

Supporting Information

The role of Co-Ga₂O₃ interfaces in methane dry reforming

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Section A DRM profile of $\text{Co}_3\text{O}_4/\beta\text{-Ga}_2\text{O}_3$ without hydrogen pre-treatment

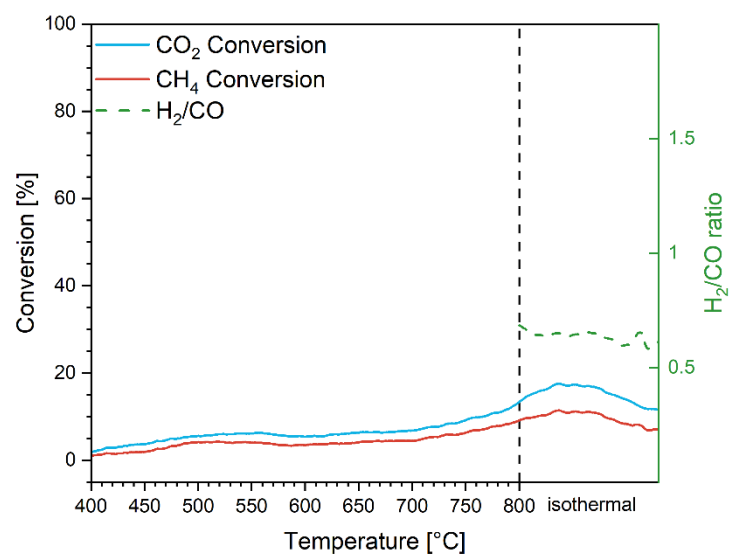


Figure S1: DRM profile of $\text{Co}_3\text{O}_4/\beta\text{-Ga}_2\text{O}_3$ without hydrogen pre-treatment. Experimental conditions as in Figure 1.

Section B Rietveld data of the ex situ collected PXRD patterns

Table S1: Rietveld data of the ex situ collected PXRD patterns

System	Phase	Weight Fraction [wt.-%]
as calcined	Co_3O_4	14.6
	Ga_2O_3	85.4
after DRM	CoGa_2O_4	42.4
	Ga_2O_3	57.6
after H_2	CoGa	23.2
	Ga_2O_3	76.8
after H_2 +DRM	$\alpha\text{-Co}$	5.4
	$\varepsilon\text{-Co}$	<0.2 below limit of quantification
	Ga_2O_3	94.5

Section C Reference catalytic measurements of blank reactor, SiO_2 , $\beta\text{-Ga}_2\text{O}_3$, Co_3O_4 , and CoGa_2O_4

