Activation of Triply Periodic Minimal Surface (TPMS) microarchitectures with $LaNiO_3$-based perovskites for low temperature ammonia decomposition

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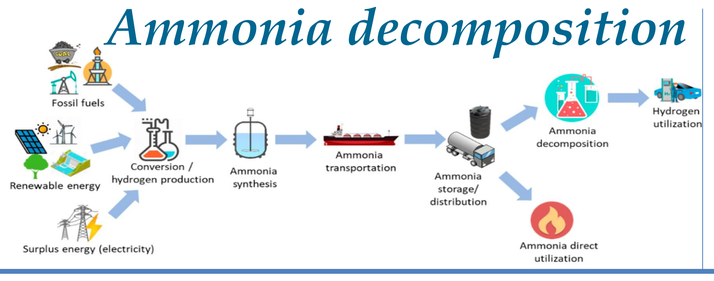
INTRODUCTION

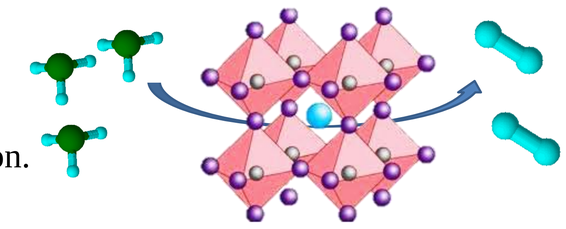
The present work deals with the synthesis, characterization, of $LaNiO_3$ based perovskites with varying A site dopant (Mg,Sr,Ce,Y) and investigation of catalytic ammonia decomposition in the temperature range of 300-600 °C. The second part of the work include catalytic activation of (by a wash-coating method) of Triply Periodic Minimal Surface (TPMS) microarchitectures 3D-printed in a cylindrical shape (Ø = 1cm, Length = 1.5 cm), in Ni-alloy and with various structural parameters (porosity, cell type). The general aim is to intensify the hydrogen generation with structured catalysts with geometries that allow the integration with H_2 selective membranes in a membrane-based reactor to increase productivity at low temperatures (300-450°C).

Ammonia decomposition



Perovskites

- ✓ Perovskite general formula ABO_3
- ✓ A site or B sites doping can tune the chemical properties
- ✓ They can produce size controlled nanoparticles with uniform spatial distribution.
- ✓ Transition metal will be strong anchoring on the metal oxide support.

