The French Research
network on Hydrogen energy

UNITÉ DE CATALYSE
ET CHIMIE DU SOLIDE

Project FLEXISOC

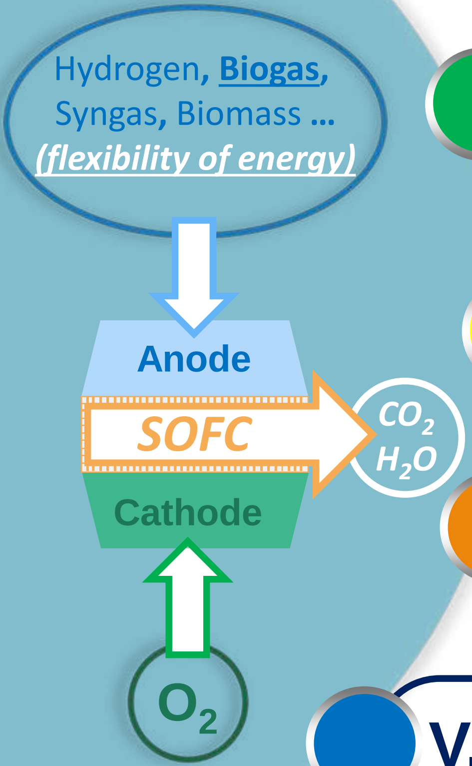
High throughput approach to optimize Ni-based catalyst for dry reforming of methane: impact of Nickel-support interaction

Yuanshuang ZHENG, Theresa AL-BAYEH, Marcia ARAQUE-MARIN*

Wednesday, in Saint-Gilles, 24th May 2023

Université de Lille
RÉPUBLIQUE FRANÇAISE
cnrs
UNIVERSITÉ D'ARTOIS
centralelille
institut Chevreul
anr agence nationale de la recherche
AU SERVICE DE LA SCIENCE

Table of Contents



Hydrogen, **Biogas**, Syngas, Biomass …
(flexibility of energy)

Anode

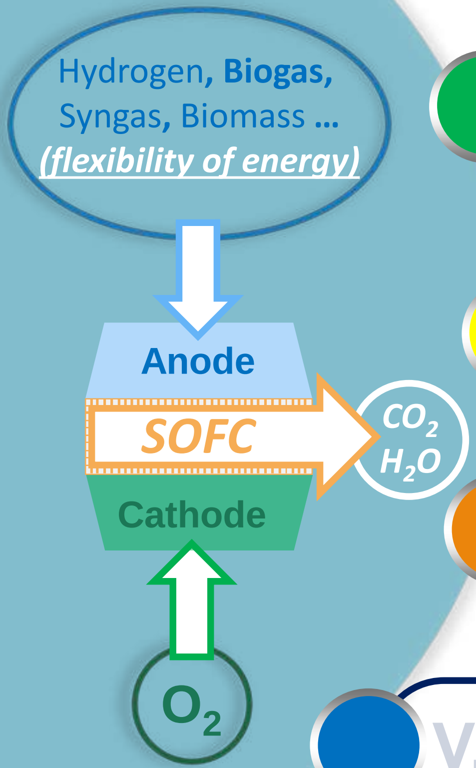
SOFC

Cathode

CO_2
H_2O

O_2

Table of Contents


Hydrogen, **Biogas,** Syngas, Biomass …
(flexibility of energy)

Anode

SOFC

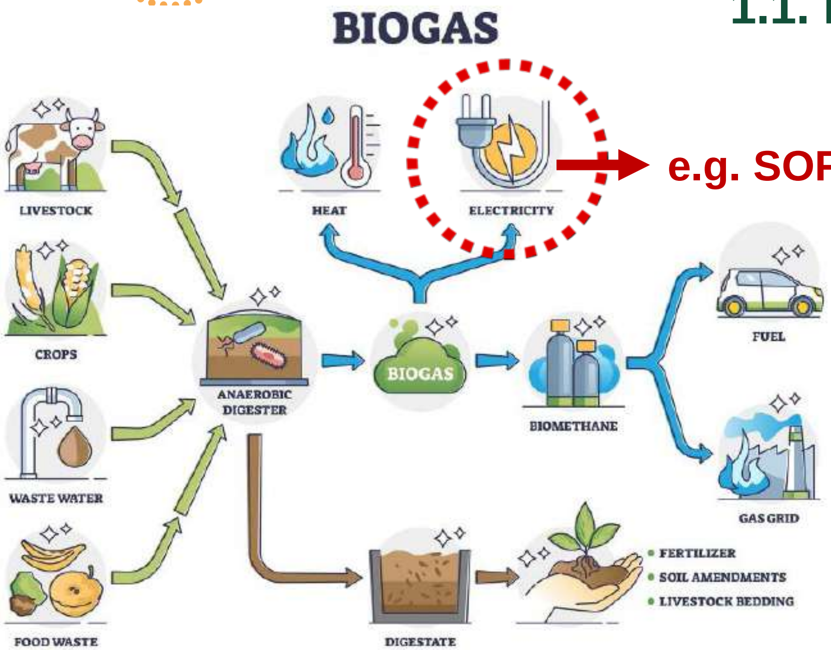
Cathode

CO_2
H_2O

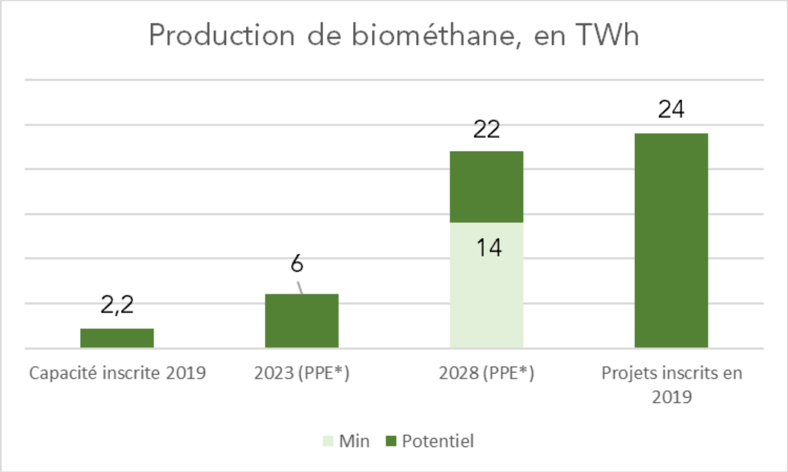
O_2

I. Introduction

1.1. Biogas as a flexible energy source for SOFC



e.g. SOFC



Biogas: Future plan & Situation in France [2]: (Biomethane as Main component of Biogas)

- Production above government forecasts
- With more and more competitive price

PPE (Programmations pluriannuelles de l'énergie)
Evolution of the purchase price – biogaz

Biogas production grows and prices fall :

- The Multiannual **Energy** Program defines objectives that the sector will exceed from 2023. Projections for the sector aim to reach **12 TWh in 2023** and **30 TWh in 2030**.
- The production **price** should **fall by 40% by 2028** due to the industrialization of the sector and processes.

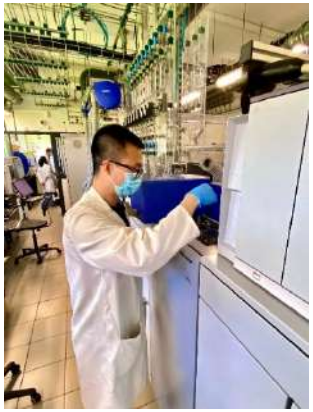
---

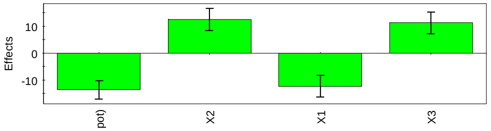
[1] – Kougias, P.G. et al., Biogas and its opportunities—A review. *Front. Environ. Sci. Eng.* 12, 14 (2018).

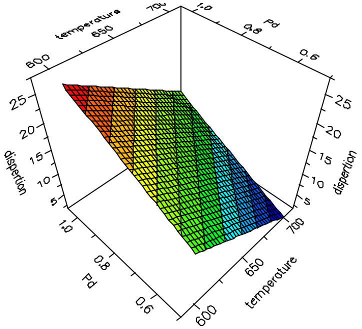
[2] – GRDF: Le biométhane atteindra les objectifs de la PPE* 2028 avec 4 ans d'avance

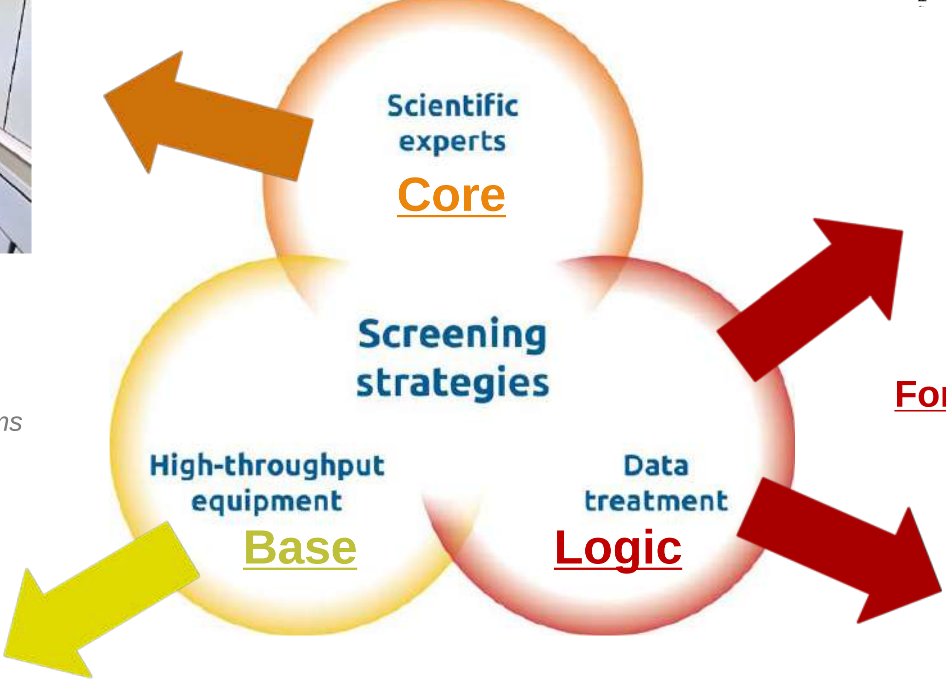
I. Introduction

1.2. High throughput technology









Scientific experts

Core

Screening strategies

High-throughput equipment

Base

Data treatment

Logic

Catalyst design

Formulation des materials

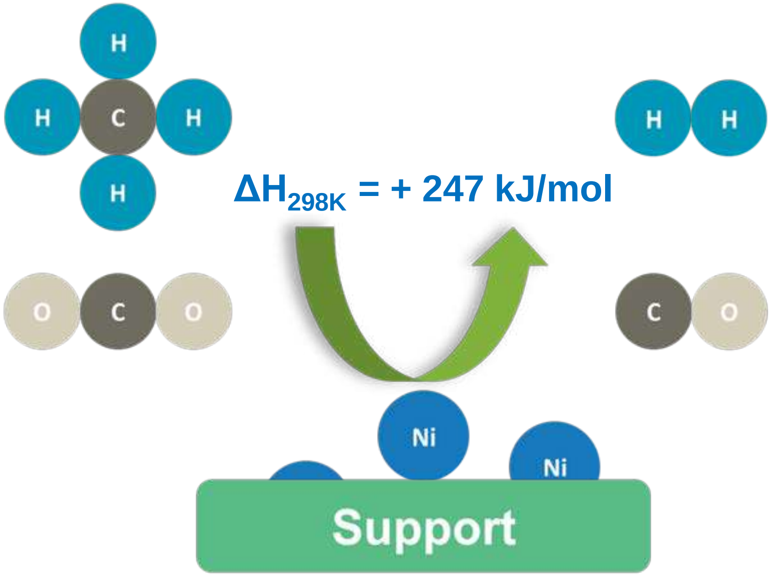
Flowrence 1220 – Avantium Systems

Control & monitoring

REALCAT platform was funded by the French National Research Agency (ANR-11-EQPX-0037) within the frame of the ‘Future Investments’ program (PIA). The Nord-Pas-de-Calais Region and the FEDER are acknowledged for their financial contribution to the equipment of the platform.

