



Waste biorefinery technologies for accelerating sustainable energy processes

Valorization of CO_2 through dry reforming of CH_4 : Design of $\text{Ni/La}_2\text{O}_3$ catalysts as a function of the preparation method.

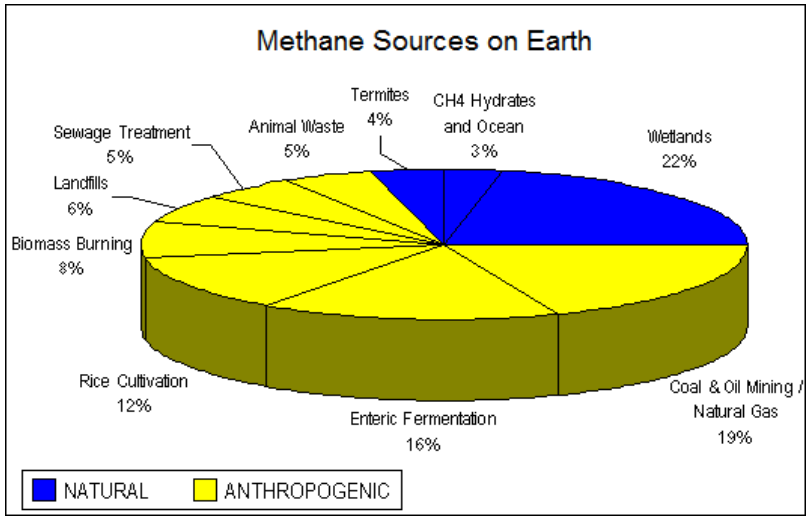
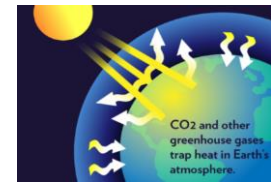
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5th October 2023

CH₄ and CO₂ are the most abundant greenhouse gases and are the main contributors to the recent climate change issues (Noor et al., 2013).



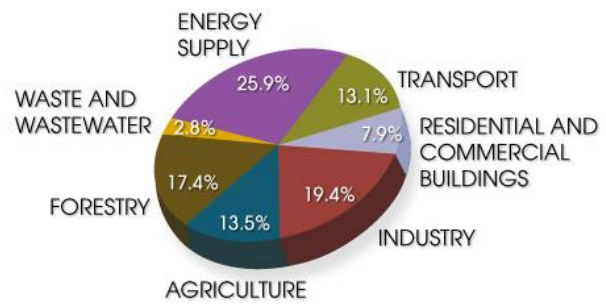
CH₄ is responsible of about 20% of the overall global warming (Wuebbles and Hayhoe, 2002).

Conversion of CH₄ and CO₂ to syngas a building block for Fisher-Tropsch synthesis



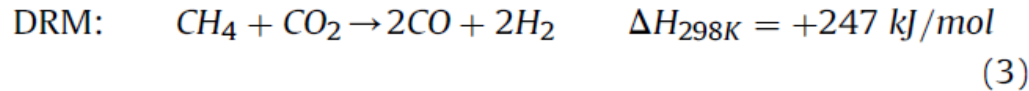
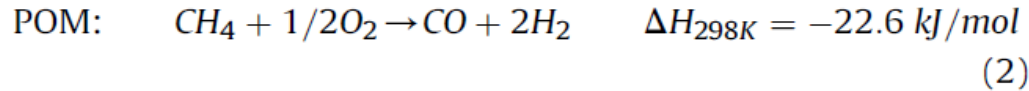
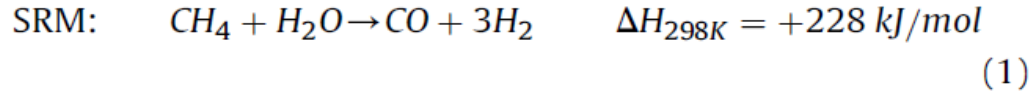
**Methanol
Fuels,
Hydrocarbons
Oxygenates**

Sources of World's CO₂ Emissions



The reforming is the most common method used in industries to produce syngas via the following three reforming processes

The details of the main reactions for reforming processes are summarized as followings:



Among the various strategies SRM is the predominant industrial process for manufacturing hydrogen and syngas.

