137   (WDXRF). From each sample in powder form, a boron glass pearl was prepared by

138   fusion in an induction micro-furnace, by mixing the sample with the flux agent

139   Spectromelt A12 (Merck) in an approximate proportion of 20:1. Chemical analysis of

140   each pearl was performed under vacuum, using a PANalytical AXIOS sequential

141   WDXRF spectrometer, equipped with a Rh tube and three different detectors (gas flow,

142   scintillation and Xe sealed).

143   Structural properties were determined by X-Ray diffraction, Raman spectroscopy, and

144   transmission electron microscopy. XRD analysis were performed on a X'PERT-PRO X-

145   Ray diffractometer using Cu Kα radiation (λ = 1.5406 Å) and a Ni filter. The X-Ray

146   tube was operated at 40 kV and 40 mA of current. The samples were scanned from an

147   initial value of $2\theta = 5°$ to a final value of $2\theta = 80°$, with a step size of 0.026° and a

148   counting time of 2.0 seconds for each step. Phase identification was performed by

149   comparison of the obtained diffraction patterns with JCPDS (Joint Committee on

150   Powder Diffraction Standards) database cards. A longer counting time (26.8 s) was

151   applied to perform a detailed XRD analysis over the xCe-Al supported cobalt catalysts.

152   The cell size of the cobalt spinel phase was obtained by profile matching of the detailed

153   XRD patterns using FullProf.2k software. Additionally, the analysis by Raman

154   spectroscopy was carried out by using a Renishaw InVia Raman spectrometer, coupled

155   to a Leica DMLM microscope. The excitation wavelength was 514 nm (ion-argon laser,

156   Modu-Laser). The spatial resolution was 2 microns. For each spectrum 20 seconds were

157   employed and five scans were accumulated with the 10% of the maximum power of the

158   514 nm laser in a spectral window of 150-1200 cm^{-1}.

159   Transmission electron microscopy (TEM) investigations were performed using a Philips

160   CM200 microscope equipped with LaB_6 crystal as electron source and operating at

161   200 kV. Bright field images were acquired using a high resolution CCD camera.

162   HRTEM measurements were carried out with a FEI Titan Cubed G2 60-300 electron

163   microscope at 300 kV equipped with a high-brightness X-FEG Schottky field emission

164   electron gun and a monochromator and CEOS GmbH spherical aberration (Cs)

165   corrector on the image side. The images were recorded on a charge-coupled device

166   (CCD) camera (2kx2k Gatan UltraScanTM 1000). X-Ray photoelectron spectroscopy

167   (XPS) measurements were carried out in a Kratos AXIS Supra spectrometer using a

168   225 W Al KAl Kα radiation source with a pass energy of 160 eV for the general survey

169   and 20 eV for the specific spectra.

170   Redox properties and Co species distribution was investigated by means of two

171   temperature-programmed techniques on a Micromeritics Autochem 2920 apparatus.

172   Temperature-programmed reduction with hydrogen (H_2-TPR) was performed using a

173   5%H_2/Ar mixture as the reducing gas. The analysis protocol involved an initial pre-

174   treatment step with a 5%O_2/He mixture at 300 °C for 30 minutes. After cooling down to

175   room temperature with flowing He, the TPR experiment was performed with a heating

176   rate of 10 °C min^{-1} up to 950 °C for all samples, and that temperature was then

177   maintained for 10 minutes. The water produced throughout the whole experiment was

178   eliminated using a cold trap, to avoid interference with the TCD detector. Additional

179   information regarding the activation of methane was obtained by means of temperature

180   programmed reaction with a 5%CH_4/He mixture in the absence of oxygen (CH_4-TPRe)

181   coupled to mass spectrometry (MKS Cirrus Quadrupole Mass Spectrometer). The

182   experiments were carried out up to 600 °C with a heating ramp of 10 °C min^{-1} followed

183   by an isothermal step at 600 °C for 30 minutes.

184

185   *2.3.   Catalytic activity determination*

186   The activity of the prepared catalysts was tested in a bench-scale fixed bed tubular

187   reactor (PID Eng&Tech S.L.) in the 200-600 °C temperature range. For each reaction

188 experiment, 1 g of catalysts with a particle size of 0.25-0.3 mm was diluted with 1 g of

189 inert quartz with a particle size of 0.5-0.8 mm, and the mixture was placed in a

190 Hastelloy X tube with a K type thermocouple located inside the catalytic bed. The

191 feedstream composition used was 1%CH_4, 10%O_2 and N_2 as balance gas, and it was fed

192 to the reactor with a total flow of 500 mL min^{-1}, which accounted for a space velocity of

193 300 mL CH_4 h^{-1} g^{-1}. The corresponding gas hourly space velocity calculated as a

194 function of the total flow rate was approximately 60,000 h^{-1}. Additionally, stability tests

195 were conducted over a prolonged period of time (150 hours) at 450 and 525 °C under

196 dry and cycling dry/humid (10%vol. H_2O) conditions. Methane conversion values were

197 obtained from the methane concentrations measured by a microGC equipped with a

198 TCD. For each temperature value or reaction time interval, the chromatographic

199 analysis were performed in triplicate to check the reproducibility. The standard

200 deviation found was less than 1% in all cases. To ensure that the obtained kinetic results

201 were not affected by mass or heat transfer limitations, the criteria for intra and extra-

202 particle heat and mass transfer, and temperature gradients were checked, according to

203 the Eurokin procedure (Table S1, Supplementary Material).

204

205 **3. Results and discussion**

206 *3.1.   Characterisation of xCe-Al supports*

207 The composition and textural and structural properties of the ceria-modified alumina

208 supports were characterised by WDXRF, N_2-physisorption, XRD and Raman

209 spectroscopy. Firstly, it should be pointed out that the chemical analysis revealed that

210 the amount of cerium species deposited on the alumina support was very close to the

211 nominal loading, namely 5, 10, 15, 20 and 30%wt.Ce (Table 1).

212   The specific surface area, total pore volume and pore size distribution maxima are

213   summarised in Table 1. The textural properties of the pure oxides (γ-Al_2O_3 and CeO_2)

214   are included for comparative purposes. A roughly linear decrease in surface area was

215   noticed with increasing Ce content. Thus, this loss was around 25% (with respect to the

216   bare alumina) for the sample with 30%wt.Ce (139 vs 105 m^2 g^{-1}). Judging from these

217   results the impact of ceria coating was considered moderate. Accordingly, the pore

218   volume of the samples steadily decreased from 0.56 to 0.32 cm^3 g^{-1}.

219   The samples showed type IV isotherms with H2 hysteresis loops, commonly associated

220   with pore blocking over a wide pore size distribution (Figure S2, Supplementary

221   material) [26]. No significant change in the hysteresis loops was apparently detected

222   with the Ce loading. Pore size distribution was estimated according to the BJH method.

223   The samples with low Ce loadings (5-15%wt.) displayed a bimodal distribution peaking

224   at around 110 and 150 Å, similar to that exhibited by the bare alumina, thus showing

225   evidence of a good dispersion of the deposited Ce over the surface of the support. For

226   the 20Ce-Al sample, however, the pore size switched to a unimodal distribution centred

227   at 110 Å, probably due to the narrowing of the largest pores (150 Å) caused by an

228   increased cerium deposition. Finally, the 30Ce-Al sample exhibited the same maximum

229   at 110 Å but with a lower pore volume (0.25 cm^3 g^{-1}) compared with the 20Ce-Al

230   sample (0.30 cm^3 g^{-1}). Besides, this sample presented a fraction of small pores with a

231   maximum around 35 Å derived from a marked pore narrowing of the existing 110 Å

232   pores because of the massive cerium incorporation.

233   XRD patterns of the xCe-Al supports calcined at 600 ºC are shown in Figure 1. This

234   graph also includes the diffractograms of the bare alumina and bulk ceria. In all cases

235   the diffraction signals could be indexed as γ-alumina (2θ at 37.7, 45.8 and 67.3º, JCPDS

236   01-074-2206) and cerium oxide (2θ at 28.5, 33.3, 47.5, 56.4 and 76.7º, JCPDS 00-004-

237 0593). Note that no peaks attributable to other possible crystalline phases such as

238 cerium aluminate were noticed. As an additional evidence of the deposition of ceria on

239 the surface of the alumina support, it was checked that the intensity ratio of the

240 characteristic signals of CeO_2 (2θ at 47.5°) and Al_2O_3 (2θ at 45.8°) increased with

241 cerium loading. Somewhat wide CeO_2 peaks were visible, thereby suggesting that ceria

242 was present in the form of finely divided particles. An attempt was thus made to

243 estimate the mean crystallite size of ceria from the peak broadening of the most intense

244 reflection ((111) plane) using the Scherrer equation. This size was close to 10 nm for the

245 5Ce-Al, 10Ce-Al and 15Ce-Al samples, and 12 nm for the supports with a higher Ce

246 content (20Ce-Al and 30Ce-Al samples). These values were in contrast with that found

247 for the as-prepared bulk ceria (32 nm), thus evidencing a good dispersion of ceria on the

248 alumina support.

249   TABLE 1

250   FIGURE 1

251 The presence of segregated ceria was further corroborated by Raman spectroscopy.

252 Thus, all coated alumina supports showed a strong peak assigned to the F_{2g} Raman-

253 active mode characteristic of the fluorite-like lattice of CeO_2 (Figure S3, Supplementary

254 material). When compared with the Raman spectra of bulk ceria (464 cm^{-1}), the signals

255 were slightly broader and shifted to lower values (462 cm^{-1}) due to the alumina-ceria

256 interaction [27]. Moreover, two additional weak signals at 260 and 595 cm^{-1} were

257 observed. These bands corresponded to nondegenerate longitudinal optical modes of

258 CeO_2, which were linked to with oxygen vacancies from partially reduced CeO_{2-x}

259 species [28]. In view of the higher intensity of these features for the 5Ce-Al and 10Ce-

260 Al supports, the formation of Ce^{3+} species, probably in the form of stable $CeAlO_3$-like

261 species, was favoured with low Ce loadings. As aforementioned, these species were not

262 detected by XRD analysis.

263 It seems clear that this varying abundance of Ce^{3+} and Ce^{4+} as a function of the cerium

264 content should be consistent with the specific hydrogen uptake of the supports estimated

265 by H_2-TPR. In this way, Figure 2 shows the reduction profiles of bulk ceria and the

266 various Ce-coated alumina supports. The CeO_2 sample exhibited a weak signal at 450-

267 500 ℃ that corresponded to the surface reduction of the oxide whereas the intense H_2

268 uptake peaking at about 800 ℃ was related to the reduction of the bulk [29]. For the

269 xCe-Al supports, these two reduction events were also observed. However, while the

270 surface reduction occurred at 450-500 ℃ as well, the bulk reduction only required 650-

271 700 ℃, probably due to the relatively small crystallite size of deposited ceria (10-

272 12 nm). In addition, a small shoulder above 850 ℃ related to the formation of $CeAlO_3$

273 as a result of the interaction of CeO_2 and Al_2O_3 ($2CeO_2 + Al_2O_3 + H_2 \rightarrow 2CeAlO_3 +$

274 H_2O) was noted [30]. The generation of this perovskite phase during the reduction

275 process was further confirmed by subsequent XRD analysis of the samples after the H_2-

276 TPR run. Hence, weak diffraction signals assignable to $CeAlO_3$ were visible on all xCe-

277 Al supports (2θ at 23.6, 33.5, 41.4 and 60.1°, JCPDS 00-048-0051) (Figure S4,

278 Supplementary material). In view of the similar shape of all H_2-TPR traces, it could be

279 assumed the redox characteristics of deposited cerium species, with no marked shift in

280 the reduction temperatures, remained invariant although the degree of reduction

281 substantially varied as a function of the cerium loading.