I. Introduction

1.3. Dry reforming of methane by supported Ni-catalyst



ΔH_{298K} = + 247 kJ/mol

Dry reforming of methane

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$$

- Hydrogen production
- Strong endothermic reaction (energy storage)
- Conversion of two greenhouse gases

Challenges for long-life SOFC anode materials: Ni-catalysts

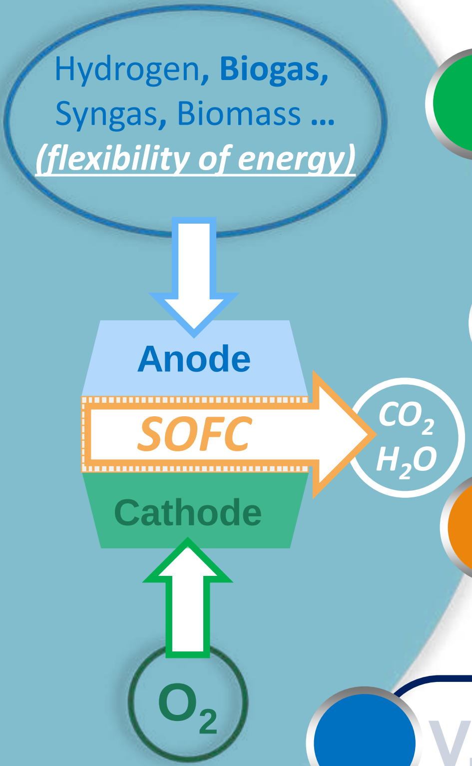
- Avoid coke deposit
- Avoid sulfur poisoning

$$CH_4 Conversion\ (\%) = \frac{CH_{4,in} - CH_{4,out}}{CH_{4,in}} \text{ x } 100\%$$

$$CO_2 Conversion\ (\%) = \frac{CO_{2,in} - CO_{2,out}}{CO_{2,in}} \text{ x } 100\%$$

$$Yield\ of\ H_2 (\%) = \frac{H_{2,out}}{2CH_{4,in}} \text{ x } 100\%$$

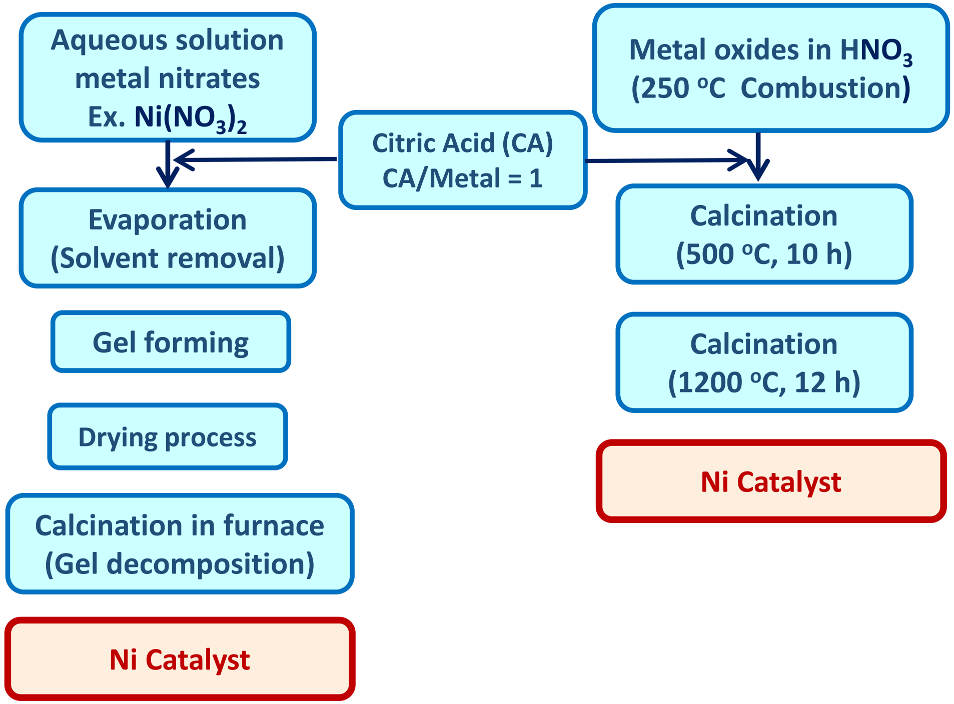
Table of Contents



II. Pathway to catalyst synthesis

2.1. Sol-gel route & impregnation method

1. Sol-gel (citric acid routes)



Aqueous solution metal nitrates Ex. $Ni(NO_3)_2$

Citric Acid (CA) CA/Metal = 1

Evaporation (Solvent removal)

Gel forming

Drying process

Calcination in furnace (Gel decomposition)

Ni Catalyst

Metal oxides in HNO_3 (250 °C Combustion)

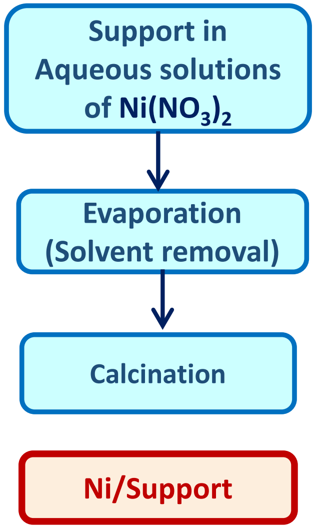
Calcination (500 °C, 10 h)

Calcination (1200 °C, 12 h)

Ni Catalyst

The sol-gel method can promote **strong interaction** between the **active nickel species** and the **support**, the modification of catalyst can change the surface defects and increase the oxygen vacancies.

2. Impregnation



Support in Aqueous solutions of $Ni(NO_3)_2$

Evaporation (Solvent removal)

Calcination

Ni/Support

The impregnation method can anchor the **nickel species on the catalyst surface** but **weakening interaction with the support** could lead to particle accumulation and loss of active nickel species.

---

1 – P. B. Managutti et al., ACS Appl. Mater. Interfaces 2021, 13, 35719–35728.

2 – P. B. Managutti et al., ACS Appl. Mater. Interfaces 2023. xx, xxxxx-xxxxx.

II. Pathway to catalyst synthesis

2.2. Coprecipitation & mechanochemical approach

3. Coprecipitation

Adding dropwise a solution containing dissolved precursor salts [Ex. **$Ni(NO_3)_2$**] into triethylamine diluted in methanol solution

↓

Solvent removal by filtration

↓

Drying at 100 °C for 24h

↓

Calcination in furnace in air at 500 °C for 4h

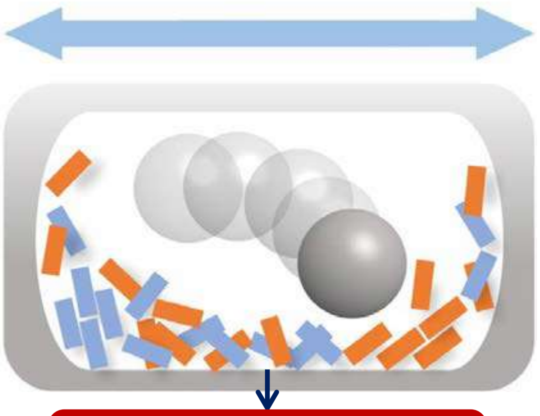
↓

Ni Catalyst

The conventional coprecipitation method is suitable for preparation of Ni doped catalyst from cerium zirconium **solid solution**, and take advantage of the **high oxygen mobility** and relative **high temperature stability** of cerium zirconium support.

4. Ballmill

Mechanochemical approach



↓

Ni Catalyst

The Ballmill mechanochemical method provides a more **uniform synthesis** method of different mixed oxides and better **control of the distribution of catalyst particles** and catalytic oxides [1].

Condition:

~ 1.7 g powder (1.5 g support + 0.186 g NiO).

~ 20 g ball (zirconia ø = 5 mm).

~ 2 g ethanol as solution.

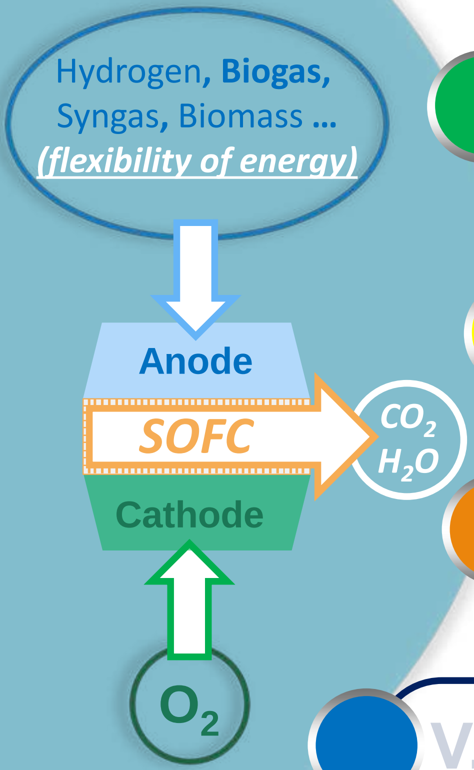
~ 2 hours grinding

Figure – HOKKAIDO UNIVERSITY

Mechanochemical: VD: Dr. Victor Duffort;

Coprecipitation: LD: Dr. Louise Duhamel.

Table of Contents



III. High throughput approach of catalysts

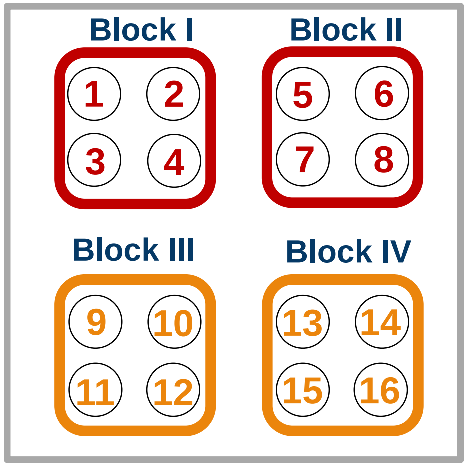
3.1. Catalysts for high throughput screening

Reactor No.	Catalyst	Synthesis	Pretreatment Temperature	Characterizations	Reaction
1	$CeNi_{0.1}$	Coprecipitation	750 ºC	XRF	Obtained
2	$La_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$	Sol-gel	750 ºC	XRF	Obtained
3	**$Pr_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$**	**Sol-gel**	**750 ºC**	**XRF/H_2-TPR**	**Obtained**
4	**$La_{0.5}Sr_{1.5}Mn_{0.7}Ni_{0.3}O_4$**	**Sol-gel**	**750 ºC**	**XRF/H_2-TPR**	**Obtained**
5	$Pr_{1.5}Sr_{1.5}Mn_{1.5}Ni_{0.4}Fe_{0.1}O_7$	Sol-gel	750 ºC	XRF	Obtained
6	$Pr_{0.5}Sr_{1.5}Mn_{1.5}Ni_{0.25}Fe_{0.25}O_7$	Sol-gel	750 ºC	XRF	Obtained
7	SiC	-	750 ºC	-	Obtained
8	YSZ	Commercial	750 ºC	XRF	Obtained
9	elcogen half-cell YSZ_Ni	Commercial	450 ºC	XRF	Obtained
10	cellules GDC/NiO FENTO	Commercial	450 ºC	XRF	Obtained
11	8YSZ_NiO, 10%Ni	Ballmill	450 ºC	XRF/H_2-TPR	Obtained
12	**HSA GDC+NiO, 10% Ni**	**Ballmill**	**450 ºC**	**XRF/H_2-TPR**	**Obtained**
13	**Ni-CZS**	**Pseudo Sol-gel**	**450 ºC**	**XRF/H_2-TPR**	**Obtained**
14	LSA GDC+NiO, 10%Ni	Ballmill	450 ºC	XRF/H_2-TPR	Obtained
15	Ni/YZ	Impregnation	450 ºC	XRF/H_2-TPR	Obtained
16	**$CeZr_{0.5}Ni_{0.5}$**	**Coprecipitation**	**450 ºC**	**XRF/H_2-TPR**	**Obtained**

3, 4, 12, 13 and 16: high & medium conversion of CH_4 & CO_2 .

