

## SUPPLEMENTARY DATA

# Bulk Co<sub>3</sub>O<sub>4</sub> for Methane Oxidation: Effect of the Synthesis Route on Physico-Chemical Properties and Catalytic Performance

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Table S1. Criteria for accurate analysis of intrinsic reaction rates of the foam catalysts (as estimated for the CC catalyst at 375 °C).

Figure S1. N<sub>2</sub> physisorption isotherms of the bulk Co<sub>3</sub>O<sub>4</sub> catalysts.

Figure S2. XRD patterns of the bulk Co<sub>3</sub>O<sub>4</sub> catalysts.

Figure S3. Raman spectra of the bulk Co<sub>3</sub>O<sub>4</sub> catalysts.

Figure S4. CH<sub>4</sub>-TPRe profiles of the bulk Co<sub>3</sub>O<sub>4</sub> catalysts.

Figure S5. Close-up view of the CH<sub>4</sub>-TPRe profiles in the 300-500 °C range of the CC catalyst before and after the stability test.

**Table S1:** Criteria for accurate analysis of intrinsic reaction rates of the foam catalysts (as estimated for the CC catalyst at 375 °C)

Criteria	Recommendation	At 375 °C	Least favourable conditions
Minimum bed length	Bodenstein parameter < $L_{\text{bed}}/d_{\text{particle}}$	4.5 < 79.5	55.6 < 79.5 <sup>b</sup>
Minimum reactor diameter	$d_{\text{tube}}/d_{\text{particle}} > 10$	31.2 <sup>a</sup>	31.2 <sup>a</sup>
Extraparticle mass transfer	Carberry number < 0.05/n	0.0042	0.046 <sup>b</sup>
Extraparticle heat transfer	$\gamma \beta_e C_a < 0.05$	0.0017	0.028 <sup>c</sup>
Intraparticle mass transport	Wheeler-Weisz modulus < 0.15	$4.3 \cdot 10^{-4}$	$8.0 \cdot 10^{-4d}$
Intraparticle heat transport	Mears parameter < 0.1	$2.0 \cdot 10^{-6}$	$4.2 \cdot 10^{-6d}$
Radial temperature gradient	Radial gradient < 0.05	0.004	0.0057 <sup>d</sup>
Intraparticle temperature gradient	Temperature gradient < 0.3	0.15	0.175 <sup>c</sup>
Bed dilution	Bed dilution parameter < 0.05	0.047	0.047

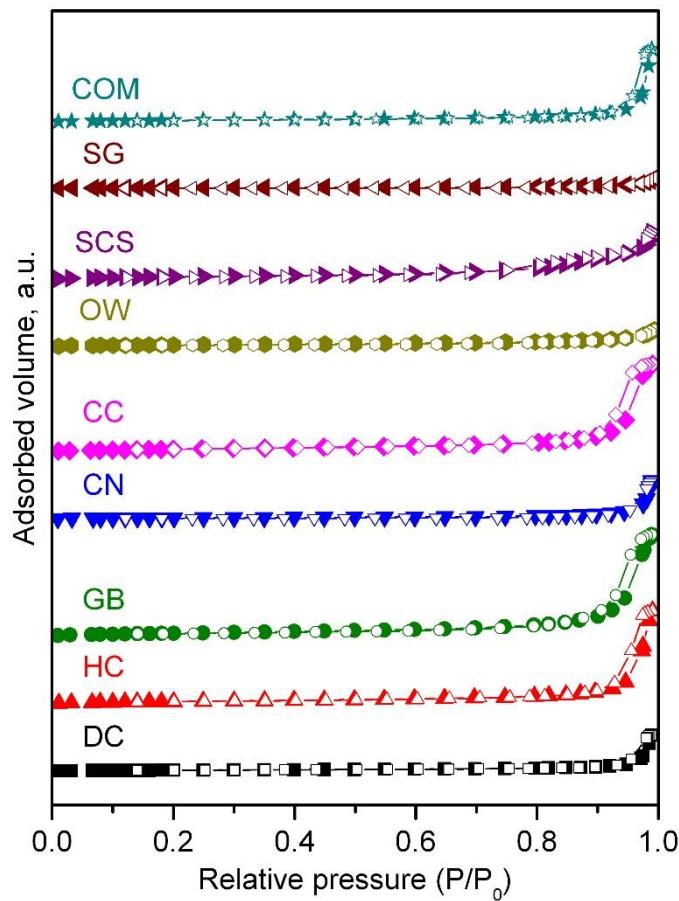
<sup>a</sup>The value of this ratio is 25.4 if the thermocouple is taken into consideration for calculation of reactor diameter.

<sup>b</sup>Determined at 500 °C.