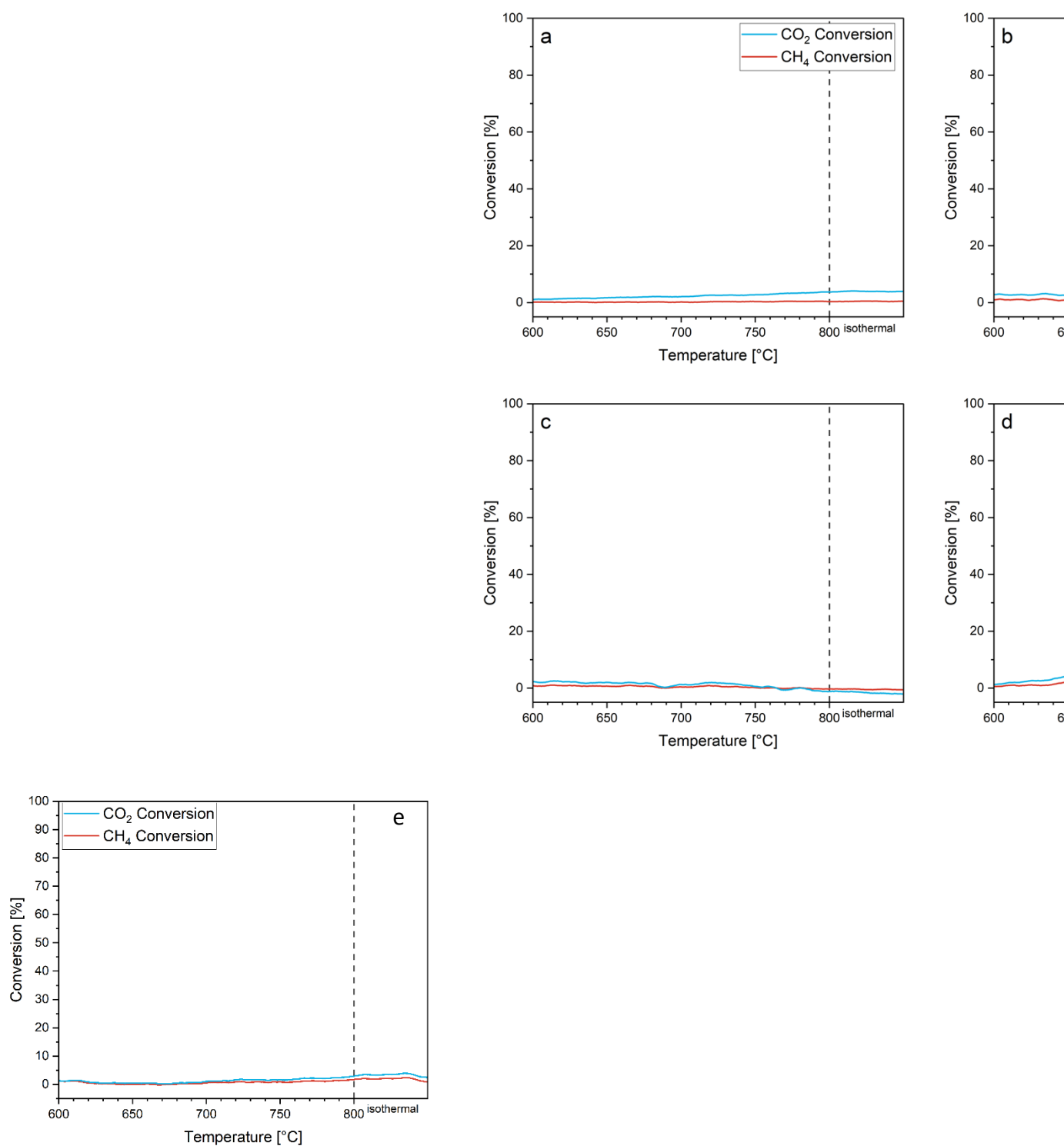


Figure S2: DRM profiles of $\beta\text{-Ga}_2\text{O}_3$ (Panel a), SiO_2 (Panel b), blank reactor (Panel c), Co_3O_4 (Panel d) and CoGa_2O_4