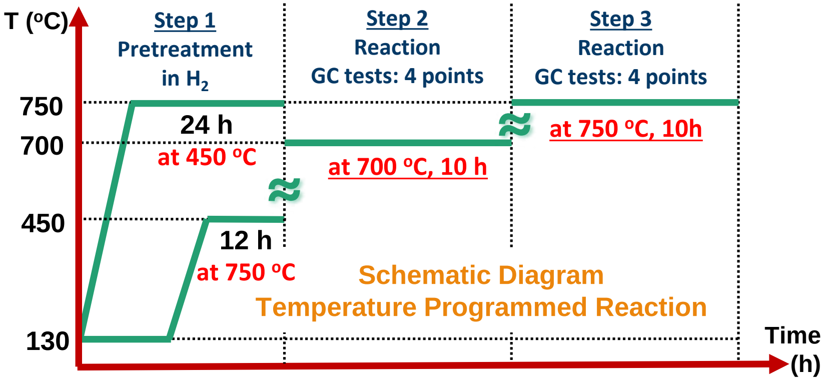
III. High throughput approach of catalysts

3.2. Conditions of high throughput screening

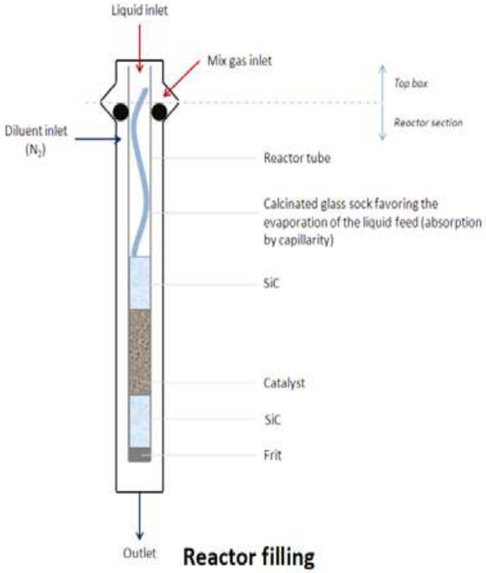


Blocks & Reactors composition

Pretreatment in H_2	Block I & II	Block III & IV
Temperature	750 ^{o}C	450 ^{o}C
Duration	24h	12h
Block	I and II	III and IV



Schematic Diagram
Temperature Programmed Reaction

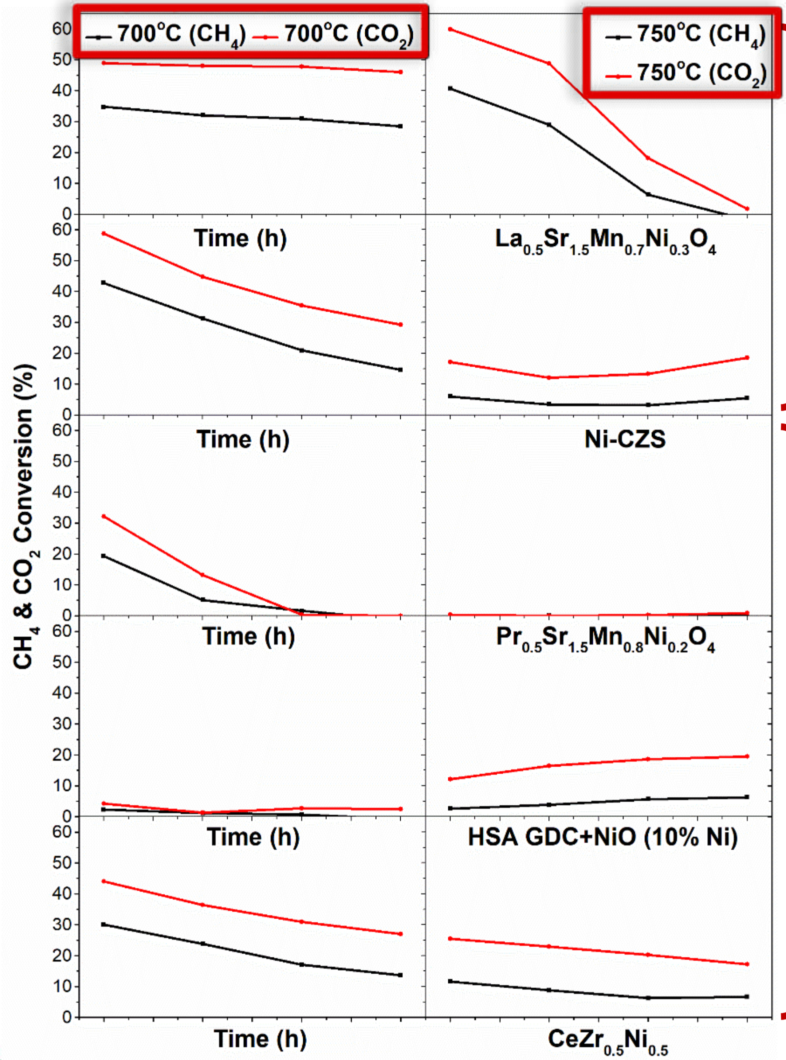


Reactor filling

Catalytic test	Test 1	Test 2
Temperature	700 ^{o}C	750 ^{o}C
Duration	10h	10h
Catalyst mass	20 mg	
CH_4 & CO_2	6.67 ml/min (0.4 L/h) per gas per reactor	
He	3.33 ml/min (0.2 L/h) per gas per reactor	
GC test	4 points/catalyst, ~10 min/analysis	
GHSV	35 000h^{-1}	

III. High throughput approach of catalysts

3.3. Results of CH_4 & CO_2 conversion of high throughput screening



High conversion

Medium conversion

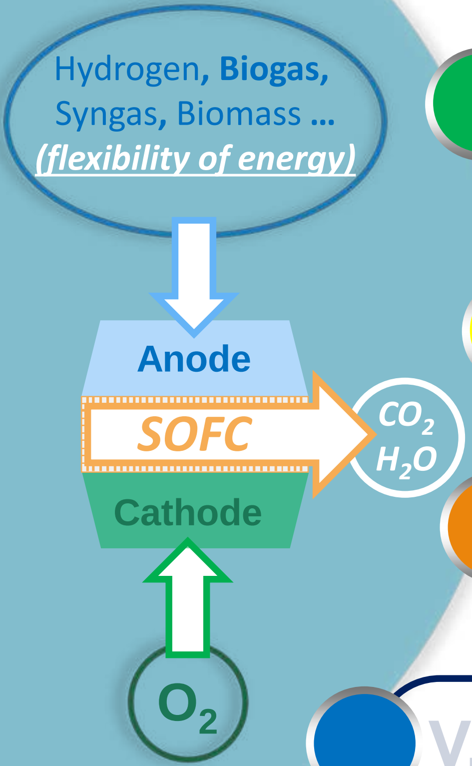
Description:
Catalytic conversions rate (high & medium) of **CH_4 & CO_2** of **5** typical **pre-reduced catalysts**

Discussion:
Global catalytic activity at **700 ºC** and **750 ºC** of CH_4 and CO_2 conversions illustrate different trends due to diverse **synthesis methods**, **physicochemical properties** and **elemental composition.**

Conclusion:
The **modified perovskite (Site-A & Site-B elemental substitution)** and **cerium zirconium solid solution (Gd & Sm incorporation)** show relatively **better conversion** rate.

Need to do:
Elemental analysis in first & H_2-TPR to study reduction properties.

Table of Contents



Hydrogen, **Biogas**, Syngas, Biomass **…**
(flexibility of energy)

Anode

SOFC

Cathode

CO_2
H_2O

O_2

IV. Elemental analysis & Reducibility

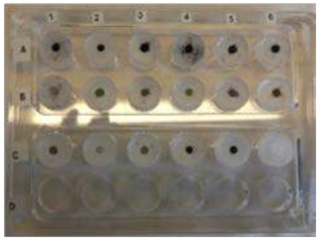
4.1. Nickel based catalysts – XRF elemental analysis

Analyser: M4 Tornado – Bruker

How ? – 1.X-ray spectrometer. 2.Sample support. 3.fluorescence X detection.

Why ? – an energy dispersive micro X-ray spectrometer that can be used for **mass elemental analysis** of **metal** materials:

Advantages: Efficient and nondestructive



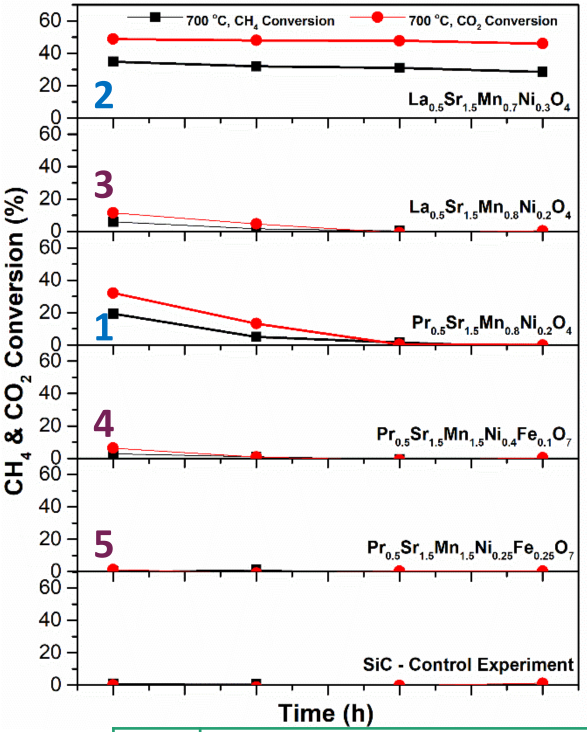
1. Generally, the **Ni elemental proportion** in metals calculated by theory is **close** to XRF analysis results.
2. Considering the HT reaction results, the XRF results of divers catalyst has positive significance for **optimizing catalyst composition (Goal of this study)** for **reducing Ni** content and **selection** of **supports**, preventing sintering and avoiding carbon deposition.

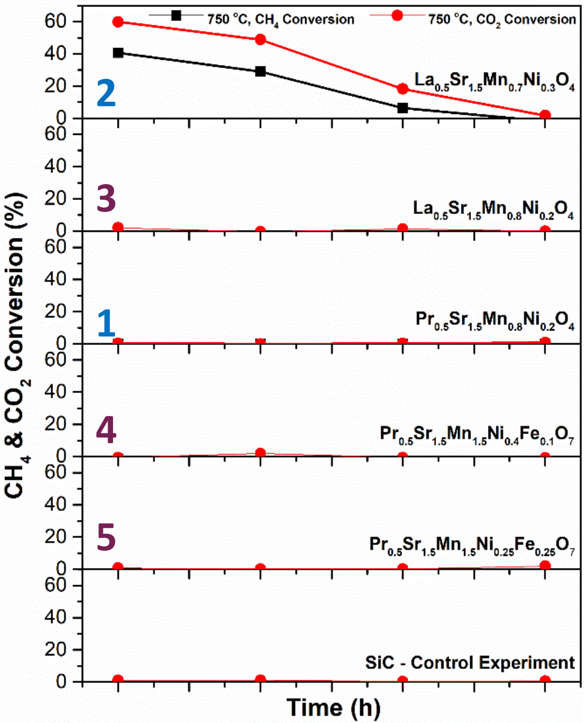
Catalysts	Theoretical Ni (metal mass %)	XRF Ni (metal mass %)
Ni/YZ	10%	9.4%
Ni-CZS	10%	11.5%
8YSZ_Ni 10%Ni	10%	9.3%
HSA GDC+NiO 10%Ni	12.4% NiO	12.3% NiO
LSA GDC+NiO 10%Ni	12.4% NiO	12.4% NiO
$Pr_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$	4.6%	4.3%
$La_{0.5}Sr_{1.5}Mn_{0.7}Ni_{0.3}O_4$	6.8%	6.3%
$CeZr_{0.5}Ni_{0.5}$	13.6%	15.1%
YSZ	Commercial	0
$CeNi_{0.1}$	4%	2.7%
Ni/CY	10%	11.4%
Ni/CGO	10%	14.3%
elcogen half-cell YSZ_Ni	Commercial	37.1%
cellules GDC/NiO FENTO	Commercial	58%
$La_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$	4.6%	4.1%
$Pr_{1.5}Sr_{1.5}Mn_{1.5}Ni_{0.4}Fe_{0.1}O_7$	5.2%	4.6%
$Pr_{1.5}Sr_{1.5}Mn_{1.5}Ni_{0.25}Fe_{0.25}O_7$	3.2%	3.1%
$Pr_{0.5}Sr_{1.5}Mn_{0.9}Ni_{0.1}O_4$	2.3%	2.1%

Elcogen: Commercial supplier. Cellules: Commercial ceramic cellules.
8YSZ: 8 mol% Y_2O_3 stabilized ZrO_2. LSA: 12 m^2/g. HSA: 23 m^2/g.