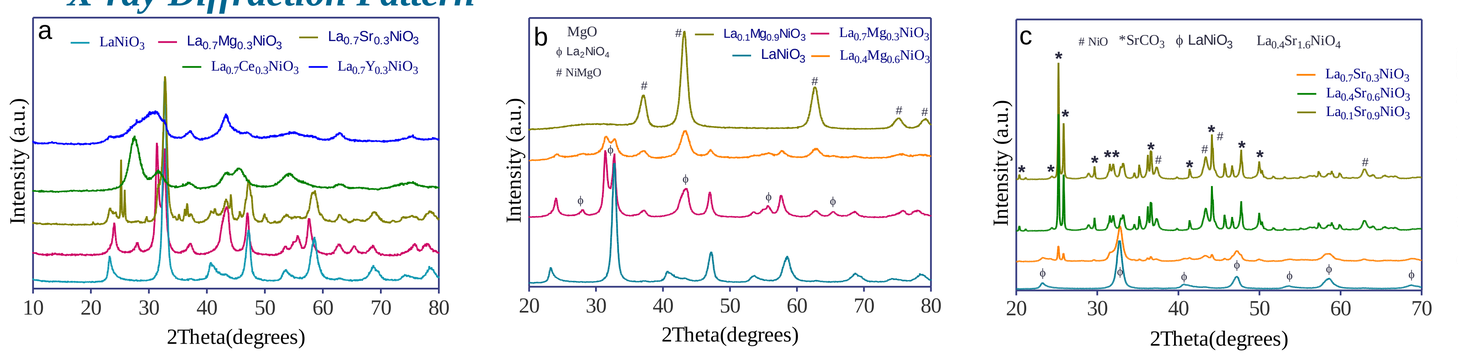


RESULTS

• *Synthesis of perovskites*

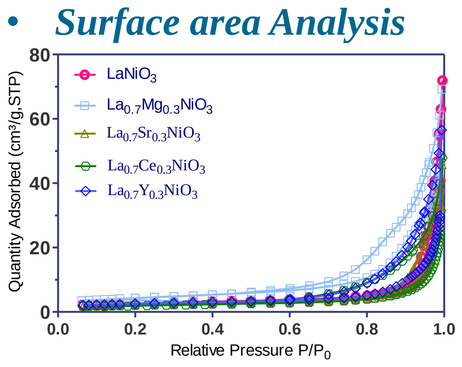
Sol-gel combustion synthesis

• *X-ray Diffraction Pattern*



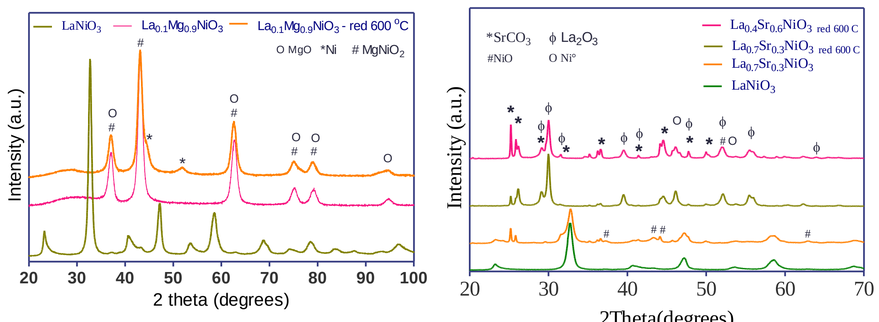
a) X-ray diffraction pattern of a) initial perovskites with general formula $La_{0.7}A_{0.3}NiO_3$ (Mg,Sr,Y,Ce) b)$La_{1-x}Mg_xNiO_3$ perovskites c) $La_{1-x}Sr_xNiO_3$ perovskites(x=0.3,06,0.9)

• *Surface area Analysis*



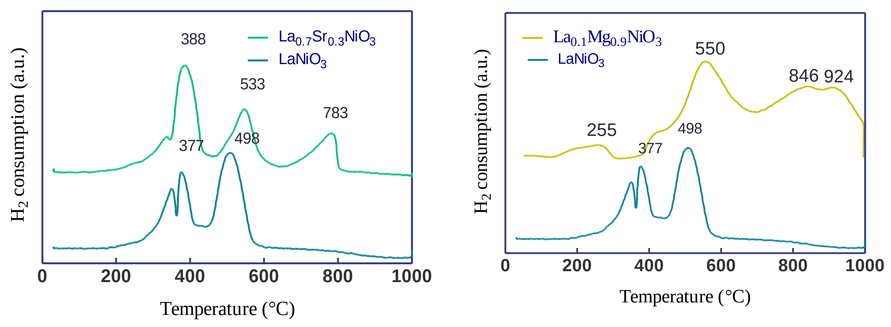
The nitrogen adsorption desorption analysis of the $La_{0.7}A_{0.3}NiO_3$ (Mg,Sr,Y,Ce)

Catalyst	Crystallite size of NiO (nm)	BET (m^2/g)
$La_{0.1}Mg_{0.9}NiO_3$	7.7	47
$LaNiO_3$	-	9
$La_{0.7}Mg_{0.3}NiO_3$	9.2	15
$La_{0.7}Y_{0.3}NiO_3$	7.6	8
$La_{0.7}Ce_{0.3}NiO_3$	18	7
$La_{0.7}Sr_{0.3}NiO_3$	13	7