Section D Details of the Co/SiO₂ catalyst

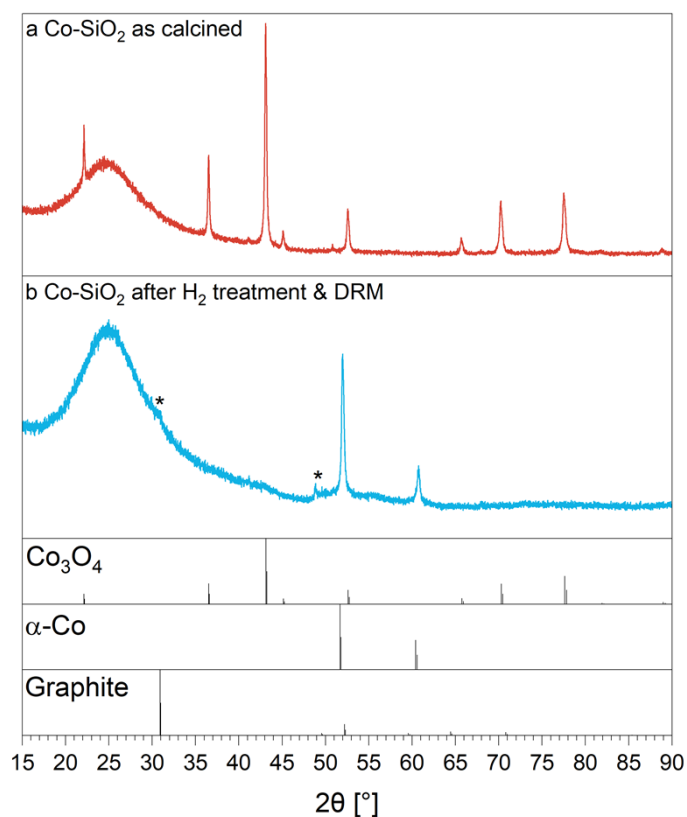


Figure S3: XRD patterns of Co₃O₄/SiO₂ in Panel **a**: as-calcined state, Panel **b**: after DRM operation at 800 °C with prior hydrogen reduction at 450 °C. The asteriks marks the respective reflections of graphite. Structure ICSD-Numbers & references: graphite 76767 [1], Co₃O₄ 36256 [62], α-Co 136039 [70].

[1] P. Trucano, R. Chen, Structure of graphite by neutron diffraction, *Nature* 1975, **258**, 136-137