Renewable and Sustainable Energy Reviews 149 (2021) 111330

Steam reforming of methane: Current states of catalyst design and process upgrading


Haotian Zhang¹, Zhuxing Sun¹, Yun Hang Hu^{*}



CATALYSTS AND SUPPORTS USED

VIII B

26 Fe	27 Co	28 Ni
44 Ru	45 Rh	46 Pd
76 Cs	77 Ir	78 Pt



Catalysts: Ni → active and cheap

Problem: deactivation due to nickel sintering, oxidation and poisoning due to carbon deposition

B. Abdullah et al. / Journal of Cleaner Production 162 (2017) 170–185

Reactions in dry (CO₂) reforming of methane.

Rxn Num	Rxn Name	Rxn Equation	ΔH _{298K} (kJmol ⁻¹)
Main reaction			
1	Dry reforming of methane	CH ₄ + CO ₂ ↔ 2CO + 2H ₂	+247
<i>Side reaction that leads to the decrease in H₂/CO ratio to <1</i>			
2	Reverse water-gas-shift (RWGS)	CO ₂ + H ₂ ↔ CO + H ₂ O	+41
<i>Side reactions that lead to formation of coke (carbon)</i>			
3	Decomposition of methane	CH ₄ ↔ C + 2H ₂	+74.9
4	Disproportionation of CO*	2CO ↔ C + CO ₂	-172.4
5	Hydrogenation of CO ₂	CO ₂ +2H ₂ ↔ C + 2H ₂ O	-90
6	Hydrogenation of CO**	H ₂ + CO ↔ H ₂ O + C	-131.3

*Boudouard reaction

**Reverse C gasification

- **Boudouard reaction and CH₄ decomposition are mostly responsible for carbon formation in the range 550-700 °C. [Energy Fuels 1996;10(4):896–904].**

Optimization of Ni-Based Catalysts for Dry Reforming of Methane via Alloy Design: A Review

LiNan Huang, Danyang Li, Dong Tian, Lei Jiang, Zhiqiang Li, Hua Wang, and Kongzhai Li*

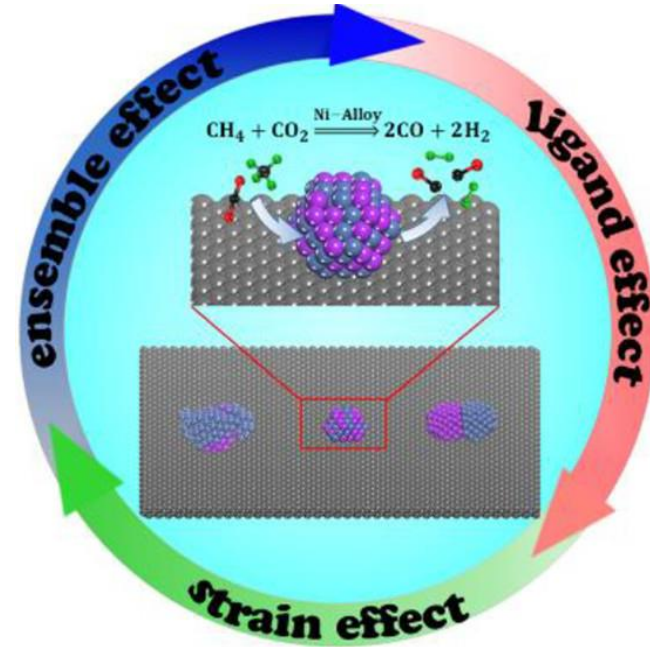
Energy Fuels 2022, 36, 10, 5102–5151



Rapid deactivation of Ni-based catalysts caused by carbon deposition and/or active metal sintering: main drawback for large-scale application of DRM.



The design of bimetallic alloy catalysts has been considered as an effective strategy to improve the activity and stability of Ni-based catalysts.



**Ni/La₂O₃ catalysts for dry reforming of methane:
Effect of La₂O₃ synthesis conditions on the
structural properties and catalytic performances**

M. Grabchenko, G. Pantaleo, F. Puleo, O. Vodyankina, L.F. Liotta*, International Journal of Hydrogen Energy, Volume 46, 2021, 7939-7953



Aim of the work

✓ Investigation of the effects of the experimental conditions used during La₂O₃ preparation:

✓ Acid pH conditions (pH ~ 2)

✓ Basic pH conditions (pH ~ 9)



✓ Study of Nickel (10wt%) catalysts supported over La₂O₃ for DRM

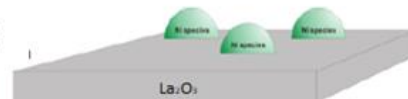


La₂O₃ CA 800 °C
La₂O₃ CA-NH₃ 800 °C

Deposition of 10% wt Ni



Incipient Wetness
Impregnation (IWI)



10%Ni-La₂O₃ CA 600 °C
10%Ni-La₂O₃ CA-NH₃ 600 °C

WIRE

Table 1 – Textural properties of La CA and La CA-NH₃ and Ni supported catalysts (as calcined).

