Ammonia as a carrier for hydrogen production by using Perovskites

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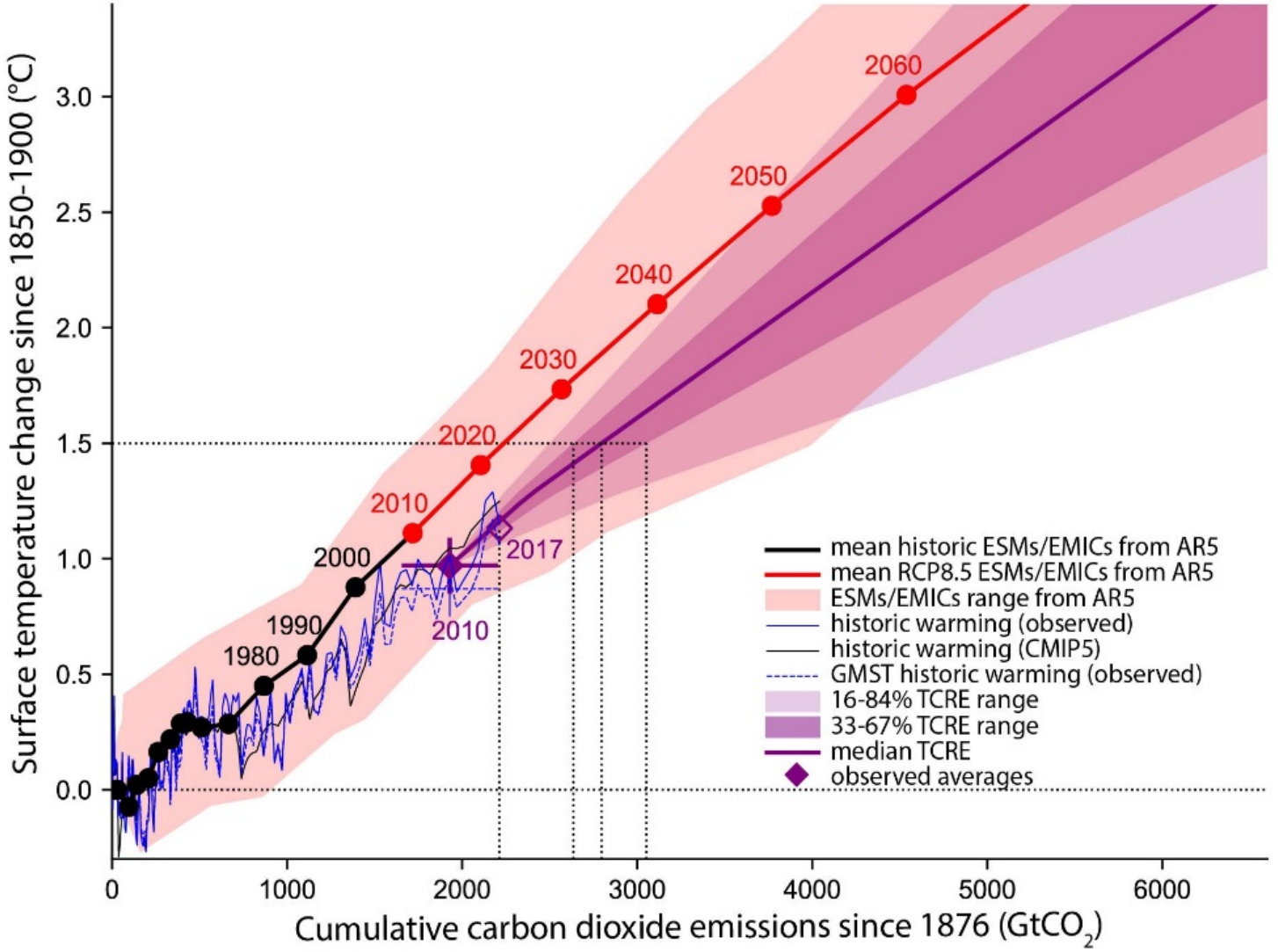
8TH INTERNATIONAL CONFERENCE ON SUSTAINABLE SOLID WASTE MANAGEMENT

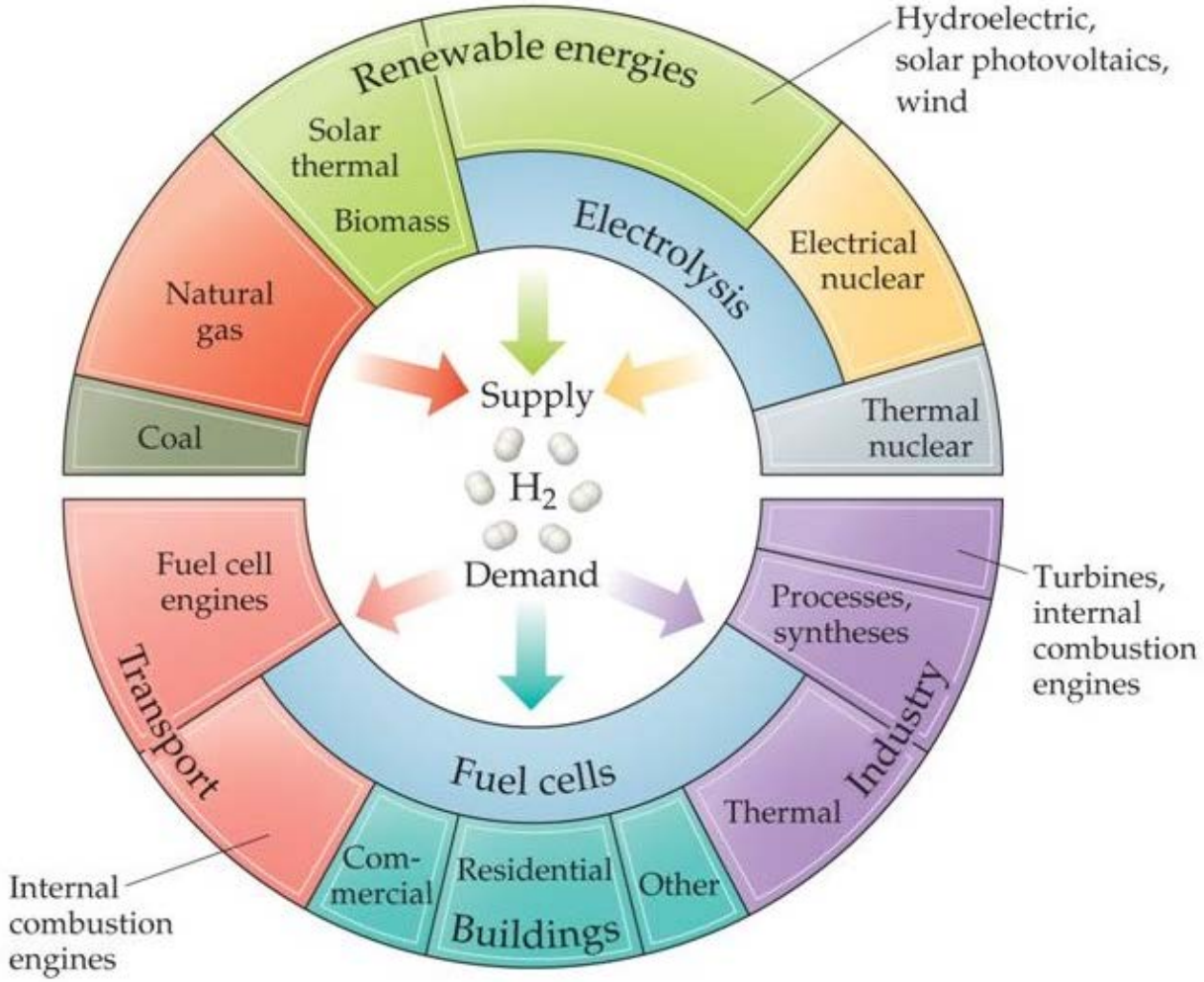
23-26 JUNE 2021, THESSALONIKI, GREECE

Environmental issues



UN. Intergovernmental Panel on Climate Change, Global Warming of 1.5 °C, 2019.

