

SUPPLEMENTARY INFORMATION

Improving the catalytic performance of Co/BaCeO₃ catalyst for ammonia synthesis by Y-modification of the perovskite-type support

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Table S2. Structural parameters of the BaCe_{1-x}Y_xO_{3-δ} (x=0–0.30) supports based on the Rietveld analysis.

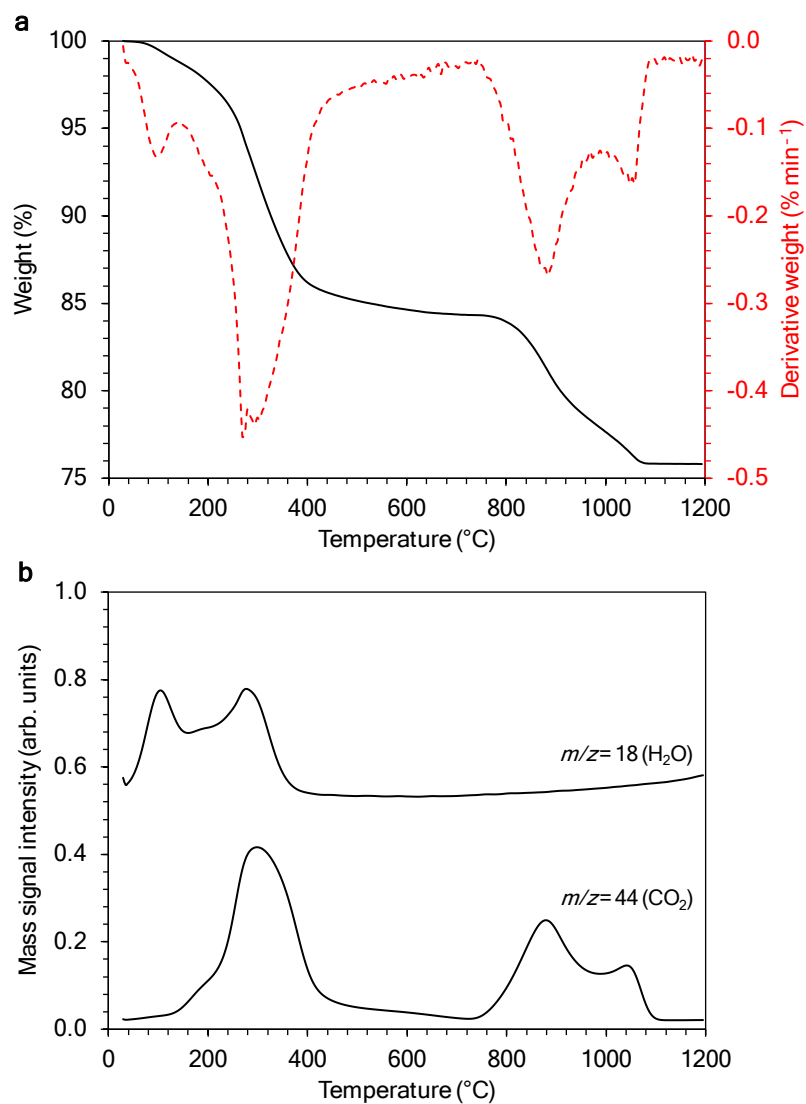


Figure S1. TGA-MS profile of thermal decomposition of the $\text{BaCe}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ ($x=0$) support precursor obtained by co-precipitation (according to the procedure described in section 2.1). (a) mass loss curve (TG) and derivative of mass loss curve (DTG) during sample heating, (b) mass signals of water vapour ($m/z=18$) and carbon dioxide ($m/z=44$) evolved during sample heating (measurement conditions: 50 mg sample, flow 100 mL min⁻¹ of air, heating 10 °C min⁻¹ in the temperature range of 30–1200 °C).

