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Coke-resistant Rh and Ni catalysts supported on γ-Al_2O_3 and CeO_2 for biogas oxidative steam reforming

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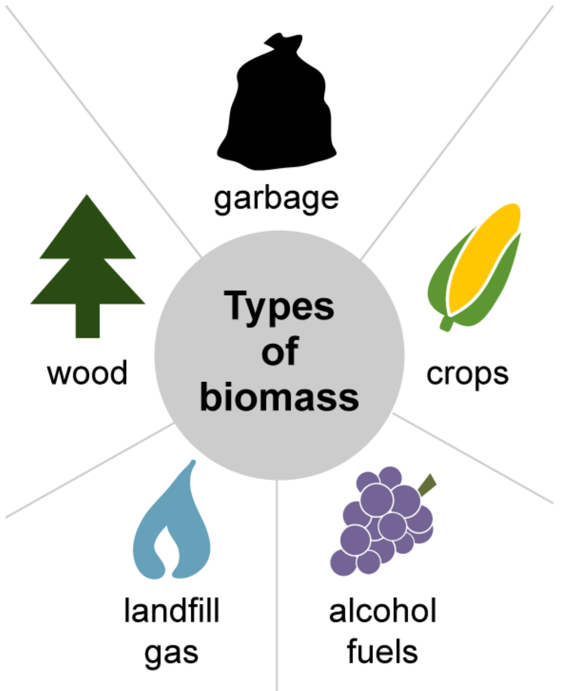
University of Salerno, Italy
Department of Industrial Engineering
Proceed Lab

Processes & Catalysis for Energy & Environment depollution

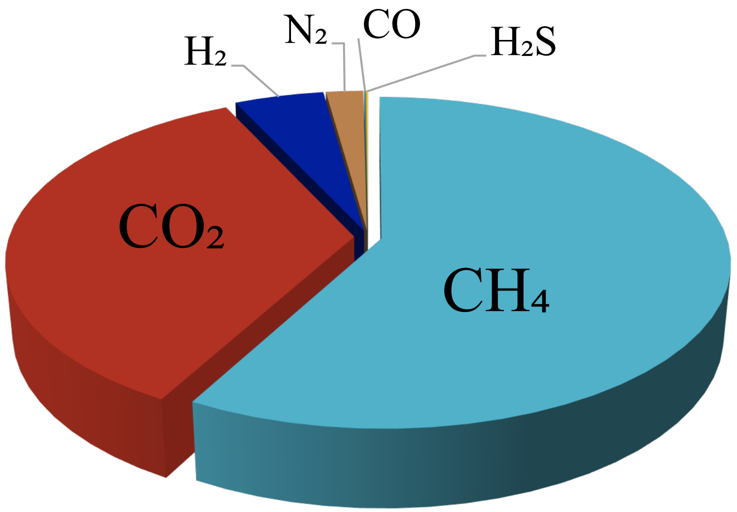
Biogas

Source

Anaerobic biomass digestion



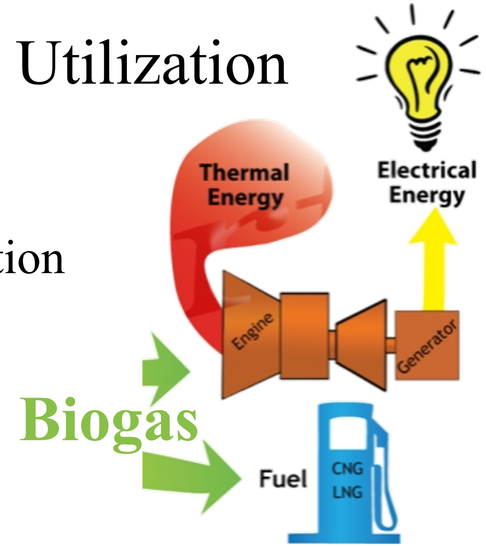
Composition



CH_4 rich gas

Utilization

Co-generation plants



CH_4 substitute in reforming processes

Hydrogen production

Biogas towards H_2

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

Methane dry reforming

drawbacks

- high endothermicity
- catalyst stability issues

high T (sintering phenomena)