Hydrogen economy



Int. J. Electrochem. Sci. Int. J. 6 (2011) 5830–5917.

Production from renewable energy sources

Clean, sustainable and renewable energy carrier

Storage and transport issues

Hydrogen economy

- Thermochemical process
- CO_x emissions

Grey and blue H_2

Green H_2

- Water electrolysis
- From biomass

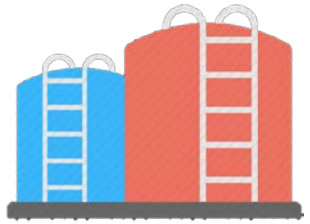
Hydrogen economy

- Thermochemical process
- CO_x emissions

Grey and blue H_2

Green H_2

- Water electrolysis
- From biomass

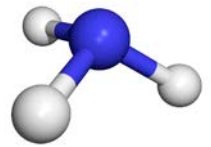


- Liquid (low temperatures) or compressed (high pressure)

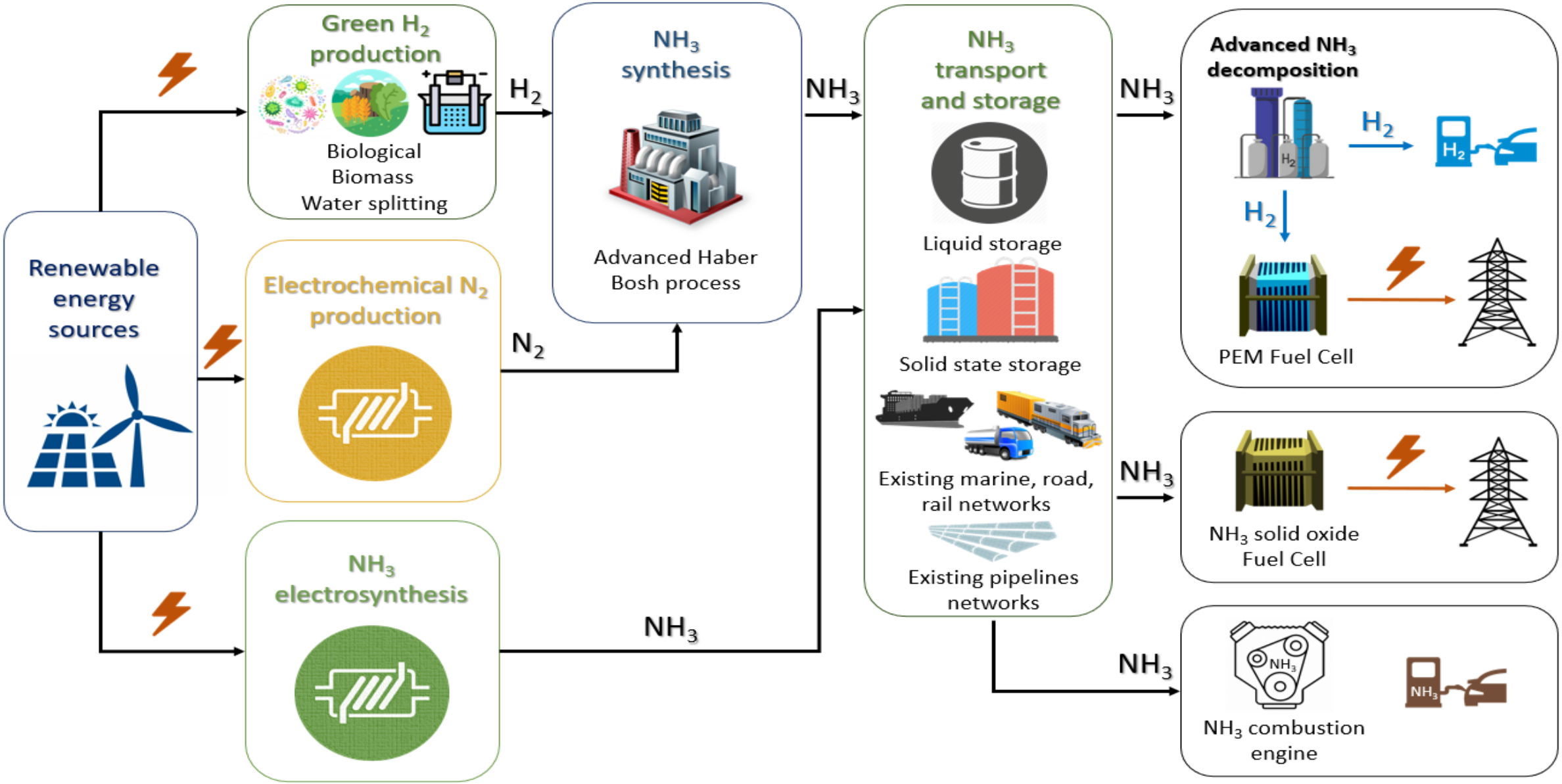
Conventional transport

Modern transport

- Adsorption
- H_2-rich molecules

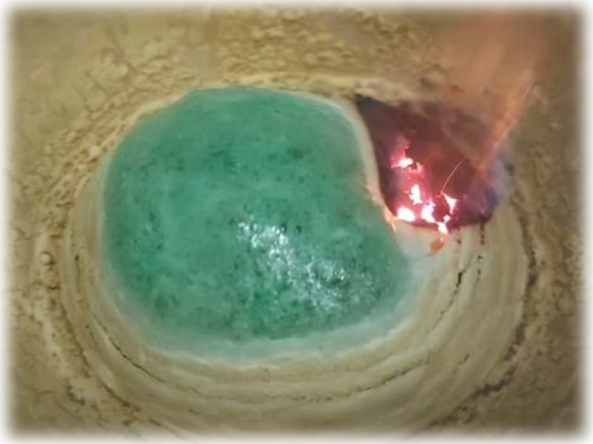


NH_3 as hydrogen carrier

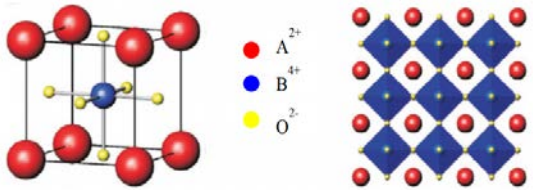


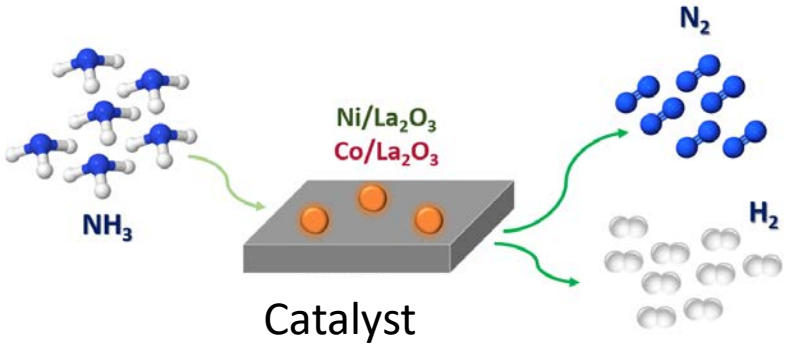
Perovskite-type oxides ($LaBO_3$) by the self-combustion method

Self-combustion method



Perovskites ($LaNiO_3$ and $LaCoO_3$)