282   FIGURE 2

283 The overall H_2 consumption of the samples expectedly increased with the cerium

284 content, from 0.09 mmol H_2 g^{-1} over the 5Ce-Al sample to 0.94 mmol H_2 g^{-1} over the

285 30Ce-Al sample (Table 1). However, more notable differences in reducibility were

286   noticed when the specific uptake was examined. Hence, this intrinsic consumption

287   largely depended on the Ce content of the support (Figure S5, Supplementary material).

288   Note that this property for the as-synthesised pure bulk CeO_2 was 1.8 mmol H_2 g_{Ce}^{-1}.

289   The consumption progressively increased from 1.9 mmol H_2 g_{Ce}^{-1} (5Ce-Al) to 3.2-

290   3.5 mmol H_2 g_{Ce}^{-1} over the 20Ce-Al and 30Ce-Al samples. The low H_2 consumption

291   observed for the 5Ce-Al and 10Ce-Al supports was coherent with a favoured presence

292   of Ce^{3+} species on these samples, in the form of CeO_{2-x} species with a strong interaction

293   with the alumina, as evidenced by Raman spectroscopy. For higher Ce concentrations,

294   the predominant cerium species was segregated CeO_2.

295   *3.2.   Characterisation of Co/xCe-Al catalysts*

296   The addition of cobalt oxide (in the 27.2-29.5%wt. range as determined by WDXRF) to

297   the ceria-modified alumina supports (the actual Ce loading of the catalysts were in the

298   3.1-18.2%wt. range as determined by WDXRF as well) resulted in a notable, almost

299   linear loss of surface area of the resulting catalysts (73-102 m^2 g^{-1}) (Table 2). With

300   respect to the corresponding support (105-139 m^2 g^{-1}), this accounted for a decline by

301   20-30%. This negative effect on surface area was comparable to that noticed for the

302   Co/Al_2O_3 catalyst (22%). As for the pore volume, the Co/30Ce-Al sample presented the

303   lowest value (0.25 cm^3 g^{-1}) while no significant differences were found among the other

304   four samples (0.30-0.32 cm^3 g^{-1}).

305   TABLE 2

306   The deposition of cobalt species preferentially occurred on the wider pores (150 Å) of

307   the modified alumina supports with a bimodal pore size distribution, namely 5Ce-Al,

308   10Ce-Al and 15Ce-Al (Figure S6, Supplementary material). In fact, the profiles of these

309   catalysts showed a unimodal distribution peaking at 110 Å. In the case of the Co/20Ce-

310   Al sample the addition of cobalt to this modified support, characterised by a unimodal

311 distribution with a maximum at 110 Å, resulted in a shift of the pore size distribution to

312 slightly lower values (around 90 Å). This shift was not observed over the Co/30Ce-Al

313 catalyst with respect to its counterpart alumina support (30Ce-Al), thus suggesting that

314 cobalt oxide was partially present on the external surface of this sample.

315 Figure 3 shows the diffractograms of the Co/xCe-Al catalysts. For comparative

316 purposes, the patterns of the Co/Al_2O_3 and Co/CeO_2 samples were included as well.

317 Along with the characteristic features of the ceria phase ($2\theta = 28.5, 33.3, 47.5, 56.4$ and

318 $76.7°$), a set of signals at $2\theta = 31.3, 37.0, 45.1, 59.4$ and $65.3°$ were clearly

319 distinguished. These were related to a spinel-like cobalt phase, namely Co_3O_4 (JCPDS

320 00-042-1467) and/or $CoAl_2O_4$ (JCPDS 00-044-0160). The formation of cobalt

321 aluminate was plausible due to the interaction of Co_3O_4 and Al_2O_3 at high temperatures

322 [31]. Unfortunately, it was not possible to differentiate between these two oxides since

323 both phases crystallise in the cubic structure. Obviously, the formation of $CoAl_2O_4$ was

324 only ruled out in the case of the $30Co/CeO_2$ sample. After the addition of cobalt the

325 crystallite size of CeO_2, which was in 9-14 nm range, was not appreciably modified

326 when compared with the corresponding xCe/Al support (10-12 nm). As for the size of

327 the spinel-like cobalt phase estimated from the peak broadening of the signal at $37.1°$, it

328 remained almost constant (23-24 nm) irrespective of the composition of the support.

329 Only for the Co/30Ce-Al catalyst the size was considerably larger (31 nm), probably

330 due to the high cerium loading.

331   FIGURE 3

332 The Raman spectra of the cobalt catalysts supported on pure alumina (Co/Al_2O_3), pure

333 ceria (Co/CeO_2) and ceria/alumina (Co/xCe-Al) are included in Figure 4. As a

334 reference, the spectrum of pure Co_3O_4 is shown as well. Apart from a relatively weak

335 band at 462 cm^{-1} (F_{2g} mode of CeO_2), all supported catalysts displayed the five Raman

336 actives modes associated with Co_3O_4, namely three F_{2g} modes located at 194, 519 and

337 617 cm^{-1}, and the E_g and A_{1g} modes at 479 and 687 cm^{-1}, respectively [32,33]. Except

338 from the Co/CeO_2 catalyst, two shoulders at 705 and 725 cm^{-1} attached to the A_{1g}

339 vibration mode were visible. These two signals suggested the presence of cobalt

340 aluminate [34,35]. It was found out that the intensity of these features was more notable

341 over the Co/Al_2O_3 and Co/5Ce-Al samples, and tended to decrease when ceria was

342 deposited with a higher loading (>10%wt.Ce, more significantly for 30%wt.Ce).

343 Although the formation of this undesired cobalt phase was not completely inhibited, it

344 seemed that incorporated ceria acted as an efficient physical barrier to prevent the

345 reaction between Co_3O_4 and Al_2O_3 to some extent. From a catalytic point of view, the

346 ceria coating of the alumina support would favour an increase in the amount of highly

347 active Co_3O_4 at the cost of $CoAl_2O_4$.

348   FIGURE 4

349 A closer inspection of the dependence of the A_{1g} mode with the Ce content of the

350 catalysts could be helpful in determining a possible distortion of the Co_3O_4 lattice due to

351 the partial insertion of cerium cations. This effect was analysed in terms of the shift and

352 the full width at half maximum (FWHM) of this signal (Figure S7, Supplementary

353 material). On one hand, it was observed that the location of the band varied from

354 689 cm^{-1} in the Co/Al_2O_3 and bulk Co_3O_4 samples to 681 cm^{-1} in the Co/CeO_2 sample,

355 thus pointing out that the lattice of Co_3O_4 was much more affected by the presence of

356 CeO_2. As the Ce/Co molar ratio of the Co/xCe-Al catalysts increased the band

357 progressively shifted to lower values, from 689 cm^{-1} for Co/Al_2O_3 to 688-685 cm^{-1} for

358 Co/5Ce-Al, Co/10Ce-Al and Co/15Ce-Al, and to 682-680 cm^{-1} for Co/20Ce-Al,

359 Co/30Ce-Al and Co/CeO_2. It should be noticed that the other Raman active modes (F_{2g}

360 and E_g) shifted as well. This redshift of the Co_3O_4 signals could be attributed to the

361 distortion of the spinel lattice, possibly due to insertion of Ce ions [36]. Consistently,

362 the FWHM values of this band were higher for the Ce-rich cobalt catalysts (25-26 cm^{-1}

363 compared with 14-19 cm^{-1} for Co/5Ce-Al, Co/10Ce-Al and Co/15Ce-Al).

364 The structural change of the Co_3O_4 lattice was further confirmed by the estimation of

365 the cell parameter of the Co spinel from XRD patterns. As aforementioned, the detected

366 diffraction signals could be assigned to both Co_3O_4 and $CoAl_2O_4$. Consequently, the

367 position shifts that denote the change in the cell size could be initially attributed to

368 distortion of both phases. However, since only the Raman vibration modes of Co_3O_4

369 phase (and not those of $CoAl_2O_4$ phase) evidenced changes with the addition of Ce, the

370 shift in the diffraction signals was assumed to occur only due to distortion of the cobalt

371 oxide phase. Thus, the cell size of Co_3O_4 in the Co/xCe-Al catalysts was found to be

372 larger than that of the catalyst supported over bare alumina (8.077 Å), as shown in

373 Figure S8 (Supplementary material). More importantly, for the Co/20Ce-Al and

374 Co/30Ce-Al samples, the cell size displayed a maximum value (8.092 Å), which

375 evidenced the largest lattice distortion, in accord with the results obtained from Raman

376 spectroscopy. The enlargement of the unit cell of Co_3O_4 has been previously reported

377 by other authors [37,38] and is associated with the larger ionic radius of Ce^{4+} ions

378 (101 pm), with respect to Co^{2+} and Co^{3+} ions (79 and 69 pm, respectively). Note that

379 this eventual insertion of Ce^{4+} ions into the spinel lattice would be accompanied by an

380 increase in the amount of Co^{3+} so as to maintain the charge balance [39].

381 HAADF-STEM images along with the corresponding EDX maps of the Co/xCe-Al

382 catalysts are shown in Figure 5. This analysis evidenced that cobalt species were indeed

383 located on the surface of the ceria-modified alumina with a low presence of segregated

384 entities. In addition, it was noteworthy that some regions of the support were not

385 massively covered by cobalt. The spinel active phase was present as crystallites with

386 average sizes around 20-25 nm, which was in good agreement with XRD results

387 (Table 2), that tended to aggregate into larger patches of 100-150 nm. Only for the

388 Co/30Ce-Al sample, segregated Co_3O_4 crystallites with sizes up to 50-60 nm were

389 marginally observed. As for the cerium, it was homogeneously distributed on the

390 support in the form of quite small crystallites (smaller than 5 nm). Additionally, CeO_2

391 clusters of about 10 nm were also detected, in line with XRD results (Table 2). For the

392 Co/30Ce-Al sample, the size of the clusters increased up to 20 nm, as also evidenced by

393 XRD analysis.

394 Finally, Figure S9 (Supplementary material) shows some selected HRTEM images,

395 where the lattice fringes of Co_3O_4 and CeO_2 could be resolved, along with their

396 corresponding Fast Fourier Transform (FFT) spot patterns. For the cobalt spinel, two

397 lattice spaces, namely 0.29 and 0.24 nm, were identified, which corresponded to the

398 {220} and the {311} planes, respectively. On the other hand, for the ceria two lattice

399 spaces of 0.31 and 0.27 nm were observed, which corresponded to the {111} and {200}

400 planes, respectively.