coke formation

Water addition

$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$

Methane steam reforming

Oxygen addition

$$CH_4 + 1/2\ O_2 \rightleftarrows CO + 2H_2$$

Methane partial oxidation

advantages

- mild reduction in endothermicity
- catalyst stability

higher hydrogen yield

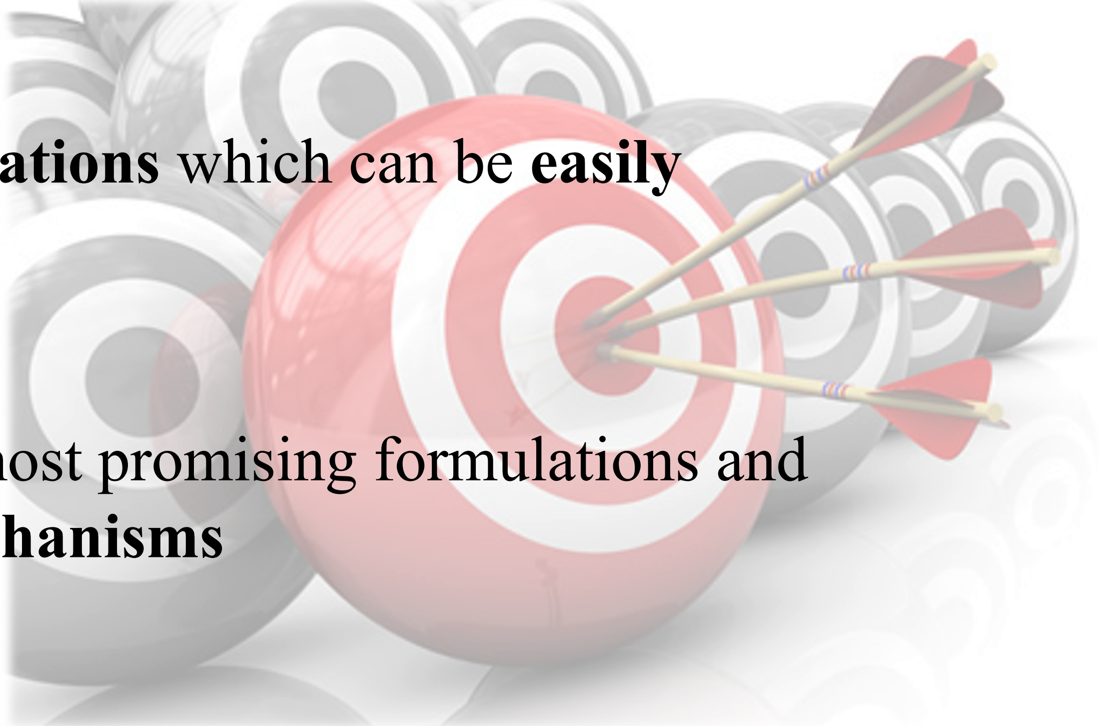
coke gasification

Aims of this work

- Study of the biogas oxidative steam reforming (BOSR) reaction in different catalyzed systems

- Research of **highly active catalytic formulations** which can be **easily empolyed** in the industrial sector

- Investigation of the **aging stability** of the most promising formulations and evaluation of the **deactivation driving mechanisms**



Biogas oxidative steam reforming

$$CH_4 + yCO_2 + xH_2O + \alpha O_2 \rightleftarrows aCO + bCO_2 + cCH_4 + dH_2O + eH_2 + fC_{(s)}$$

Active species: Ni, Rh

- Ni: typical active metal in reforming processes
  cheap and easily available
- Rh: high activity and stability towards POX

Supports: Al_2O_3, CeO_2

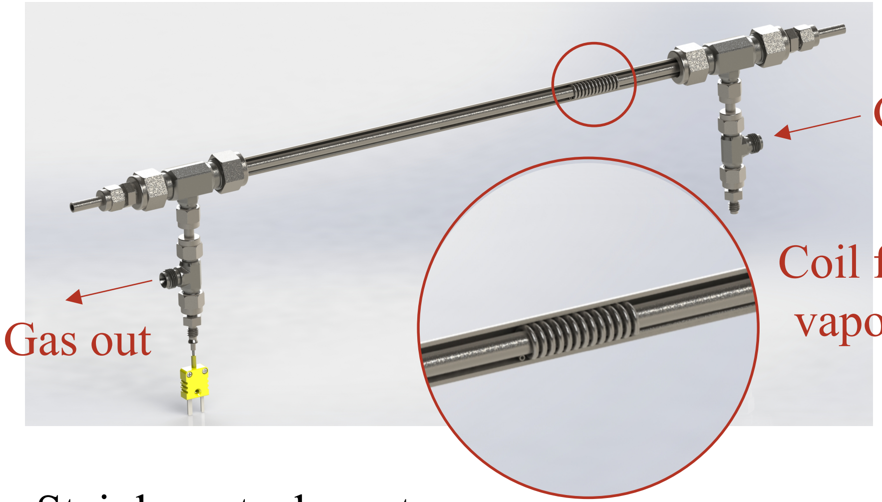
- Al_2O_3: typical support in reforming processes
  cheap and easily available
  high SSA → good dispersion
- CeO_2: reduce the coke deposition