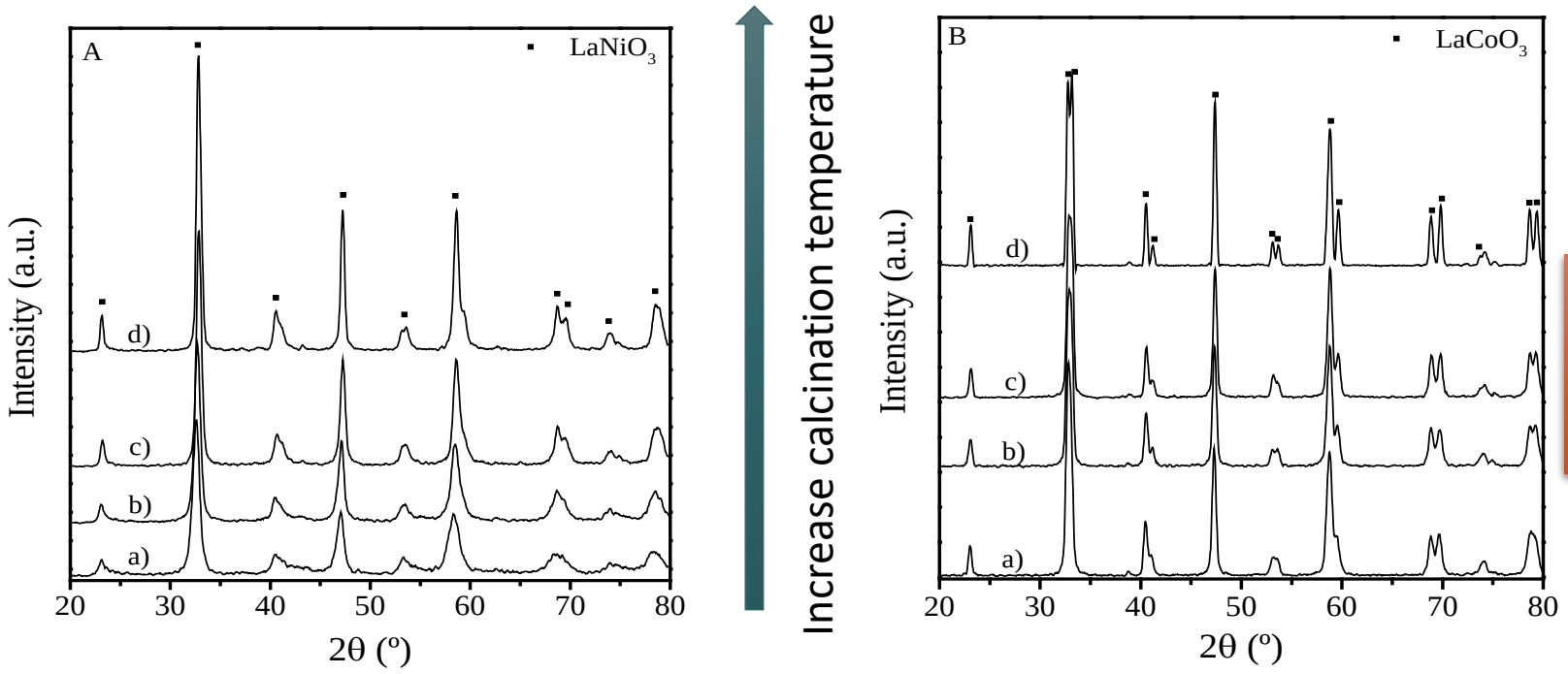
Perovskite-type oxides ($LaBO_3$) by the self-combustion method

Influence of metal (Ni or Co)

Influence of calcination temperature

28 Ni Nickel

Rhombohedral $LaNiO_3$ (R-3m, 33-0711)

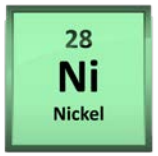


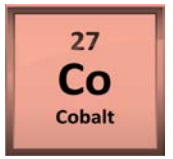
27 Co Cobalt

Rhombohedral $LaCoO_3$ (R-3m, 48-0123)

XRD pattern of A) $LaNiO_3$ y B) $LaCoO_3$ perovskites calcined at **a) 650, b) 700, c) 750 and d) 900 ºC**

Perovskite-type oxides ($LaBO_3$) by the self-combustion method → Influence of metal (Ni or Co) → Influence of calcination temperature →





Calcination temperature (°C)	$LaNiO_3$			$LaCoO_3$		
	Crystal size (nm) (2θ=47.4°)	S_{BET} *($m^2 \cdot g^{-1}$)*	V_p *($cm^3 \cdot g^{-1}$)*	*Crystal size (nm) (2θ=47.5°)*	S_{BET} *($m^2 \cdot g^{-1}$)*	V_p *($cm^3 \cdot g^{-1}$)*
650	11.3	11.1	0.062	26.1	10.3	0.059
700	14.4	9.7	0.059	25.1	13.4	0.094
750	16.8	7.8	0.057	28.7	13.2	0.077
900	23.8	3.2	0.025	40.7	3.5	0.012

Perovskite-type oxides ($LaBO_3$) by the self-combustion method

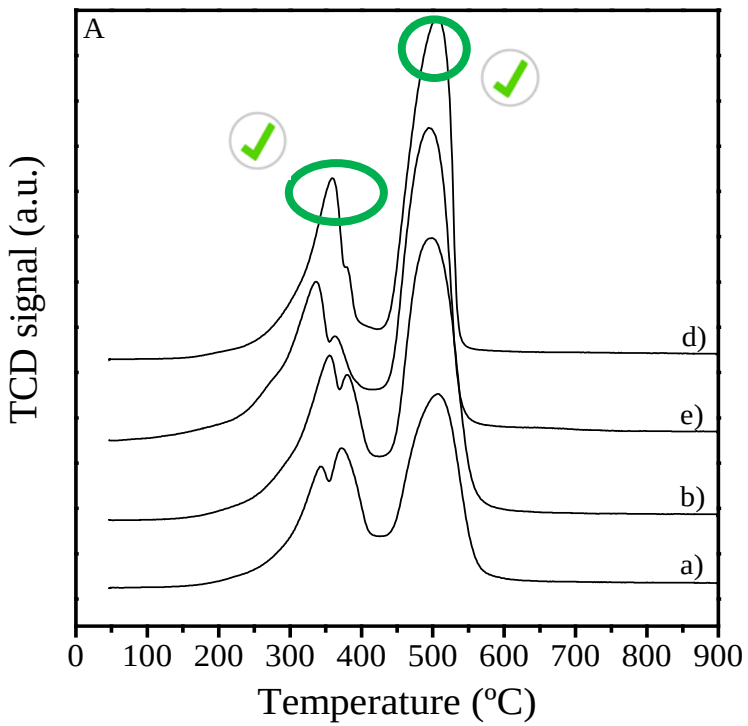
Influence of metal (Ni or Co)