401 FIGURE 5

402 The surface structure and composition was investigated by XPS. The distribution of

403 cobalt and oxygen species was determined from the Co2p and O1s spectra of the

404 samples, respectively (Figure S10, Supplementary material). In particular, the Co $2p_{3/2}$

405 signal could be deconvoluted in five different contributions. The two signals located at

406 lower binding energies, namely 779.5 and 780.7 eV, were attributed to the presence of

407 Co^{3+} and Co^{2+} cations in a spinel phase, respectively, while the signal centred at about

408 782.3 eV was attributed to the presence of CoO species [40]. The presence of this oxide

409 was comparable on all samples, and it accounted for around 5‑8% of the total detected

410 signal. Finally, the two signals located at higher binding energies (785.5 and 789.5 eV)

411 were identified as the satellite signals from Co^{2+} and Co^{3+} ions, respectively [41]. On

412 the other hand, the O 1s spectra showed three different signals located at 529.8, 530.8

413 and 532.4 eV, respectively. The first signal was assigned to oxygen species from the

414 spinel lattice (O_{latt}), the second one was related to weakly adsorbed oxygen species on

415 the surface (O_{ads}) and the last feature was attributed to the presence of hydroxyl groups

416 from adsorbed water [42].

417 Table 3 includes the surface molar composition of the investigated catalysts. The bulk

418 composition as determined by WDXRF is also included for comparative purposes.

419 Initially the properties of the reference supported catalysts, namely Co/Al_2O_3 and

420 Co/CeO_2 samples, will be discussed. The Co/Al_2O_3 sample showed a surface Co^{3+}/Co^{2+}

421 molar ratio of 0.67, which was noticeably lower compared with that of the Co/CeO_2

422 catalyst (0.95). Taking the latter value as representative of the supported Co_3O_4 oxide

423 phase, the low value of the alumina-supported catalyst was in agreement with the

424 significant presence of $CoAl_2O_4$, where cobalt cations are in the +2 oxidation state, as

425 suggested by Raman spectroscopy. As the formation of cobalt aluminate involves a

426 gradual diffusion of Co cations into the alumina structure, this necessarily resulted in a

427 lower presence of cobalt on the surface, with a Co/Al molar ratio of 0.32. Furthermore,

428 the relative abundance of surface cobalt increased for the Ce-containing samples as

429 revealed by their higher Co/(Ce+Al) molar ratios (up to 0.84 for the Co/20Ce-Al

430 sample). This finding was coherent with a less favoured formation of cobalt aluminate

431 due to the barrier effect of ceria, in line with the results derived from Raman

432 spectroscopy.

433 <div align="center">TABLE 3</div>

434 On the other hand, the Co^{3+}/Co^{2+} molar ratio of the Co/xCe-Al catalysts, except for the

435 Co/5Ce-Al sample), was higher (0.99-1.38) than that of the Co/CeO_2 catalyst. This fact

436   revealed that some cerium cations were likely incorporated into the Co_3O_4 lattice, as

437   previously suggested by XRD. This partial insertion necessarily implied an increase in

438   the abundance of Co^{3+} cations at the cost of Co^{2+} cations to maintain the charge balance.

439   This higher abundance of Co^{3+} species on the surface of the samples with increasing Ce

440   loading was accompanied by a concomitant more notable presence of lattice oxygen

441   species in the Co/xCe-Al catalysts (Table 3). These type of oxygen species are usually

442   involved in the oxidation of methane by a Mars–van Krevelen mechanism. As shown in

443   Figure 6, the relative presence of both species increased with cerium loading and was

444   optimised for the Co/20Ce-Al catalyst.

445   FIGURE 6

446   The nature of deposited cobalt species and their interaction with underlying ceria-coated

447   alumina was examined by H_2-TPR analysis (Table 4). Initially the behaviour of cobalt

448   catalysts supported on pure alumina or ceria (Co/Al_2O_3 and Co/CeO_2, respectively) was

449   compared. Besides, the reduction profile of bulk ceria was taken into consideration

450   (Figure S11, Supplementary material). Both cobalt catalysts displayed a notable H_2

451   uptake between 200-600 ℃ that was related to the reduction of precipitated Co_3O_4. This

452   contribution showed two more or less discernible peaks at 310 and 380 ℃, which were

453   indicative of the sequential reduction to CoO and metallic Co, respectively [32,43].

454   Except for a small band observed at 800 ℃ (this peak corresponded to the reduction of

455   ceria support), the Co/CeO_2 catalyst did not consume hydrogen between 600-800 ℃.

456   The overall H_2 uptake was 7.6 mmol H_2 g^{-1}. Interestingly, it was found that when

457   subtracting the amount of H_2 theoretically required for full reduction of deposited

458   Co_3O_4 (equivalent to 22.6 mmol H_2 g_{Co}^{-1}, according to following the equation

459   $Co_3O_4 + 4H_2 \rightarrow 3Co + 4H_2O$) from the overall H_2 consumption of the sample, the H_2

460   consumption related to the reduction of the support could be estimated. This value was

461   1.8 mmol H_2 g_{Ce}^{-1}, that coincided with the specific consumption measured for the pure

462   CeO_2 support. These results led us to conclude that no mutual effects on the reducibility

463   of both cobalt oxide and ceria existed for this catalyst.

464   In the case of Co/Al_2O_3, an additional peak between 550-750 ℃ was clearly

465   ascertained. This was assigned to the presence of significant quantities of $CoAl_2O_4$

466   derived from the strong interaction between Co_3O_4 and Al_2O_3, as also evidenced by

467   Raman spectroscopy. In fact, the total measured amount of H_2 (5.6 mmol H_2 g^{-1}) was

468   rather far from the stoichiometric uptake (6.8 mmol H_2 g^{-1}) when assuming that the

469   cobalt phase was exclusively Co_3O_4. These findings led to the conclusion that the

470   reducibility of free Co_3O_4 (cobalt species whose reduction occurred at 200-600 ℃) was

471   much more favoured when cobalt was deposited over ceria instead of alumina, although

472   the interaction between cobalt and ceria did not seem to enhance the redox properties of

473   the Co_3O_4 deposited over pure ceria in comparison with pure Co_3O_4. Simultaneously,

474   the reducibility of ceria was also not improved.

475   TABLE 4

476   The H_2-TPR profiles of the cobalt catalysts supported on ceria-alumina also consisted of

477   two H_2 uptakes at 200-550 ℃ and 550-800 ℃ (Figure 7). The total H_2 consumption of

478   the samples is given in Table 4. In all cases the H_2 uptake was larger than that shown by

479   the Co/Al_2O_3 sample. A significant increase by 5-16% was found with the amount of

480   cerium in the support. Above 15%wt.Ce the consumption was rather similar (6.5-

481   6.7 mmol H_2 g^{-1}). While no significant changes in the reduction onset temperature

482   (about 250 ℃) were observed, the relative contribution of these reduction events

483   seemed to be shifted in favour of the low-temperature band with the Ce loading

484   (Table 4). The observed increase in the H_2 uptake at low temperature could be

485   rationalised in terms of a favoured reduction of Co_3O_4 with a distorted lattice due to

486 cerium doping as revealed by XRD and XPS analysis. Another plausible phenomenon

487 that would contribute to a higher reducibility between 200 and 500 ºC could be a larger

488 extent of ceria reduction owing to the transfer of hydrogen by metallic cobalt onto the

489 ceria surface [44,45]. On the other hand, and in agreement with Raman spectroscopy,

490 the interaction between Co_3O_4 and Al_2O_3 to give $CoAl_2O_4$ was somewhat inhibited by

491 deposited ceria, thereby resulting in a decreased H_2 uptake at high temperatures.

492 In sum, the presence of ceria deposited on the alumina surface resulted in remarkable

493 changes in the redox properties by distorting the Co_3O_4 crystalline lattice and/or

494 promoting the ceria reducibility and/or inhibiting the formation of $CoAl_2O_4$. These

495 positive effects eventually led to a larger abundance of highly active oxygen, in the

496 form of lattice oxygen species as evidenced by XPS analysis, over the Co/xCe-Al

497 catalysts in comparison with the Co/Al_2O_3 counterpart.

498   FIGURE 7

499 More useful insights on the influence of the catalyst composition on the reactivity of

500 available oxygen species for methane oxidation were obtained by CH_4-TPRe analysis

501 coupled to mass spectrometry. The analysis was performed between 50 and 600 ºC with

502 a subsequent isothermal step at this temperature for 30 minutes. The evolution of CO_2

503 (m/z = 44) and CO (m/z = 28) was monitored (Figure 8). CO_2 formation occurred at two

504 clearly distinct temperature windows, namely 425-500 ºC (only CO_2 was detected) and

505 above 580 ºC (both CO and CO_2 were detected accompanied by H_2 as well, not shown

506 in Figure 8). In the low temperature range both Co/Al_2O_3 and Co/CeO_2 catalysts led to

507 the generation of CO_2 at about 485 ºC, which was attributed to the oxidation of methane

508 by oxygen species associated with Co^{3+} ions. Table 4 includes the O_2 consumption

509 corresponding to this generation of CO_2 for all examined catalysts. Note that the lowest

510 value (0.28 mmol O_2 g_{Co}^{-1}) corresponded to the Co/Al_2O_3 sample in agreement with the

511   marked presence of $CoAl_2O_4$. When cerium was added to the alumina support, the CO_2

512   formation was more evident ant took place at significantly lower temperatures. Figure 6

513   revealed that the extent of CH_4 oxidation was noticeably favoured with the presence of

514   lattice oxygen species. On the other hand, the reduction process interestingly occurred at

515   465 ℃ over the Co/20Ce-Al sample and consumed the largest amount of oxygen

516   (0.88 mmol O_2 g_{Co}^{-1}). Moreover, the temperature of the onset of reduction (marked by

517   arrows in Figure 8) was significantly lower for the Co/20Ce-Al and Co/30Ce-Al

518   samples (around 350 °C) in comparison with the rest of the samples (around 400 °C).

519   As stated above, the generation of CO_2 was also visible at higher temperatures owing to

520   the oxidation of methane by oxygen species associated with Co^{2+} ions [46]. This mass

521   signal was detected at 600 °C during the isothermal period. Exceptionally, CO_2 was

522   detected at 580 °C over the Co/20Ce-Al catalyst, thereby suggesting a higher mobility

523   of the oxygen species in this sample. In all cases, the high-temperature oxidation was

524   accompanied by the generation of CO and H_2 to some extent that could be due to partial

525   oxidation or cracking of methane in the presence of metallic or oxygen-deficient cobalt

526   species [47]. In fact, the diffraction pattern of the samples after the CH_4-TPRe run

527   evidenced the formation of graphitic carbon (signal at $2\theta = 26.6°$) due to the occurrence

528   of these two reactions [48].