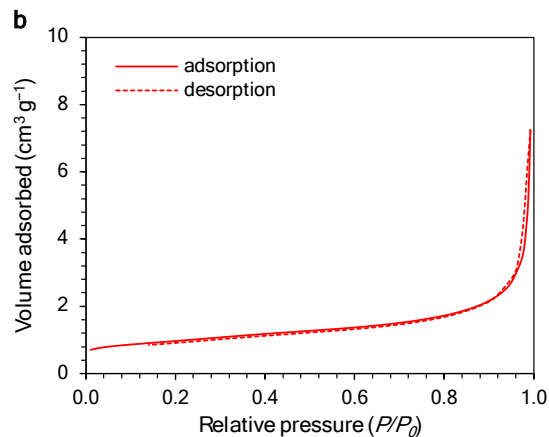
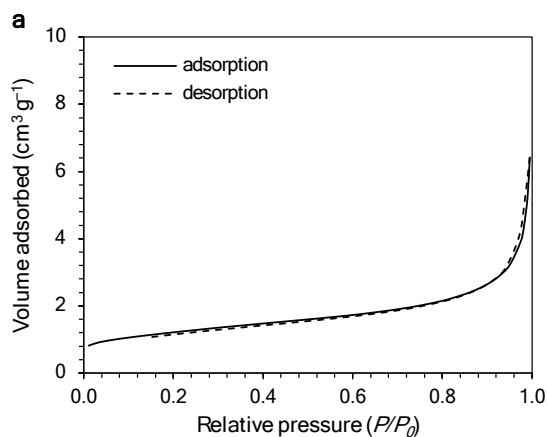


Figure S2. Exemplary N₂ adsorption-desorption isotherms of (a) BaCe_{1-x}Y_xO_{3-δ} (x=0) and (b) BaCe_{1-x}Y_xO_{3-δ} (x=0.10) supports.

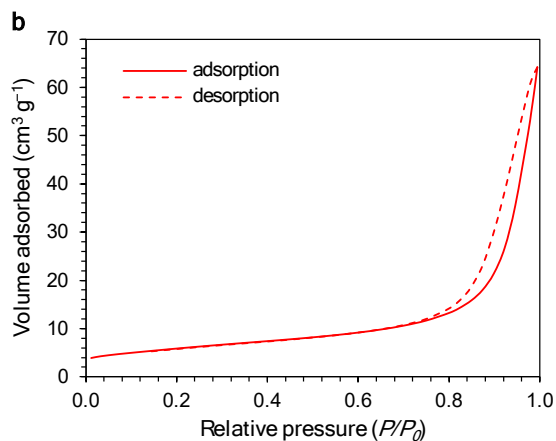
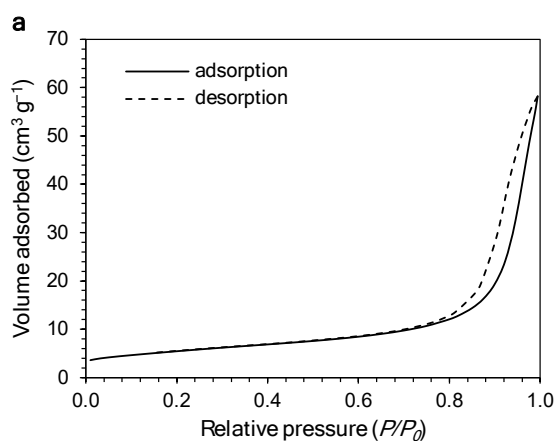


Figure S3. Exemplary N₂ adsorption-desorption isotherms of (a) Co/BaCe_{1-x}Y_xO_{3-δ} (x=0) and (b) Co/BaCe_{1-x}Y_xO_{3-δ} (x=0.10) catalyst precursors.