IV. Elemental analysis & Reducibility

4.1. Nickel incorporated perovskites – XRF elemental analysis vs. reactivity





No.	Catalysts	Theoretical Ni (metal mass %)	XRF Ni (metal mass %)
1	$Pr_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$	4.6%	4.3%
2	$La_{0.5}Sr_{1.5}Mn_{0.7}Ni_{0.3}O_4$	6.8%	6.3%
3	$La_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$	4.6%	4.1%
4	$Pr_{1.5}Sr_{1.5}Mn_{1.5}Ni_{0.4}Fe_{0.1}O_7$	5.2%	4.6%
5	$Pr_{1.5}Sr_{1.5}Mn_{1.5}Ni_{0.25}Fe_{0.25}O_7$	3.2%	3.1%

Ruddlesden-Popper perovskites :
$A_{n+1}B_nO_{(3n+1)\pm\delta}$

(2) $La_{0.5}Sr_{1.5}Mn_{0.7}Ni_{0.3}O_4$ showed best activity and stability generally. When 750 °C increasing conversion in first but decreasing. Ni inverse exsolution [1,2]

(1) $Pr_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$ & (3) $La_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$ showed activity when 700 °C, but nearly no conversion when 750 °C.

(1) $Pr_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$ vs. (3) $La_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$
Pr substitution: positive impact for
Formula **$A_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$**

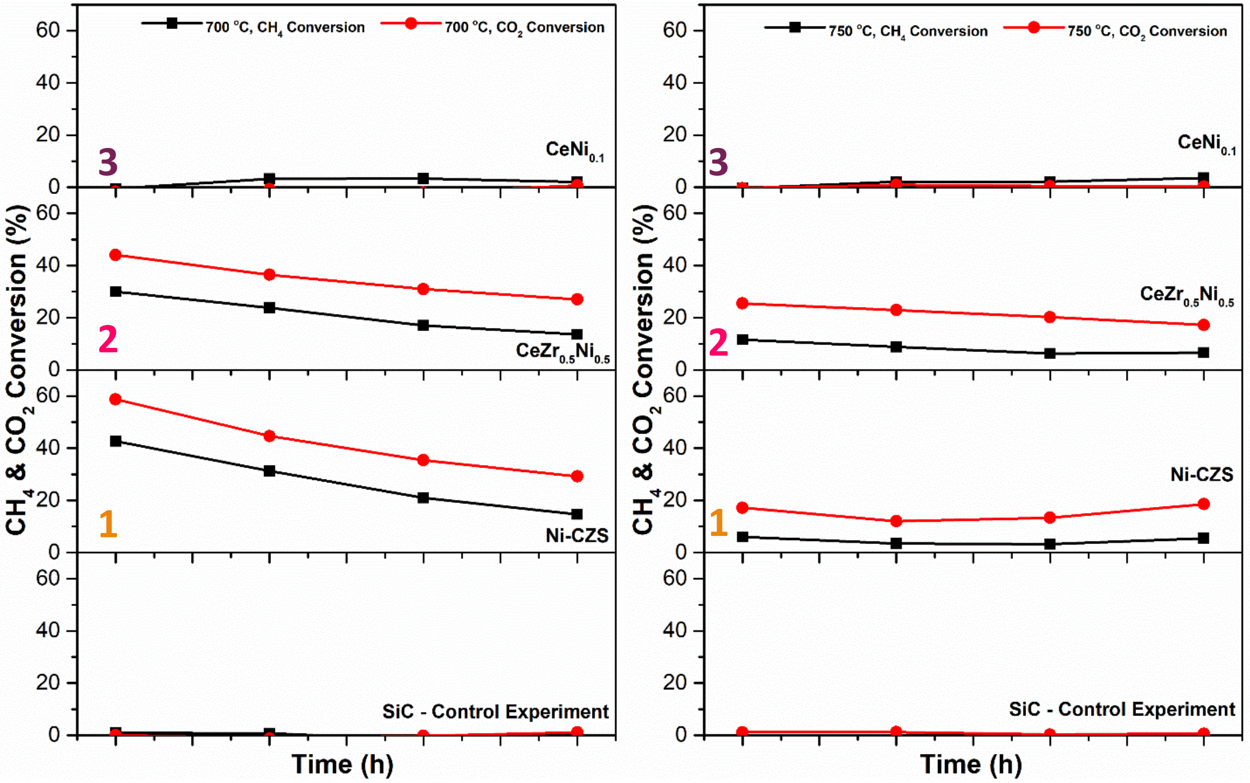
(2) $La_{0.5}Sr_{1.5}Mn_{0.7}Ni_{0.3}O_4$ vs. (3) $La_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$
More Ni doping: positive impact for
Formula **$La_{0.5}Sr_{1.5}Mn_xNi_{1-x}O_4$**

(4) $Pr_{1.5}Sr_{1.5}Mn_{1.5}Ni_{0.4}Fe_{0.1}O_7$ vs. (5) $Pr_{1.5}Sr_{1.5}Mn_{1.5}Ni_{0.25}Fe_{0.25}O_7$
More Ni doping is better to
Formula **$Pr_{1.5}Sr_{1.5}Mn_{1.5}Ni_xFe_{1-x}O_7$**
Fe doping goal : for coke oxydation.

1 – P. B. Managutti et al., ACS Appl. Mater. Interfaces 2021, 13, 35719–35728.
2 – P. B. Managutti et al., ACS Appl. Mater. Interfaces 2023.
3 – Y-M Park et al., Inter. Jour. of Hydrogen Energy,36, 15, 2011, 9169-9179.

IV. Elemental analysis & Reducibility

4.1. Nickel incorporated Cerium solid oxide – XRF elemental analysis vs. reactivity



No.	Catalysts	Theoretical Ni (metal mass %)	XRF Ni (metal mass %)
1	Ni-CZS	10%	11.5%
2	$CeZr_{0.5}Ni_{0.5}$	13.6% (No counting O)	15.1% (No counting O)
3	$CeNi_{0.1}$	4%	2.7%

Catalysts based on cerium oxide

On the whole :

Ni-incorporation into cerium oxide : **positive impact** for **cerium based solid oxide**.

Global profiles :

Increasing temperature from 700 °C to 750 °C : **negative impact** for **cerium based solid oxide**.

$CeZr_{0.5}Ni_{0.5}$ vs. $CeNi_{0.1}$:

Zr doping in cerium oxide : **positive** impact for dry reforming of methane reactivity.

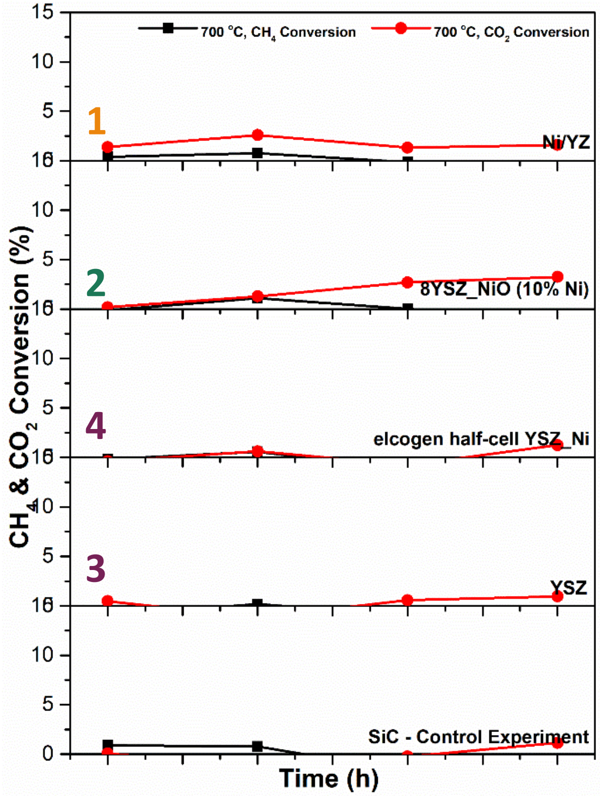
$CeZr_{0.5}Ni_{0.5}$ vs. Ni-CZS :

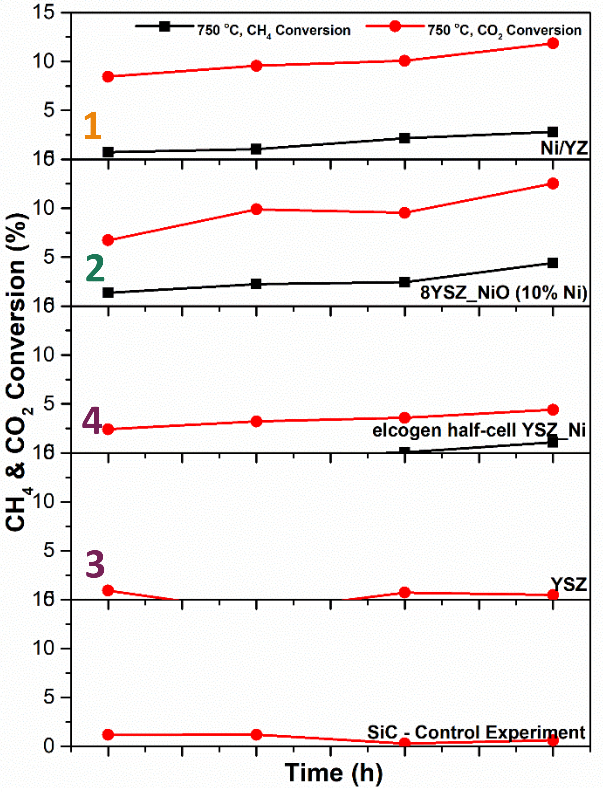
Sm doping in cerium zirconium oxide : **positive** impact for dry reforming of methane reactivity.

1 – Y-M Park et al., Inter. Jour. of Hydrogen Energy, Vol 36, 15, 2011, 9169-9179.

IV. Elemental analysis & Reducibility

4.1. Nickel based catalysts – XRF elemental analysis vs. reactivity





1. Sic vs. **(3) YSZ support : no activity.**
2. **(4) Commercial one (elcogen half-cell YSZ_Ni) with high Nickel doping 37% percentage : nearly no conversion at 700 ºC & such low conversion at 750 ºC.**
3. **(1) Ni/YZ & (2) 8YSZ_Ni 10%Ni : increasing conversion from 700 ºC to 750 ºC.**
4. **(1) Ni/YZ & (2) 8YSZ_Ni 10%Ni : similar activity** during HT tests **because of Ni species on surface of YSZ**

Catalysts based on YSZ support

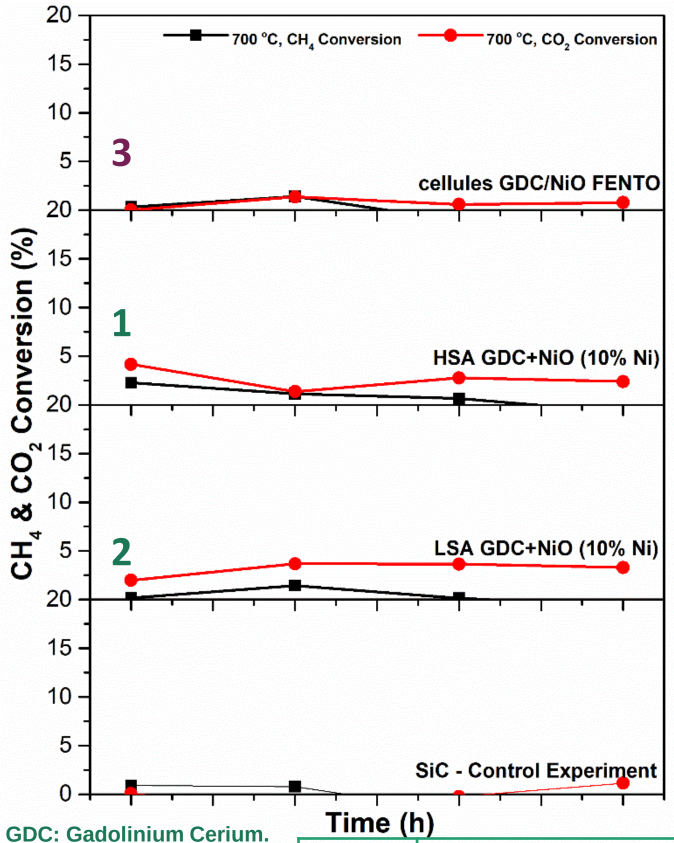
No.	Catalysts	Theoretical Ni (metal mass %)	XRF Ni (metal mass %)
1	Ni/YZ	10%	9.4%
2	8YSZ_Ni 10%Ni	10%	9.3%
3	YSZ	Commercial	0
4	elcogen half-cell YSZ_Ni	Commercial	37.1%

