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10	Performance and stability of wet-milled CoAl ₂ O ₄ , Ni/CoAl ₂ O ₄ and
11	Pt,Ni/CoAl ₂ O ₄ for soot combustion
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26 Figure S1. a) XRD patterns of the mechanically activated support and the 27 supported catalysts, and JCPD standards for CoAl₂O₄, α -Al₂O₃, Pt, and Ni. 28 Figure S1 shows the XRD patterns of the support and the catalysts. Both 29 30 supported samples exhibit the characteristic peaks of the CoAl₂O₄ spinel (JCPDS) File Nos. 00-044-0160) and the α -alumina (JCPDS File Nos. 00-046-1212) 31 phases present in the mechanically activated cobalt aluminate. However, the 32 33 presence of Pt or Ni crystalline phases cannot be determined, due to the low amount and/or high dispersion of the metals. XPS analyses of the fresh and used 34 samples reveal traces of zirconia contamination attributed to the milling 35 procedure [1], and indicate that all the samples had a normal spinel structure and 36 Co²⁺ cations in tetrahedral sites (Figure S2) [2,3]. The intensity of the Pt 4d and 37 38 Ni 2p peaks was not sufficient to assess the oxidation state before and after reaction by deconvolution of the platinum and nickel spectra into the individual 39 components. 40



43 Figure S2.- a, c, e) Survey XPS spectra. b, d, f) XPS spectra of Co 2p core levels.

Table S1: Elemental composition (at %) of the samples based on XPS analysis
(traces of Zr not quantified).

Sample	C (at. %)	O (at. %)	AI (at. %)	Co (at. %)	Co:Al
CoAl₂O₄ fresh	17.31	44.43	32.62	5.63	1:6
CoAl ₂ O ₄ -700	20.73	44.18	31.06	4.02	1:8
Pt,Ni/CoAl₂O₄ fresh	16.17	43.70	35.06	5.07	1:7
Pt,Ni/CoAl₂O₄ used	16.43	45.82	33.28	4.46	1:7
Ni/CoAl ₂ O ₄ fresh	12.18	43.46	38.15	6.20	1:6
Ni/CoAl₂O₄ used	12.91	44.77	37.69	4.63	1:8

XPS analyses of the fresh and used samples reveal some zirconia contamination 47 attributed to the milling procedure [1] and indicate that all the samples had a 48 normal spinel structure and Co²⁺ cations in tetrahedral sites (Figure S2). Firstly, 49 in cobalt aluminate the Co 2p_{3/2} peak is perfectly symmetric because cobalt only 50 has a single oxidation state [4]. Moreover, for these samples, the data give an 51 energy splitting $\Delta E=15.6$ eV, which is characteristic of Co²⁺ only, and no 52 additional signatures for the Co³⁺ state are noticed. Finally, these structures 53 clearly show two intense satellites which are representative of tetrahedral 54 55 coordinated Co²⁺ cations [5]. Table S1 contains the quantitative elemental analysis obtained from the XPS spectra. The starting Co:Al ratio is in agreement 56 with the CoAl₂O₄ structure that ends with aluminum atoms in octahedral positions 57 [2]. The slight variation of the Co:Al ratio after use, from 1:6 - 1:8, confirms that 58 the materials surface is essentially stable. The intensity of the Pt 4d and Ni 2p 59

peaks was not sufficient to assess the oxidation state before and after reaction
by deconvolution of the platinum and nickel spectra into the individual
components.



65 Figure S3.- a) HAADF-STEM image of Pt,Ni/CoAl₂O₄ catalyst. b-c) EDX mapping

66 analyses for Ni (green) and Pt (gray) of the area.

Figure S3a shows an STEM-HAADF (Scanning Transmission Electron Microscopy-High Angle Annular Dark Field) illustrative image of a region with brighter spots dispersed all over the CoAl₂O₄ that correspond to Pt and Ni, according to the EDX mapping of these elements in the region. The semiquantitative distribution of the metals along the CoAl₂O₄ support determined by EDX is 65% Pt and 35% Ni.



Figure S4.- Soot combustion with O_2 (in the absence of NO) without catalyst and over the Pt,Ni/CoAl₂O₄ and Ni/CoAl₂O₄ catalysts under tight and loose contact conditions. The temperature of maximum CO₂ production is indicated.

The catalytic performance of the samples in the absence of NO_x, only with O₂, is 78 shown in **Figure S4**. Apparently, the presence of the metal does not significantly 79 contribute to the direct oxidation mechanism, as the conversion without NOx is 80 81 similar to that obtained with the bare spinel [6], and only under tight contact, which maximizes the soot-catalyst interface, key for the active-oxygen mechanism of 82 soot combustion [7], slightly different from that of the uncatalysed reaction. On 83 the contrary, the presence of platinum and/or nickel in the spinel structure does 84 greatly increase the concentration of reactive NO₂ species during the reaction, 85 and thus the enhancement in the soot combustion capacity takes place via this 86 reaction route. 87

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- 89 Table S2: Quantification of the weight loss generated during the methodology
- 90 employed to recharge the reactor.

Sample	Initial weight (g)	Final weight (g)
CoAl ₂ O ₄	1.100	1.067
Pt,Ni/CoAl ₂ O ₄	1.100	1.074
Ni/CoAl₂O₄	1.100	1.073
Pt/α-Al ₂ O ₃	1.100	1.056

The methodology employed to recharge the reactor with soot in loose contact caused the loss of some mass of the reused SiC and catalyst mixture that must be attributed to a loss of catalyst, as SiC particles have a bigger particle and come off very easily. The weight loss was quantified, but the values obtained, included in the **Table S2**, may be slightly underestimated, as some quartz fibers may be present in the unloaded material.