X-ray diffraction pattern after reduction at 600 °C

• *Temperature programmed reduction*

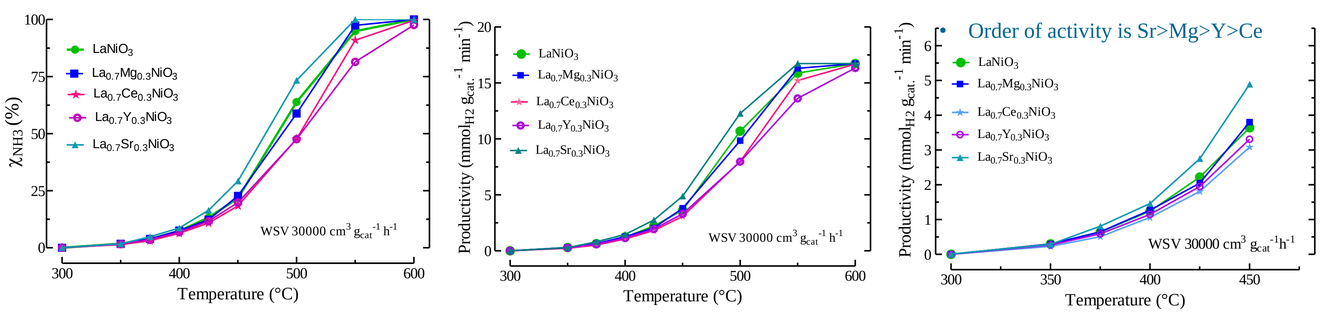


- The reducibility of Ni shifted to lower temperature

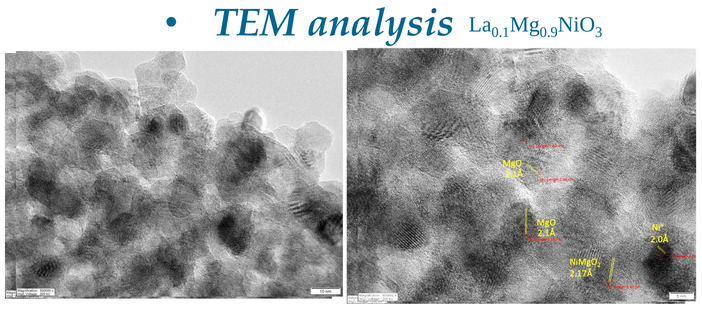
• *Lab-scale testing of the prepared perovskites*

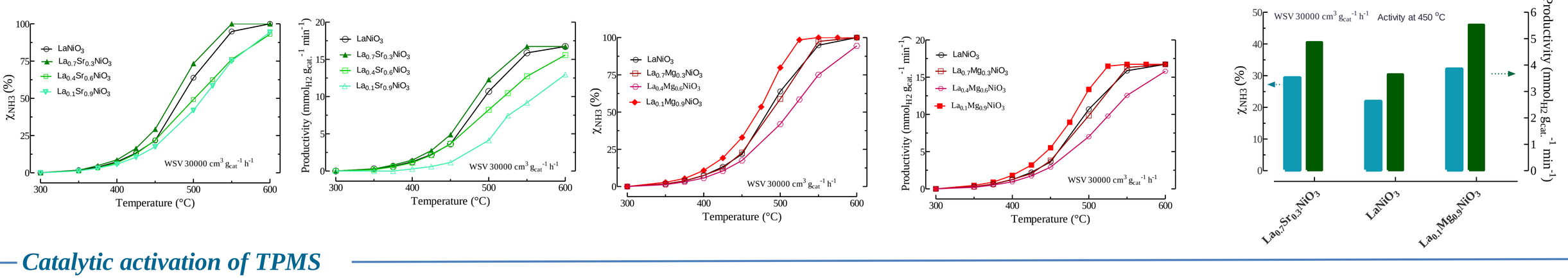
Operative conditions	
Temperature	400 - 600 (°C)
Pressure	1 (bar)
WSV	30000 ($cm^3\ g_{cat}^{-1}\ h^{-1}$)
Total IN Flow	100 cm^3/min
NH_3/He	Gas cylinder 50%/50% vol.
Catalysts size	Pellets: 50-70 mesh
Reactor	Quartz tube: Ø = 0.6 cm, L=200cm (Cat. = 0,2 g , quartz: 0.2g)

- The size of the Ni partice is around 7- 10 nm after reduction
- Order of activity is Sr>Mg>Y>Ce