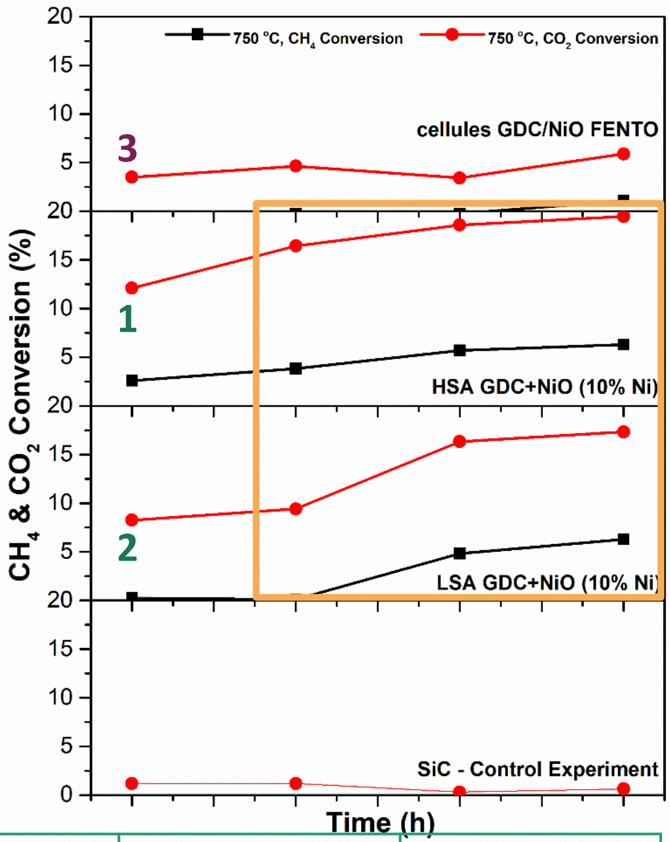
Elcogen: Commercial supplier. Cellules: Commercial ceramic cellules.
8YSZ: 8 mol% Y_2O_3 stabilized ZrO_2.

1 – Y-M Park et al., Inter. Jour. of Hydrogen Energy, 36, 15, 2011, 9169-9179.

IV. Elemental analysis & Reducibility

4.1. Nickel based catalysts – XRF elemental analysis vs. reactivity





1. **(3) Commercial one** (cellules GDC/NiO FENTO) with **high Ni doping 58% percentage : nearly no conversion** at **700 ºC** & **such low conversion** at **750 ºC.**
2. **(1, 2) HSA/LSA GDC+NiO 10%Ni : increasing conversion from 700 ºC to 750 ºC ; increasing activity at 750 ºC. (But what we want is low temperature reaction goal)**
3. Conversion of (1) HSA GDC+NiO 10%Ni > (2) LSA GDC+NiO 10%Ni **: High specific surface area** showed **positive impact.**

GDC: Gadolinium Cerium.

Catalysts based on Gd doped cerium oxide

No.	Catalysts	Theoretical Ni (metal mass %)	XRF Ni (metal mass %)
1	HSA GDC+NiO 10%Ni	12.4% NiO	12.3%
2	LSA GDC+NiO 10%Ni	12.4% NiO	12.4%
3	cellules GDC/NiO FENTO	Commercial	58%

Cellules: Commercial ceramic cellules.

LSA: low specific surface area 12 m^2/g.
HSA: high specific surface area 23 m^2/g.

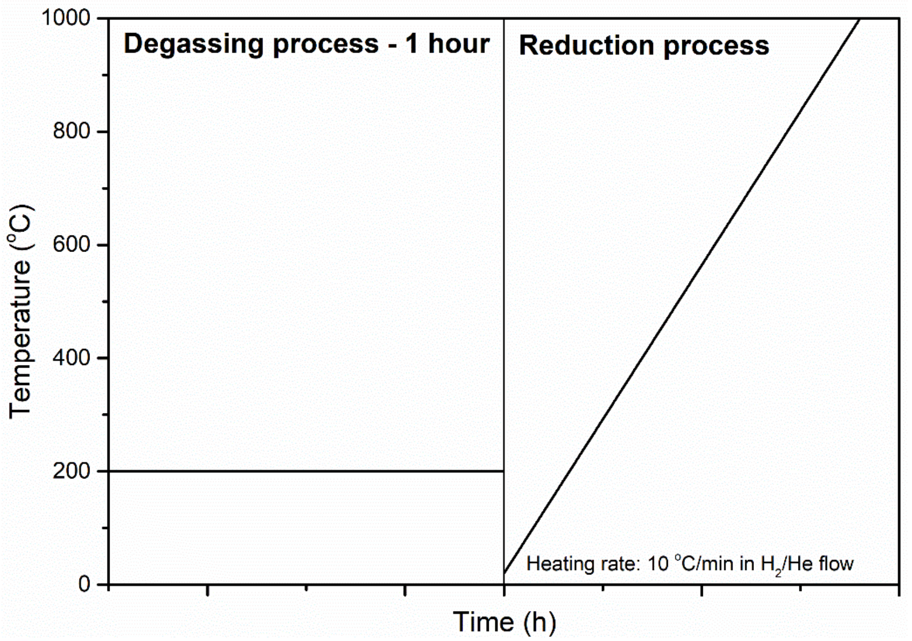
1 – *Y-M Park et al., Inter. Jour. of Hydrogen Energy, Vol 36, 15, 2011, 9169-9179.*

IV. Elemental analysis & Reducibility

4.2. Nickel based catalysts reducibility by H_2 Thermal Programmed Reduction

H_2-TPR Protocol

Step	Temperature	Time/Rate
Degassing	200 °C	1 hour
Reduction	Amb. – 1000 °C	10 °C/min



What is H_2-TPR:
an thermal-analytical technique that examines the **reduction properties of metal oxides** in hydrogen under varying thermal conditions, an **important factor** in catalysis studies.

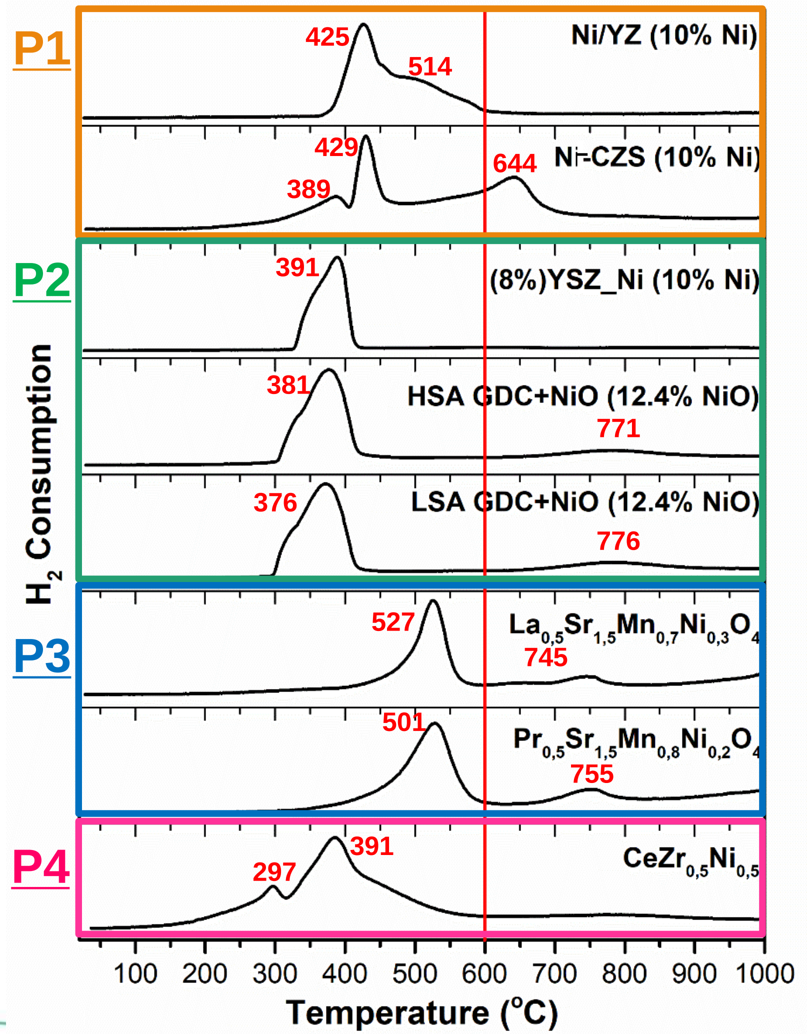
How is H_2-TPR: ~ 50 mg catalyst inside U type quartz tube on AutoChem 2920 in 5% H_2/He flow

Why is H_2-TPR:
to clarify the different interaction capacity between nickel species and divers support through study of reduction peak temperature.

IV. Elemental analysis & Reducibility

4.2. Nickel based catalysts reducibility by H_2 Thermal Programmed Reduction

P1, P2, P3, P4: Catalysts from 4 different laboratories.



Catalyst	Total H_2 amount (mmol/g)	H_2 amount (mmol/g) (< 600 °C)	H/Metal Molar Ratio
Ni/YZ	1.4	1.4	1.65
Ni-CZS	2.0	1.6	0.77
8YSZ_Ni 10%Ni	1.7	1.7	2.04
HSA GDC+NiO 10% Ni	2.1	1.7	0.67
LSA GDC+NiO 10% Ni	1.9	1.6	0.59
$Pr_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$	1.1	1.0	0.74
$La_{0.5}Sr_{1.5}Mn_{0.7}Ni_{0.3}O_4$	1.3	1.0	0.86
$CeZr_{0.5}Ni_{0.5}$	2.5	2.2	0.83

General H_2-TPR profiles: [1, 2, 3, 4]

1. Ni species main reduction **< 600 °C** (also **Project Goal**).
2. **H/Metal molar ratio**: Hydrogen consumption per unit molar metals.

a) When only Ni: **H/Ni = 2**, $Ni^{2+} + H = Ni^0 + 2H^+$;
b) When only Ce: **H/Ce = 1**, $Ce^{4+} + H = Ce^{3+} + H^+$ (Superficial & Bulk);
c) When only Mn: **H/Mn = 1**, $Mn^{4+} + H = Mn^{3+} + H^+$ (Superficial) & **H/Mn = 1**, $Mn^{3+} + H = Mn^{2+} + H^+$ (Interficial & Bulk);

Attention: **Synergic impact** of **Cerium** and **Manganese** species **incorporation** which also **participate in reduction**.

1 – *Y. Wei et al., applied catalysis a: general 2020, 549, 117439.*
2 – *Ma, Y et al., Catal Lett 150, 1418–1426 (2020).*
3 – *Horlyck, J et al. Top Catal 61, 1842–1855 (2018).*
4 – *S. Das et al., Chem. Commun., 2019, 55, 6074.*

YZ/YSZ: Yttria-stabilized zirconia;
GDC: Gadolinium Cerium;
CZS: Cerium Zirconium Samarium.

VD: Victor Duffort;
LD: Louise Duhamel.

