

Supporting information

CO₂ hydrogenation at atmospheric pressure and low temperature using plasma-enhanced catalysis over supported cobalt oxide catalysts

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Supporting information consists of 14 pages, 11 figures and 7 tables.

This document contains supplementary data on the characterization of the catalysts (XRD patterns, XPS data, temperature programmed reduction profiles, nitrogen adsorption-desorption isotherms, and HRTEM and STEM images). This document also includes the catalytic tests of plasma alone compared to MgO and Al₂O₃, and the stability test of 15% Co_xO_y/MgO catalyst. The energy efficiency values of all tested catalysts and the plasma electrical diagnostics results when packing the most relevant catalysts are also included.

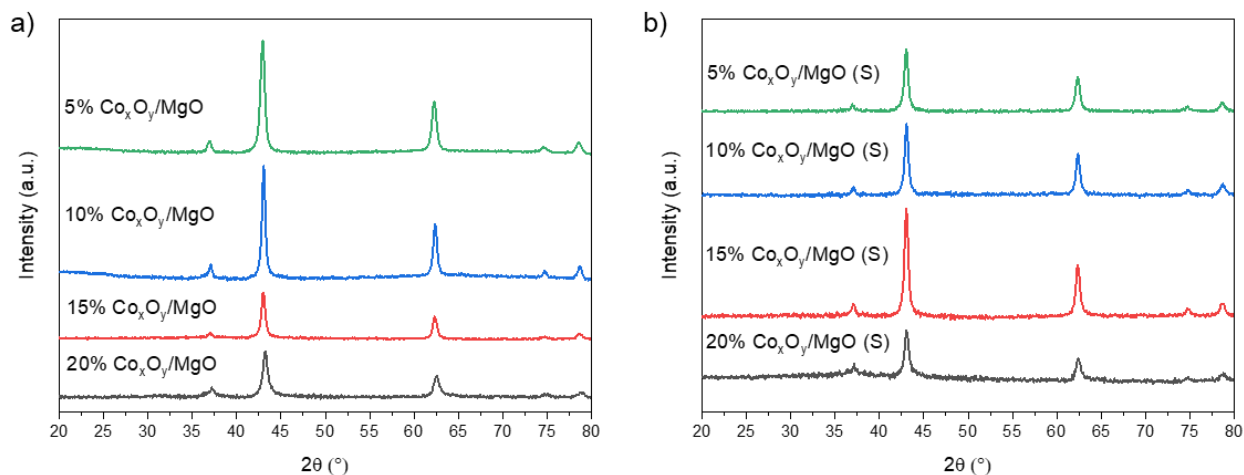


Figure S1. XRD patterns of (a) fresh and (b) spent Co_xO_y/MgO catalysts with different cobalt loadings. In all the cases, only the diffraction peaks corresponding to the MgO phase are visible, at $2\theta = 36.9^\circ, 42.9^\circ, 62.2^\circ, 74.6^\circ$ and 78.6° . The main diffraction peaks of Co₃O₄ and CoO species overlap with the pattern of MgO.

Table S1. Co₃O₄ and CoO relative atomic percentage of fresh and spent Co_xO_y/MgO catalysts, obtained from XPS analysis.

Catalyst	Co ₃ O ₄ relative atomic percentage (%)	CoO relative atomic percentage (%)
5% Co _x O _y /MgO	74.6	25.4
5% Co _x O _y /MgO (spent)	17.6	82.4
10% Co _x O _y /MgO	74.1	25.9
10% Co _x O _y /MgO (spent)	28.7	71.3
15% Co _x O _y /MgO	61.3	38.7
15% Co _x O _y /MgO (spent)	33.6	66.4
20% Co _x O _y /MgO	77.9	22.1
20% Co _x O _y /MgO (spent)	76.4	23.6