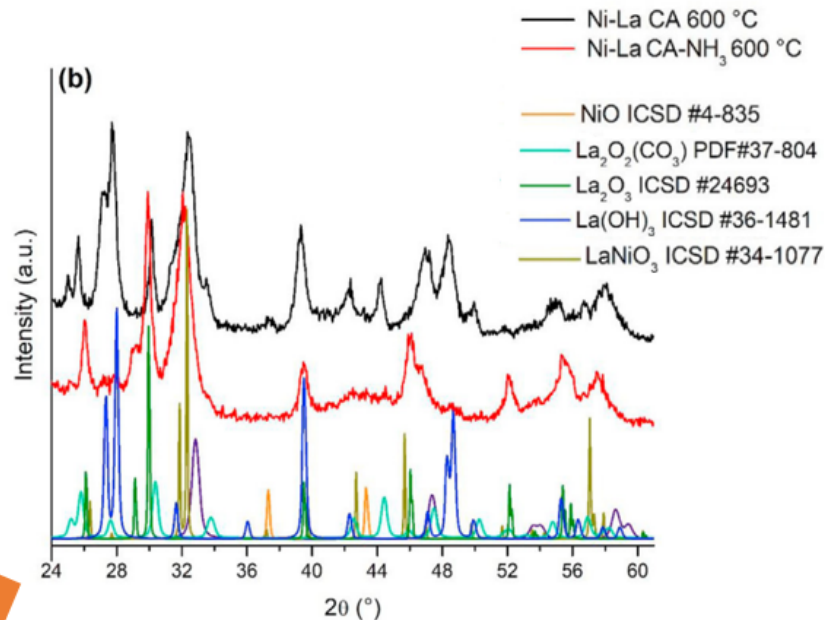
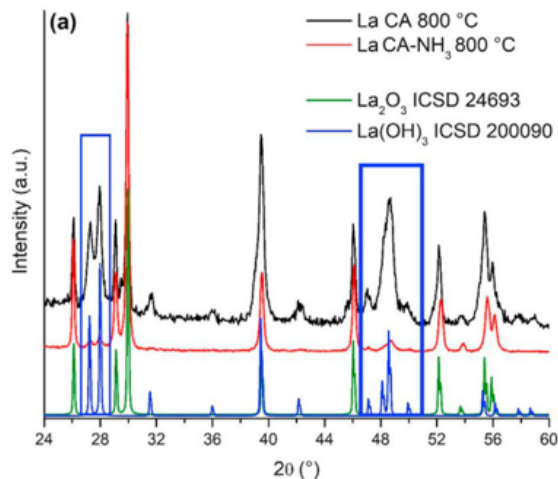
Samples	SSA (m ² /g)	Mean pore size (nm)	Cumulative pore volume (cm ³ /g)	Crystallite size (nm)		
				La ₂ O ₃	La(OH) ₃	NiO
La CA	9.0	8.2	0.055	49.0	25.0	–
La CA-NH ₃	15.2	7.4	0.058	34.5	3.0	–
Ni-La CA	8.3	8.5	0.047	nd	19.0	8.0
Ni-La CA-NH ₃	10.5	9.0	0.052	20.0	15.0	nd

XRD characterization

Peaks attributed to La₂O₃ and La(OH)₃ were detected in both supports calcined at 800 °C.