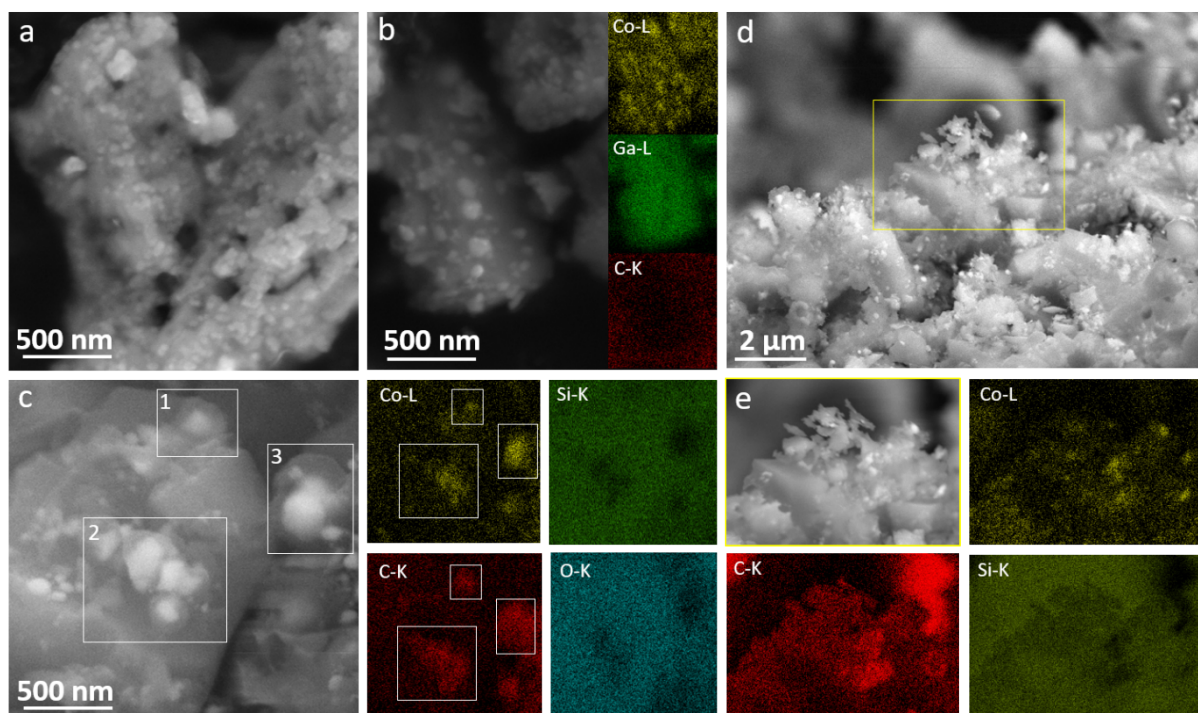


Figure S4: SEM analysis of $\text{Co}_3\text{O}_4/\beta\text{-Ga}_2\text{O}_3$ and the $\text{Co}_3\text{O}_4/\text{SiO}_2$ reference powder catalyst in the as-calcined state and after a hydrogen pre-reduction (1 bar flowing H_2 , 550 °C, 1 h for $\text{Co}_3\text{O}_4/\beta\text{-Ga}_2\text{O}_3$; 1 bar flowing H_2 , 450 °C, 10 min for $\text{Co}_3\text{O}_4/\text{SiO}_2$) – DRM cycle (conditions as in Figure 1). Panel **a**: $\text{Co}_3\text{O}_4/\beta\text{-Ga}_2\text{O}_3$ as-calcined. Panel **b**: $\text{Co}_3\text{O}_4/\beta\text{-Ga}_2\text{O}_3$ after reduction at 550 °C/ DRM operation. Panel **c**: $\text{Co}_3\text{O}_4/\text{SiO}_2$ after reduction at 450 °C/ DRM operation. Panel **d** and **e**: Detail of the catalyst shown in Panel **c**. Panels **b**, **c** and **e** exhibit EDX maps of the Co-L, Ga-L, Si-K, C-K and O-K edges. The insets in Panel **c** (marked 1,2 and 3) are added as a guide to the eye to pinpoint the exact same locations in the EDX maps. Panel **e** is a magnification of the yellow rectangle shown in Panel **d**.

Section E: XRD pattern of the as-synthesized untreated CoGa intermetallic compound

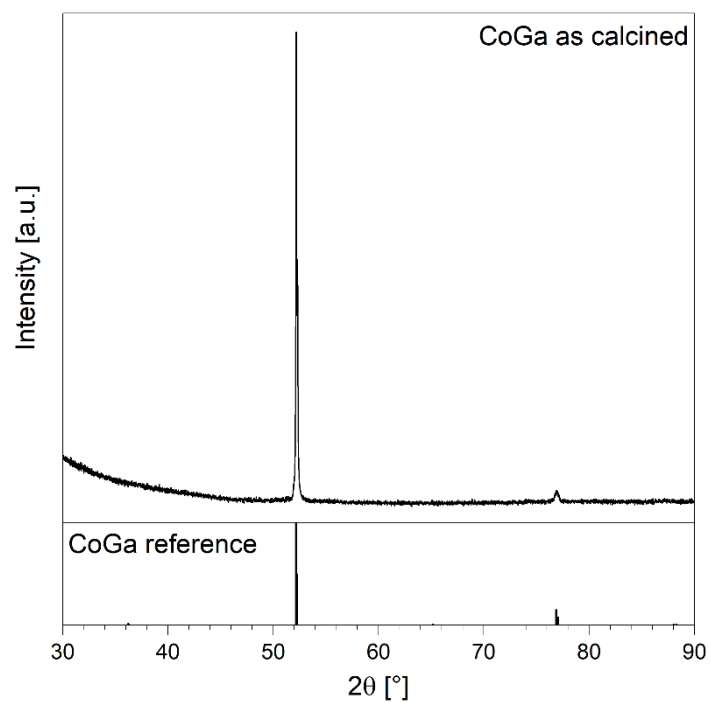


Figure S5: XRD pattern of the as-synthesized untreated CoGa intermetallic compound.

Structure ICSD-Number & reference: CoGa 657494 [67].