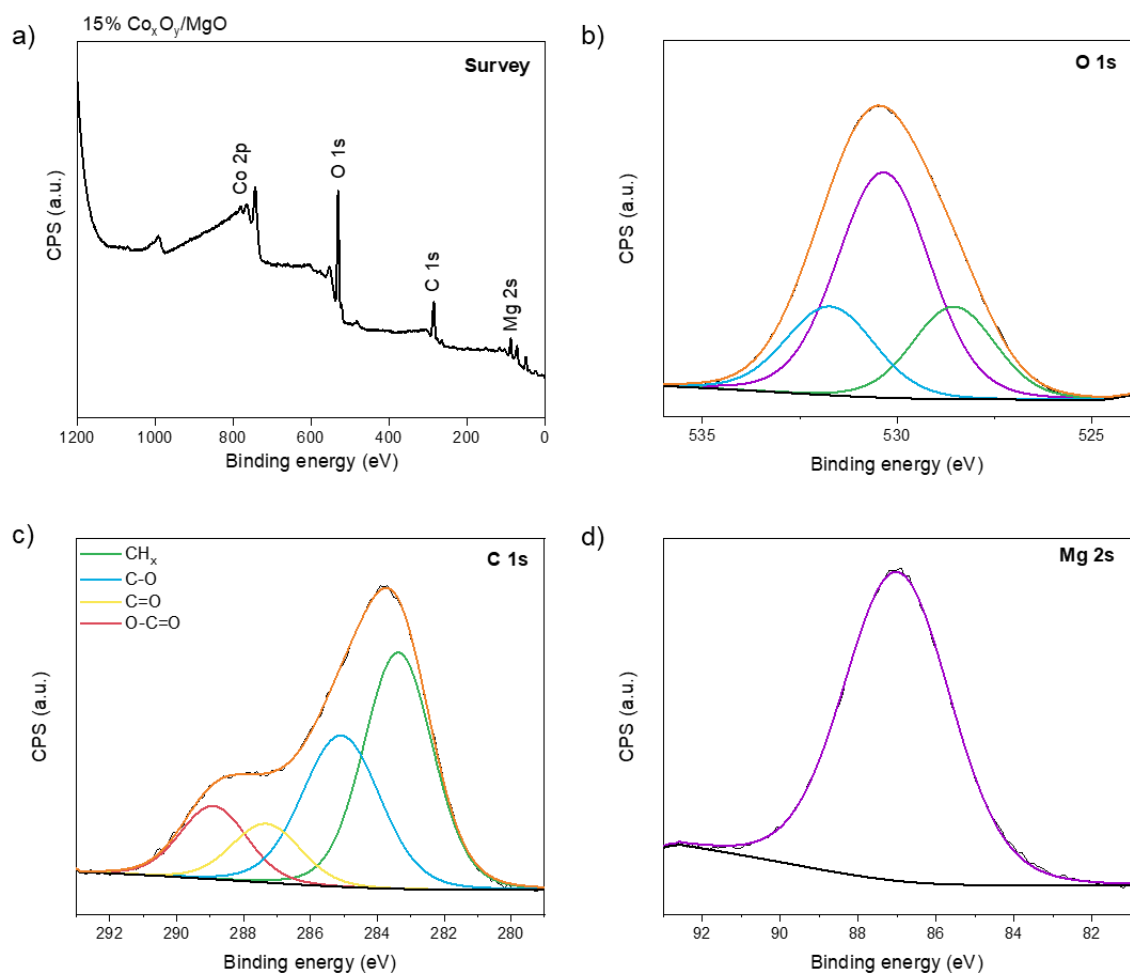


Figure S2. XPS spectra of fresh 15% $\text{Co}_x\text{O}_y/\text{MgO}$ catalyst. a) survey, b) O 1s, b) C 1s and d) Mg 2s.

Table S2. Binding energies and atomic fractions (in brackets) of 5% Co_xO_y/MgO catalyst (fresh and spent), from XPS analysis.

5% Co_xO_y/MgO fresh	5% Co_xO_y/MgO spent
Binding energy (eV)	Binding energy (eV)
O1s: 530.28 (54.69%) 528.58 (14.33%) 531.72 (30.98%)	O1s: 530.43 (38.64%) 528.78 (16.23%) 531.7 (45.13%)
C1s: 284.13 (57.98%) 289.12 (18.23%) 285.42 (14.12%) 287.26 (9.67%)	C1s: 283.77 (45.79%) 289.28 (11.98%) 285.37 (31.85%) 287.73 (10.38%)
Mg2s: 87.53 (100%)	Mg2s: 87.56 (100%)
Co2p: 780.5 (8.14%) 796.00 (4.00%) 780.07 (23.94%) 795.57 (11.77%) 784.90 (39.83%) 803.26 (12.32%)	Co2p: 780.5 (28.17%) 796.00 (13.85%) 780.35 (6.02%) 795.85 (2.96%) 785.63 (37.88%) 803.67 (11.11%)

Table S3. Binding energies and atomic fractions (in brackets) of 10% Co_xO_y/MgO catalyst (fresh and spent), from XPS analysis.