Influence of calcination temperature

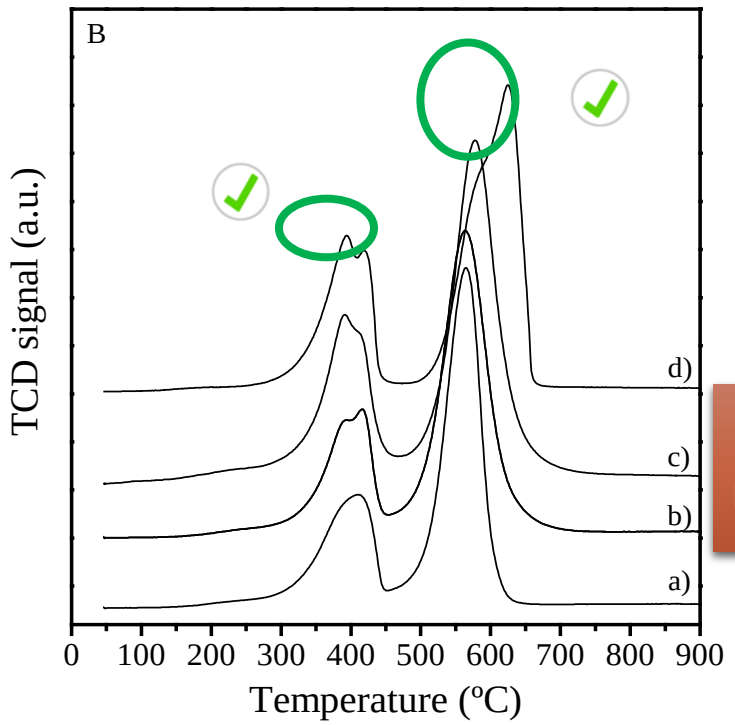
28 Ni Nickel

~ 350 °C
$LaNiO_3 \rightarrow La_2Ni_2O_5$

~ 510 °C
$La_2Ni_2O_5 \rightarrow Ni^0 / La_2O_3$



Increase calcination temperature



27 Co Cobalt

300-400 °C
$LaCoO_3 \rightarrow La_2Co_2O_5$

475-600 °C
$La_2Co_2O_5 \rightarrow Co^0 / La_2O_3$

H_2-TPR profiles of A) $LaNiO_3$ y B) $LaCoO_3$ perovskites calcined at **a) 650, b) 700, c) 750 and d) 900 °C**

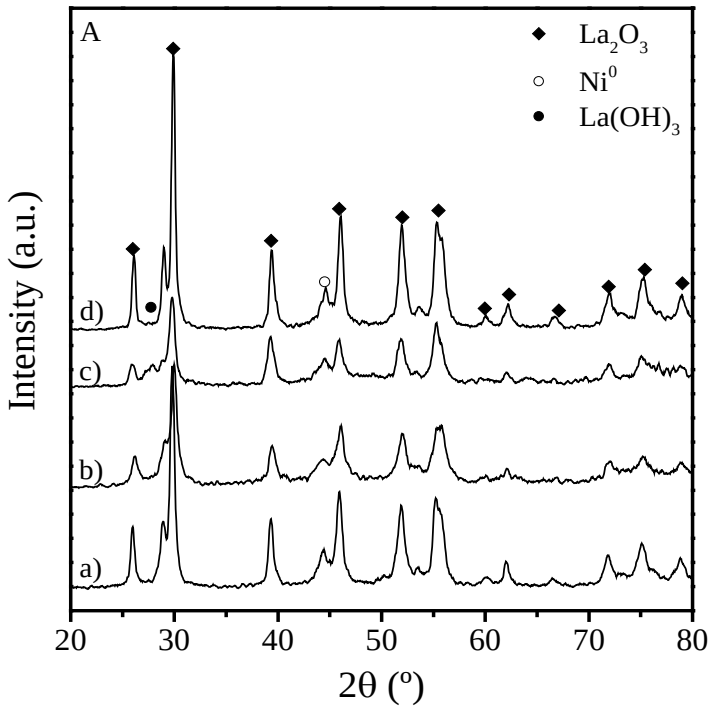
Perovskite-type oxides ($LaBO_3$) by the self-combustion method

Influence of metal (Ni or Co)

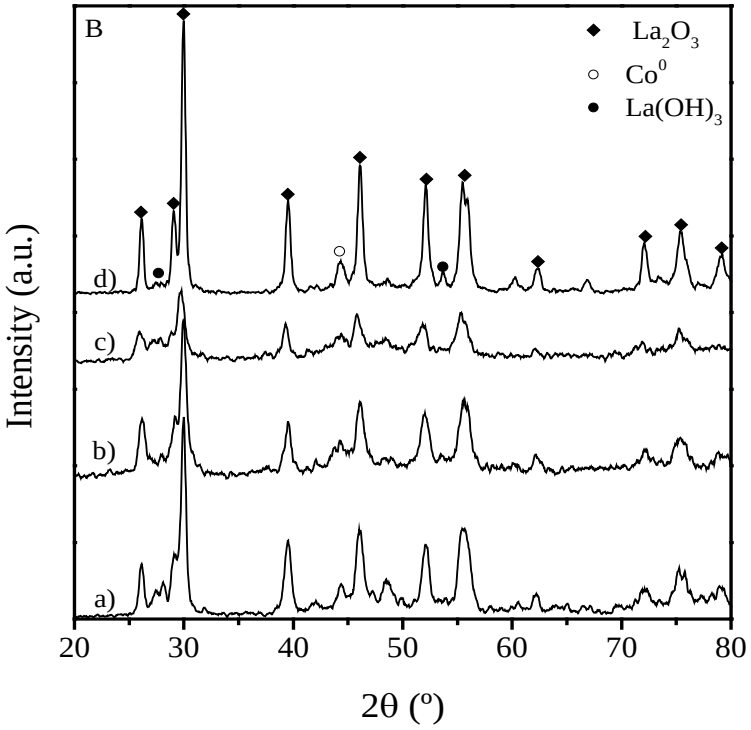
Influence of calcination temperature

28 Ni Nickel

Ni^0/La_2O_3



Increase calcination temperature



27 Co Cobalt

Co^0/La_2O_3

XRD pattern of A) $LaNiO_3$ y B) $LaCoO_3$ perovskites calcined at **a) 650, b) 700, c) 750 and d) 900 ºC** and reduced at 550 ºC and 600 ºC, respectively.

Perovskite-type oxides ($LaBO_3$) by the self-combustion method → Influence of metal (Ni or Co) → Influence of calcination temperature

Samples	Crystal size (nm)		
	La_2O_3 ($2\theta = 29.9^o$)	Ni^0 ($2\theta = 44.5^o$)	Co^0 ($2\theta = 44.3^o$)
$LaNiO_3$ 650 °C	15.6	5.5	-
$LaNiO_3$ 700 °C	14.4	8.1	-
$LaNiO_3$ 750 °C	14.0	9.7	-
$LaNiO_3$ 900 °C	22.6	10.7	-
$LaCoO_3$ 650 °C	22.5	-	9.8
$LaCoO_3$ 700 °C	18.9	-	8.5
$LaCoO_3$ 750 °C	11.1	-	9.0
$LaCoO_3$ 900 °C	23.3	-	11.9

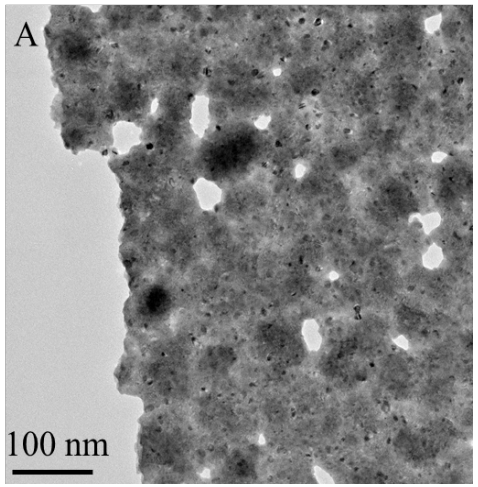
28 Ni Nickel

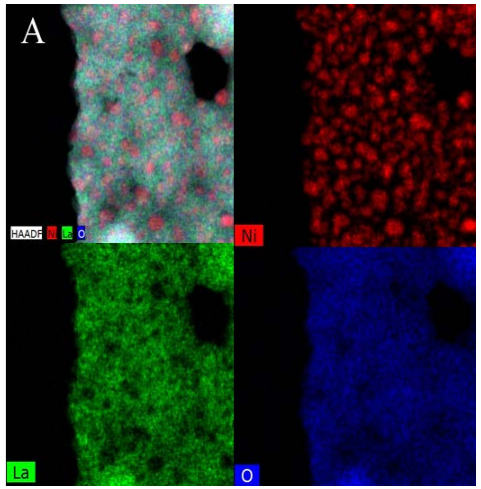
27 Co Cobalt

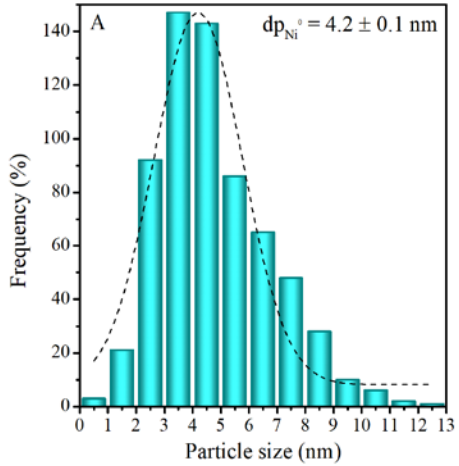
Perovskite-type oxides ($LaBO_3$) by the self-combustion method