Preparation method: wet impregnation

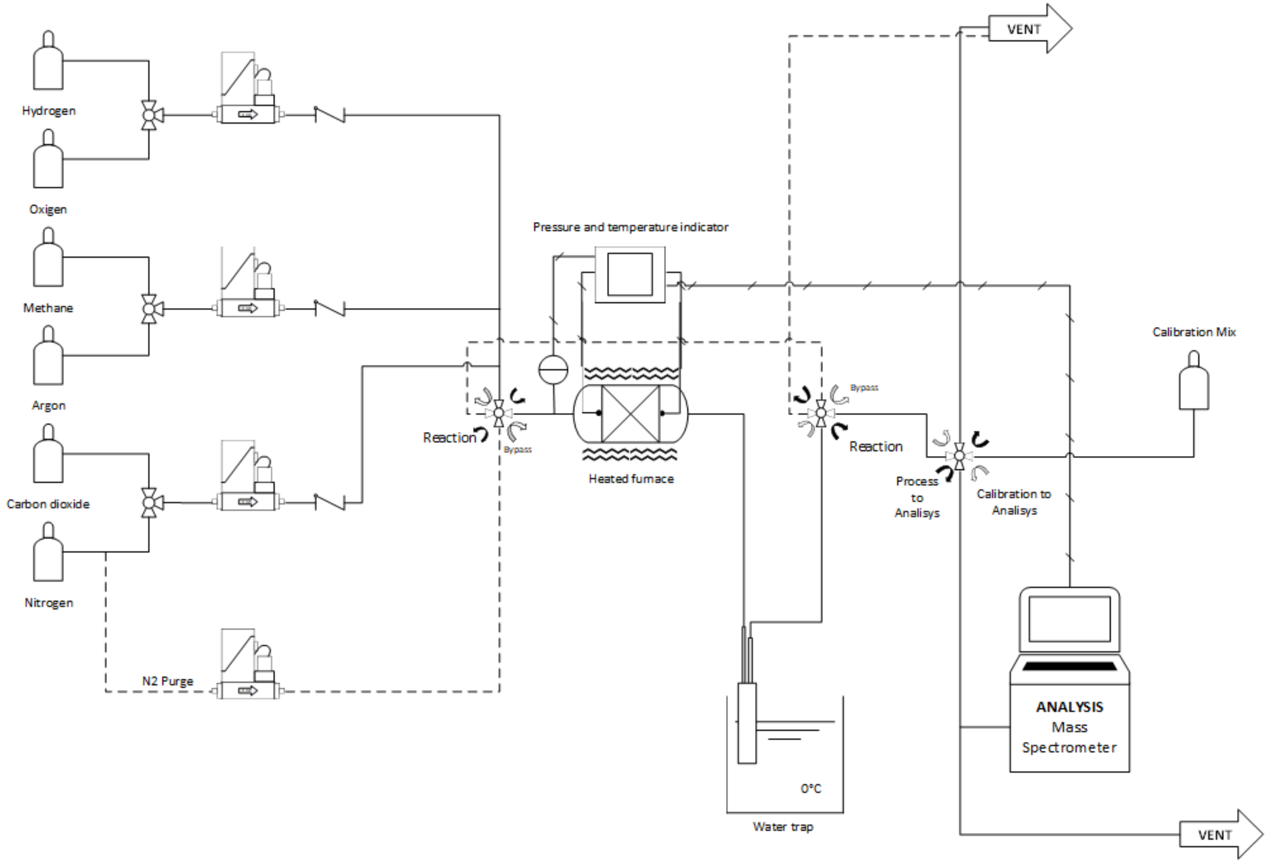
Bimetallic formulations: subsequent impregnations

Sample	Nominal metal loading (wt%)	
	Ni	Rh
10%Ni/Al_2O_3	10	-
5%Ni/Al_2O_3	5	-
0.5%Rh/Al_2O_3	-	0.5
0.5%Rh-5%Ni/Al_2O_3	5	0.5
5%Ni/CeO_2	5	-
0.5%Rh-5%Ni/CeO_2	5	0.5

