Supplementary Materials: Methanation of CO_2 over cobalt-lanthanide aerogels: effect of calcination temperature

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Table S1. Surface area of the aerogels as prepared and after calcination treatment.

Catalyst	Surface Area ($m^2 \cdot g^{-1}$)		
	Aerogels	Calcined	
		500 °C	900 °C
Co-La	145.5 ± 0.3	47.8 ± 1.3	5.2 ± 0.3
Co-Ce	160.1 ± 0.7	64.9 ± 1.3	6.8 ± 0.2
Co-Sm	120.1 ± 1.1	10.8 ± 0.6	3.9 ± 0.3
Co-Gd	130.8 ± 0.9	31.9 ± 1.1	5.4 ± 0.2
Co-Dy	104.2 ± 0.4	28.3 ± 0.4	4.8 ± 0.4
Co-Yb	133.4 ± 4.3	40.5 ± 1.7	9.8 ± 0.5

Table S2. EDS analysis of cobalt-lanthanide aerogels calcined at 500 °C.

Catalyst	EDS Values (wt.%) *				
	Co	Ln	O	Cl	Co/Ln Ratio**
Co_3O_4.3LaOCl	25.0 (21.8)	45.8 (51.3)	17.6 (13.8)	11.60 (13.1)	1.3
Co_3O_4.3CeO_2	26.2 (23.4)	59.8 (55.5)	14.0 (21.1)	-	1.0
Co_3O_4.3SmOCl	25.4 (20.9)	56.8 (53.3)	7.5 (13.2)	10.3 (12.6)	1.1
Co_3O_4.GdOCl	18.9 (20.4)	57.4 (54.3)	14.8 (13.0)	8.9 (12.3)	0.9
Co_3O_4.3DyOCl	24.9 (20.0)	67.9 (55.2)	1.9 (12.7)	5.3 (12.1)	1.0
Co_3O_4.3YbOCl	23.0 (19.3)	58.8 (56.8)	12.7 (12.3)	5.5 (11.6)	1.1

*Theoretical values. **Atomic ratio

Table S3. EDS analysis of cobalt-lanthanide aerogels calcined at 900 °C.

Catalyst	EDS Values (wt.%) *			
	Co	Ln	O	Co/Ln ratio**
$LaCoO_3$	29.0 (24.0)	59.6 (56.5)	11.4 (19.5)	1.1
Co_3O_4.3CeO_2	26.3 (23.4)	69.1 (55.5)	4.6 (21.1)	0.9
$SmCoO_3$	26.9 (22.9)	60.1 (58.4)	13.0 (18.7)	0.9
$GdCoO_3$	25.1 (22.3)	64.9 (59.5)	10.0 (18.2)	1.0
$DyCoO_3$	23.2 (21.9)	63.5 (60.3)	13.3 (17.8)	1.0
2Co_3O4.3Yb_2O_3	22.1 (21.3)	67.4 (62.4)	10.5 (16.3)	1.0

*Theoretical values. **Atomic ratio.

Table S4. Estimated cobalt particles size of cobalt-lanthanide aerogels calcined at 500 °C and 900 °C.

Catalyst	*Co_3O_4 Particle Size*		*Co Particle Size* #	
	Calcined 500 °C	Calcined 900 °C	Calcined 500 °C	Calcined 900 °C
Co_3O_4	21.1 ± 0.1	-	- (-)	25.6 ± 0.7 (23.4 ± 0.5)
Co-La	13.4 ± 0.4	44.5 ± 0.8	12.5 ± 0.3 (16.0 ± 0.7)	- (-)

Co-Ce	23.0 ± 0.4	37.0 ± 0.2	- (-)	- (32.5±0.8)
Co-Sm	15.2 ± 0.3	32.7 ± 1.0 *	- (-)	- (-)
Co-Gd	15.2 ± 0.3	46.5 ± 1.1 *	- (-)	- (-)
Co-Dy	17.2 ± 0.2	53.1 ± 0.8 *	- (-)	- (-)
Co-Yb	17.1 ± 0.3	47.8 ± 1.0	- (-)	38.6 ± 0.8 (31.3 ± 0.7)

*these compounds are in perovskite phase ($LnCoO_3$). #between parenthesis the values obtained after reaction with pre-reduction treatment.

Table S5. H_2-TPR consumption of hydrogen obtained and expected for the aerogels calcined at 500 °C.