Influence of metal (Ni or Co)

Influence of calcination temperature



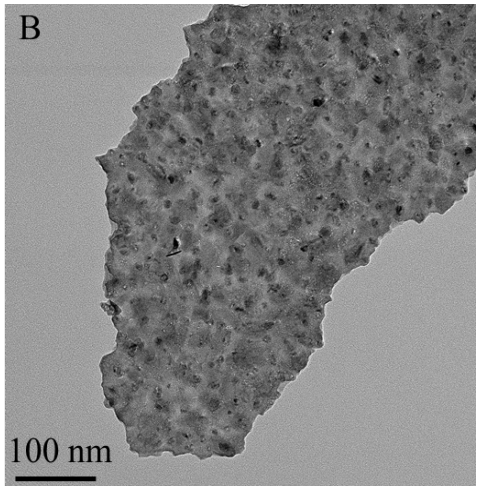


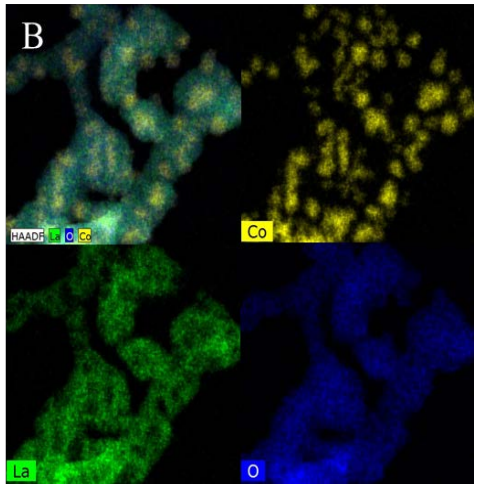


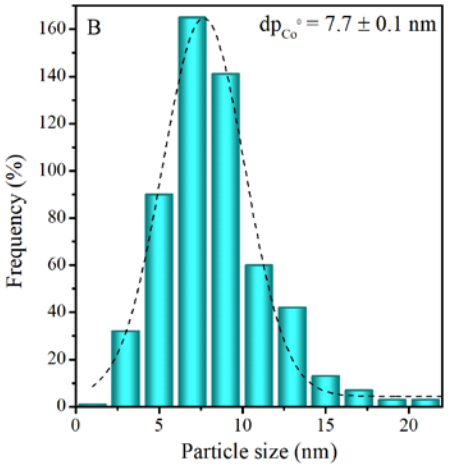
Ni^0/La_2O_3

Lower particles size (4.2 nm)

Co^0/La_2O_3



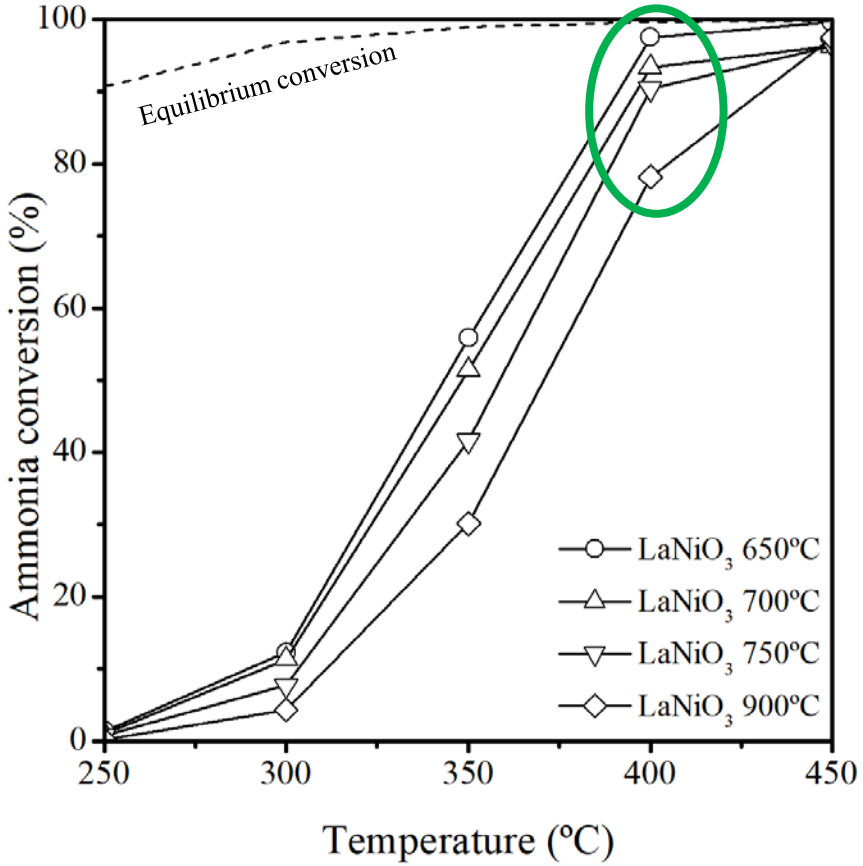


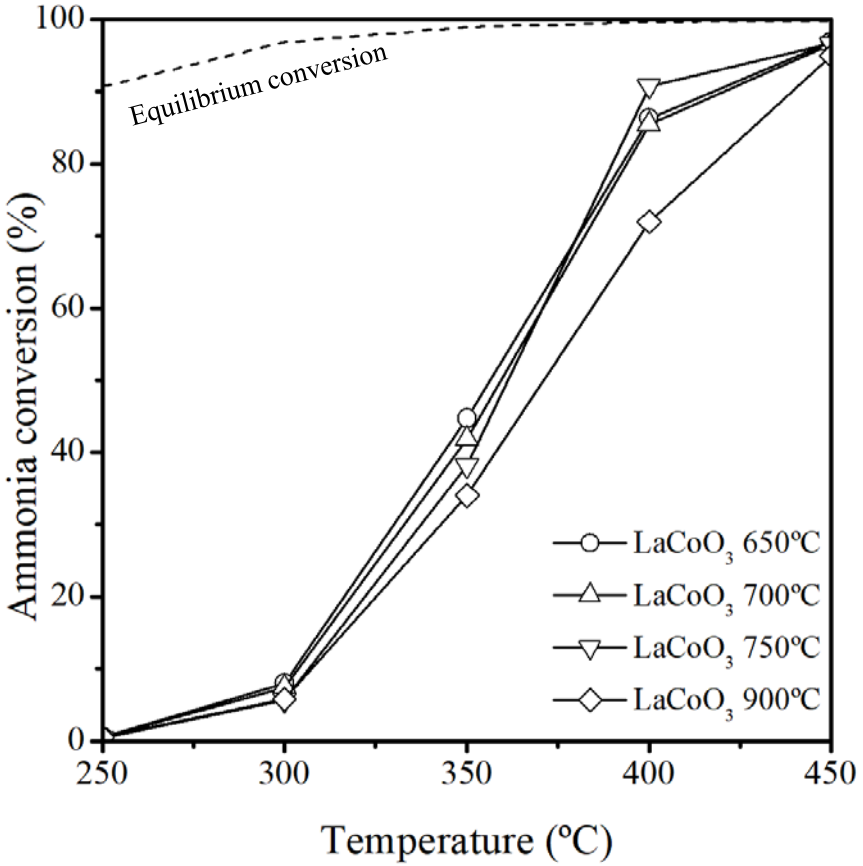


Perovskite-type oxides ($LaBO_3$) by the self-combustion method

Influence of metal (Ni or Co)