10% Co_xO_y/MgO fresh	10% Co_xO_y/MgO spent
Binding energy (eV)	Binding energy (eV)
O1s: 530.25 (47.51%) 528.59 (30.55%) 531.87 (21.93%)	O1s: 530.35 (65.21%) 528.52 (20.48%) 531.78 (14.3%)
C1s: 283.42 (38.95%) 288.04 (38.99%) 285.12 (14.88%) 288.04 (7.19%)	C1s: 283.16 (60.49%) 288.39 (13.54%) 284.64 (16.15%) 286.06 (9.82%)
Mg2s: 87.06 (100%)	Mg2s: 87.30 (100%)
Co2p: 780.16 (7.03%) 795.66 (3.46%) 779.56 (20.09%) 795.06 (9.88%) 783.73 (46.69%) 802.10 (12.86%)	Co2p: 780.61 (25.21%) 796.11 (12.40%) 779.58 (10.13%) 795.08 (4.98%) 785.55 (36.20%) 802.53 (11.08%)

Table S4. Binding energies and atomic fractions (in brackets) of 15% Co_xO_y/MgO catalyst (fresh and spent), from XPS analysis.

15% Co_xO_y/MgO fresh	15% Co_xO_y/MgO spent
Binding energy (eV)	Binding energy (eV)
O1s: 530.27 (74.11%) 528.34 (19.96%) 532.47 (5.93%)	O1s: 530.35 (57.38%) 528.55 (21.07%) 531.72 (21.55%)
C1s: 283.38 (44.08%) 288.9 (13.2%) 285.08 (31.82%) 287.32 (10.90%)	C1s: 283.38 (62.09%) 288.9 (17.25%) 285.08 (11.45%) 287.32 (9.21%)
Mg2s: 87.01 (100%)	Mg2s: 87.26 (100%)
Co2p: 780.04 (11.70%) 795.54 (5.75%) 779.51 (18.57%) 795.01 (9.13%) 783.87 (46.67%) 801.84 (8.18%)	Co2p: 780.05 (18.64%) 795.55 (9.15%) 779.52 (9.4%) 795.34 (4.62%) 784.29 (12.11%) 801.89 (46.11%)

Table S5. Binding energies and atomic fractions (in brackets) of 15% Co_xO_y/MgO catalyst (fresh and spent), from XPS analysis.

20% Co_xO_y/MgO fresh	20% Co_xO_y/MgO spent
Binding energy (eV)	Binding energy (eV)
O1s: 530.34 (70.32%) 528.32 (19.04%) 532.57 (10.64%)	O1s: 530.56 (66.54%) 528.51 (18.79%) 532.60 (14.67%)
C1s: 283.38 (37.34%) 288.92 (4.93%) 285.33 (47.13%) 287.27 (10.59%)	C1s: 283.59 (26.77%) 288.92 (7.43%) 285.2 (55.15%) 287.38 (10.65%)
Mg2s: 87.05 (100%)	Mg2s: 87.21 (100%)
Co2p: 780.00 (8.00%) 795.50 (3.93%) 779.02 (28.28%) 794.52 (13.9%) 784.94 (3.58%) 802.88 (12.3%)	Co2p: 780.40 (7.95%) 795.90 (3.91%) 779.68 (25.75%) 795.18 (12.66%) 784.69 (37.82%) 802.71 (11.92%)

Table S6. Atomic fractions of Co, Mg, O and C on the surface of the catalysts, and the intensity ratios between cobalt and support particles of fresh and spent $\text{Co}_x\text{O}_y/\text{MgO}$ catalysts, obtained from XPS analysis.

Catalyst	Atomic fraction (%) on the surface				$I_{\text{Co}}/I_{\text{Mg}}$
	Co	Mg	O	C	
5% $\text{Co}_x\text{O}_y/\text{MgO}$	0.16	34.05	37.87	27.92	0.005
5% $\text{Co}_x\text{O}_y/\text{MgO}$ (spent)	0.15	27.45	35.78	26.62	0.006
10% $\text{Co}_x\text{O}_y/\text{MgO}$	0.20	32.11	35.77	31.92	0.006
10% $\text{Co}_x\text{O}_y/\text{MgO}$ (spent)	0.19	28.13	27.99	43.59	0.007
15% $\text{Co}_x\text{O}_y/\text{MgO}$	0.24	29.55	36.39	33.82	0.008
15% $\text{Co}_x\text{O}_y/\text{MgO}$ (spent)	0.26	31.16	35.27	32.02	0.008
20% $\text{Co}_x\text{O}_y/\text{MgO}$	0.30	30.91	32.21	36.58	0.010
20% $\text{Co}_x\text{O}_y/\text{MgO}$ (spent)	0.31	31.41	32.05	36.22	0.010