IV. Elemental analysis & Reducibility

4.2. Nickel based catalysts reducibility – Reaction pretreatment (450 ºC & 12 h)

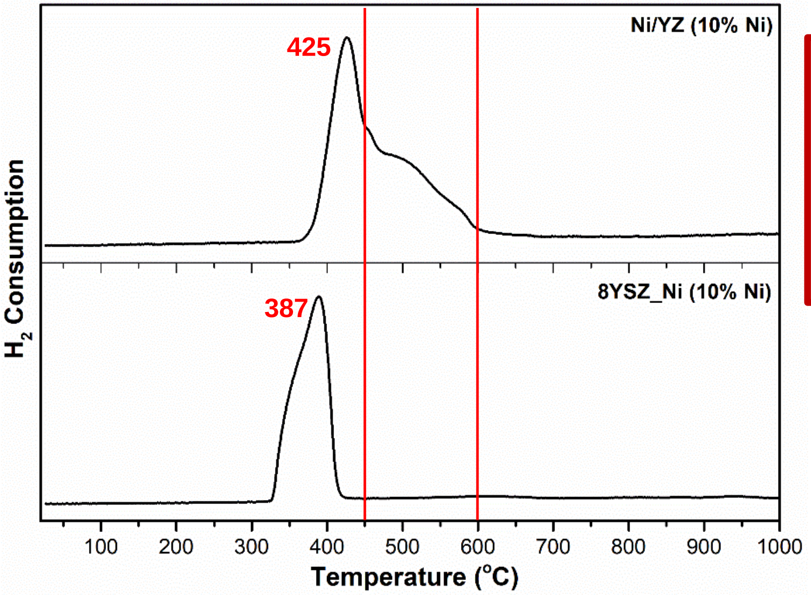
Catalysts based on YSZ support

Catalyst	Synthesis / Ni position	Total H_2 amount (mmol/g)	H_2 amount (mmol/g) (< 600 ºC)	H/Metal Molar Ratio
Ni/YZ	**Impregnation/ Support surface**	**1.4**	**1.4**	**1.7**
8YSZ_Ni 10%Ni	**Mechanochemical / Support surface**	**1.7**	**1.7**	**2.0**

Metal reduction: $\mathbf{Ni^{2+} + H = Ni^{0} + 2H^{+}}$:

Theoretical molar ratio H/Ni = 2

YZ/YSZ support : Chemically stable (20-1000 ºC)



1. Ni species main reduction < 600 ºC (also **Project Goal**).
2. **H/Metal** molar ratio : **Ni/YZ** (**1.7**) **< 8YSZ_Ni** (**2.0**).
3. **Reaction pretreatment (450 ºC & 12 h)** :
   a. Ni/YZ : Slightly incomplete reduction (**1.7**).
   b. 8YSZ_Ni (10% Ni) : Complete reduction (**2.0**).

Because of different synthesis methods [4] :

1. Impregnation : Ni species in porous structure of YZ.
2. Mechanochemical : Ni particles mainly on YSZ surface.
3. 450 ºC is incomplete reduction for Ni/YZ.

---

1 – Y. Wei et al., applied catalysis a: general 2020, 549, 117439.

2 – Ma, Y et al., Catal Lett 150, 1418–1426 (2020).

3 – Horlyck, J et al. Top Catal 61, 1842–1855 (2018).

4 – S. Das et al., Chem. Commun., 2019, 55, 6074.

YZ/YSZ: Yttria-stabilized zirconia.

IV. Elemental analysis & Reducibility

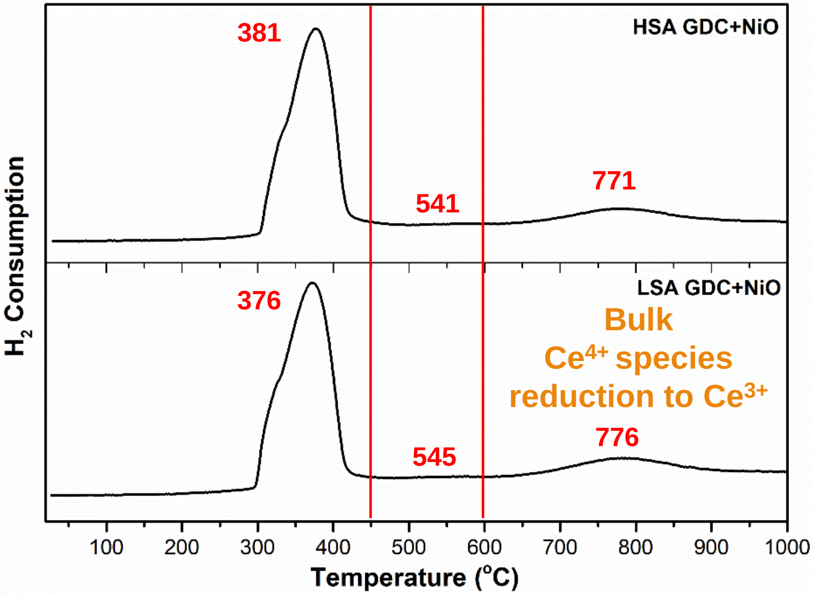
4.2. Nickel based catalysts reducibility – Reaction pretreatment (450 ºC & 12 h)

Catalysts based on Gd doped cerium oxide

GDC: Gadolinium Cerium.

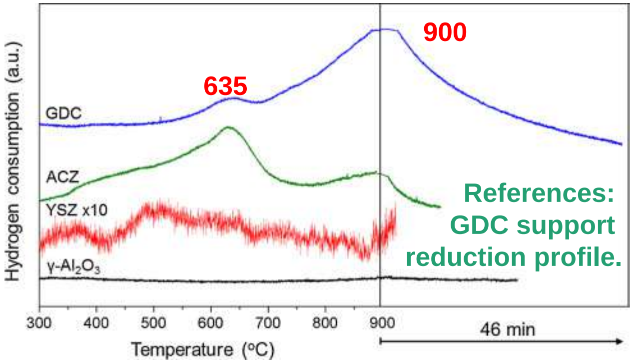
LSA: low specific surface area 12 m^2/g.
HSA: high specific surface area 23 m^2/g.

Catalyst	Synthesis / Ni position	Total H_2 amount (mmol/g)	H_2 amount (mmol/g) (< 600 ºC)	H/Metal Molar Ratio
HSA GDC+NiO 10% Ni	Mechanochemical / Support surface	2.1	1.7	0.67
LSA GDC+NiO 10% Ni	Mechanochemical / Support surface	1.9	1.6	0.59



Bulk Ce^{4+} species reduction to Ce^{3+}

Metal reduction – 1 : $Ni^{2+} + H = Ni^0 + 2H^+$:
Theoretical molar ratio H/Ni = 2 ;
Metal reduction – 2 : $Ce^{4+} + H = Ce^{3+} + H^+$
(Superficial & Bulk) :
Theoretical molar ratio H/Ce = 1 .
Gd incorporation in CeO_2 : 635 & 900 ºC [5].



References: GDC support reduction profile.

1. HSA/LSA GDC+NiO at lower temperature than GDC support : **interaction by Ni doping in GDC**.
2. Reaction pretreatment (450 ºC & 12 h) : Nearly complete reduction of Ni species.
3. **HSA** GDC+NiO presented the **slightly better reducibility** than **LSA** GDC+NiO from H/Metal molar ratio (**0.67 > 0.59**) due to more contact surface.

---

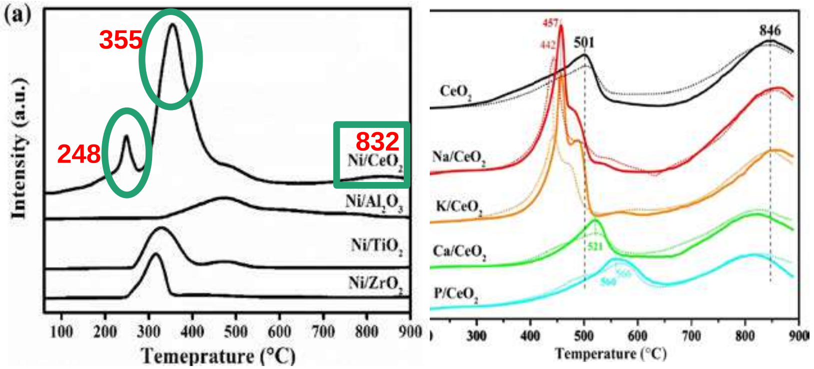
1 – Y. Wei et al., applied catalysis a: general 2020, 549, 117439.
2 – Ma, Y et al., Catal Lett 150, 1418–1426 (2020).
3 – Horlyck, J et al. Top Catal 61, 1842–1855 (2018).
4 – S. Das et al., Chem. Commun., 2019, 55, 6074.
5 – I. V. Yentekakis et al., App. Catal. B: Environ. 192, 5 9 2016, 357-364.

IV. Elemental analysis & Reducibility

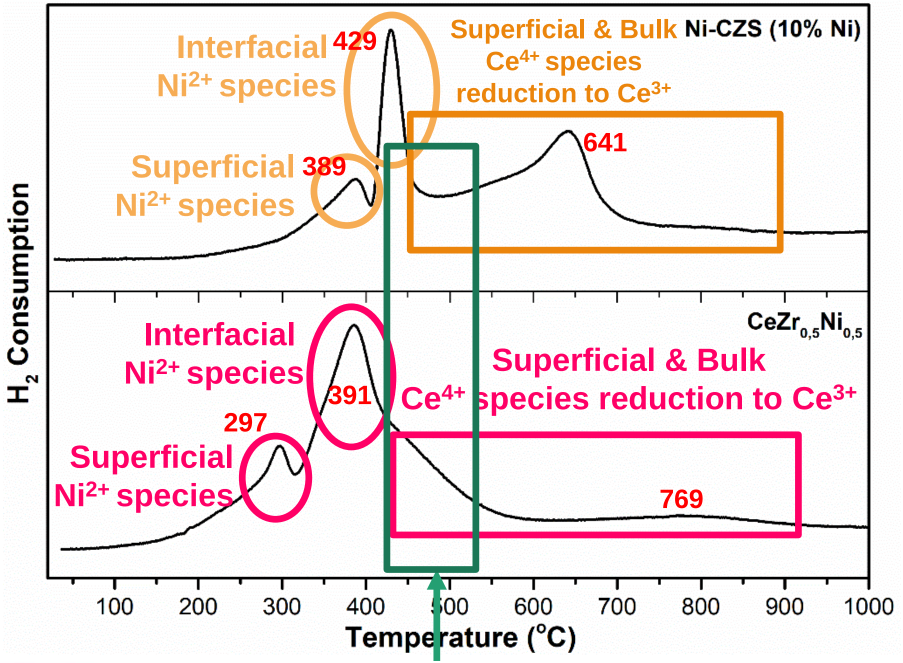
4.2. Nickel based catalysts reducibility – Reaction pretreatment (450 °C & 12 h)

Catalysts based on cerium zirconium oxide

Catalyst	Synthesis / Ni position	Total H_2 amount (mmol/g)	H_2 amount (mmol/g) (< 600 °C)	H/Metal Molar Ratio
(10%Ni) Ni-CZS	Pseudo sol-gel / doping in support	2.0	1.6	0.77
(10%Ni) $CeZr_{0.5}Ni_{0.5}$	Coprecipitation / doping in support	2.5	2.2	0.83



References: (1) Ni/CeO_2 & (2) CeO_2 reduction profile.



Superimposed zone of Ni & Ce reduction

Metal reduction – 1 : $Ni^{2+} + H = Ni^0 + 2H^+$:

Theoretical molar ratio H/Ni = 2 ;

Metal reduction – 2 : $Ce^{4+} + H = Ce^{3+} + H^+$ (Superficial & Bulk) :

Theoretical molar ratio H/Ce = 1 .

Cerium Zirconium solid solution: **oxygen mobility (Cerium), stability (Zirconium) and surface & structure defect (Samarium)**.

1. Ref (1,2) vs. samples : **Nickel doping into structure** presented **stronger interaction** between nickel species and support, **Ni^{2+} reduction appeared at higher temperature**.
2. Ref (2) vs. samples : Ni and Sm doping **improved Ce^{4+} species reduction to Ce^{3+} species.**
3. $CeZr_{0.5}Ni_{0.5}$ and Ni-CZS hold **similar H/Metal ratio** : coprecipitation similar interaction vs. Sol-gel.

---

1 – Y. Wei et al., applied catalysis a: general 2020, 549, 117439.
2 – Ma, Y et al., Catal Lett 150, 1418–1426 (2020).
3 – Horlyck, J et al. Top Catal 61, 1842–1855 (2018).
4 – S. Das et al., Chem. Commun., 2019, 55, 6074.
5 – I. V. Yentekakis et al., App. Catal. B: Environ. 192, 5 9 2016, 357-364.

CZS: Cerium Zirconium Samarium.