Section F Isothermal mass spectra during reduction and DRM conditions at 800 °C

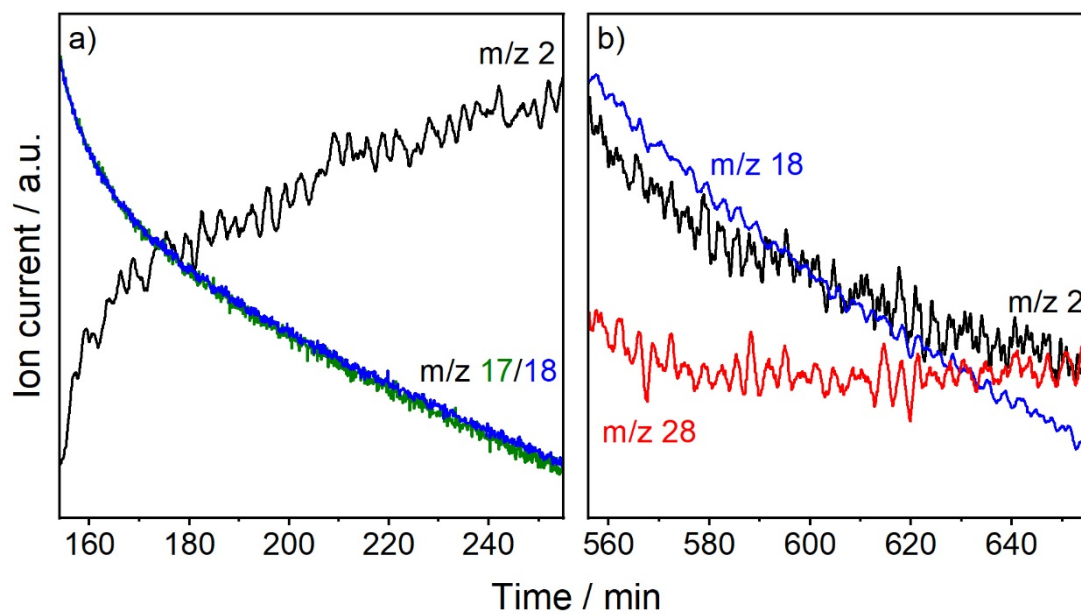


Figure S6: Isothermal mass spectra during (a) reduction and (b) DRM conditions, both at 800°C.

Section G XRD Characterization after re-cooling

The XRD patterns during cooling down after reduction and DRM can be observed on Figure S7 and S8, respectively. From both figures no new structural change can be observed, besides what was pointed out previously. In both figures, the reflections underwent to thermal shrinking during the cooling down part.

Regarding Figure S7, the reflection of CoGa starting at 51.6° 2θ should increase to very high intensities (as can be observed in Figure 3b). However, it can be observed a ‘dark zone’ in the regions above 51.8° which it is attributed to the misalignment of the height of the sample and the detector due to thermal expansion during reduction. This effect ‘hides’ the reflection corresponding to CoGa and the intensity increase related to it, which is observed in Figure 3b by comparing both plots at 800 and 50° C. This effect can also be observed in Figure 3a (first part of the reduction), but is not observable during the DRM step (Figure 4a and Figure S8) since a second sample alignment was done to correct these misalignment effects just before the DRM step (at 50° C).