Influence of calcination temperature





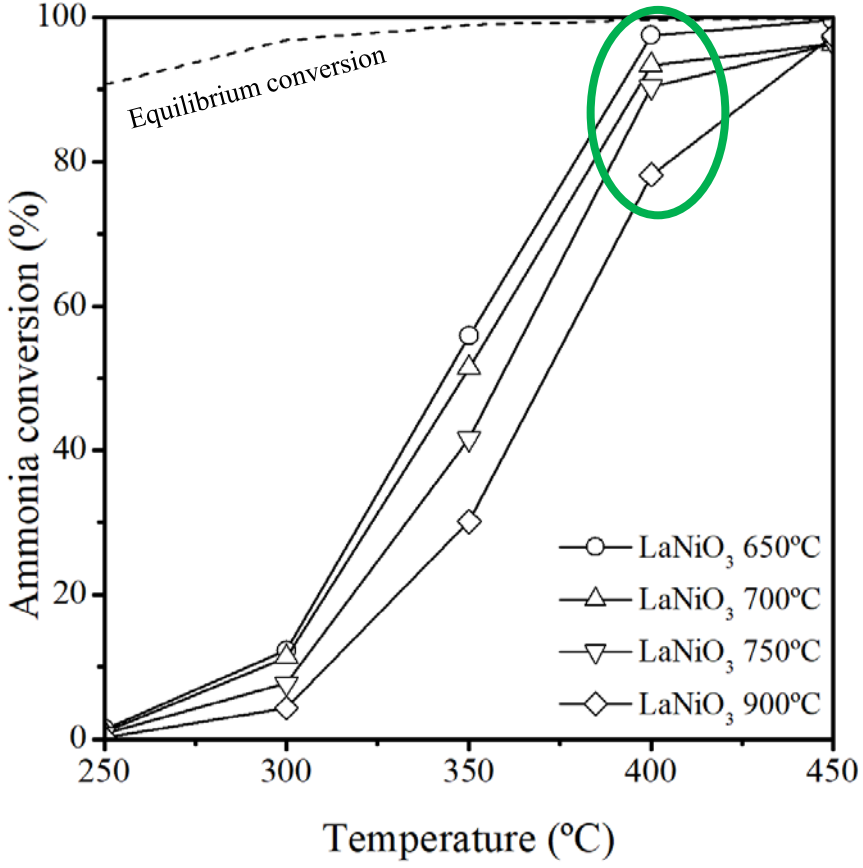
Fixed-bed reactor. P=1 atm; 5 v/v%NH_3-Ar; GHSV=75.000 mL·g_{cat}^{-1}·h^{-1}

Reaction products were analysed on-line by using gas chromatograph (Agilent 7820A)

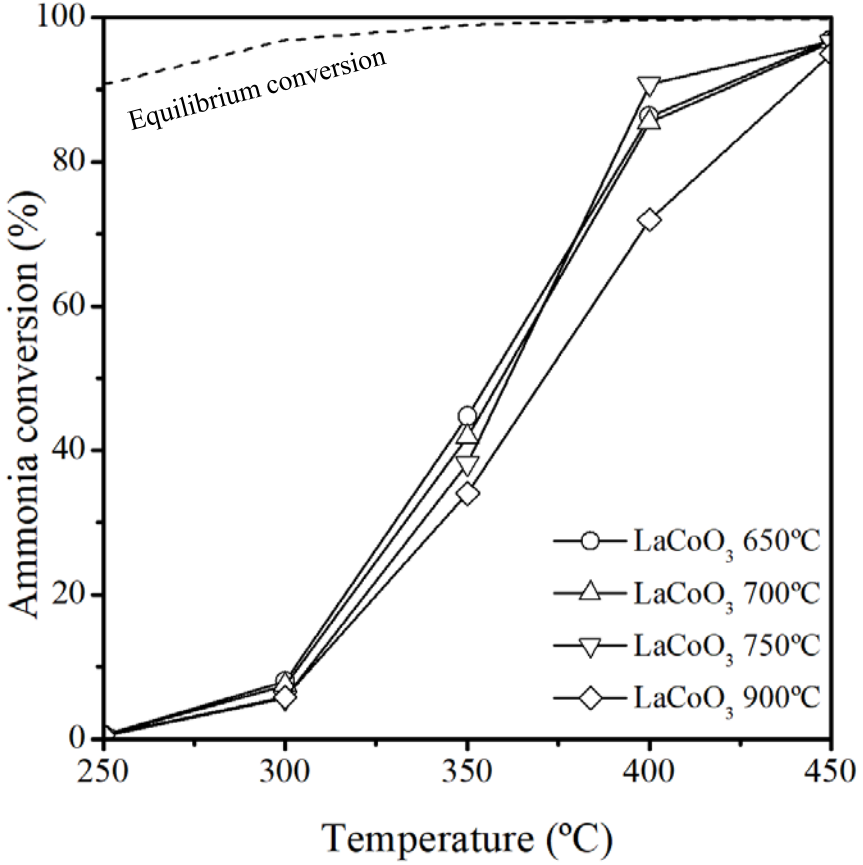
Perovskite-type oxides ($LaBO_3$) by the self-combustion method

Influence of metal (Ni or Co)

Influence of calcination temperature



28 Ni Nickel > 27 Co Cobalt



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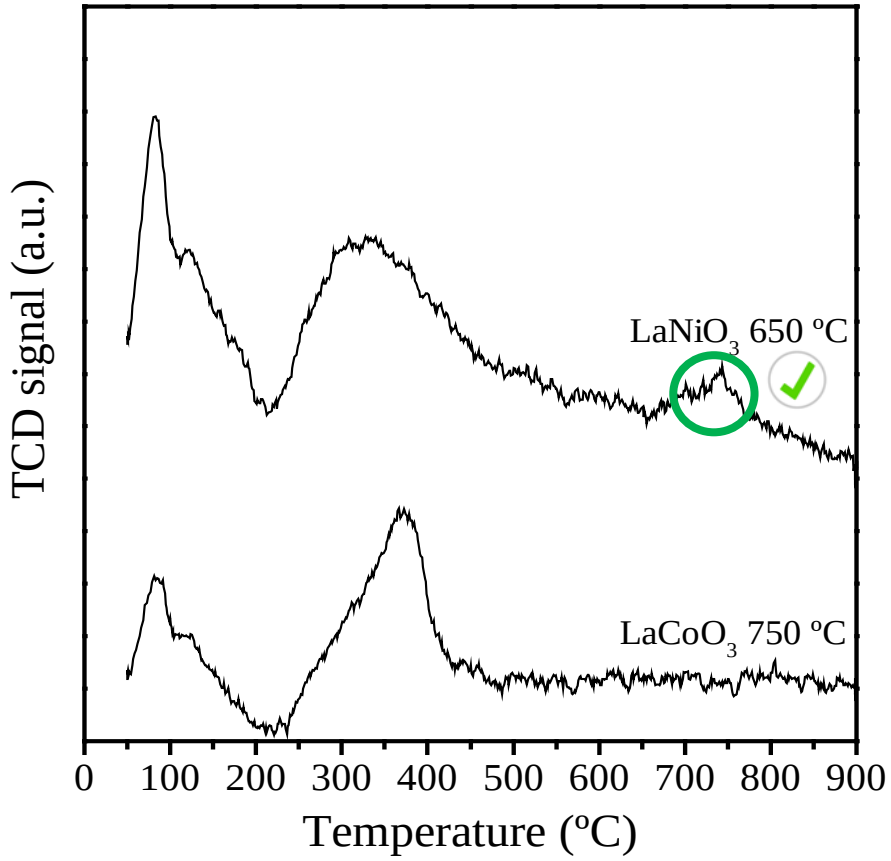
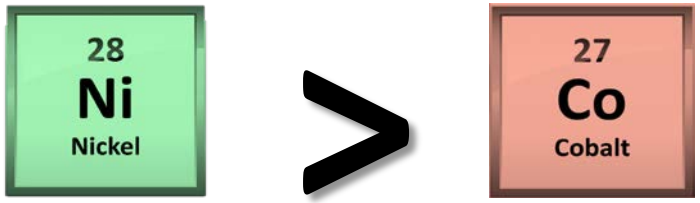
Perovskite-type oxides ($LaBO_3$) by the self-combustion method