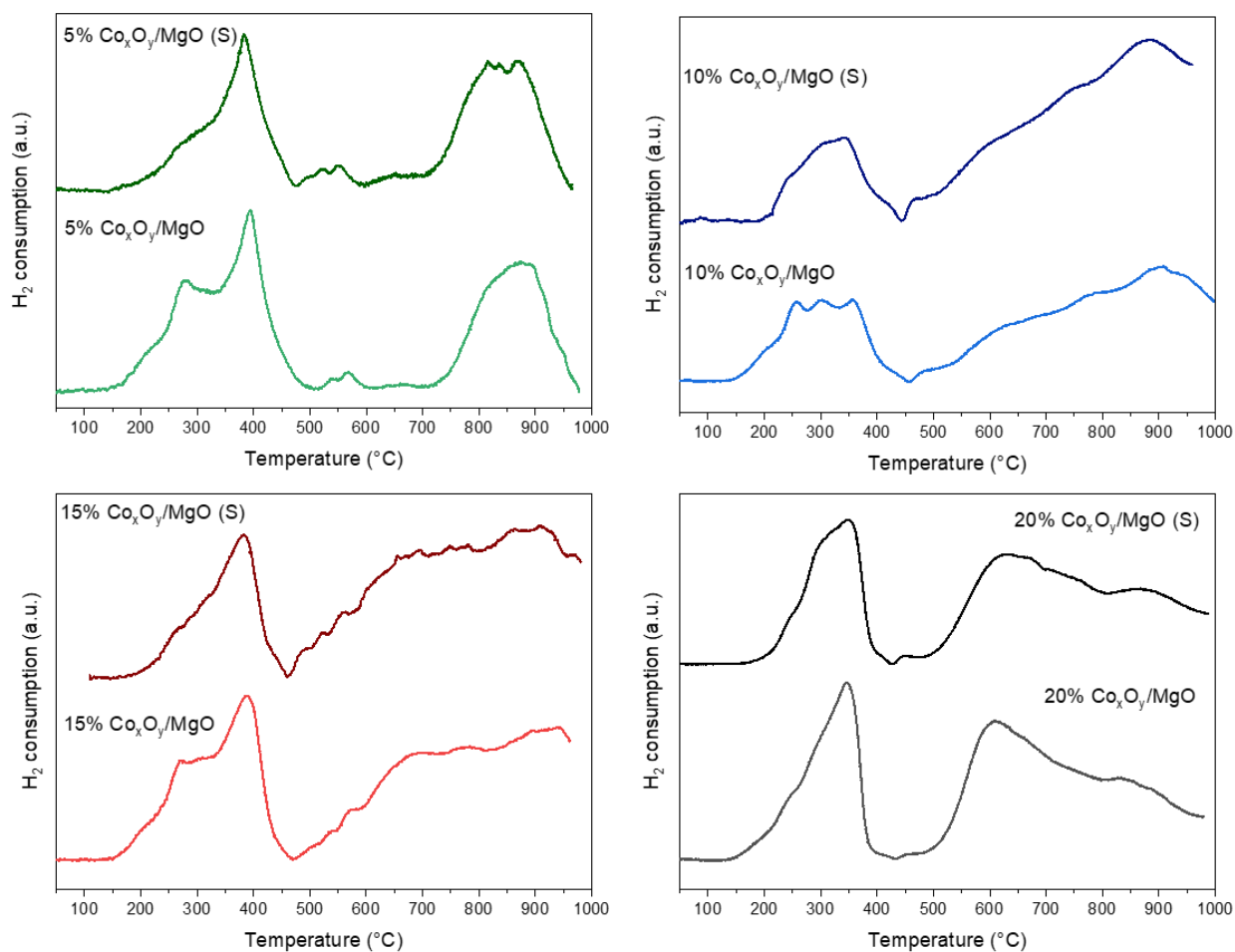


Figure S3. H₂-TPR profiles of the fresh Co_xO_y/MgO catalysts (bottom light colored lines) and the Co_xO_y/MgO catalysts after exposure to H₂/CO₂ DBD plasma for 1.5 h (spent (S), top dark colored lines).