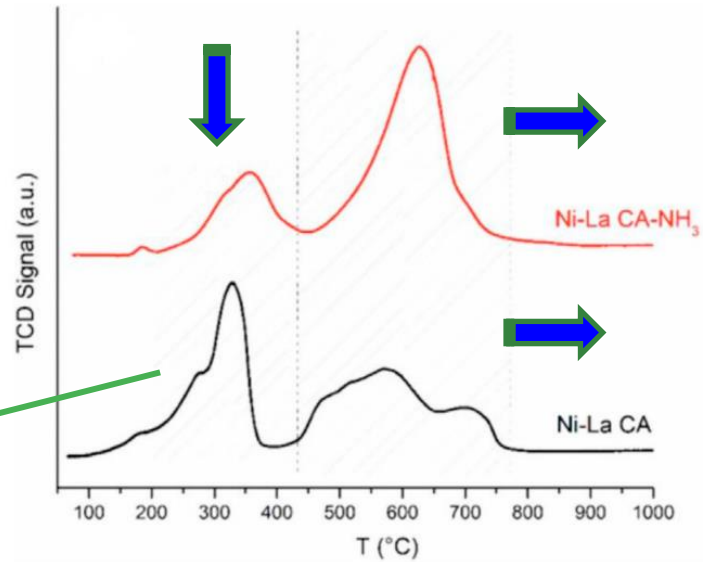
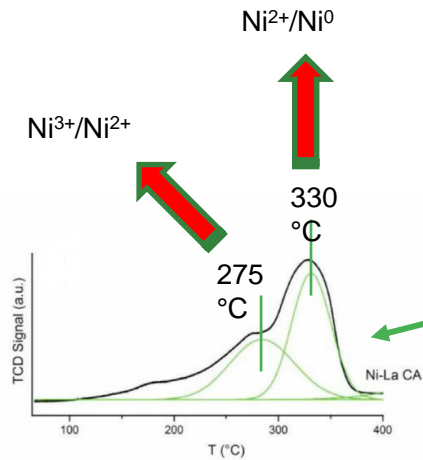
Peaks of La(OH)₃ were more intense in the case of the La CA; in the LaCA-NH₃ the La₂O₃ phase is favored with respect to La(OH)₃

NiLaCA-NH₃ contains LaNiO₃ along with La(OH)₃ and La₂O₃, no NiO. La(OH)₃, LaNiO₃ and NiO were detected as the main phases in NiLaCA. La₂O₃ was also present



Investigation of calcined catalysts by H₂-TPR

Large crystallites scarcely interacting with the support

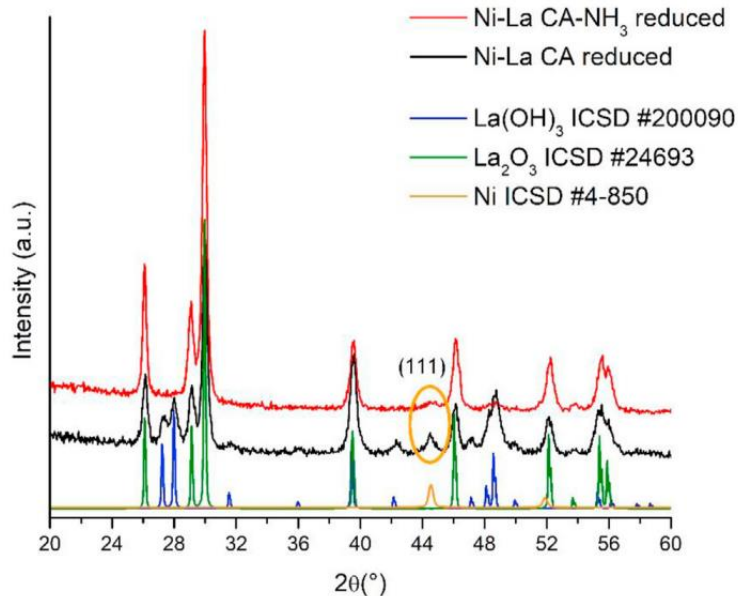


Small crystallites strongly interacting with the support

XRD of reduced catalysts

Before each catalytic test in DRM, the catalysts were pretreated at 350 °C for 30 min in 5 vol% O₂/He flow and then at 750 °C for 1h in 5%H₂/Ar flow.