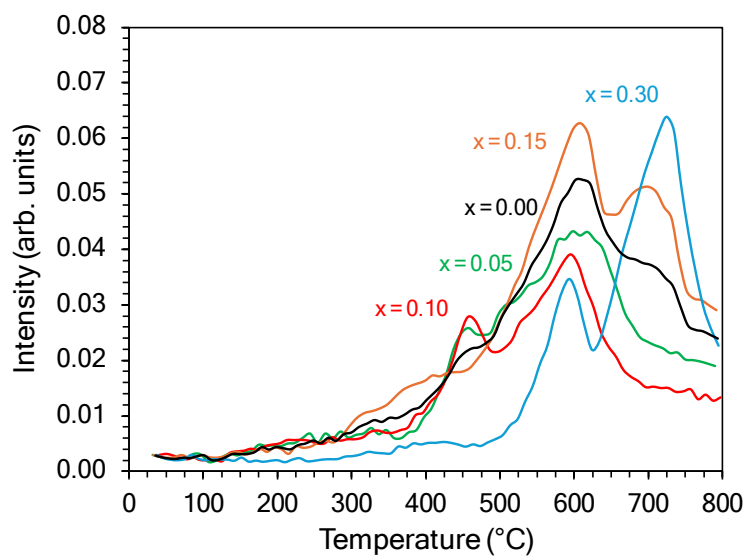


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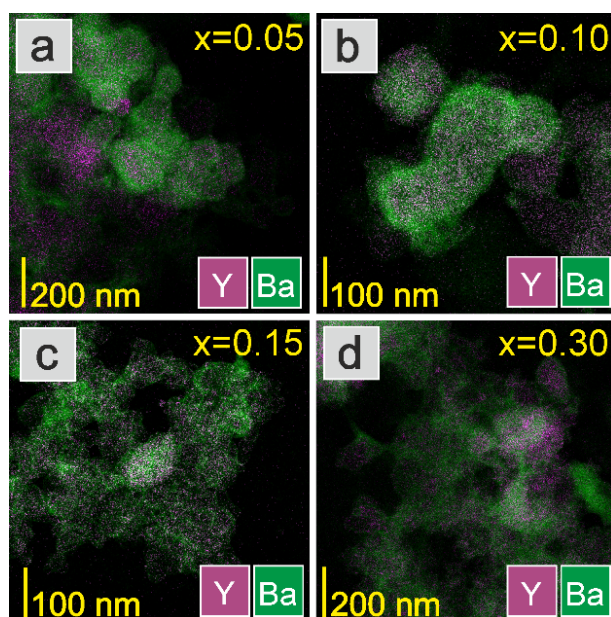


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Table S1. Average reaction rate (r_{NH_3}) of ammonia synthesis reaction over catalysts with different active metals (10 wt% of Co, Ni, Mo, or Fe) supported on $\text{BaCe}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ ($x=0.10$). Activation conditions: 470 °C (72 h) → 520 °C (24 h) → 550 °C (48 h) → 600 °C (24 h), flow of H_2/N_2 mixture (75/25 mol%, 30 $\text{dm}^3 \text{h}^{-1}$), atmospheric pressure. Measurement conditions: 470°C, 6.3 MPa, flow of H_2/N_2 mixture (75/25 mol%, 70 $\text{dm}^3 \text{h}^{-1}$).

Catalyst	Active phase	r_{NH_3} ($\text{g}_{\text{NH}_3} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$)
Mo/BaCe _{0.90} Y _{0.10} O _{3-δ}	Mo	0.01
Ni/BaCe _{0.90} Y _{0.10} O _{3-δ}	Ni	0.14
Fe/BaCe _{0.90} Y _{0.10} O _{3-δ}	Fe	0.32
Co/BaCe _{0.90} Y _{0.10} O _{3-δ}	Co	2.66

Table S2. Structural parameters of the $\text{BaCe}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ ($x=0-0.30$) supports based on the Rietveld analysis.

Support	x	Phase	a /Å	b /Å	c /Å	b /°	V /Å ³
BaCeO ₃	0.00	<i>Pmcn</i>	8.7745(2) ^a	6.2323(2)	6.2131(2)	-	339.77(2)
BaCe _{0.95} Y _{0.05} O _{3-δ}	0.05	<i>Pmcn</i>	8.7745(2)	6.2326(2)	6.2148(1)	-	339.88(1)
BaCe _{0.90} Y _{0.10} O _{3-δ}	0.10	<i>Pmcn</i>	8.7760(2)	6.2366(1)	6.2174(1)	-	340.25(1)
BaCe _{0.85} Y _{0.15} O _{3-δ}	0.15	<i>Pmcn</i>	8.7567(5)	6.222(1)	6.218(1)	-	338.74(9)
BaCe _{0.70} Y _{0.30} O _{3-δ}	0.30	<i>I2/m</i>	6.2478(4)	8.7676(6)	6.2215(4)	90.946(4)	340.76(4)

^a Uncertainty of the last digit (within parentheses).