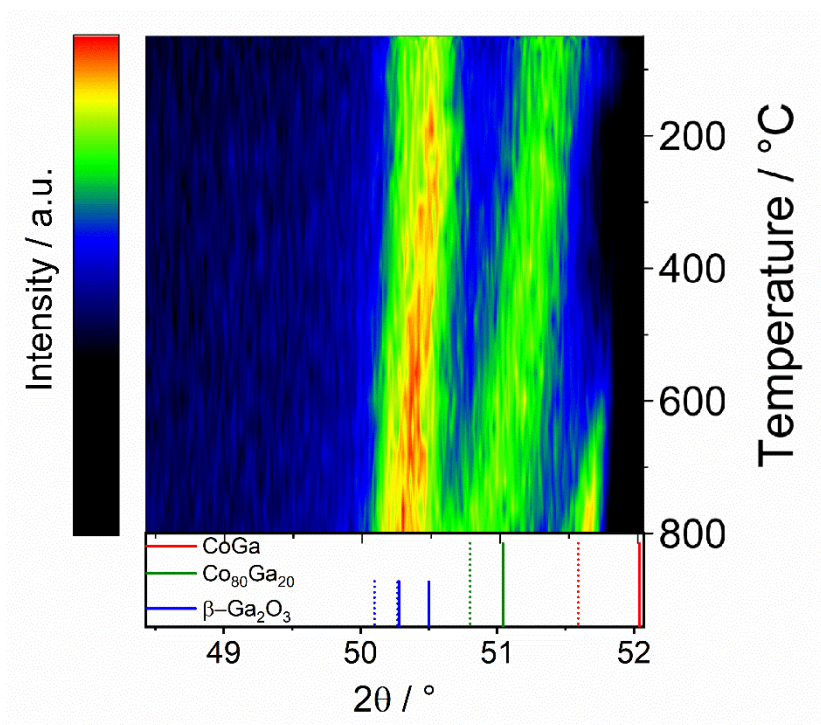


Figure S7: In situ XRD patterns collected on $\text{Co}_3\text{O}_4/\beta\text{-Ga}_2\text{O}_3$ during reduction in hydrogen while cooling down from 800 to 50 °C. The dotted lines in the inset are the calculated XRD patterns of the modified lattice parameters due to thermal expansion. [References from the XRD patterns are the same as the main publication].

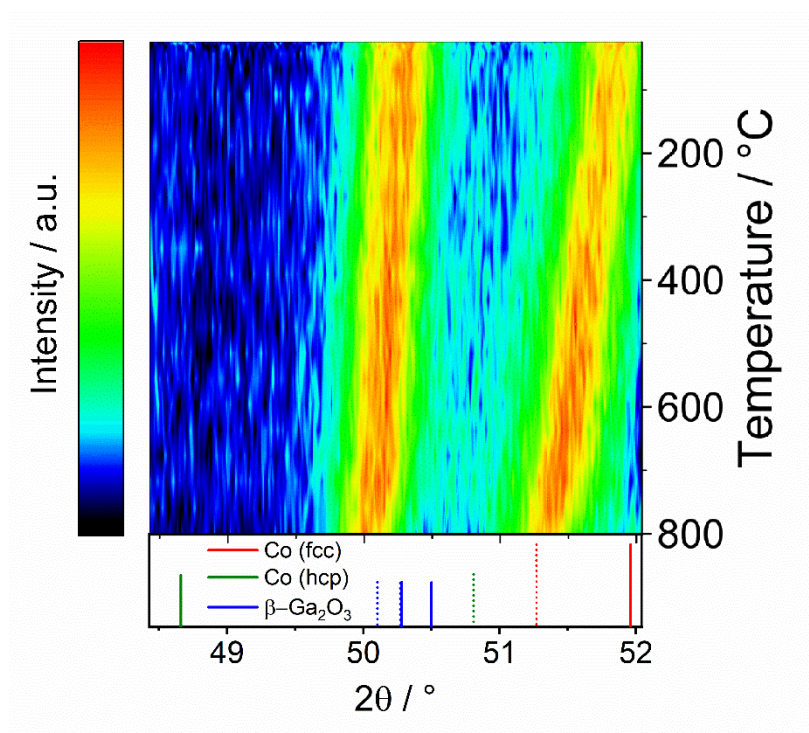


Figure S8: In situ XRD patterns collected on $\text{Co}_3\text{O}_4/\beta\text{-Ga}_2\text{O}_3$ during cooling down from 800 to 50 °C after DRM. The dotted lines in the inset are the calculated XRD patterns of the modified lattice parameters due to thermal expansion. [References from the XRD patterns are the same as the main publication].

Section H Electron microscopy analysis of the $\text{Co}_3\text{O}_4/\beta\text{-Ga}_2\text{O}_3$ catalyst after a direct DRM treatment without hydrogen pre-reduction