Influence of metal (Ni or Co)

Influence of calcination temperature



CO_2-TPD desorption profiles



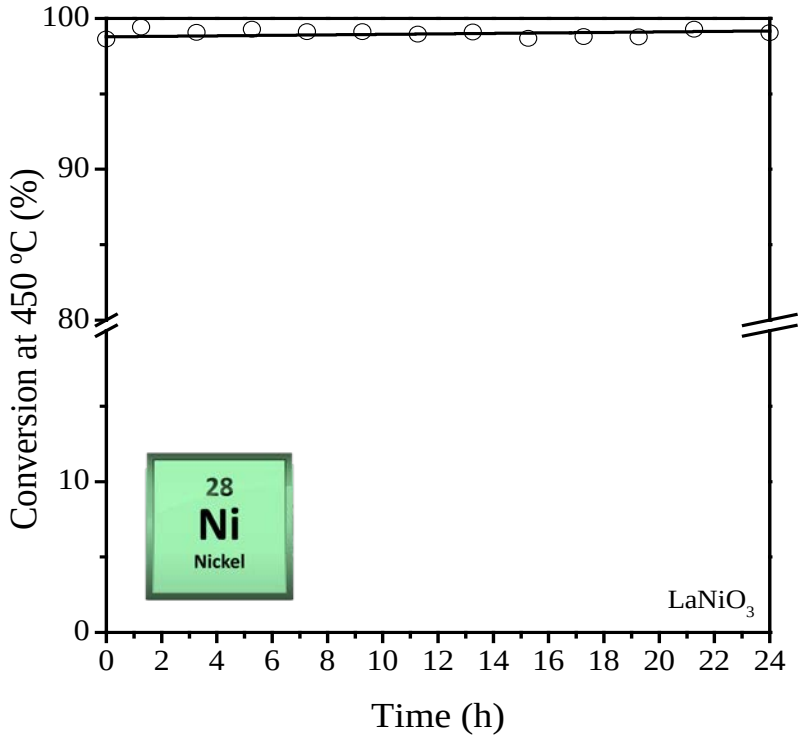
18 μmol $CO_2 \cdot g_{cat}^{-1}$ > 9.6 μmol $CO_2 \cdot g_{cat}^{-1}$

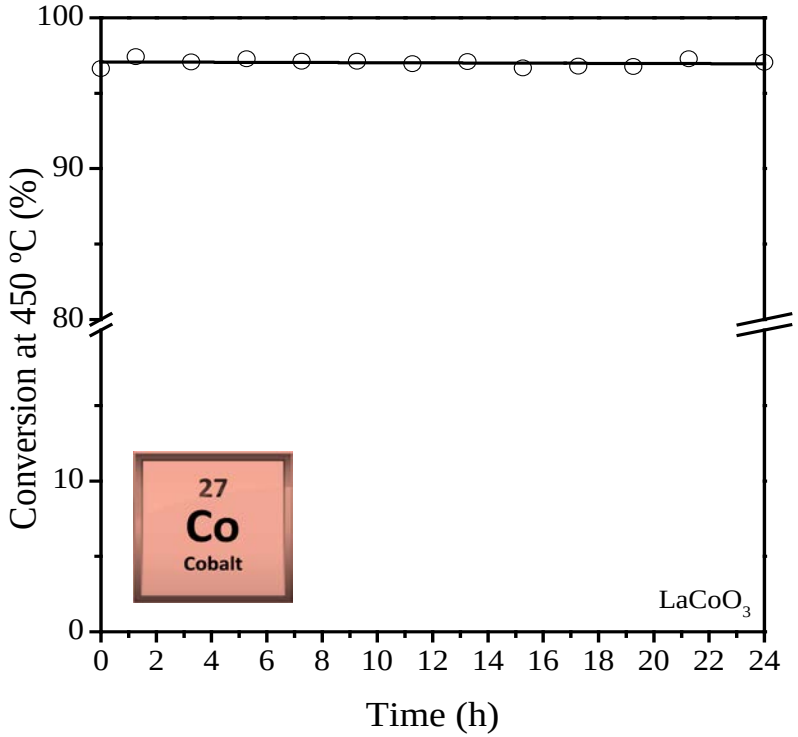
Basicity

Perovskite-type oxides ($LaBO_3$) by the self-combustion method

Influence of metal (Ni or Co)