Catalyst	Uptake H_2 (*μmoles*)	Theoretical Moles (*μmoles*)	Exp./Theor. Ratio	Tm (° C)
Co_3O_4	79.5	84.7	0.94	334.7
Co_3O_4.3LaOCl	151.2	176.0	0.87	449.1
Co_3O_4.3CeO_2	115.0	183.1	0.62	395.7
Co_3O_4.3SmOCl	159.5	183.7	0.87	567.3
Co_3O_4.3GdOCl	143.7	151.1	0.95	549.5
Co_3O_4.3DyOCl	77.7	90.2	0.86	560.4
Co_3O_4.3YbOCl	174.4	212.2	0.82	487.6

Table S6. H_2-TPR consumption of hydrogen obtained and expected for the aerogels calcined at 900 °C.

Catalyst	Uptake H_2 (*μmoles*)	Theoretical Moles (*μmoles*)	Exp./Theor. Ratio	Tm (°C)
Co_3O_4	17.6	18.3	0.96	378.0
$LaCoO_3$	100.2	112.3	0.89	613.8
Co_3O_4.3CeO_2	110.2	119.7	0.92	379.5
$SmCoO_3$	116.1	118.3	0.98	550.1
$GdCoO_3$	84.7	89.8	0.96	519.2
$DyCoO_3$	109.1	112.5	0.99	540.5
2Co_3O_4.3Yb_2O_3	87.1	88.9	0.98	386.9

Table S7. Dehydrogenation / dehydration of 2-propanol over cobalt-lanthanide aerogels calcined at 500 °C, at 250 °C under oxidative atmosphere (between parentheses under inert atmosphere).

Catalyst	Conversion (%)	Selectivity (%)		νA/νP
		Acetone (A)	Propene (P)	
Co_3O_4	70.4 (11.1)	99.4 (99.5)	0.2 (0.7)	457.9 (135.1)
Co_3O_4.3LaOCl	58.8 (2.1)	99.5 (95.7)	0.2 (4.3)	412.3 (22.3)
Co_3O_4.3CeO_2	23.9 (3.4)	98.6 (95.8)	0.4 (3.0)	281.4 (31.7)
Co_3O_4.3SmOCl	24.9 (1.3)	98.4 (87.7)	0.8 (12.3)	121.9 (7.1)
Co_3O_4.3GdOCl	25.0 (0.4)	99.4 (67.4)	0.6 (32.6)	167.2 (2.1)
Co_3O_4.3DyOCl	0.2 (0.2)	85.5 (83.5)	14.5 (16.5)	8.1 (5.4)
Co_3O_4.3YbOCl	5.0 (1.6)	94.3 (94.2)	2.0 (5.8)	47.7 (16.4)

Table S8. Dehydrogenation / dehydration of 2-propanol over cobalt-lanthanide aerogels calcined at 900 °C, at 250 °C under oxidative atmosphere (between parentheses under inert atmosphere).

Catalyst	Conversion (%)	Selectivity (%)		νA/νP
		Acetone (A)	Propene (P)	
Co_3O_4	18.5 (2.8)	98.9 (89.4)	0.7 (3.4)	144.7 (26.0)
$LaCoO_3$	12.2 (0.5)	98.4 (87.5)	1.0 (12.5)	108.8 (7.0)
$Co_3O_4.3CeO_2$	21.6 (4.0)	99.3 (98.2)	0.5 (1.8)	213.9 (53.2)
$SmCoO_3$	6.4 (0.8)	96.7 (93.5)	1.6 (6.5)	60.8 (14.5)
$GdCoO_3$	10.4 (0.8)	97.5 (91.0)	0.8 (9.0)	123.0 (10.1)
$DyCoO_3$	2.5 (0.3)	94.4 (55.4)	2.5 (44.6)	37.3 (1.2)
$2Co_3O_4.3Yb_2O_3$	2.1 (0.2)	95.6 (76.6)	4.4 (23.4)	21.8 (3.3)