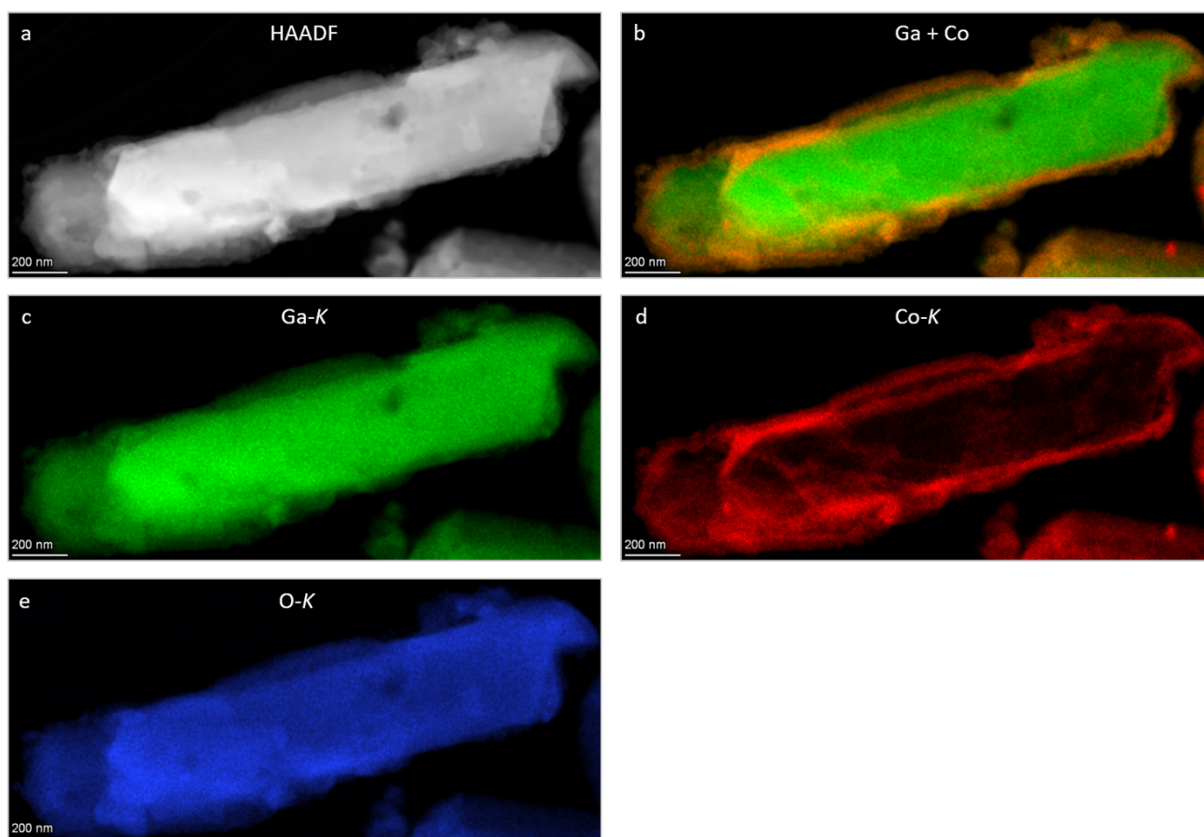


Figure S9: Mesoscale electron microscopy analysis of $\text{Co}_3\text{O}_4/\beta\text{-Ga}_2\text{O}_3$ catalyst after a direct DRM treatment with out hydrogen pre-reduction. Panel a: HAADF. Panel b: Overlay of the Ga-K and Co-K EDX intensities. Panels c-d: Individual Ga-K (c), Co-K (d) and O-K (e) EDX intensities.