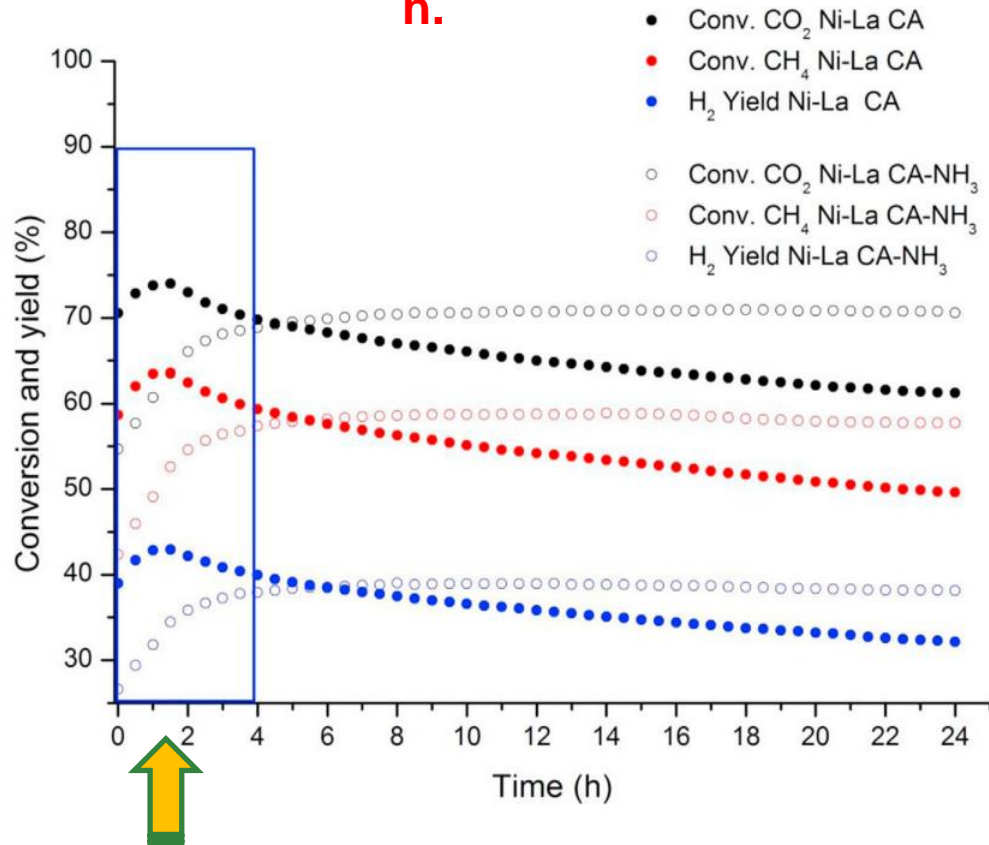
WIRE



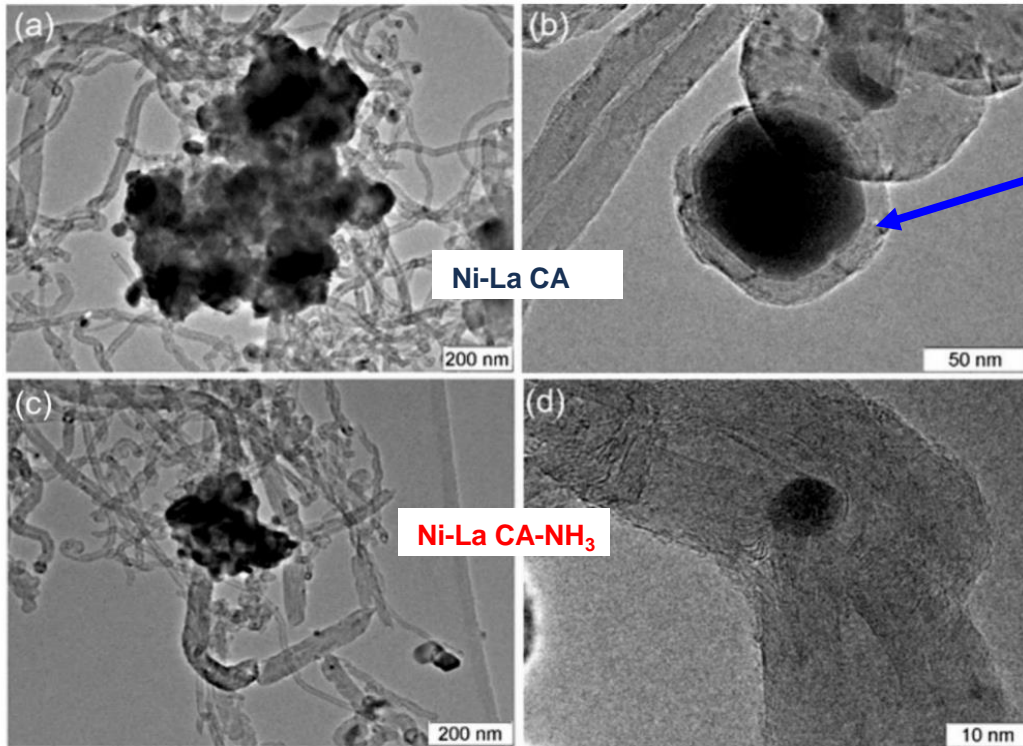
NiLa CA-NH₃: La₂O₃ and weak and large feature of metallic Ni were detected (~ 2 nm by HRTEM).