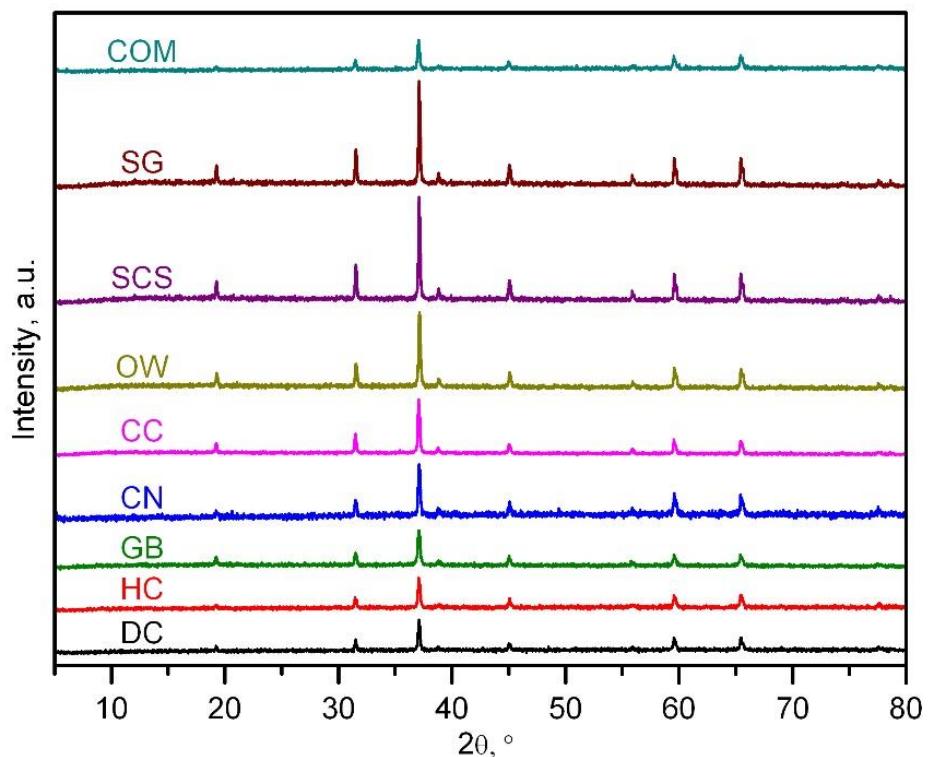
<sup>c</sup>Determined at 600 °C.

<sup>d</sup>Determined at 450 °C.

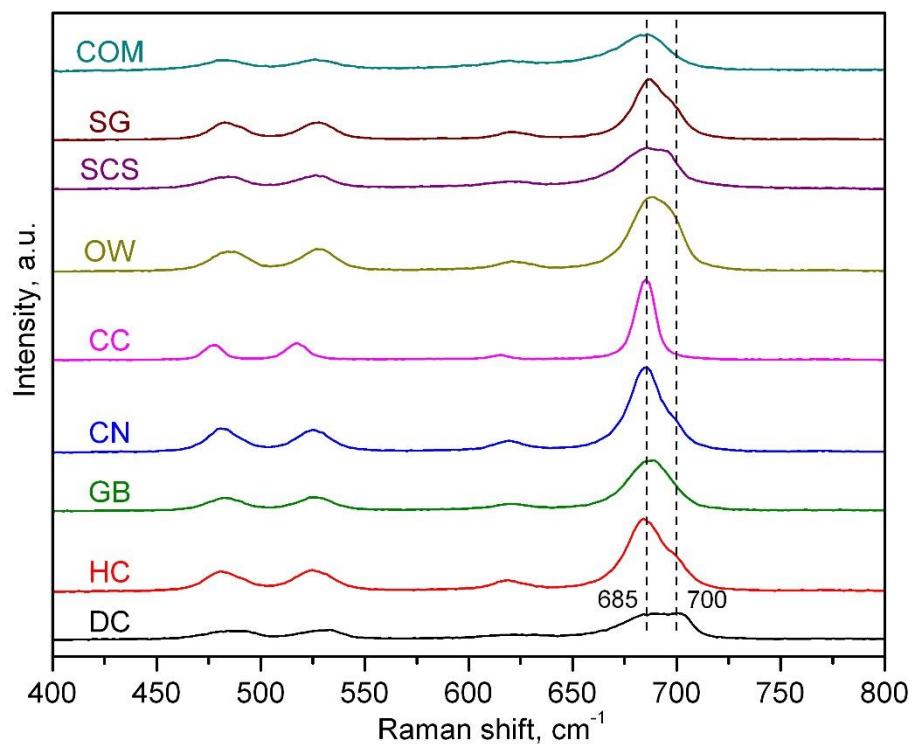
For the definition of each parameter the readers should refer to Eurokin - <http://eurokin.org/>; J. Perez-Ramirez, R.J. Berger, G. Mul, F. Kapteijn, J.A. Moulijn, *Catalysis Today* 60 (2000) 93–109 or A. Aranzabal, J.A. González-Marcos, J.L. Ayastuy, J.R. González-Velasco, *Chem. Eng. Sci.* 61 (2006) 3564–3576.