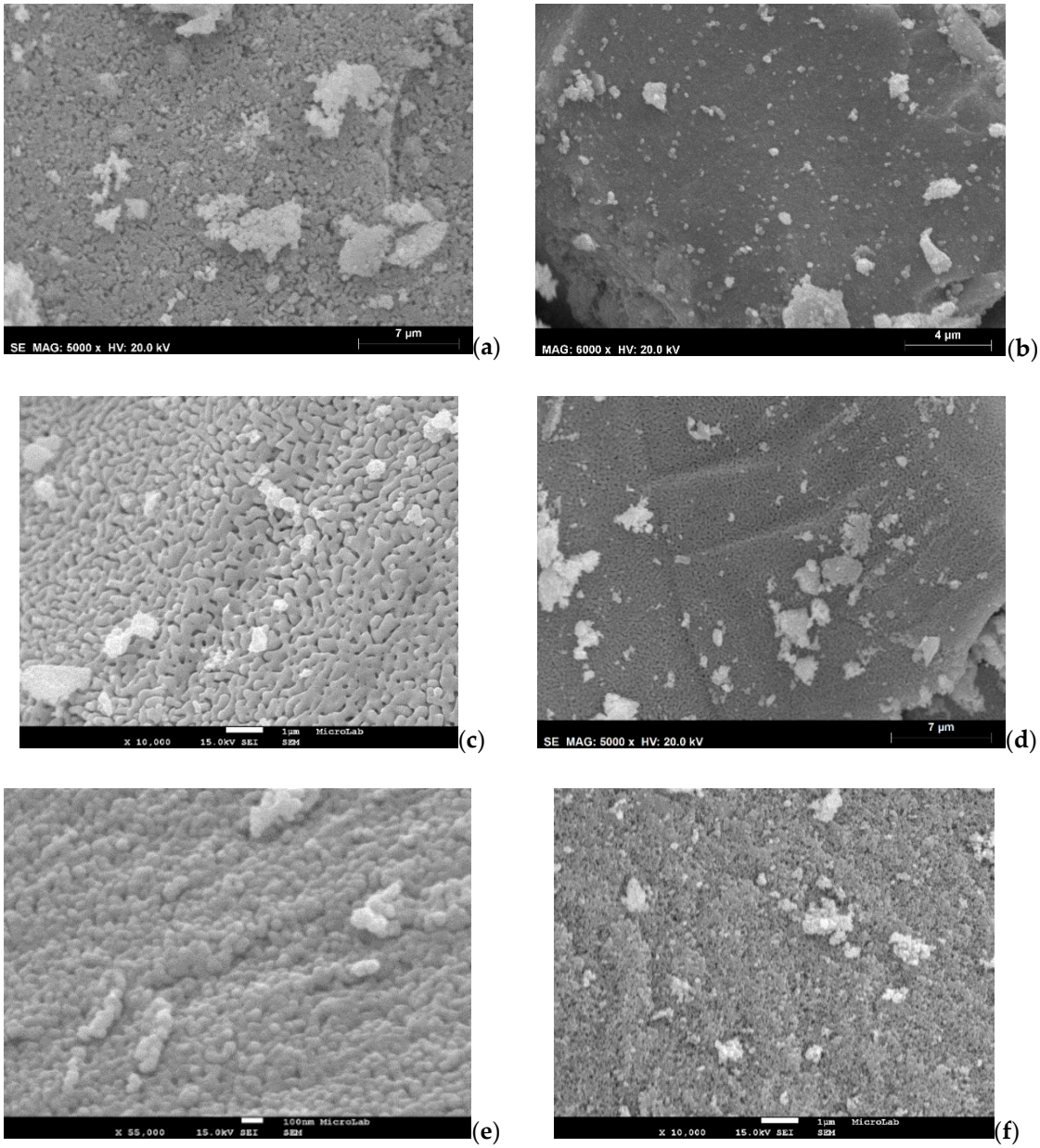

Figure S2. SEM images of the aerogels calcined at 900 °C: Co-La (**a**), Co-Ce (**b**), Co-Sm (**c**); Co-Gd (**d**), Co-Dy (**e**) and Co-Yb (**f**).