529   FIGURE 8

530

531   *3.3.   Catalytic behaviour of Co/xCe-Al catalysts*

532   The performance of the synthesised cobalt catalysts was examined by their

533   corresponding light-off curves at 300 mL CH_4 g^{-1} h^{-1} (30000 mL g^{-1} h^{-1}) in the 200-

534   600 °C temperature range (Figure 9). Each catalyst was subjected to at least three

535   consecutive runs. It was found that the corresponding light-off curves were all

536 comparable after the second cycle. The representative light-off curve of each catalyst

537 corresponded to the third consecutive run. For the sake of comparison the conversion-

538 temperature profiles of the Co/Al_2O_3, Co/CeO_2 and bulk CeO_2 catalysts are also

539 included. It must be noticed that all catalysts exhibited a 100% selectivity towards CO_2,

540 irrespective of their cerium loading. While a negligible activity in the whole

541 temperature range was noticed for bare ceria, the cobalt catalyst supported over

542 uncoated alumina (Co/Al_2O_3) gave a T_{50} value at around 550 °C. However, this sample

543 did not achieve a 100% conversion at the highest investigated temperature (only around

544 80% at 600 °C). Interestingly, all Co/xCe-Al catalysts evidenced a better behaviour

545 irrespectively the ceria loading, with T_{50} values in the 480-540 °C temperature range

546 and a conversion higher than 95% at 600 °C. On the other hand, the observed higher

547 efficiency of the Co/CeO_2 sample (T_{50} of 500 °C) with respect to its counterpart

548 supported on pure alumina indicated that a cobalt-ceria interaction was catalytically

549 more preferable. The following overall trend was found: Co/20Ce-Al (480 °C) >

550 Co/15Ce-Al (490 °C) > Co/30Ce-Al (495 °C) > $Co/CeO_2 \approx$ Co/10Ce-Al (505 °C) >

551 Co/5Ce-Al (525 °C) > $Ce-Al_2O_3$ (550 °C). Thus, an optimum cerium loading (20%wt.)

552 deposited on alumina was defined.

553   FIGURE 9

554 A clearer evidence of the superior performance of the Co/20Ce-Al catalyst was given by

555 the analysis of the specific reaction rate shown by each Co/xCe-Al sample (Figure 10).

556 This reaction rate was calculated under differential conditions (conversion <15%) at

557 400 °C. A volcano-type relationship was distinctly seen, given that the reaction rate

558 progressively increased with Ce loading between 0 and 20%wt. (as referred to the

559 alumina support) from 1.2 to 3.3 $mmol_{CH4}$ g_{Co}^{-1} h^{-1}, to then decrease significantly for the

560 samples with a higher Ce concentration (2.9 $mmol_{CH4}$ g_{Co}^{-1} h^{-1}). This trend was also

561   consistent with the intrinsic activity shown by the cobalt catalyst supported on pure

562   ceria (2.1 $mmol_{CH4}\ g_{Co}^{-1}\ h^{-1}$). The results evidenced a promoted activity of Co_3O_4 when

563   supported on ceria-coated alumina. The positive effect of ceria coating was mainly

564   ascribed to the enhanced reactivity of the oxygen species of Co_3O_4 as also shown in

565   Figure 10. Hence, a marked dependence of the intrinsic activity with the amount of O_2

566   consumed at low temperatures (< 500 °C) in the CH_4-TPRe runs was evidenced. As

567   aforementioned, ceria addition was useful for partially reducing the amount of inactive

568     $CoAl_2O_4$ and simultaneously inducing a distortion of the structure of Co_3O_4. Both

569   phenomena ultimately led to catalysts with an enhanced oxidation ability. The apparent

570   activation energy of the reaction over the investigated cobalt catalysts was evaluated by

571   applying the integral method. A first pseudo-order for methane and a zero pseudo-order

572   for oxygen were assumed on the basis of a simplified Mars–van Krevelen kinetics for

573   this reaction studied with a high O_2/CH_4 molar ratio [49,50]. The corresponding plots

574   for the linearized kinetic equation of the integral reactor are shown in Figure S12,

575   Supplementary material. The values for the apparent activation energy were in the 80-

576   83 $kJ\ mol^{-1}$ range for all catalysts, which were coherent with the value obtained with a

577   bulk Co_3O_4 catalyst (78 $kJ\ mol^{-1}$) [24].

578   FIGURE 10

579   Finally, the stability of the most active sample (Co/20Ce-Al) was examined under two

580   different scenarios. On one hand, the evolution of conversion with time on stream of a

581   fresh sample was followed at 450 °C for 60 hours. Then, the reaction temperature was

582   increased up to 525 °C and the sample was maintained at this temperature during

583   additional 90 hours. Results from this experiment carried out under dry conditions are

584   shown in Figure 11. A relatively constant conversion level around 30% was observed at

585   450 °C with no clear evidences of deactivation. After raising the temperature at 525 °C,

586   a progressive loss of conversion from 78% to 64% (25 hours), and to 58% (25 hours)

587   was noticed. Then, conversion remained stable for the remaining 40 hours of the

588   stability test.

589   In a second scenario a fresh sample was also evaluated during a prolonged time span

590   (150 hours), in the absence or presence of water (10%) in the feed stream. Figure 11

591   includes the evolution of methane conversion during the stability test, where dry and

592   humid conditions were cycled each 25 hours at constant temperature (525 °C). The

593   results revealed a significant deactivation for the first 25 hours under dry conditions,

594   with a conversion decrease from 80 to 64%. Note that the conversion profile for this

595   time interval was virtually identical to that observed for the same conditions used in the

596   first stability test. When water was added to the gas stream, the impact on conversion

597   was considerable as conversion fell down to about 30%. When dry conditions were re-

598   established, methane conversion was partially recovered to give a stable value close to

599   52%. However, this was a little bit far from 58% dictated by the run carried out under

600   exclusively dry conditions. Once again, the admission of water led to an inhibition of

601   activity as conversion was 25%. When water admission was stopped, conversion again

602   increased (up to 48%), and finally decreased down to around 20% in the presence of

603   water. These results evidenced that the suggested inhibiting effect of water was not only

604   due to competition effects with methane for surface adsorption but it was also affecting

605   the physico-chemical properties of the catalyst [51,52].

606   FIGURE 11

607   The used samples from the two long-term stability tests conducted under dry and

608   dry/humid conditions, namely Co/20Ce-Al(d) and Co/20Ce-Al(d/h) samples, were

609   characterised by N_2 physisorption, XRD and CH_4-TPRe. Attention was paid on the

610   eventual changes on the surface area, the crystallite size of oxide phases and the amount

611   of active oxygen species al low temperatures (<550 °C). It was found that the

612   composition of the feed stream clearly affected the physico-chemical properties of the

613   sample (Table S2, Supplementary material). Thus, a decrease in the surface area was

614   observed (from 93 to 85 $m^2\,g^{-1}$ over Co/20Ce-Al(d)), which was slightly larger

615   (79 $m^2\,g^{-1}$) when the sample operated in the presence of large amounts of steam.

616   However, both deposited ceria and cobalt spinel phase exhibited a high thermal stability

617   in view of their relatively invariable crystallite size (12 and 23 nm, respectively). The

618   negative impact of water was reflected in the amount and reactivity of active oxygen

619   species as estimated by CH_4-TPRe analysis. The corresponding profiles are included in

620   Figure S13, Supplementary material and revealed that the O_2 consumption at low

621   temperatures decreased by 4% for the Co/20Ce-Al(d) sample and 16% for the Co/20Ce-

622   Al(d/h) sample. Moreover, a concomitant shift of the peak temperatures for this uptake

623   was noticed from 465 to 470 °C over the Co/20Ce-Al(d) sample and 480 °C over the

624   Co/20Ce-Al(d/h) sample.

625

626   **Conclusions**

627   The effect of cerium deposition on alumina-supported cobalt oxide catalysts for the

628   complete oxidation of lean methane was studied. The addition of cerium (5-30%wt.) to

629   the alumina was carried out prior to the deposition of cobalt (30%wt.) by a precipitation

630   synthesis route. The textural properties of the modified supports were hardly modified

631   with respect to those of bare alumina, due to the good dispersion of ceria over the

632   surface of the alumina. This dispersion also was responsible for a relatively strong

633   interaction between alumina and deposited ceria that resulted in an increased Ce^{3+}

634   content, especially at low Ce loadings (5-15%wt.). For higher Ce loadings (20-30%wt.)

635 the cerium-alumina interaction was weaker, thus resulting in a deposited ceria with a

636 higher Ce^{4+} content and better reducibility with respect to pure bulk ceria.

637 When cobalt was deposited over the modified supports, a dual effect of ceria was

638 evidenced. On one hand, ceria was found to act as a physical barrier between alumina

639 and deposited cobalt, reducing the cobalt-alumina interaction and the subsequent cobalt

640 aluminate formation, more remarkably with higher Ce loadings (20-30%wt.). On the

641 other hand, the interaction between cobalt and ceria led to a partial incorporation of

642 cerium ions into the structure of the cobalt oxide. Both findings ultimately led to a

643 larger abundance of Co^{3+} and therefore to a promoted mobility of the lattice oxygen

644 species with ceria loading. Consequently, cobalt catalysts supported over ceria-alumina

645 were significantly more active than that supported over bare alumina. The best

646 behaviour was found for the Co/20Ce-Al sample. Furthermore, this sample exhibited a

647 relatively good thermal stability for prolonged reaction time intervals (150 h) under dry

648 conditions. However, the presence of water vapour markedly affected the catalytic

649 performance although this negative effect was partially reversible.

650

656

657 **Appendix A. Supplementary data**

658 Supplementary data associated with this article can be found in the online version.

659

27

660   **References**

661   [1]   G. Zhai, J. Wang, Z. Chen, W. An, Y. Men, Chem. Eng. J. 337 (2018) 488-498.
662   https://doi.org/10.1016/j.cej.2017.12.141.

663   [2]   B. Bai, H. Arandiyan, J. Li, Appl. Catal. B Environ. 142-143 (2013) 677-683.
664   https://doi.org/10.1016/j.apcatb.2013.05.056.

665   [3]   G. Ercolino, P. Stelmachowski, G. Grzybek, A. Kotarba, S. Specchia, Appl. Catal.
666   B Environ. 206 (2017) 712-725. https://doi.org/10.1016/j.apcatb.2017.01.055.

667   [4]   K. Lehtoranta, T. Murtonen, H. Vesala, P. Koponen, J. Alanen, P. Simonen, T.
668   Rönkkö, H. Timonen, S. Saarikoski, T. Maunula, K. Kallinen, S. Korhonen,
669   Emiss. Control Sci. Technol. 3 (2017) 142-152. https://doi.org/10.1007/s40825-
670   016-0057-8.

671   [5]   M. Keenan, R. Pickett, E. Tronconi, I. Nova, N. Kinnunen, M. Suvanto, T.
672   Maunula, K. Kallinen, R. Baert, Top. Catal. 62 (2019) 273-281.
673   https://doi.org/10.1007/s11244-018-1127-7.

674   [6]   J. Chen, H. Arandiyan, X. Gao, J. Li, Catal. Surv. Asia 19 (2015) 140-171.
675   https://doi.org/10.1007/s10563-015-9191-5.

676   [7]   F. Zasada, J. Janas, W. Piskorz, M. Gorczynska, Z. Sojka, ACS Catal. 7 (2017)
677   2853-2867. https://doi.org/10.1021/acscatal.6b03139.