NiLa CA: La₂O₃ and La(OH)₃ phases and a peak of metallic Ni corresponding to particles with mean size of ~20 nm as estimated by Scherrer's equation

Long run tests at 650 °C for 24 h.

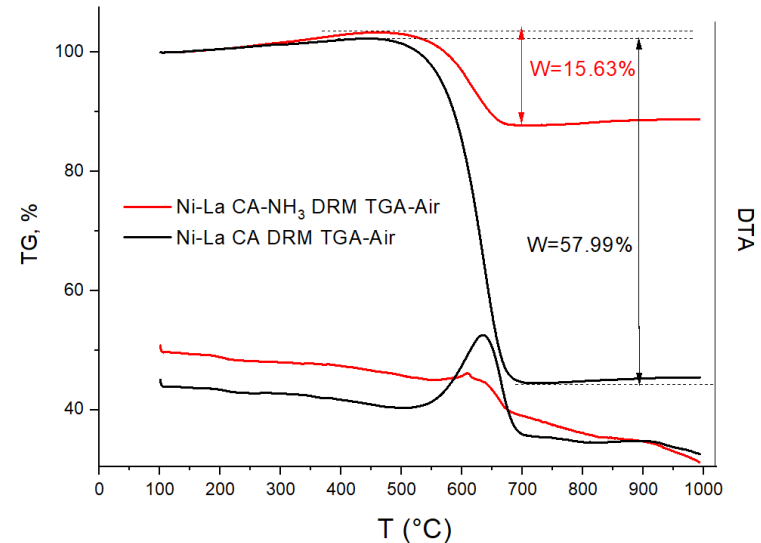


The lower catalytic activity of Ni-La CA-NH₃ can be due to very small Ni particles interacting with the support that are activated after 4h long run