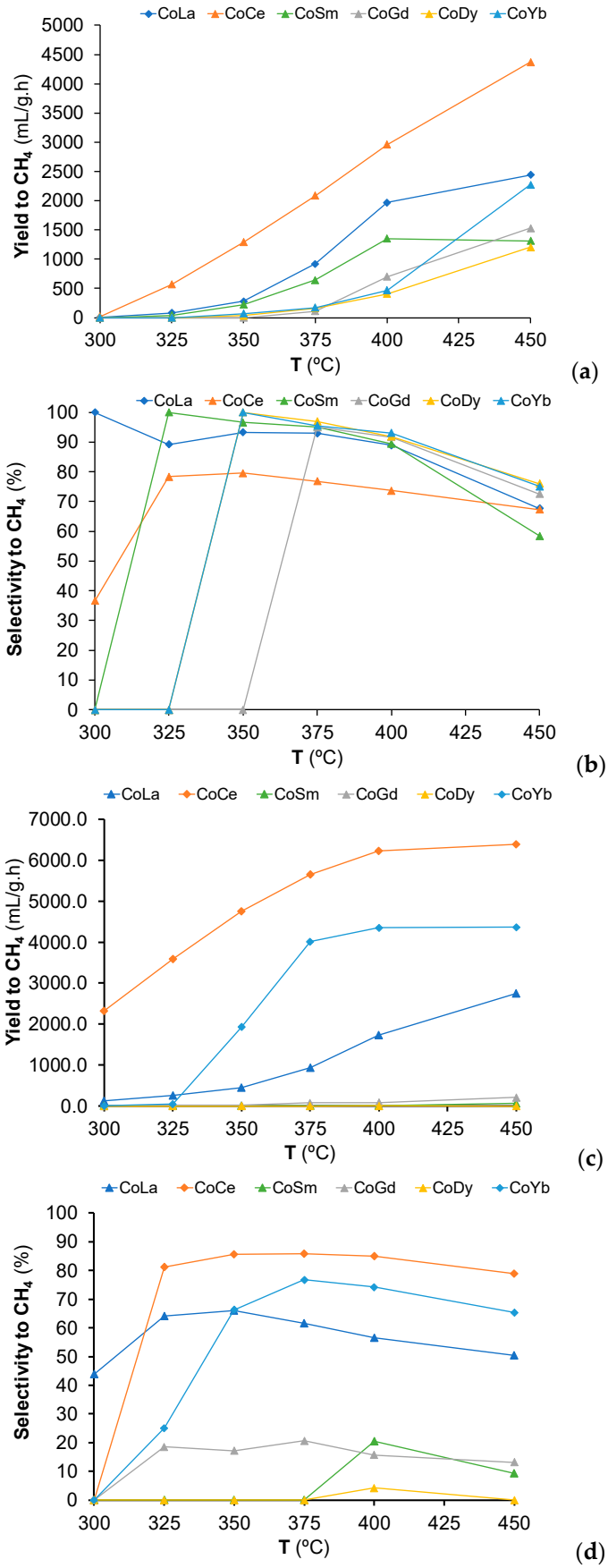

Figure S3. Temperature effect on yield and selectivity to methane of the cobalt-lanthanide aerogels calcined at 500 °C (**a**, **b**) and at 900 °C (**c**, **d**).

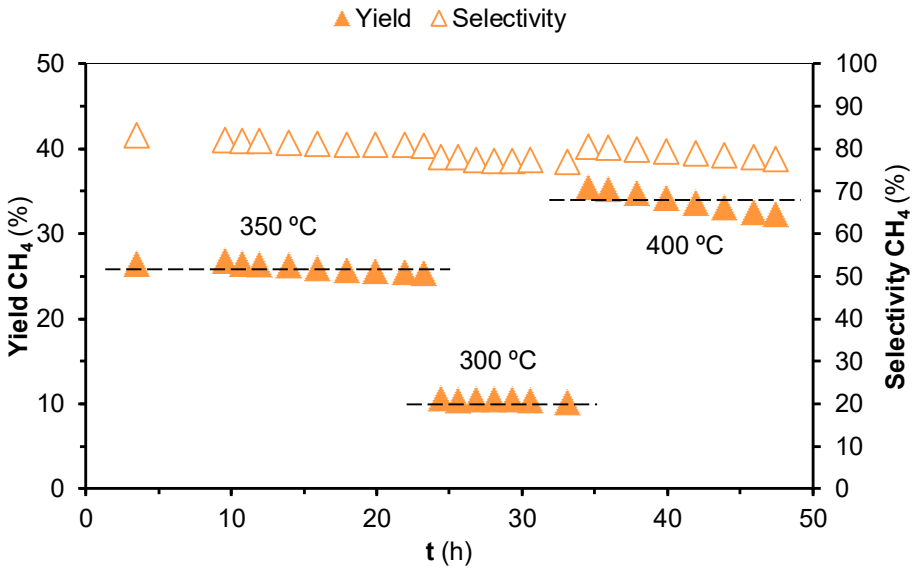

Figure S4. Stability of the bimetallic Co-Ce aerogel calcined at 900 °C, without pre-reduction, at different temperatures (H_2/CO_2=4, GHSV=15000 mL CO_2 / g_{cat}.h).