678   [8]   F. Zasada, W. Piskorz, J. Janas, J. Grybos, P. Indyka, Z. Sojka, ACS Catal. 5
679   (2015) 6879-6892. https://doi.org/10.1021/acscatal.5b01900.

680   [9]   L.F. Liotta, G. Di Carlo, G. Pantaleo, A.M. Venezia, G. Deganello, Appl. Catal. B
681   Environ. 66 (2006) 217-227. https://doi.org/10.1016/j.apcatb.2006.03.018.

682   [10] Z. Pu, H. Zhou, Y. Zheng, W. Huang, X. Li, Appl. Surf. Sci. 410 (2017) 14-21.
683   https://doi.org/10.1016/j.apsusc.2017.02.186.

684   [11] Z. Chen, S. Wang, W. Liu, X. Gao, D. Gao, M. Wang, S. Wang, Appl. Catal. A
685   Gen. 525 (2016) 94-102. https://doi.org/10.1016/j.apcata.2016.07.009.

686   [12] Q. Wang, Y. Peng, J. Fu, G.Z. Kyzas, S.M.R. Billah, S. An, Appl. Catal. B
687   Environ. 168-169 (2015) 42-50. https://doi.org/10.1016/j.apcatb.2014.12.016.

688   [13] G. Grzybek, K. Ciura, S. Wójcik, J. Gryboś, P. Indyka, M. Inger, K. Antoniak-
689   Jurak, P. Kowalik, A. Kotarba, Z. Sojka, Catal. Sci. Technol. 7 (2017) 5723-5732.
690   https://doi.org/10.1039/C7CY01575E.

691   [14] I. Zacharaki, C.G. Kontoyannis, S. Boghosian, A. Lycourghiotis, C. Kordulis,
692   Catal. Today 143 (2009) 38-44. https://doi.org/10.1016/j.cattod.2008.09.026.

693 [15] B. Solsona, T.E. Davies, T. Garcia, I. Vázquez, A. Dejoz, S.H. Taylor, Appl.
694   Catal. B Environ. 84 (2008) 176-184.
695   https://doi.org/10.1016/j.apcatb.2008.03.021.

696 [16] L.F. Liotta, G. Pantaleo, A. Macaluso, G. Di Carlo, G. Deganello, Appl. Catal. A
697   Gen. 245 (2003) 167-177. https://doi.org/10.1016/S0926-860X(02)00652-X.

698 [17] J. Cheng, J. Yu, X. Wang, L. Li, J. Li, Z. Hao, Energ. Fuels 22 (2008) 2131-2137.
699   https://doi.org/10.1021/ef8000168.

700 [18] S. Park, G. Kwak, Y. Lee, K. Jun, Y.T. Kim, Bull. Korean Chem. Soc. 39 (2018)
701   540-547. https://doi.org/10.1002/bkcs.11431.

702 [19] J. Park, S. Yeo, T. Kang, I. Heo, K. Lee, T. Chang, Fuel 212 (2018) 77-87.
703   https://doi.org/10.1016/j.fuel.2017.09.090.

704 [20] Y. Zhang, H. Xiong, K. Liew, J. Li, J. Mol. Catal. A Chem. 237 (2005) 172-181.
705   https://doi.org/10.1016/j.molcata.2005.04.057.

706 [21] V. Garcilaso, J. Barrientos, L.F. Bobadilla, O.H. Laguna, M. Boutonnet, M.A.
707   Centeno, J.A. Odriozola, Renew. Energ. 132 (2019) 1141-1150.
708   https://doi.org/10.1016/j.renene.2018.08.080.

709 [22] M.A. Ulla, R. Spretz, E. Lombardo, W. Daniell, H. Knözinger, Appl. Catal. B
710   Environ. 29 (2001) 217-229. https://doi.org/10.1016/S0926-3373(00)00204-6.

711 [23] S. Ji, S. Ji, H. Wang, E. Flahaut, K.S. Coleman, M.L.H. Green, Catal. Lett. 75
712   (2001) 65-71. https://doi.org/10.1023/A:1016711207912.

713 [24] A. Choya, B. de Rivas, J.R. González-Velasco, J.I. Gutiérrez-Ortiz, R. López-
714   Fonseca, Appl. Catal. B Environ. 237 (2018) 844-854.
715   https://doi.org/10.1016/j.apcatb.2018.06.050.

716 [25] A. Choya, B. de Rivas, J.I. Gutiérrez-Ortiz, R. López-Fonseca, Catalysts 8 (2018)
717   427. https://doi.org/10.3390/catal8100427.

718 [26] K.M.S. Khalil, J. Colloid Interf. Sci. 307 (2007) 172-180.
719   https://doi.org/10.1016/j.jcis.2006.11.039.

720 [27] Q. Yu, X. Wu, C. Tang, L. Qi, B. Liu, F. Gao, K. Sun, L. Dong, Y. Chen, J.
721   Colloid Interf. Sci. 354 (2011) 341-352.
722   https://doi.org/10.1016/j.jcis.2010.10.043.

723 [28] A. Martínez-Arias, M. Fernández-García, L.N. Salamanca, R.X. Valenzuela, J.C.
724   Conesa, J. Soria, J. Phys. Chem. B 104 (2000) 4038-4046.
725   https://doi.org/10.1021/jp992796y.

726 [29] B. de Rivas, C. Sampedro, E.V. Ramos-Fernández, R. López-Fonseca, J. Gascon,
727   M. Makkee, J.I. Gutiérrez-Ortiz, Appl. Catal. A Gen. 456 (2013) 96-104.
728   https://doi.org/10.1016/j.apcata.2013.02.026.

729 [30] M. Gil-Calvo, C. Jiménez-González, B. de Rivas, J.I. Gutiérrez-Ortiz, R. López-
730   Fonseca, Ind. Eng. Chem. Res. 56 (2017) 6186-6197.
731   https://doi.org/10.1021/acs.iecr.7b00986.

732 [31] Y. Ji, Z. Zhao, A. Duan, G. Jiang, J. Liu, J. Phys. Chem. C 113 (2009) 7186-7199.
733   https://doi.org/10.1021/jp8107057.

734 [32] Q. Liu, L. Wang, M. Chen, Y. Cao, H. He, K. Fan, J. Catal. 263 (2009) 104-113.
735   https://doi.org/10.1016/j.jcat.2009.01.018.

736 [33] D.K. Chlebda, R.J. Jędrzejczyk, P.J. Jodłowski, J. Łojewska, J. Raman Spectrosc.
737   48 (2017) 1871-1880. https://doi.org/10.1002/jrs.5261.

738 [34] X. Jiang, Y. Ma, Y. Chen, Y. Li, Q. Ma, Z. Zhang, C. Wang, Y. Yang,
739   Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 190 (2018) 61-67.
740   https://doi.org/10.1016/j.saa.2017.08.076.

741 [35] V. D'Ippolito, G.B. Andreozzi, D. Bersani, P.P. Lottici, J. Raman Spectrosc. 46
742   (2015) 1255-1264. https://doi.org/10.1002/jrs.4764.

743 [36] Q. Zhang, S. Mo, B. Chen, W. Zhang, C. Huang, D. Ye, Mol. Catal. 454 (2018)
744   12-20. https://doi.org/10.1016/j.mcat.2018.05.006.

745 [37] D. Li, L. Wang, M. Koike, Y. Nakagawa, K. Tomishige, Appl. Catal. B Environ.
746   102 (2011) 528-538. https://doi.org/10.1016/j.apcatb.2010.12.035.

747 [38] G. Zou, Y. Xu, S. Wang, M. Chen, W. Shangguan, Catal. Sci. Technol. 5 (2015)
748   1084-1092. https://doi.org/10.1039/c4cy01141d.

749 [39] R. Dziembaj, A. Chojnacka, Z. Piwowarska, M. Gajewska, M. Swietoslawski, S.
750   Górecka, M. Molenda, Catal. Today 333 (2019) 196-207.
751   https://doi.org/10.1016/j.cattod.2018.03.042.

752 [40] J. González-Prior, R. López-Fonseca, J.I. Gutiérrez-Ortiz, B. de Rivas, Appl.
753   Catal. B Environ. 222 (2018) 9-17. https://doi.org/10.1016/j.apcatb.2017.09.050.

754 [41] M. Singh, N.K. Ralhan, S. Singh, Bull. Mater. Sci. 38 (2015) 297-301.
755   https://doi.org/10.1007/s12034-015-0872-5.

756 [42] M.C. Biesinger, B.P. Payne, A.P. Grosvenor, L.W.M. Lau, A.R. Gerson, R.S.C.
757   Smart, Appl. Surf. Sci. 257 (2011) 2717-2730.
758   https://doi.org/10.1016/j.apsusc.2010.10.051.

759 [43] C. Tang, C. Wang, S. Chien, Thermochim. Acta 473 (2008) 68-73.
760   https://doi.org/10.1016/j.tca.2008.04.015.

761 [44] Ming Meng, Y.Q. Zha, J.Y. Luo, T.D. Hu, Y.N. Xie, T. Liu, J. Zhang, Appl.
762   Catal. A Gen. 301 (2006) 145-151. https://doi.org/10.1016/j.apcata.2005.06.035.

763   [45]   H. Sohn, G. Celik, S. Gunduz, D. Dogu, S. Zhang, J. Shan, F. Feng Tao, U.S.
764   Ozkan, Catal. Lett. 147 (2017) 2863-2876. https://doi.org/10.1007/s10562-017-
765   2176-4.

766   [46]   L. Hu, Q. Peng, Y. Li, J. Am. Chem. Soc. 130 (2008) 16136-16137.
767   https://doi.org/10.1021/ja806400e.

768   [47]   A.W. Budiman, S. Song, T. Chang, C. Shin, M. Choi, Catal. Surv. Asia 16 (2012)
769   183-197. https://doi.org/10.1007/s10563-012-9143-2.

770   [48]   M. Gil-Calvo, C. Jiménez-González, B. De Rivas, J.I. Gutiérrez-Ortiz, R. López-
771   Fonseca, Chem. Eng. Trans. 57 (2017) 901-906.
772   https://doi.org/10.3303/CET1757151.

773   [49]   N. Bahlawane, Appl. Catal. B Environ. 67 (2006) 168-176.
774   https://doi.org/10.1016/j.apcatb.2006.03.024.

775   [50]   P. Stefanov, S. Todorova, A. Naydenov, B. Tzaneva, H. Kolev, G. Atanasova, D.
776   Stoyanova, Y. Karakirova, K. Aleksieva, Chem. Eng. J. 266 (2015) 329-338.
777   https://doi.org/10.1016/j.cej.2014.12.099.

778   [51]   A.K. Dalai, B.H. Davis, Appl. Catal. A Gen. 348 (2008) 1-15.
779   https://doi.org/10.1016/j.apcata.2008.06.021.

780   [52]   Ø Borg, Z. Yu, D. Chen, E.A. Blekkan, E. Rytter, A. Holmen, Top. Catal. 57
781   (2014) 491-499. https://doi.org/10.1007/s11244-013-0205-0.