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Figure S5.- Stability evaluation. a) Temperature needed for 50% soot combustion 101 under loose contact between catalyst and soot with Ni/CoAl₂O₄ and 102 Pt,Ni/CoAl₂O₄ catalysts, CoAl₂O₄ support, and Pt/Al₂O₃ reference. Solid: first use, 103 dashed: second use. b) Effect of the temperature on the BET specific surface 104 area of the prepared samples. Solid: BET measured before thermal treatment, 105 dashed: BET measured after thermal treatment of samples at 800°C. c-d) 106 Thermal analysis in air of the reduced catalysts (c) Ni/CoAl₂O₄ and (d) 107 108 Pt,Ni/CoAl₂O₄.

Figure S5a shows the T₅₀ values obtained in the first and second soot
combustion test for easier comparison, together with the BET specific surface
area values obtained as a function of the calcination temperature, Figure S5b,
and the TG-DTA results in oxidizing atmosphere, Figure S5c-d.

The reference Pt/Al₂O₃ catalyst essentially maintains its initial activity. The slight 113 114 increase of T₅₀ value in the second soot combustion test, of 24 °C, could be attributed to the methodology employed to reload the reactor and the subsequent 115 116 loss of some of the catalyst mass. Similarly, in consecutive runs with the Pt,Ni/CoAl₂O₄ catalyst, ΔT_{50} was 31 °C. However, the activity of the samples 117 without Pt markedly decreased in the second soot combustion test, with a shift in 118 T₅₀ of 84 °C for the CoAl₂O₄ sample (from 411 to 494 °C), and of 135 °C for the 119 Ni/CoAl₂O₄. 120

In order to simulate the effect of the reaction conditions on the textural properties, 121 122 the SBET of the samples was measured after calcination in air at different temperatures (Figure S5b). The specific surface area of CoAl₂O₄ is significantly 123 reduced at temperatures higher that 600 °C, which indicates that active sites are 124 125 lost; the same effect is expected during the first catalytic test. The loss of surface area can be attributed to the reconstruction of the activated CoAl₂O₄ structure 126 and the sintering of the crystallites. This would limit its ability to activate oxygen 127 and the contact with the soot after exposure at temperatures higher than 600 °C 128 129 compared with the fresh sample.



Figure S6.- Thermogravimetric behavior under air atmosphere of the fresh
samples: a) Pt/Al₂O₃, b) CoAl₂O₄, c) Pt,Ni/CoAl₂O₄, d) Ni/CoAl₂O₄, e)
Ni(5%)/CoAl₂O₄.

134 The thermal evolution of the Ni/CoAl₂O₄ and of Pt,Ni/CoAl₂O₄ catalysts in air up 135 to 1000 °C shown in **Figure S5c-d** (for other samples, see **Figure S6**) provides

further information about the effect of the reaction conditions on the samples. The 136 137 removal of absorbed water takes place from RT to near 200 °C. From this point, the differential thermal analysis shows an exothermic peak centered at 315 °C, 138 which might correspond to the combustion of organic compounds generated 139 during the milling procedure. The total weight loss of Ni/CoAl₂O₄ is 0.89 %, and 140 of Pt,Ni/CoAl₂O₄ is 0.69 %. However, the total weight loss of bare CoAl₂O₄ is 141 much higher (1.78 %, as observed in Figure S6). This effect is a direct 142 consequence of the weight gain due to the partial oxidation of Ni into NiO, related 143 to the tendency of the secondary metals during annealing to segregate to the 144 surface where oxygen is present [8], and suggests a possible cause of the 145 catalyst activity loss [9]. The same TG experiment was performed with a similar 146 147 Ni/CoAl₂O₄ sample containing 5-fold Ni loading to be able to quantify the extent 148 of the oxidation process (see **Figure S6**). In this sample, the weight gain between 200 and 950 °C, after water removal is 0.73 %. Even though a masking effect by 149 weight compensation in the first 200 °C cannot be ruled out, this value is much 150 151 lower than the weight corresponding to the complete oxidation of Ni into the partial oxidation product, NiO (1.4 %), or the total oxidation product, Ni₂O₃ (2.0 152 %). The supported Pt,Ni/CoAl₂O₄ catalyst has lower weight loss than the 153 monometallic Ni catalyst, and thus better thermal stability, despite the decrease 154 in the surface area. This suggests that the Pt nanoparticles can improve both the 155 156 activity and the stability of Ni-based catalyst.

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159 Figure S7.- O 1s XPS spectra of the catalysts samples.

The nature of the introduced crystalline disorder was studied in more detail by 160 XPS analyses of the surface. The XPS spectra of O 1s are exhibited in Figure 161 162 **S7**. The peaks at ca 531 and 532 eV were ascribed to CoAl₂O₄ lattice oxygen and chemisorbed oxygen species, respectively [10]. Compared to the CoAl₂O₄ 163 sample, the position of lattice oxygen in Ni/CoAl₂O₄ and Pt,Ni/ CoAl₂O₄ is shifted 164 165 to higher binding energy. This indicates that the introduction of metals reduced 166 the electronic density of lattice oxygen, possibly due to the formation of oxygen defects on CoAl₂O₄ [11]. 167

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