Experimental plant



Stainless steel reactor
Diameter = 1/2”
K-type TC at catalyst bed outlet section

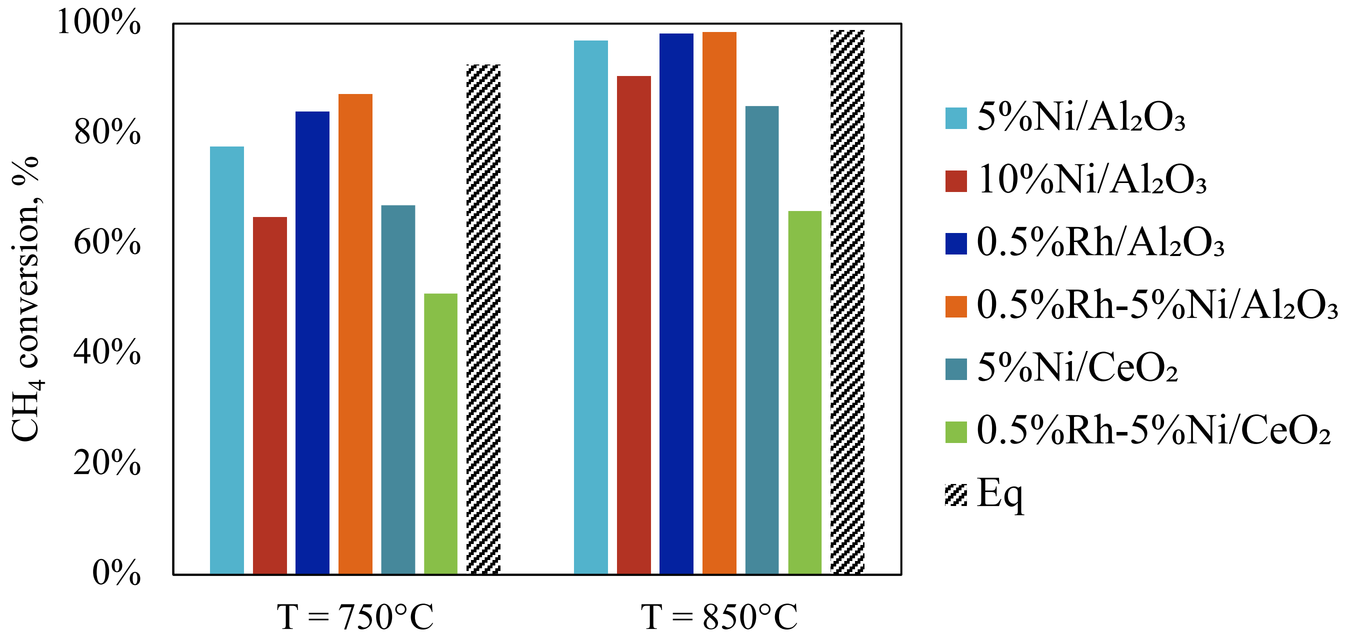


Reaction performances evaluation

$$X_{CH_4} = \frac{mol_{CH_4,in} - mol_{CH_4,out}}{mol_{CH_4,in}} \qquad Y_{H_2} = \frac{mol_{H_2,out}}{mol_{BIOGAS,fed}}$$