782
783

809

Sample	Ce, %wt.	S_{BET}, $m^2 g^{-1}$	V_{pore}, $cm^3 g^{-1}$	Pore Size Distribution maxima, Å	D_{CeO2}, nm	H_2 uptake, mmol g_{Ce}^{-1}
Al_2O_3	-	139	0.56	110, 150	-	-
5Ce-Al	5.2	128	0.51	110, 150	10	1.9
10Ce-Al	9.8	126	0.51	110, 150	9	2.1
15Ce-Al	15.3	122	0.49	110, 150	10	2.6
20Ce-Al	20.6	117	0.42	110	12	3.3
30Ce-Al	30.3	105	0.32	35, 110	12	3.1
CeO_2	81.4	8	0.03	230	32	1.8

810

811   TABLE 1

812

Sample	Ce, %wt.	Co, %wt.	S_{BET}, $m^2\,g^{-1}$	V_{pore}, $cm^3\,g^{-1}$	Pore Size Distribution maxima, Å	D_{CeO2}, nm	$D_{Co\text{-}spinel}$, nm
Co/Al$_2$O$_3$	-	27.9	108	0.29	90	-	29
Co/5Ce-Al	3.1	28.8	102	0.32	110	8	24
Co/10Ce-Al	5.9	28.9	96	0.30	110	9	24
Co/15Ce-Al	9.2	28.0	90	0.32	110	10	23
Co/20Ce-Al	12.4	29.5	93	0.30	90	11	23
Co/30Ce-Al	18.2	27.2	73	0.25	35, 110	14	31
Co/CeO$_2$	48.8	28.9	18	0.07	225	33	44

813

814   TABLE 2

815

Sample	Co, %wt.	Ce, %wt.	Al, %wt.	Co/(Ce+Al) molar ratio	Co^{3+}/Co^{2+} molar ratio	O_{ads}/O_{latt} molar ratio
Co/Al_2O_3	22.6 (27.9)	0 (0)	32.1 (37.0)	0.32	0.67	1.41
Co/5Ce-Al	26.7 (28.8)	1.3 (3.1)	23.6 (32.1)	0.51	0.91	1.30
Co/10Ce-Al	30.4 (28.9)	2.4 (5.9)	20.1 (30.0)	0.68	0.99	0.98
Co/15Ce-Al	30.1 (28.0)	3.0 (9.2)	19.4 (29.1)	0.69	1.15	0.82
Co/20Ce-Al	32.9 (29.5)	3.8 (12.4)	17.2 (26.1)	0.84	1.38	0.77
Co/30Ce-Al	29.7 (27.2)	5.3 (18.2)	18.4 (20.1)	0.70	1.17	0.88
Co/CeO_2	35.6 (28.9)	26.8 (48.8)	0 (0)	3.26	0.95	1.07

816   The values in brackets correspond to the bulk composition as determined by WDXRF.

817   TABLE 3

818

819

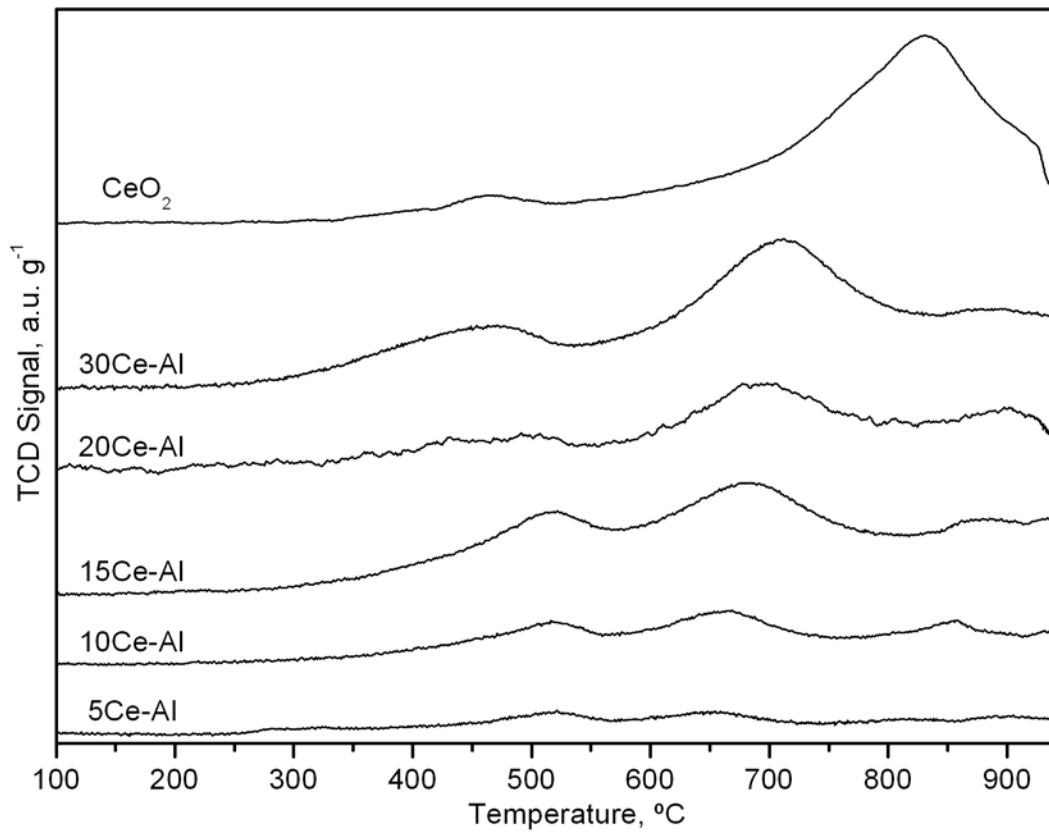| Sample	H$_2$-TPR		CH$_4$-TPRe
	H$_2$ uptake at low temperatures, mmol g^{-1}	H$_2$ uptake at high temperatures, mmol g^{-1}	O$_2$ consumption at low temperatures, mmol g$_{Co}^{-1}$
Co/Al$_2$O$_3$	2.74	2.84	0.28
Co/5Ce-Al	2.01	3.86	0.45
Co/10Ce-Al	2.83	3.27	0.68
Co/15Ce-Al	3.02	3.22	0.72
Co/20Ce-Al	3.29	3.19	0.88
Co/30Ce-Al	3.68	2.61	0.77
Co/CeO$_2$	6.77	0.82	0.70
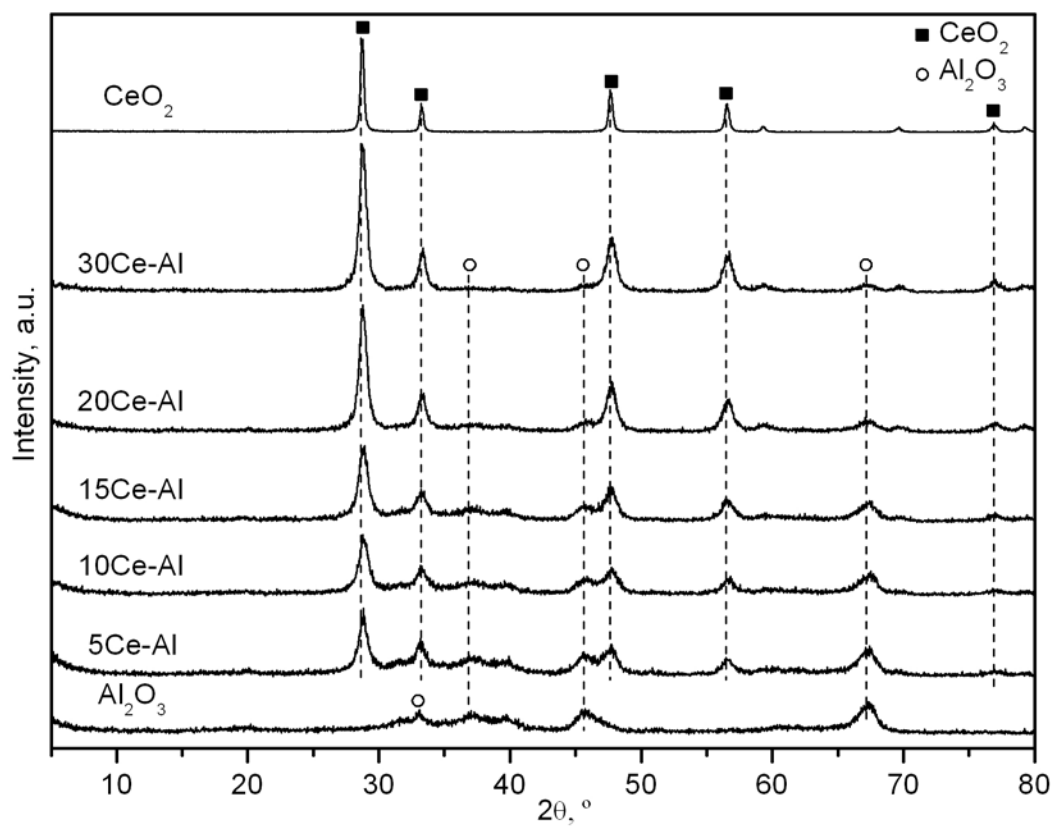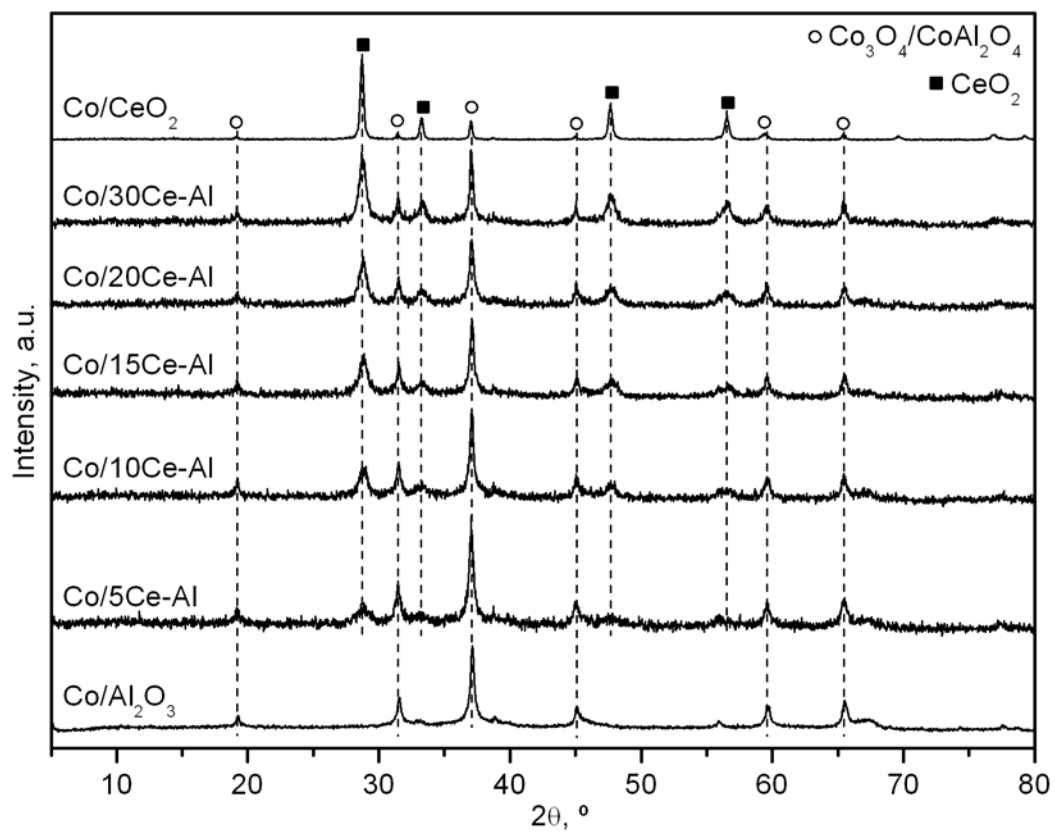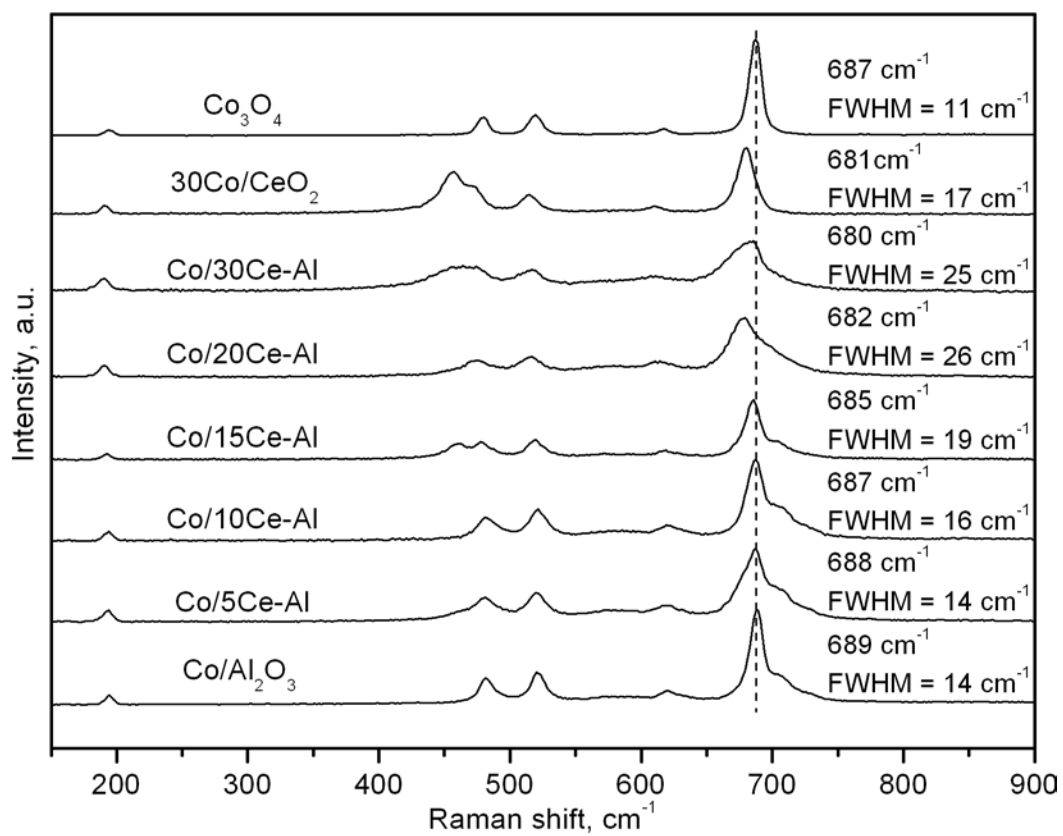
820