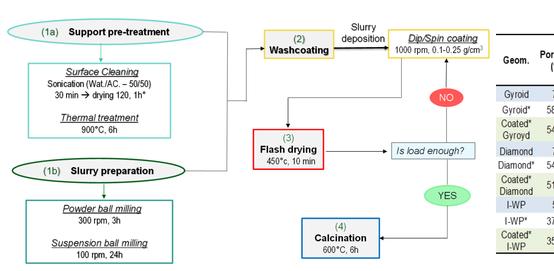


• *TEM analysis* $La_{0.1}Mg_{0.9}NiO_3$





Catalytic activation of TPMS

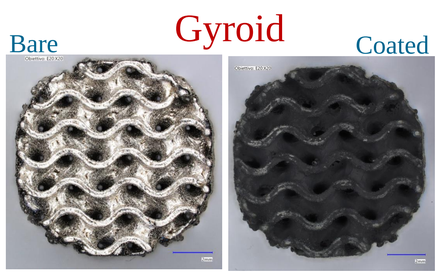


Scheme of the Dip/Spin coating method

Geom.	Porosity (%)	Unit cell (mm)	Sheet size (mm)	Pore size (mm)	Solid Vol. (mm^3)	Fluid Vol. (mm^3)	Solid Density (g/cm^3)	Surface Area (mm^2)	Specific S.A. (mm^2/mm^3)	Effective poros. ($\varepsilon_{eff.}$)	Solid Vol. (cm^3)	Area (cm^2)	Specific S.A. (cm^2/cm^3)	WC $g_{cat}/g_{cat}V_{geo}$ (g/cm^3)
Gyroid	70	3	0.30	1.20	366	811	-	2619	7.15	0.69	0.366	26.19	71.5	
Gyroid*	58.51	3	0.32	1.18	489	689	8.3777	-	-	0.59	0.489	-	-	
Coated* Gyroyd	54.49	3	0.37	1.16	536	642	8.2317	-	-	0.54	0.536	-	-	0.287 0.245
Diamond	70	3	0.23	1.27	368	809	-	3246	8.81	0.69	0.368	32.46	88.14	
Diamond*	54.53	3	0.3	1.30	535	642	8.3121	-	-	0.55	0.535	-	-	
Coated* Diamond	51.01	3	0.32	1.30	577	609	8.2008	-	-	0.51	0.577	-	-	0.292 0.249
I-WP	50	3	0.37	1.22	621	557	-	2848	4.59	0.47	0.621	28.48	46	
I-WP*	37.60	3	0.39	1.32	735	443	8.3834	-	-	0.38	0.735	-	-	
Coated* I-WP	35,07	3	0.45	1.25	765	413	8.2793	-	-	0.35	0.765	-	-	0.260 0.222

TPMS structures feature

Catalyst loading≈0.25 g/cm³

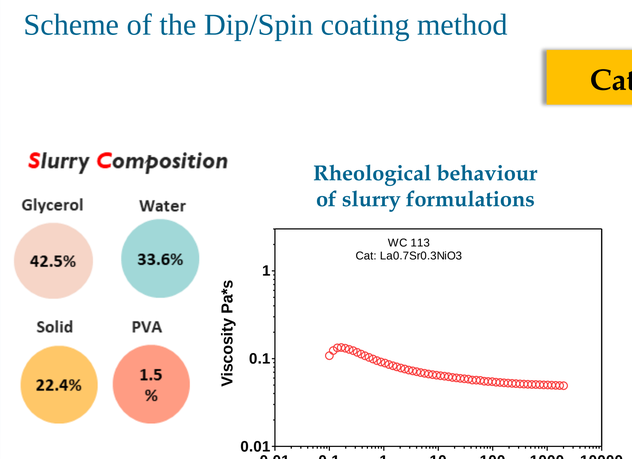


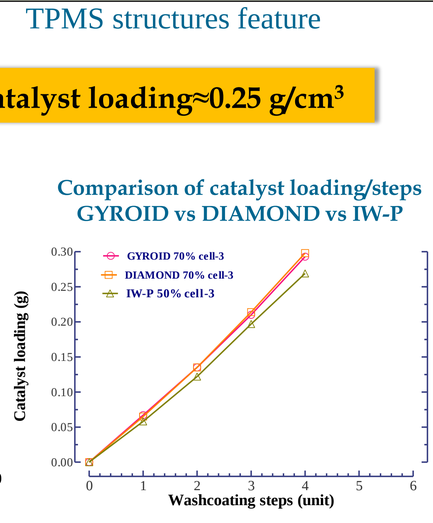
Porosity = 70%, Cell = 3mm, Sheet = 0.30mm Ø = 1cm, L = 1.5cm

Porosity = 70%, Cell = 3mm, Strut = 0.33mm Ø = 1cm, L = 1.5cm

Porosity = 50%, Cell = 3mm Sheet = 0.37mm Ø = 1cm, L = 1.5cm

Bare and coated TPMS structures





CONCLUSION

- Perovskites are promising materials for low-temperature NH_3, as they can incorporate catalytically active metals, provide a good distribution, and regulate the size of the active phase after reduction.
- Between the different formulations studied, the $La_0.1Mg_0.9NiO_3$ and $La_0.7Sr_0.3NiO_3$ perovskites exhibited promising performance at 450°C, achieving a hydrogen productivity (5.52 and 4.89 mmol $H_2 \cdot gcat^{-1}\ min^{-1}$).
- The combined dip/spin coating method can be used to obtain TPMS catalysts with homogeneous and stable catalytic layers irrespective of the geometry of the structured support.

Acknowledgements

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