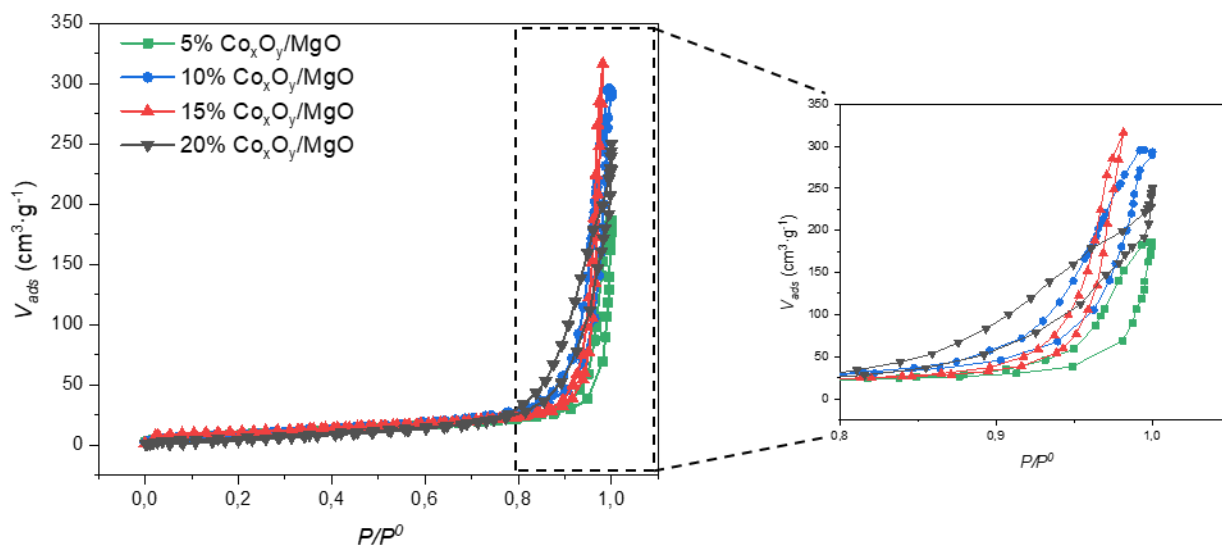


Figure S4. N_2 adsorption-desorption isotherms of the Co_xO_y/MgO catalysts with different cobalt loadings.

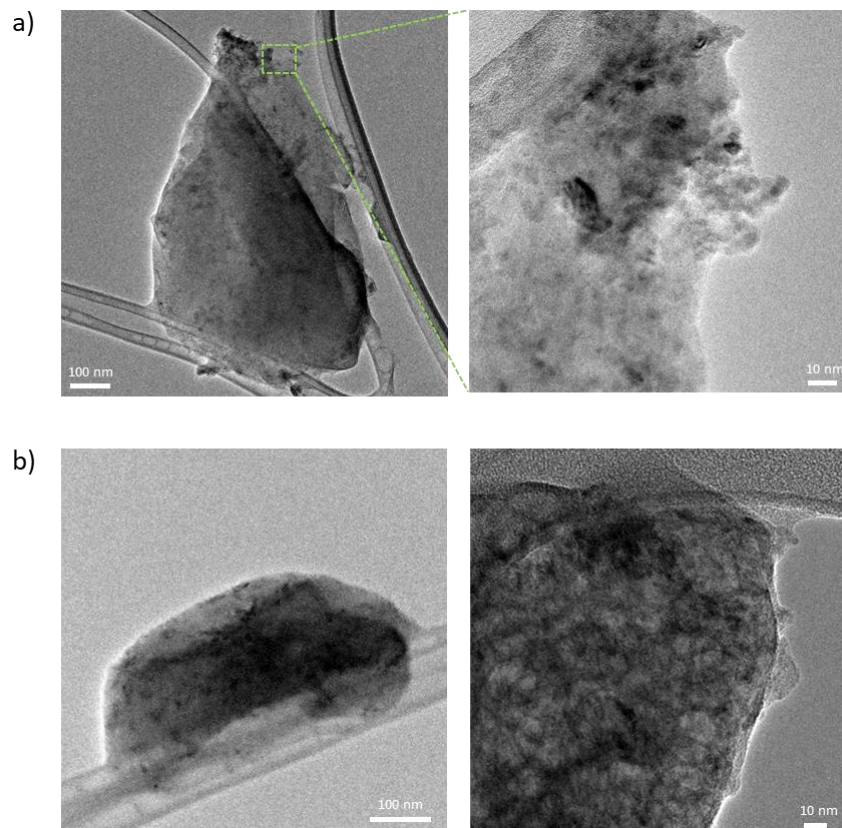


Figure S5. Representative HRTEM images of 20% Co_xO_y/MgO . a) fresh, b) after exposure to H_2/CO_2 DBD plasma for 1.5 h.