Large sintered Ni particle with size ~80 nm

TGA-air after DRM Long Run Test 650°C 24h

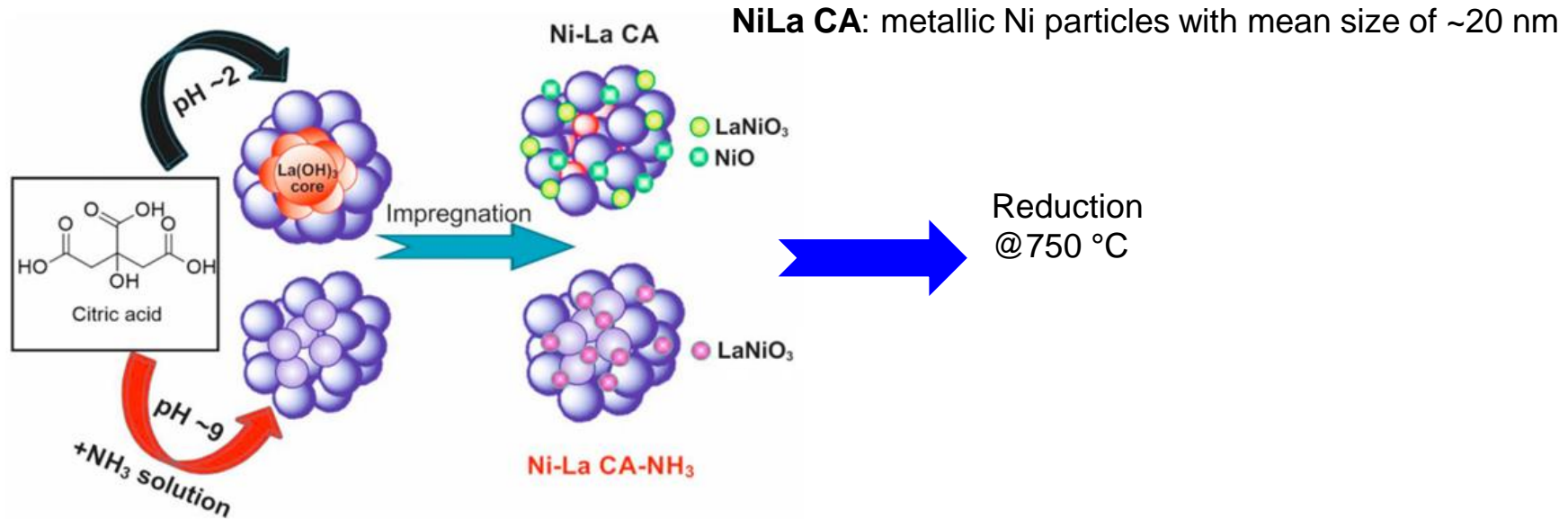


TEM HR images of carbon formation after DRM reaction over Ni-La CA (a, b) and Ni-La CA-NH₃ (c, d) catalysts

Ni-La CA: Two types of carbon, filaments and large aggregated of La₂O₃ packed with carbon

Conclusions

Effect of NH_3 addition on the structural properties of La_2O_3 oxides and the corresponding Ni catalysts.

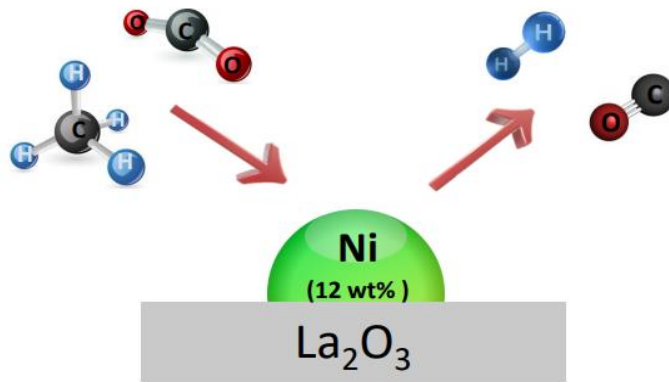


Future perspectives: investigation of other preparation methods

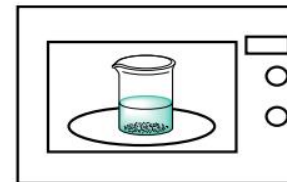
Hydrothermal synthesis (HT)



- One pot (**12Ni-La HT one**)
- Wetness impregnation (**12Ni/La HT WI**)



Microwave assisted synthesis (MW)



- One pot (**12Ni-La MW one**)
- Wetness impregnation (**12Ni/La MW WI**)

Research team @CNR-ISMN and collaboration



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Centenary !!!



*CNR Research Area
in Palermo*

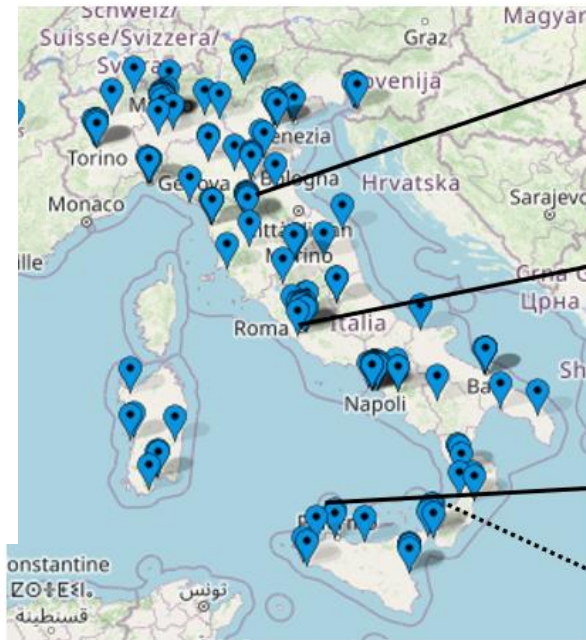
Main research fields are:

❑ **CATALYTIC PROCESSES FOR ENVIRONMENTAL PROTECTION AND ENERGY SUSTAINABILITY**

❑ MATERIALS FOR CULTURAL HERITAGE CONSERVATION

❑ EXTRACTION OF BIOACTIVE MOLECULES

❑ FUNCTIONAL HYBRID ORGANIC AND INORGANIC MATERIALS FOR HIGH-TECH TEXTILE; ENVIRONMENTAL REMEDIATION



CNR-ISMN BOLOGNA

CNR-ISMN ROMA

CNR-ISMN PALERMO

CNR-ISMN Small unit @ Messina University

More than 100 STAFF MEMBERS at CNR-ISMN;
25 people in Palermo



Greetings from Sicily and from Palermo!!