Influence of calcination temperature



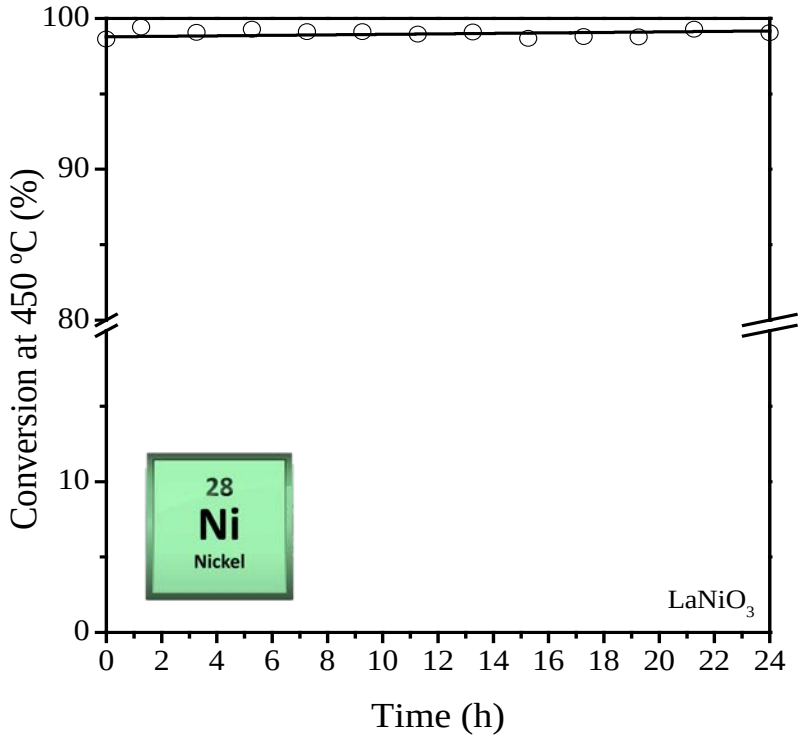


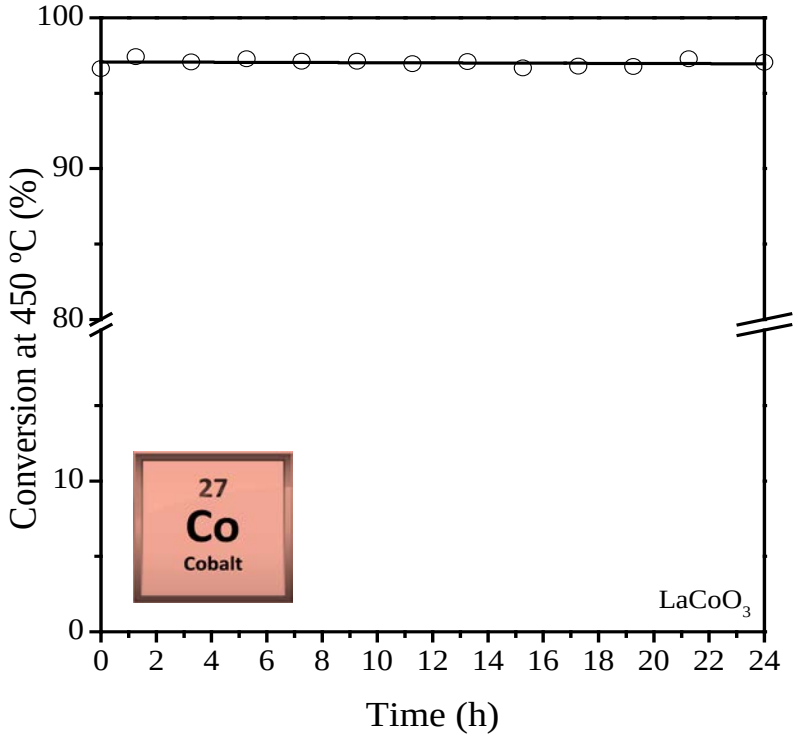
Stability test for reduced samples of $LaNiO_3$ calcined at 650 °C and $LaCoO_3$ calcined at 750 °C (0.08 g catalyst, 75000 $mL \cdot h^{-1} \cdot g_{cat}^{-1}$, atmospheric pressure).

Perovskite-type oxides ($LaBO_3$) by the self-combustion method

Influence of metal (Ni or Co)

Influence of calcination temperature





Excellent catalytic stability after 24 h

Perovskite-type oxides ($LaBO_3$) by the self-combustion method

Influence of metal (Ni or Co)

Influence of calcination temperature

Conclusion

1

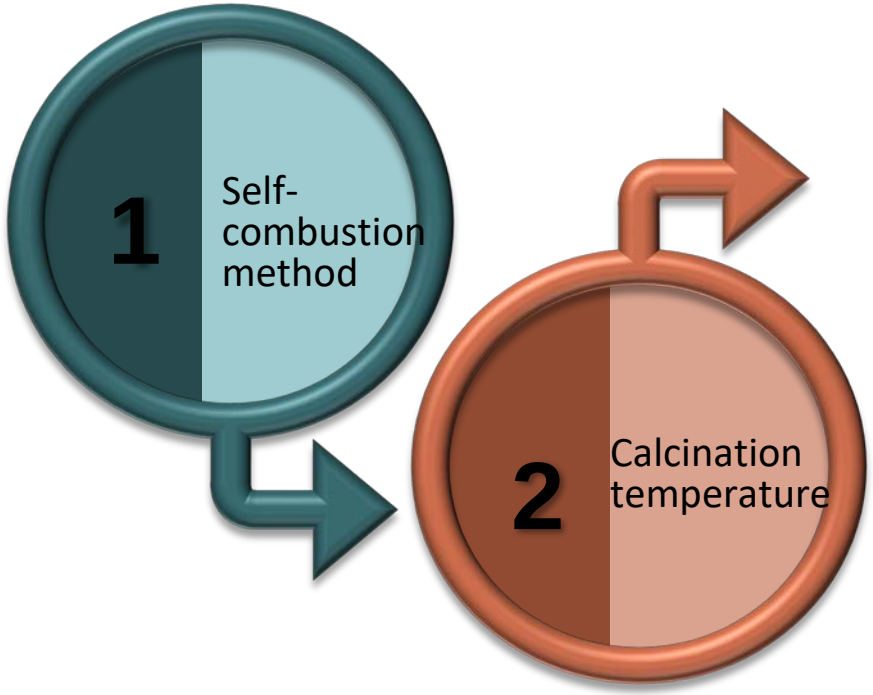
$LaNiO_3$ and $LaCoO_3$ perovskites are adequate catalytic precursors in the catalytic ammonia decomposition reaction.

Perovskite-type oxides ($LaBO_3$) by the self-combustion method

Influence of metal (Ni or Co)

Influence of calcination temperature

Conclusion



2

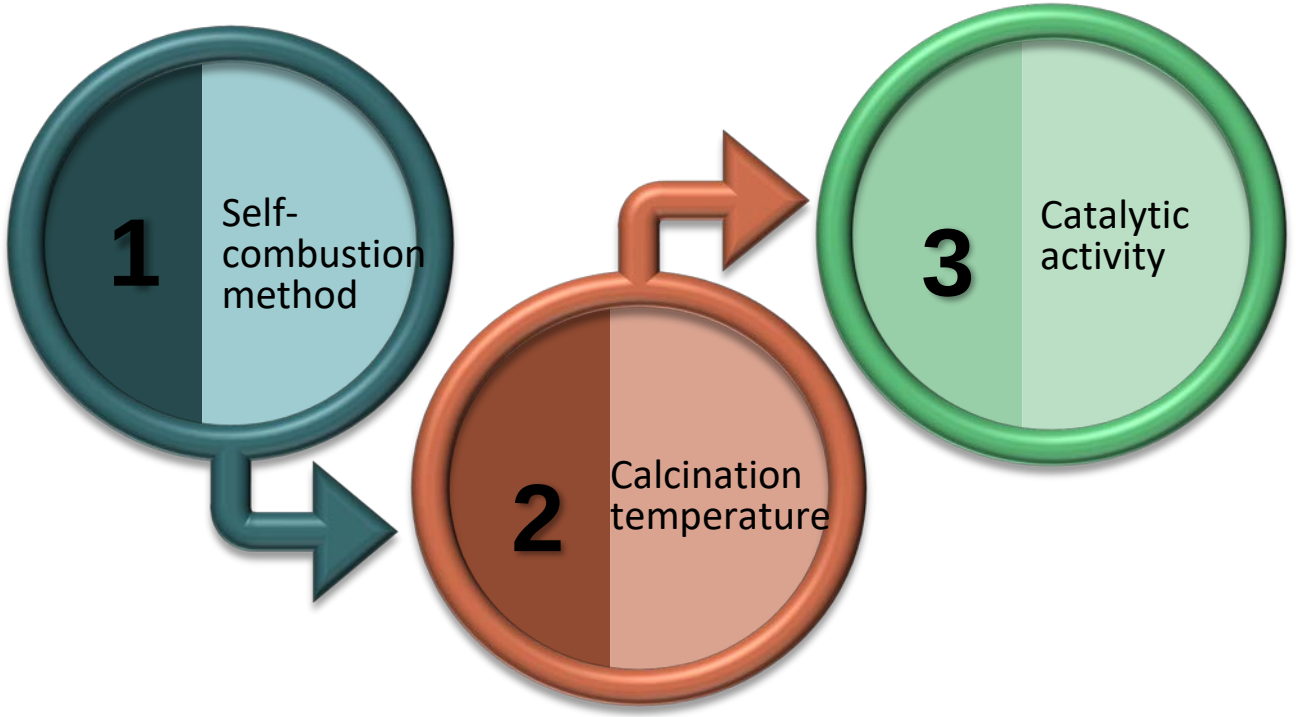
Small and well-dispersed Ni^0 particles after reduction obtained with $LaNiO_3$. For cobalt perovskites, calcination temperatures below 900 °C had no significant influence on metallic cobalt crystal size.

Perovskite-type oxides ($LaBO_3$) by the self-combustion method

Influence of metal (Ni or Co)

Influence of calcination temperature

Conclusion



3

The nickel and cobalt perovskite-derived catalysts yielded excellent H_2 production from ammonia decomposition. In particular, at 450 °C almost 100% of the ammonia was converted over the $LaNiO_3$ calcined at 650 °C.

Ammonia as a carrier for hydrogen production by using Perovskites

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