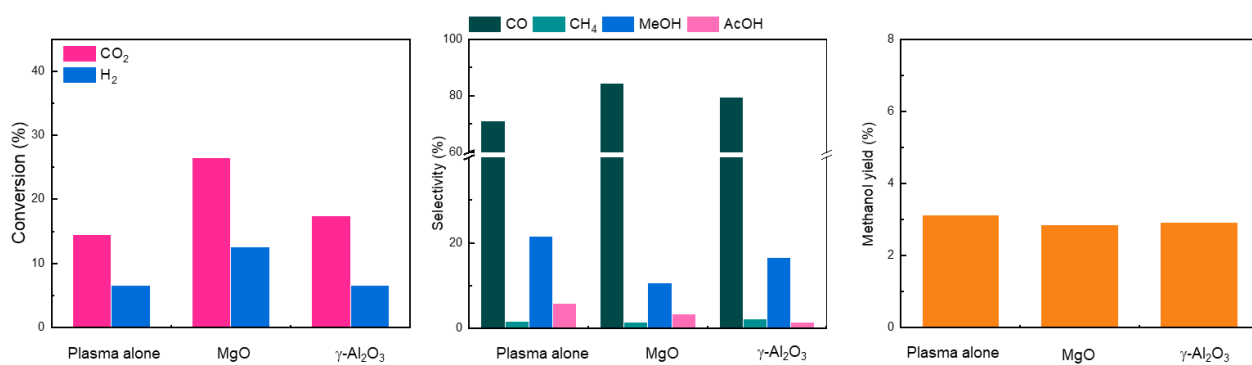


Figure S6. CO₂ and H₂ conversion, selectivity and MeOH yield plots of plasma alone, MgO and γ -Al₂O₃. Reaction conditions: 35 °C, atmospheric pressure, 500 mg catalyst, total flow 28 mL/min, H₂/CO₂ molar ratio 3:1, discharge power 10 W, reaction time 1.5 h.

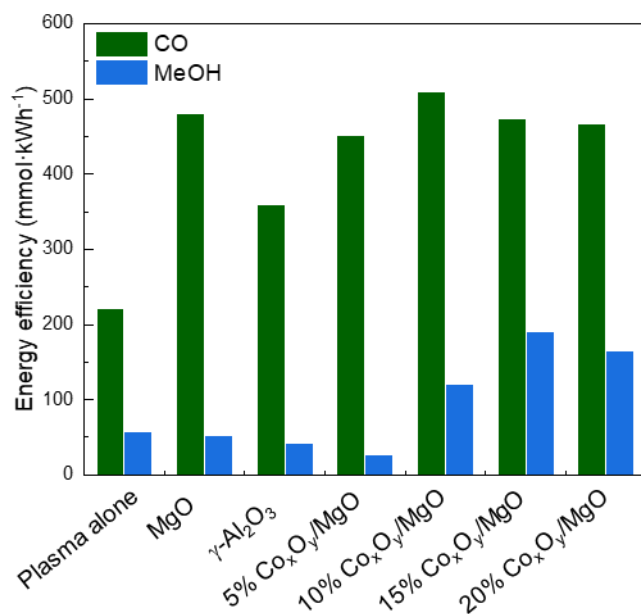


Figure S7. Energy efficiency of CO and methanol production of all tested catalysts.