821   TABLE 4

FIGURE 1

825

826   FIGURE 2

827

828

829

FIGURE 3

830

831

Co₃O₄
687 cm⁻¹
FWHM = 11 cm⁻¹

30Co/CeO₂
681 cm⁻¹
FWHM = 17 cm⁻¹

Co/30Ce-Al
680 cm⁻¹
FWHM = 25 cm⁻¹

Co/20Ce-Al
682 cm⁻¹
FWHM = 26 cm⁻¹

Co/15Ce-Al
685 cm⁻¹
FWHM = 19 cm⁻¹

Co/10Ce-Al
687 cm⁻¹
FWHM = 16 cm⁻¹

Co/5Ce-Al
688 cm⁻¹
FWHM = 14 cm⁻¹

Co/Al₂O₃
689 cm⁻¹
FWHM = 14 cm⁻¹

832

833 FIGURE 4

834

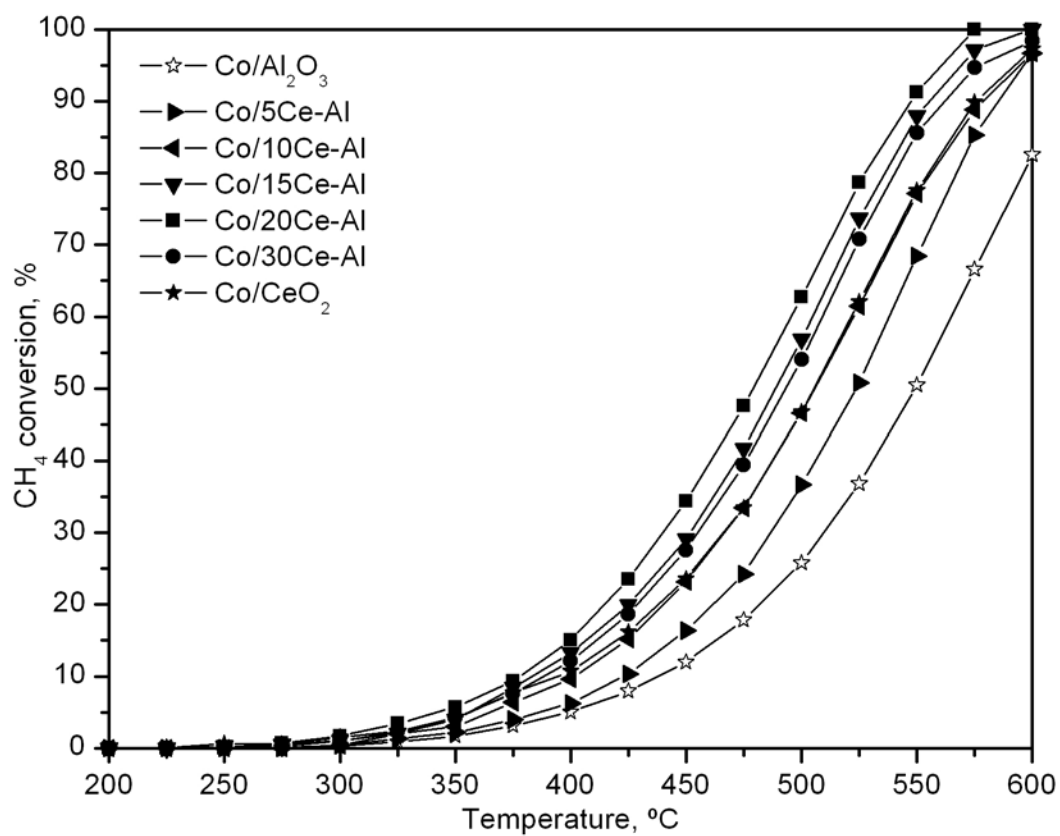FIGURE 5

838

839   FIGURE 6

840

841

FIGURE 7

842

843
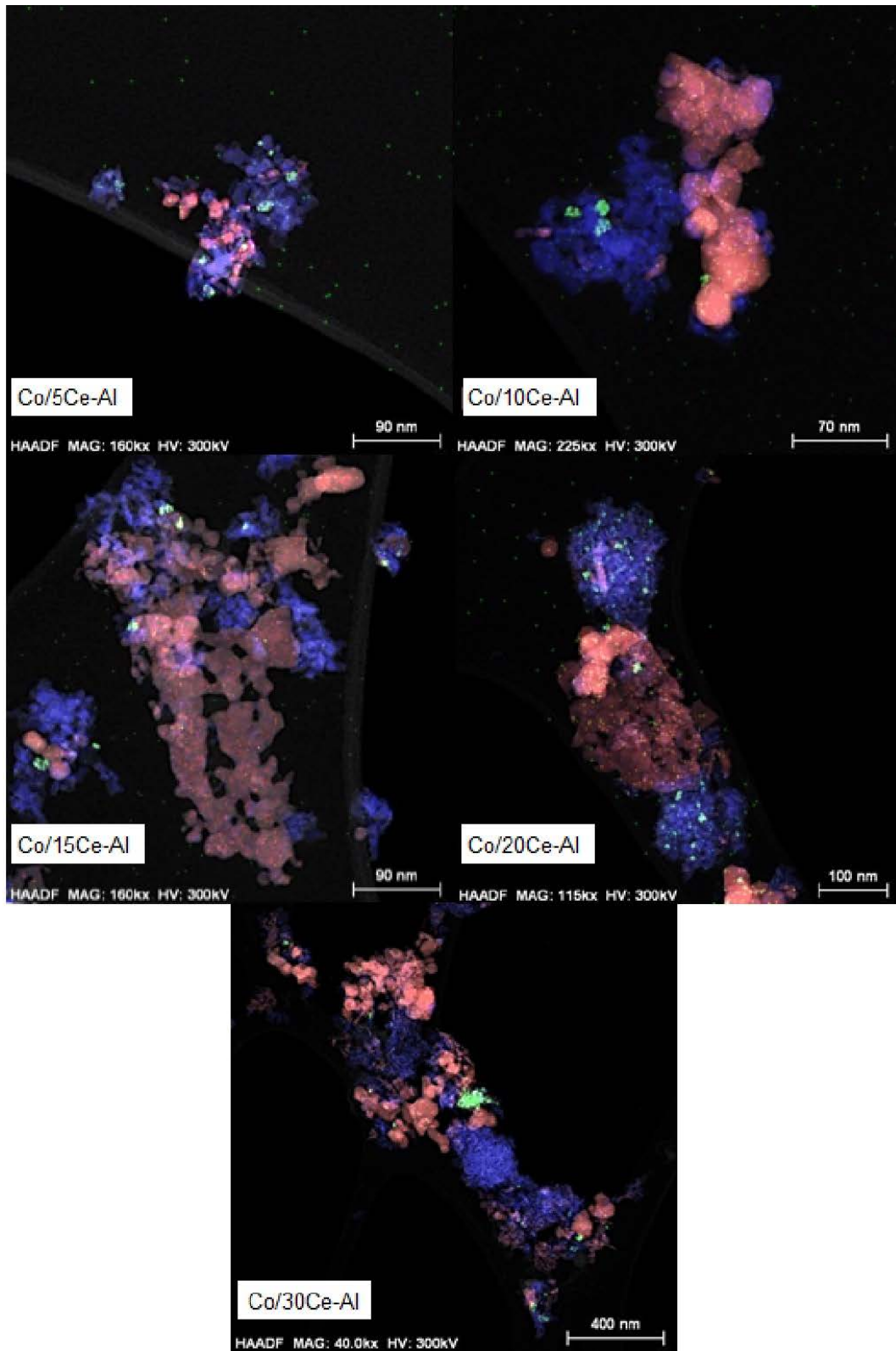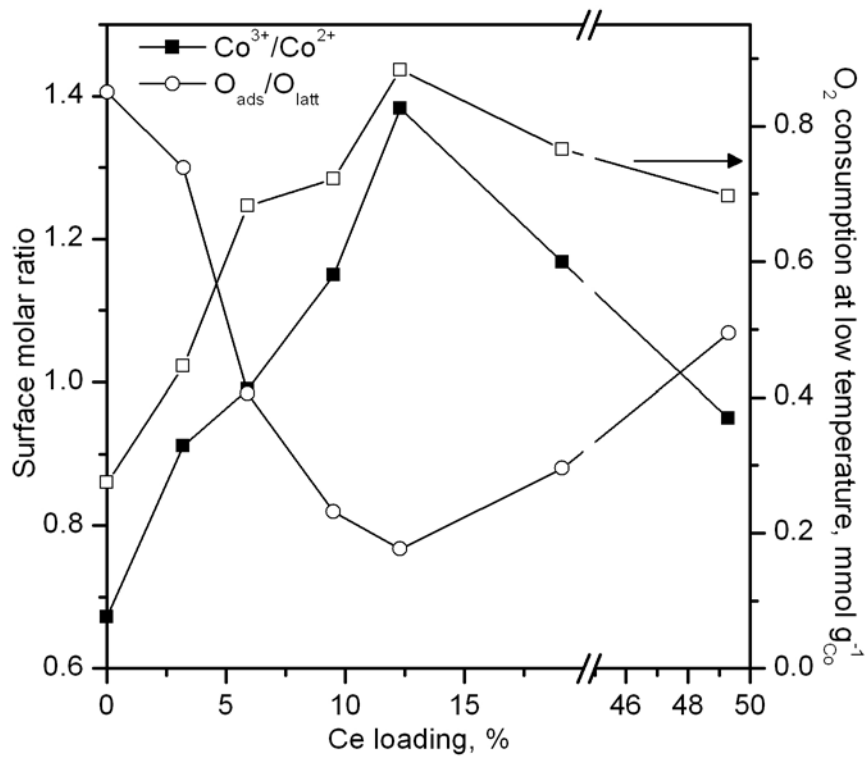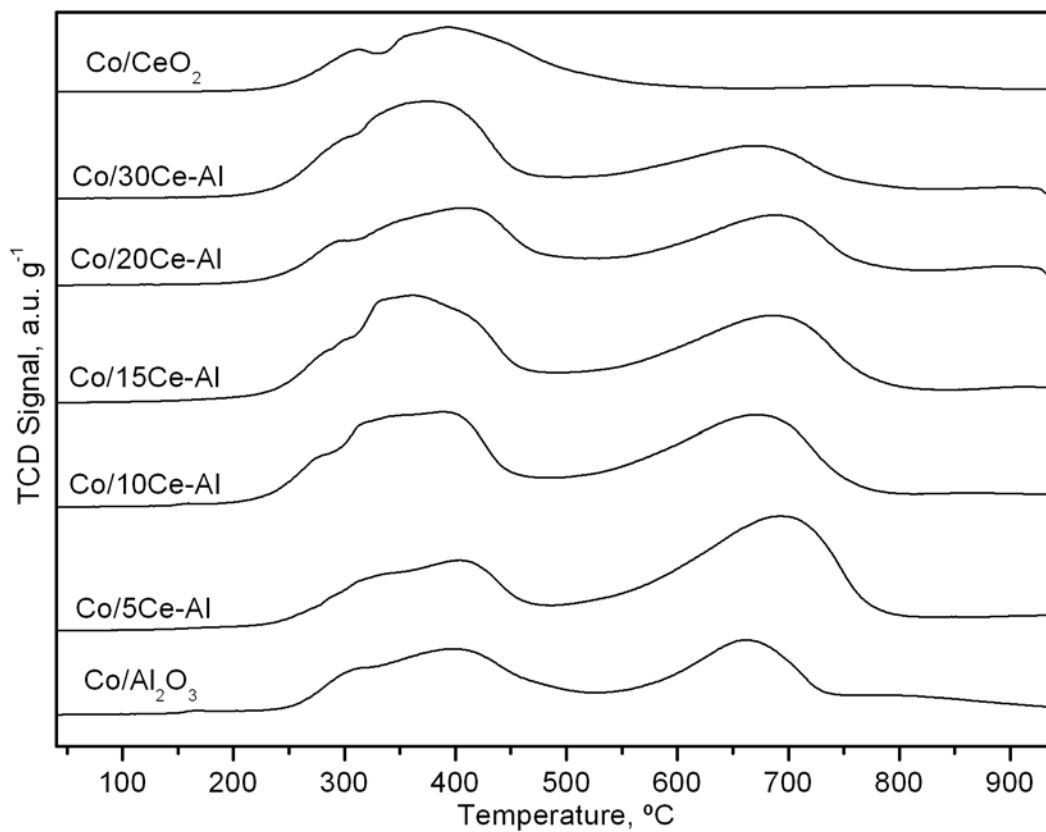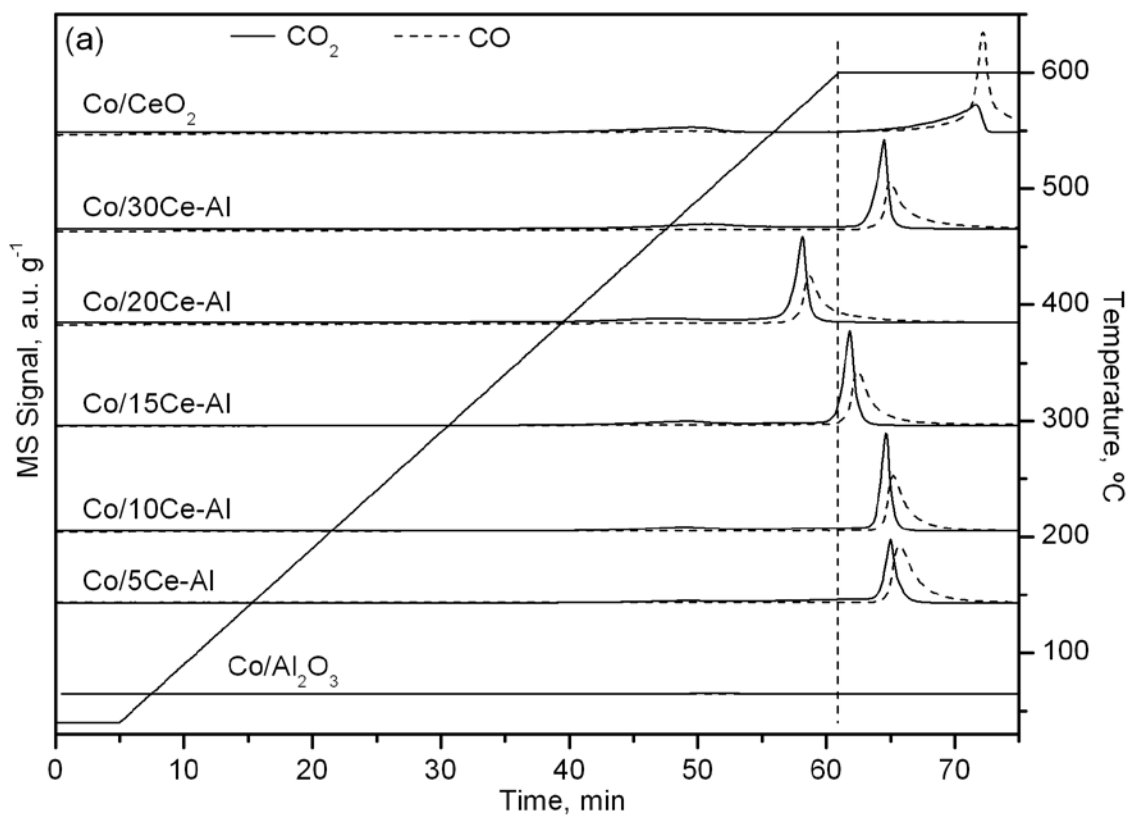
844

845

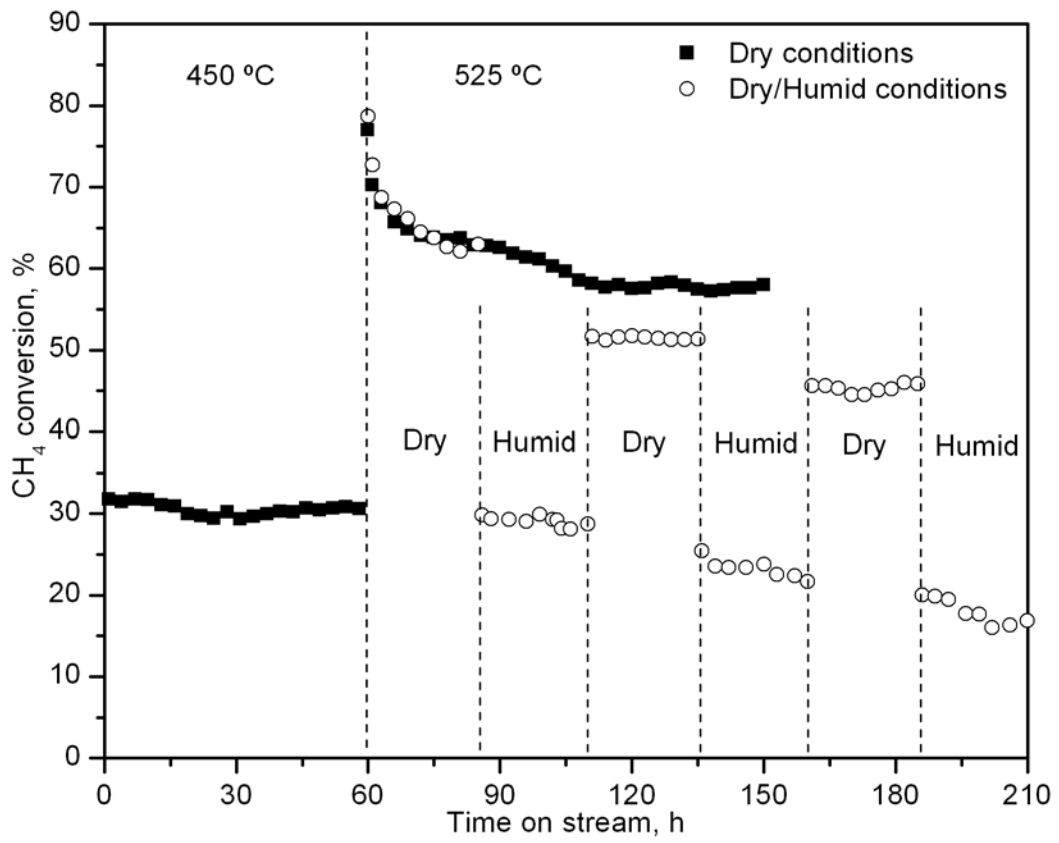846   FIGURE 8

847

848

FIGURE 9

849

850

851

852

853   FIGURE 10

854

855

FIGURE 11

856

47