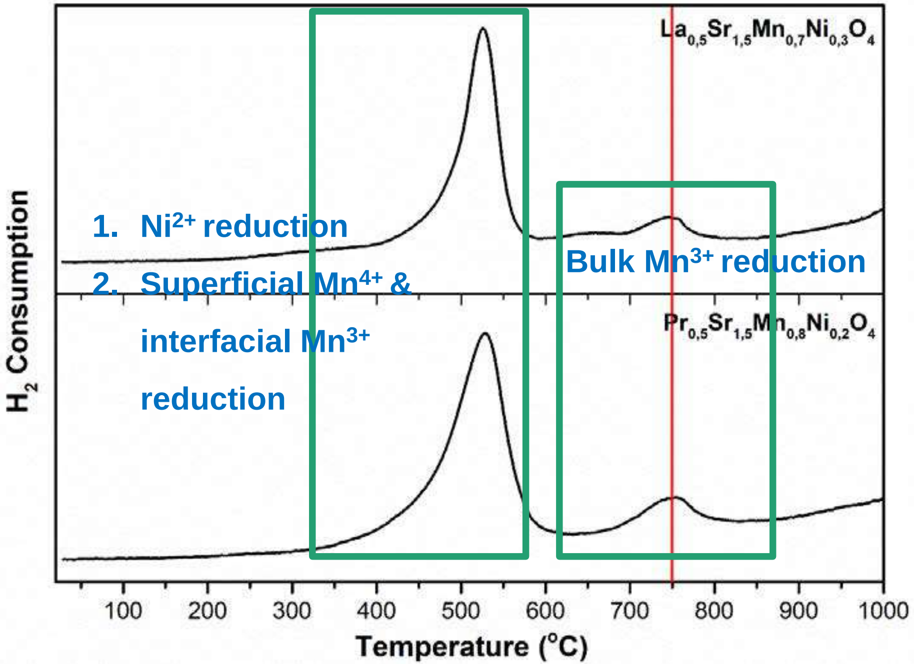
IV. Elemental analysis & Reducibility

4.2. Nickel based catalysts reducibility – Reaction pretreatment (750 ºC & 24 h)

Rudddlesden-Popper perovskites : $A_{n+1}B_nO_{(3n+1)\pm\delta}$

Catalyst	Synthesis / Ni position	Total H_2 amount (mmol/g)	H_2 amount (mmol/g) (< 750 ºC)	H/Metal Molar Ratio
$Pr_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$	Sol-gel / doping in support	1.1	1.0	0.74
$La_{0.5}Sr_{1.5}Mn_{0.7}Ni_{0.3}O_4$	Sol-gel / doping in support	1.3	1.0	0.86

Metal reduction – 1 : **$Ni^{2+} + H = Ni^0 + 2H^+$** :
Theoretical molar ratio H/Ni = 2 ;
Metal reduction – 2 : **$Mn^{4+} + H = Mn^{3+} + H^+$** (Superficial)
Theoretical molar ratio H/Ni = 1 ;
Metal reduction – 3 : **$Mn^{3+} + H = Mn^{2+} + H^+$** (Interficial & Bulk)
Theoretical molar ratio H/Ni = 1 .



1. **Ni^{2+} reduction**
2. **Superficial Mn^{4+} & interfacial Mn^{3+} reduction**

Bulk Mn^{3+} reduction

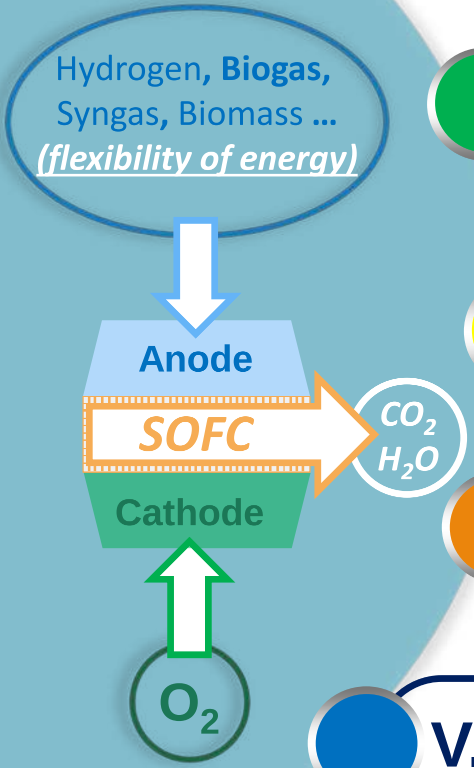
Remind of conversion corresponds to H/M ratio:
$La_{0.5}Sr_{1.5}Mn_{0.7}Ni_{0.3}O_4 > Pr_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$

1. **Pretreatment (750 ºC & 24 h)** ensured the reduction of metal oxides on surface & effect of **Exsolution of Ni species [1, 2, 4]**.
2. **Sol-gel** synthesis: **strong interaction** between **Ni** and **support** leads to high temperature reduction.
3. Different perovskite Site-A ($La_{0.5}Sr_{1.5}$ & $Pr_{0.5}Sr_{1.5}$), Site-B (Mn and Ni) incorporation determined the **similar reduction profiles & H/Metal molar ratio**.
4. Superficial ($Mn^{4+} \longrightarrow Mn^{3+}$) & interfacial ($Mn^{3+} \longrightarrow Mn^{2+}$) reduction should be taken into consideration around 500 ºC, bulk ($Mn^{3+} \longrightarrow Mn^{2+}$) reduction around 750 ºC [3].
5. Perovskite A-site substitution : surface structure defect and more oxygen vacancies [3].
6. Perovskite B-site substitution : Ni & Mn synergic effect because of C-H bond breaking by Mn [4].

---

1 – P. B. Managutti et al., ACS Appl. Mater. Interfaces 2021, 13, 35719–35728.
2 – P. B. Managutti et al., ACS Appl. Mater. Interfaces 2023.
3 – J. Wu et al., Applied Catalysis A: General, Vol 619, 2021, 118-137.
4 – Y. Zheng et al., Applied Catalysis A: General, Vol 614, 2022, 118-687.

Table of Contents



V. Conclusion & perspectives

Conclusion – HT approach to optimize Ni-catalyst for dry reforming of methane

1. Comparing parallel HT reactions, **$La_{0.5}Sr_{1.5}Mn_{0.7}Ni_{0.3}O_4$** and **Ni-CZS** showed the **best** conversion rates; **$Pr_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$, HSA GDC+NiO** and **$CeZr_{0.5}Ni_{0.5}$** exhibited relatively **moderate** conversion rates from **catalytic results** on activity & stability.
2. Among 4 synthesis methods: **Sol-gel, impregnation, coprecipitation and mechanochemical approach, Sol-gel method** showed **best** results due to **strong interaction** between nickel species and support.
3. **YSZ** presented **chemically stability** as support for Ni species.
4. **Gd & Sm incorporation** into **Ce Zr solid oxide** showed **positive impacts** on the reactivity and reducibility.
5. **Perovskite** (**$La_{0.5}Sr_{1.5}Mn_{0.7}Ni_{0.3}O_4$ & $Pr_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$**) presented **significant reactivity and reducibility** with **low Ni doping** content due to **Ni exsolution after reduction** in hydrogen and **Mn** species synergic influence on **C-H bond breaking**.
6. **H_2-TPR** : as **evidence** to confirm the conditions of the catalysts **pretreatment (450 ºC & 750 ºC).**
7. **Hydrogen consumption** & **molar ratio H/M** of H_2-TPR reflected corresponding **activity of catalysts**.
8. **Interaction strength** between the nickel species and the supports: By group: Ni-CZS > Ni/YZ; $La_{0.5}Sr_{1.5}Mn_{0.7}Ni_{0.3}O_4$ > $Pr_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$; HSA GDC+NiO > LSA GDC+NiO. (**Sol-gel & more SSA : positive**)
9. **XRF** analysis showed catalysts' metal contents in mass, the **theoretical** and **experimental** results are generally **similar** in mass nickel.

V. Conclusion & perspectives

Perspectives – HT approach to optimize Ni-catalyst for dry reforming of methane

Perspectives	Ideas	Goal
Elemental optimization	Co & Fe doping in perovskite	Avoid coke deposit
	Zr & Sm in Cerium oxide	More surface defect & active Ni metal species
Synthesis	Sol-gel with more SSA	Ni stable & active species, with low content & small nanoparticles (6-9 nm) [1]
Characterizations	XRD	Structure change during reduction or reaction
	XPS	Metal valences before vs. after reaction
	TPO	Coke deposit
	SEM/TEM	Coke deposit, particles size, exsolution
	O_2-TPD	Oxygen mobility

The French Research network on Hydrogen energy

Thanks for your kind attention

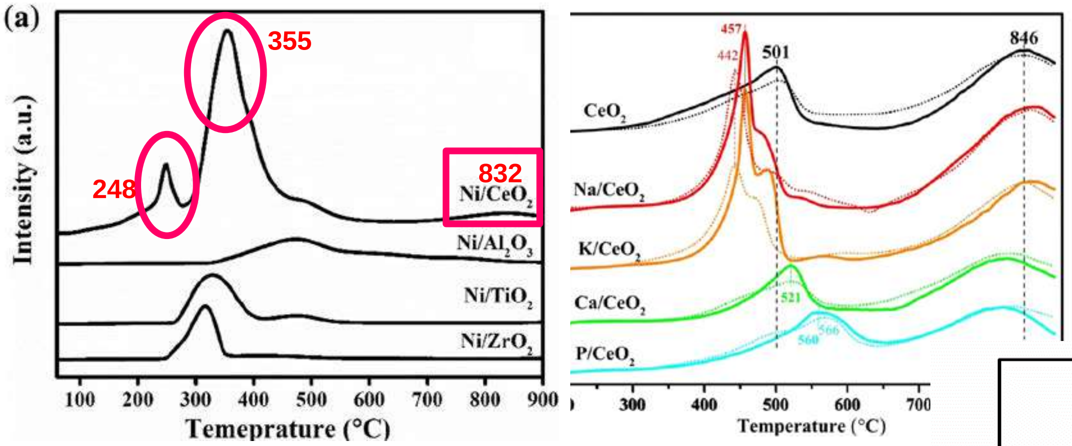
(UCCS)	(Cooperative Partners)
Thanks to Dr. Marcia ARAQUE-MARIN	Thanks to Dr. Mona BAHOUT
Thanks to Dr. Victor DUFFORT	Thanks to Dr. Annie LE GAL LA SALLE
Thanks to Dr. Svetlana HEYTE	Thanks to Dr. Anne-Cécile ROGER
Thanks to Mme. Theresa AL-BAYEH (Intern)	Thanks to Mr. Yilin LUO (Intern)

Thanks to the meeting organizers , the fundings and all the colleagues.

PEPR-H2

IV. Elemental analysis & Reducibility

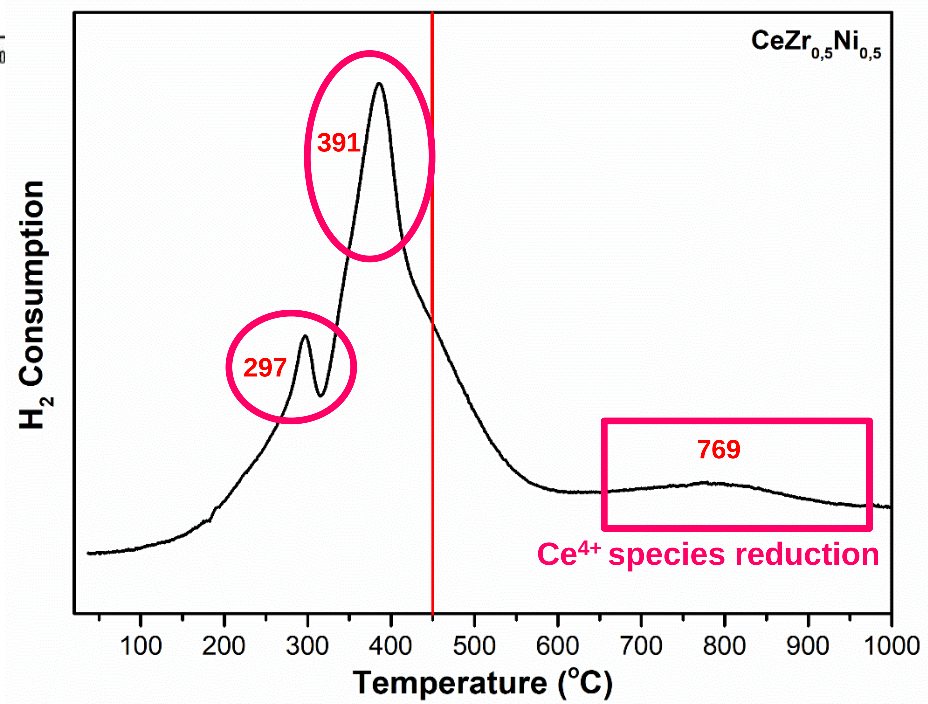
4.2. Nickel based catalysts reducibility – Reaction pretreatment (450 ^oC & 12 h)



References: CeO_2 & Ni/CeO_2 reduction profile

Catalyst	Total H_2 amount (mmol/g)	H_2 amount (mmol/g) (< 450 ^oC)	Ratio H_2/Ni
$CeZr_{0.5}Ni_{0.5}$	2.5	1.9	0.4

Ratio H_2/Ni: Ni & Ce oxide solid solution synergically participate in reduction with stronger interaction