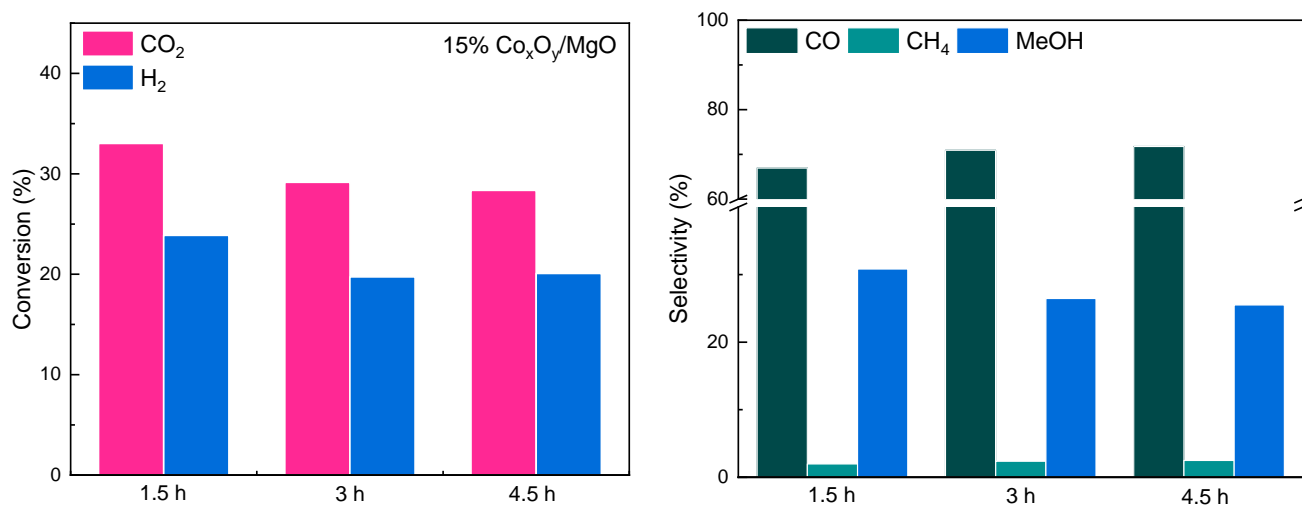


Figure S8. Stability test of 15% Co_xO_y/MgO. Reaction conditions: 35 °C, atmospheric pressure, 500 mg catalyst, total flow 28 mL/min, H₂/CO₂ molar ratio 3:1, discharge power 10 W. Data was taken after 1.5, 3 and 4.5 h of reaction.

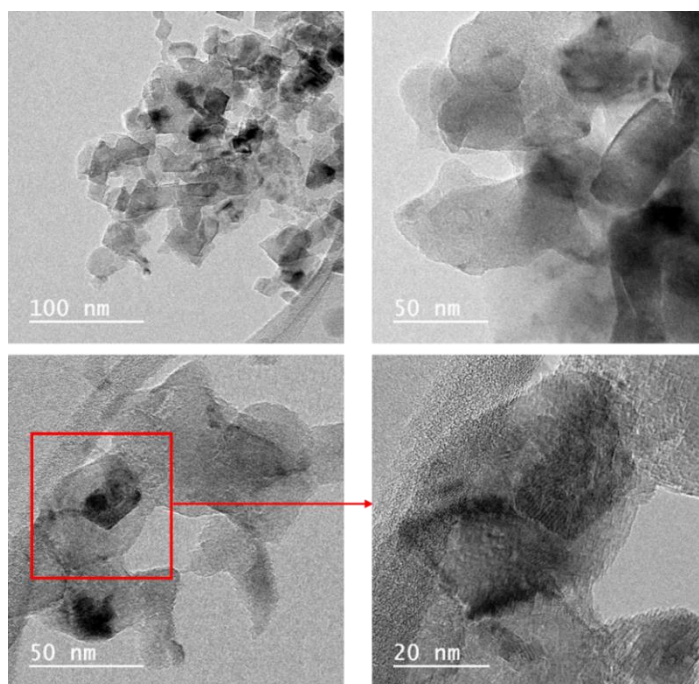


Figure S9. HRTEM images of 15% Co_xO_y/MgO spent catalyst (exposed to H₂/CO₂ DBD plasma for 1.5 h), with different magnifications.

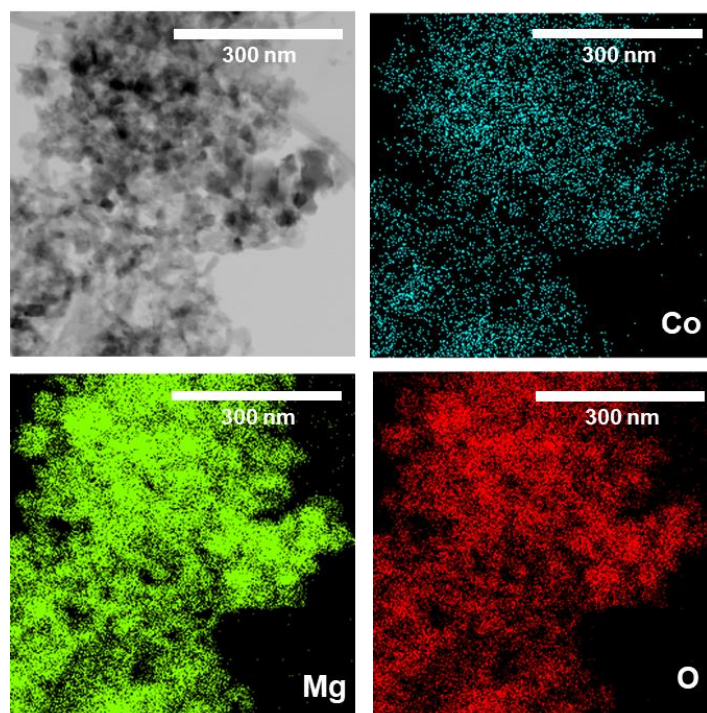


Figure S10. STEM-EDS analysis of 15% $\text{Co}_x\text{O}_y/\text{MgO}$ spent catalyst (exposed to H_2/CO_2 DBD plasma for 1.5 h).

