## **ELECTRONIC SUPPLEMENTARY INFORMATION**

## Structure-reactivity relationship in Co<sub>3</sub>O<sub>4</sub> promoted Au/CeO<sub>2</sub> catalysts for the CH<sub>3</sub>OH

## oxidation reaction revealed by in situ FTIR and operando EXAFS studies

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**Figure S1.** FTIR difference spectra collected upon CO inlet (15 mbar) at r.t. and subsequent pressure decreases down to  $1.0 \times 10^{-3}$  mbar on AuCe10Co before methanol oxidation reaction.



**Figure S2.** FTIR difference spectra collected on AuCe (section a) and AuCe10Co (section b) upon the adsorption of 5 mbar CH<sub>3</sub>OH at r.t. (blue lines) and at increasing temperature after the inlet of 5 mbar  $O_2$  on preadsorbed methanol: 50 °C (brown lines), 75 °C (violet lines), after 10 min (orange lines) and 20 min (red lines) at 100 °C.



**Figure S3.** FTIR difference spectra collected on AuCe in contact with 5 mbar methanol after 10 min at r.t. (blue line), at 50 °C (red line), at 75 °C (black line), at 100 °C (cyan line) and after 20 min at the same temperature (orange line).



**Figure S4.** FTIR difference spectra collected on AuCe10Co in contact with 5 mbar methanol after 10 min at r.t. (blue line), at 50 °C (violet line), at 75 °C (orange line) and at 100 °C (red line).



**Figure S5.** FTIR difference spectra collected on Ce10Co with the methanol/oxygen mixture after 10 min at r.t (black curve), at 50 °C (blue curve), at 75 °C (orange curve), and at 100 °C (red curve).



**Figure S6:**Immaginary part of  $k^3$ -weighted, phase uncorrected, FT of the Au L<sub>3</sub>-edge EXAFS spectra of the catalysts prepared on differently Co doped ceria substrate and submitted to thermal treatment in oxygen at 400°C. Same data reported in Figure 5a.