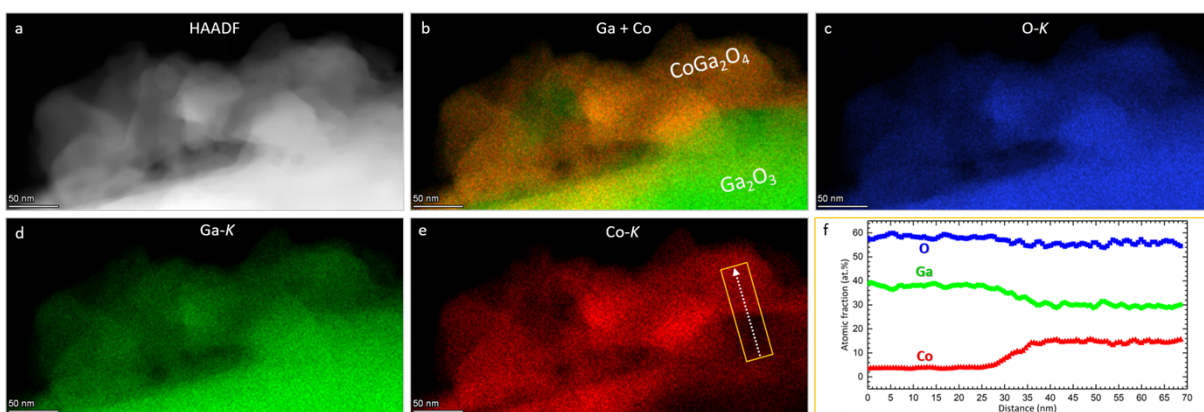


Figure S10: Nanoscale electron microscopy analysis of $\text{Co}_3\text{O}_4/\beta\text{-Ga}_2\text{O}_3$ after a direct DRM treatment without hydrogen pre-reduction. Panel a: HAADF. Panel b: Overlay of the Ga-K and Co-K EDX intensities. Panels c-d: Individual O-K (c), Ga-K (d) and Co-K (e) EDX intensities. Panel f: Line profile along the arrow shown in Panel e.

Section I Peak data of the XPS analysis

Table S2: Peak data of the Co 2p and Ga 3d XPS analysis including binding energy/ eV, full-width-at-half-maximum (FWHM), peak area/ % and peak ratio.

		<i>Comp.</i>	<i>Pos. / eV</i>	<i>FWHM</i>	<i>% Area / -</i>	<i>Ratio / -</i>
Co 2p	<i>H₂ + DRM</i>	<i>Co 2p 3/2</i>	780.38	3.87	31.93	1.00
		<i>Co 2p 3/2 sat.</i>	785.20	10.34	39.92	1.25
		<i>Co 2p 1/2</i>	795.98	4.46	17.45	0.55
		<i>Co 2p 1/2 sat.</i>	802.60	6.83	10.70	0.34
	<i>DRM</i>	<i>Co 2p 3/2</i>	780.48	3.14	33.72	1.00
		<i>Co 2p 3/2 sat.</i>	785.14	8.09	36.90	1.09
		<i>Co 2p 1/2</i>	796.21	3.10	15.25	0.45
		<i>Co 2p 1/2 sat.</i>	802.79	5.93	14.14	0.42
	<i>H₂</i>	-	-	-	-	-
		-	-	-	-	-
		-	-	-	-	-
		-	-	-	-	-
	<i>As Calcined</i>	<i>Co 2p 3/2</i>	780.45	3.95	42.33	1.00
		<i>Co 2p 3/2 sat.</i>	785.62	9.63	28.62	0.68
		<i>Co 2p 1/2</i>	795.63	3.86	19.71	0.47
		<i>Co 2p 1/2 sat.</i>	802.71	6.19	9.34	0.22
	<i>Intermetallic</i>	<i>Co met. LMM Auger</i>	775.82	2.04	6.53	0.52
		<i>Co met. 3/2</i>	778.44	2.00	16.12	1.28
		<i>Co met. 1/2</i>	790.75	2.20	4.42	0.35
		<i>Co 2p 3/2</i>	780.02	2.77	12.57	1.00
		<i>Co 2p 3/2 sat.</i>	784.50	5.83	22.76	1.81
		<i>Co 2p 1/2</i>	795.02	3.14	18.91	1.50
		<i>Co 2p 1/2 sat.</i>	800.88	4.72	18.68	1.49
Ga 3d	<i>H₂ + DRM</i>	<i>Ga³⁺ 3d 5/2</i>	1117.77	3.42	100.00	1.00
	<i>DRM</i>	<i>Ga³⁺ 3d 5/2</i>	1117.72	3.40	100.00	1.00
	<i>H₂</i>	<i>Ga³⁺ 3d 5/2</i>	1117.72	3.07	100.00	1.00