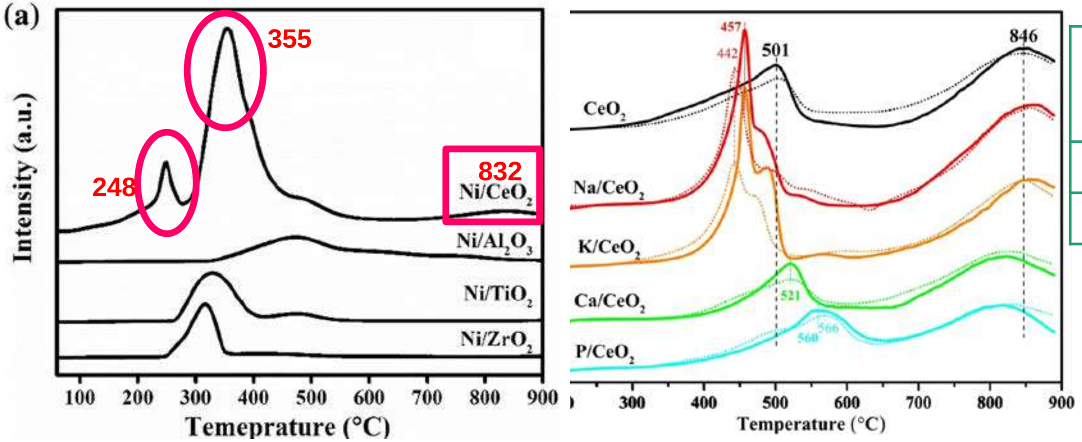
Ce^{4+} species reduction

1. Cerium Zirconium mixed oxide significant **oxygen mobility (Cerium)** and **stability (Zirconium)** which promoted Ni species catalytic activity.
2. **Nickel doping** into Cerium Zirconium mixed oxide presented **stronger interaction** between nickel species and support**, Ni^{2+} reduction appeared at higher temperature**.
3. Bulk Ce^{4+} & Ce^{2+} reduction appeared ~ 500 ^oC and > 800 ^oC. **Nickel doping improved Ce^{2+} species reduction <** 800 ^oC**.**

1 – Y. Wei et al., applied catalysis a: general., 2020, 549, 117439.
2 – Ma, Y et al., Catal Lett 150, 1418–1426 (2020).
3 – Horlyck, J et al. Top Catal 61, 1842–1855 (2018).
4 – O. H. Laguna et al., catalysis Today, 172, 2011, 118-123.
5 – He, J., et al., Environ Sci Pollut Res 28, 26018–26029 (2021).

IV. Elemental analysis & Reducibility

4.2. Nickel based catalysts reducibility – Reaction pretreatment (450 °C & 12 h)

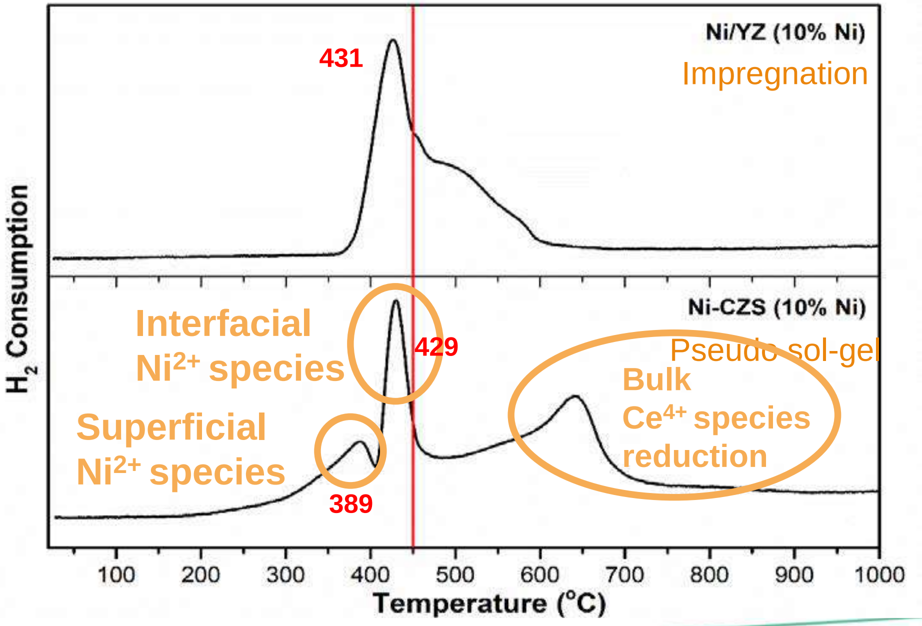


References: CeO_2 & Ni/CeO_2 reduction profile

Catalyst	Total H_2 amount (mmol/g)	H_2 amount (mmol/g) (< 450 °C)	Ratio H_2/Ni
Ni/YZ	1.4	0.76	0.8
Ni-CZS	2.0	0.8	0.1

Less hydrogen consumption per unit of Ni, more hydrogen consumption in total.

Uniformed Ni distribution on Ni-CZS



1. Impregnation – Ni species on surface: reduction happened in low < 600 °C temperature zone.
2. Pseudo sol-gel – Ni species on surface and in bulk: reduction also appeared at high > 600 °C temperature zone Ce reduction .
3. Bulk Ce^{2+} reduction > 800 °C. But **Ni & Sm doping improved Ce species reduction** < 800 °C**.** Because of surface defect & oxygen vacancies by Sm incorporation.

1 – Y. Wei et al., applied catalysis a: general 2020, 549, 117439.
2 – Ma, Y et al., Catal Lett 150, 1418–1426 (2020).
3 – Horlyck, J et al. Top Catal 61, 1842–1855 (2018).
4 – O. H. Laguna et al., catalysis Today, 172, 2011, 118-123.
5 – He, J., et al., Environ Sci Pollut Res 28, 26018–26029 (2021).

IV. Elemental analysis & Reducibility

4.2. Nickel based catalysts reducibility – Reaction pretreatment (450 ºC & 12 h)

LSA: 12 m^2/g. HSA: 23 m^2/g.

Catalyst	Total H_2 amount (mmol/g)	H_2 amount (mmol/g) (< 450 ºC)	Ratio H_2/Ni
8YSZ_Ni 10%Ni	1.7	1.6	1.0
HSA GDC+NiO 10% Ni	2.1	1.5	0.3
LSA GDC+NiO 10% Ni	1.9	1.4	0.3

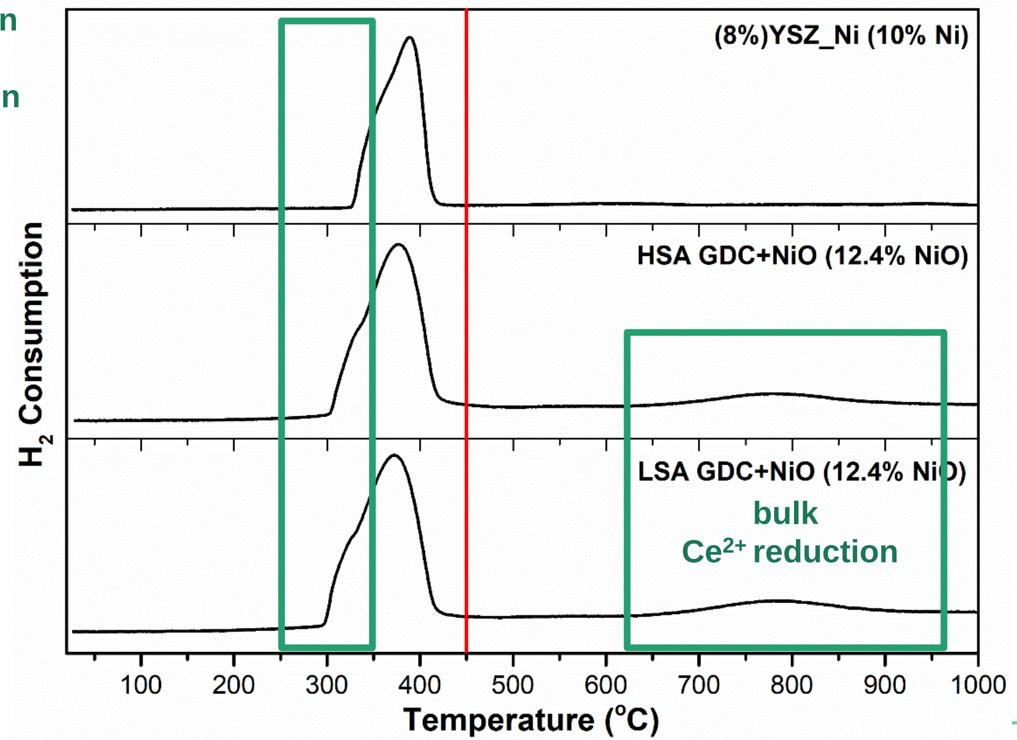
Aggregation of Ni species on 8YSZ_Ni

Uniforme Ni species distribution on HSA/LSA GDC+NiO

Ratio H_2/Ni: GDC Support (Ce species) synergically participate in reduction with stronger interaction

Less hydrogen consumption per unit of Ni, more hydrogen consumption in total.

1. HSA/LSA GDC+NiO at lower temperature and higher H_2 consumption: because of **surface defect by Gd doping in Ce oxide**.
2. Reduction at **high temperature** corresponded to **bulk Ce^{2+} reduction**.
3. Gadolinium Cerium mixed oxide support by mechanochemical route: **HSA** GDC+NiO (High specific surface area) presented the **slightly better reducibility** than **LSA** GDC+NiO (Low specific surface area).



1 – Y. Wei et al., applied catalysis a: general., 2020, 549, 117439.

2 – Ma, Y et al., Catal Lett 150, 1418–1426 (2020).

3 – Horlyck, J et al. Top Catal 61, 1842–1855 (2018).

4 – O. H. Laguna et al., catalysis Today, 172, 2011, 118-123.

V. Conclusion & perspectives

HT approach to optimize Ni-based catalyst for dry reforming of methane

Conclusion

1. Comparing parallel conversions, **$La_{0.5}Sr_{1.5}Mn_{0.7}Ni_{0.3}O_4$** and **Ni-CZS** showed the **best** conversion rates (CO_2: ~45%, CH_4: ~30% at 700 °C; CO_2: ~ 20%, CH_4: ~5% at 750 °C); **$Pr_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$, HSA GDC+NiO** and **$CeZr_{0.5}Ni_{0.5}$** exhibited relatively **moderate** conversion rates (CO_2: ~35% , CH_4: ~20% at 700 °C; CO_2: ~20% , CH_4: ~5% at 750 °C). Catalytic stability showed **interaction** between **nickel species and support**.
2. Among 4 synthesis methods: **Sol-gel, impregnation, coprecipitation and mechanochemical approach, Sol-gel method** showed **best** results due to **strong interaction** between nickel species and support.
3. **YSZ** presented **chemically stability** as support for Ni species.
4. **Gd & Sm incorporation** into **Ce Zr solid oxide** showed **positive impacts** on the reactivity and reducibility.
5. **Perovskite** (**$La_{0.5}Sr_{1.5}Mn_{0.7}Ni_{0.3}O_4$ & $Pr_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$**) presented **significant reactivity and reducibility** with **low Ni doping** content due to **Ni exsolution after reduction** in hydrogen and **Mn** species synergic influence on **C-H bond breaking**.
6. **H_2-TPR** analysis with reductive properties of the catalysts as **evidence** to confirm the conditions of the catalysts reaction **pretreatment (450 °C & 750 °C)** and **catalytic results** and presented also the nickel species **interaction** between **nickel species and support**.
7. H_2-TPR hydrogen consumption, **low H/Ni** showed more **uniformed Ni** species **distribution**.
8. Interaction strength between the nickel species and the supports: By group: Ni-CZS > Ni/YZ; $La_{0.5}Sr_{1.5}Mn_{0.7}Ni_{0.3}O_4$ > $Pr_{0.5}Sr_{1.5}Mn_{0.8}Ni_{0.2}O_4$; HSA GDC+NiO > LSA GDC+NiO.
9. The mass metal contents of the catalysts were obtained by XRF analysis, the theoretical and experimental results are generally similar in mass nickel.

Perspectives

1. Co and Fe incorporation into Ce solid solution and perovskite Site-B to test to avoid coke deposit from elemental design of catalyst.
2. Characterizations: XRD for crystal structure; XPS for metal valence state; TPO, SEM/TEM for post-catalyst for coke deposit test.