Table S7. BET surface area, cumulative pore volume and average pore diameter (from BJH analysis) values of the spent $\text{Co}_x\text{O}_y/\text{MgO}$ catalysts, derived from nitrogen sorption isotherms.

Catalyst	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	Average pore diameter (nm)
5% $\text{Co}_x\text{O}_y/\text{MgO}$ (spent)	36	0.3	52
15% $\text{Co}_x\text{O}_y/\text{MgO}$ (spent)	41	0.9	80
20% $\text{Co}_x\text{O}_y/\text{MgO}$ (spent)	35	0.2	24

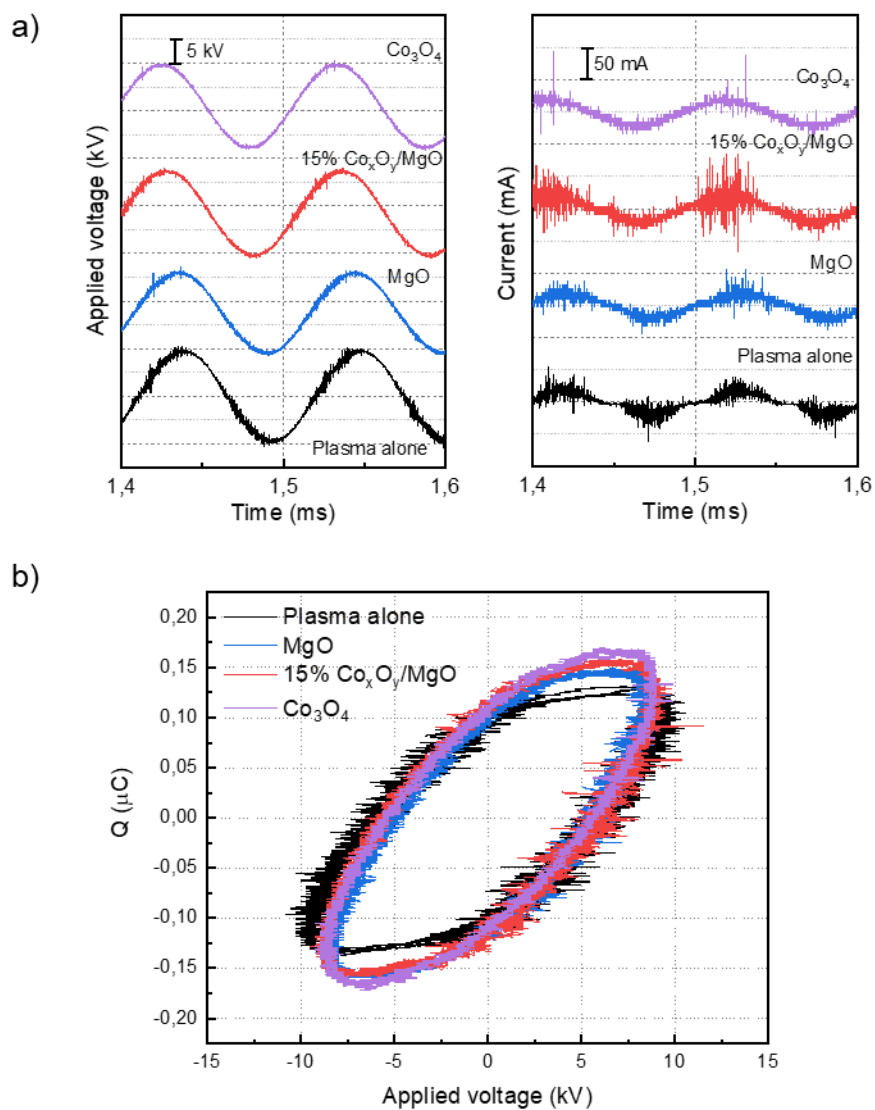


Figure S11. a) Applied voltage and current signals, and b) Q-V Lissajous plots of plasma alone, MgO, 15% $\text{Co}_x\text{O}_y/\text{MgO}$ and Co_3O_4 packing materials.