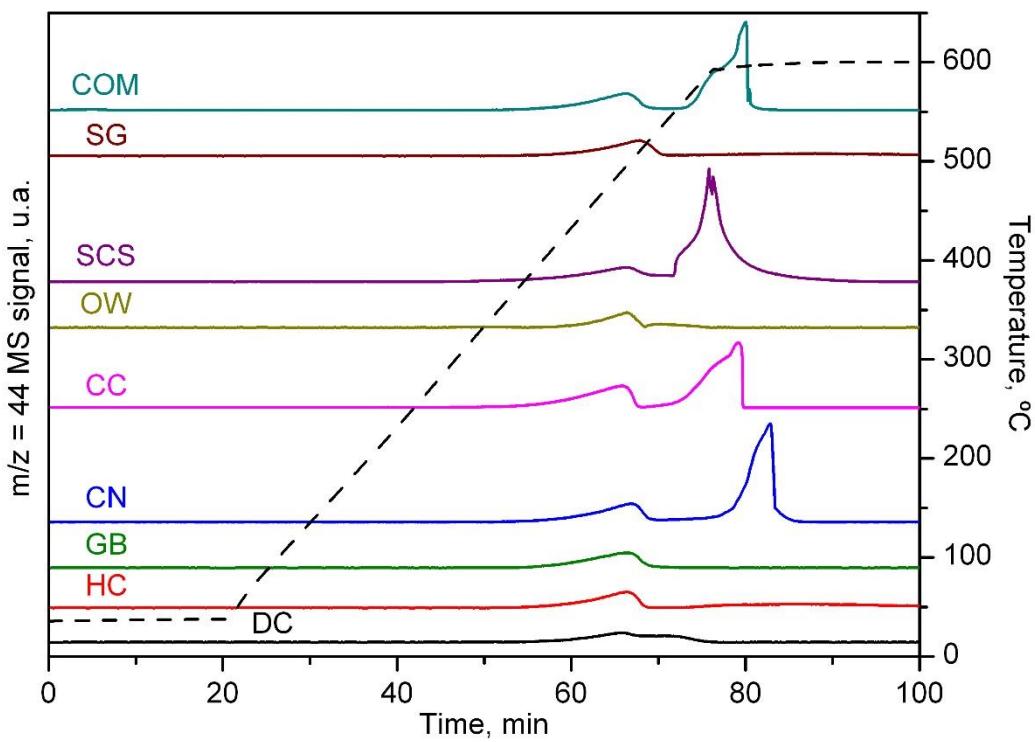
**Figure S1:**  $\text{N}_2$  physisorption isotherms of the bulk  $\text{Co}_3\text{O}_4$  catalysts.



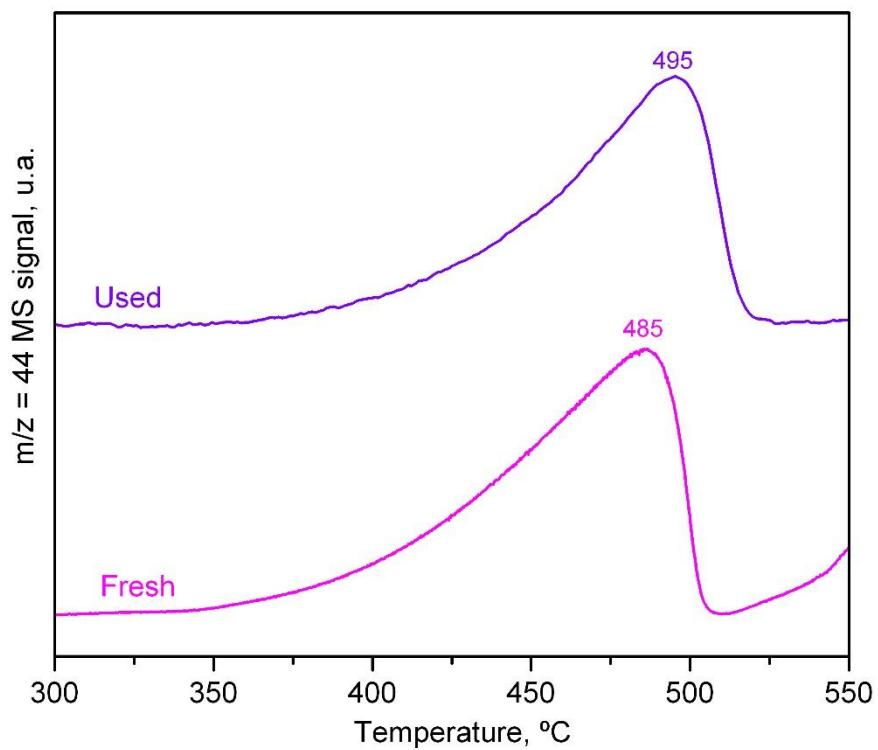
**Figure S2:**XRD patterns of the bulk  $\text{Co}_3\text{O}_4$  catalysts.



**Figure S3:** Raman spectra of the bulk  $\text{Co}_3\text{O}_4$  catalysts.



**Figure S4:** CH<sub>4</sub>-TPRe profiles of the bulk Co<sub>3</sub>O<sub>4</sub> catalysts.



**Figure S5:** Close-up view of the CH<sub>4</sub>-TPRe profiles in the 300-500 °C range of the CC catalyst before and after the stability test.