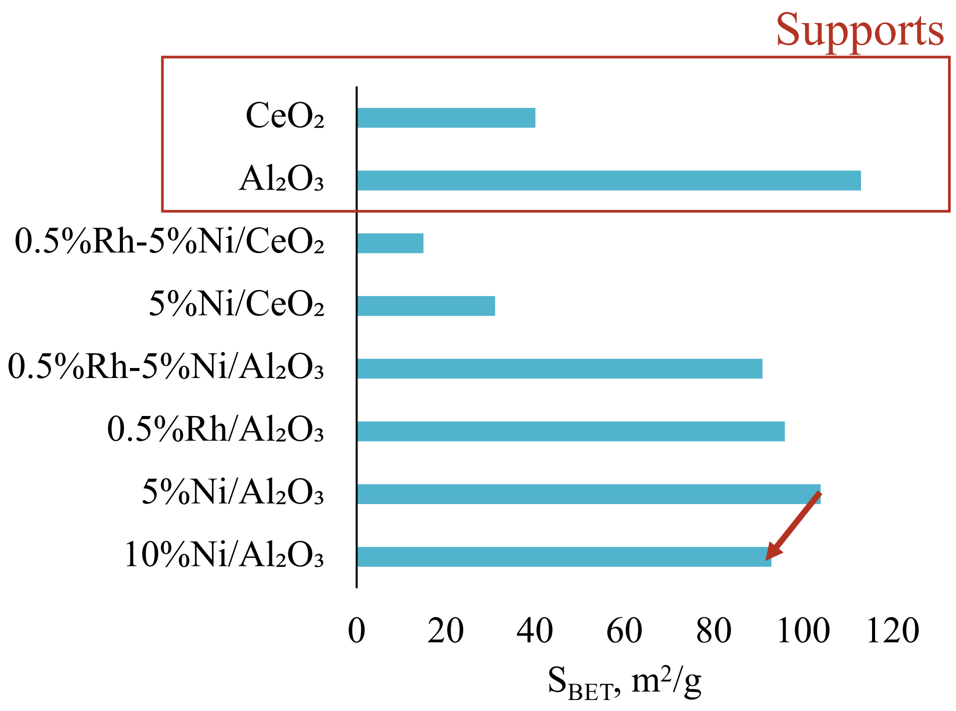
Catalytic activity tests

T = 750°C and 850°C



1. The increase in Ni loading led to a worsening of the activity
2. Rh offers a higher activity towards BOSR
3. Sinergic effect enhance the reaction performances
4. Al_2O_3 is a better support than CeO_2
5. Rh addition has a detrimental effect in CeO_2 supported catalysts

Catalytic activity tests



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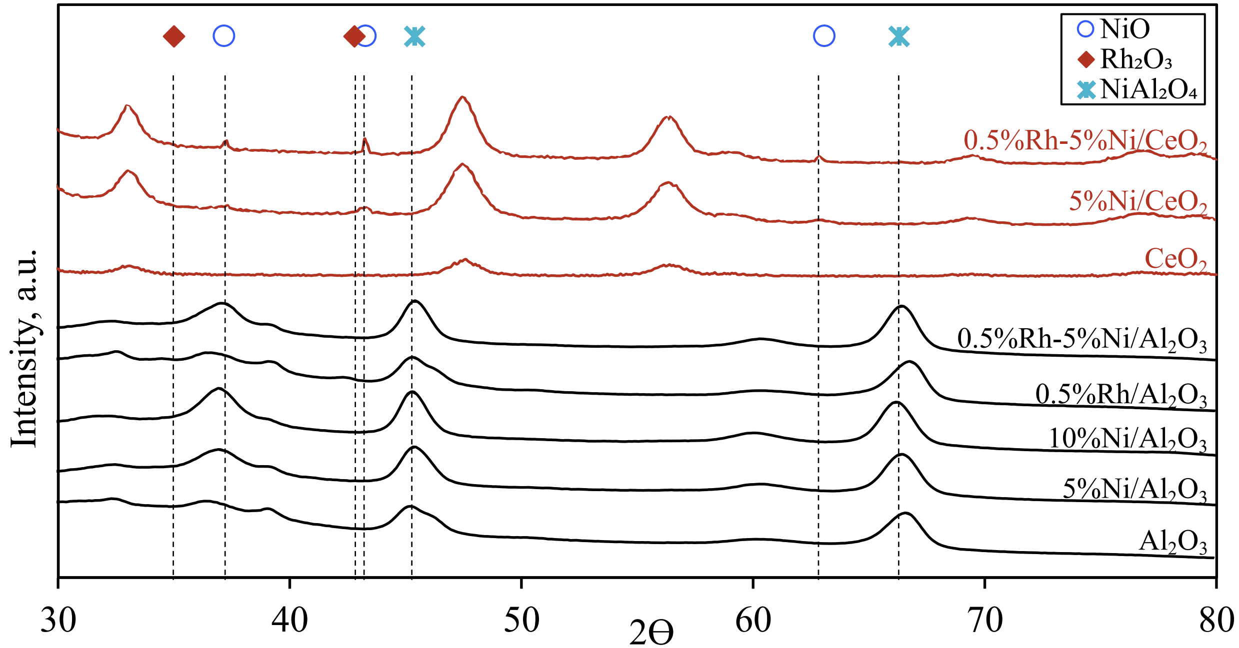
Metal dispersion is a determining factor

Catalytic activity tests

Rh-Al_2O_3 interactions are effective towards the reactants activation

Rh-Ni interactions are different on Al_2O_3 and on CeO_2, in addition to the worse dispersion



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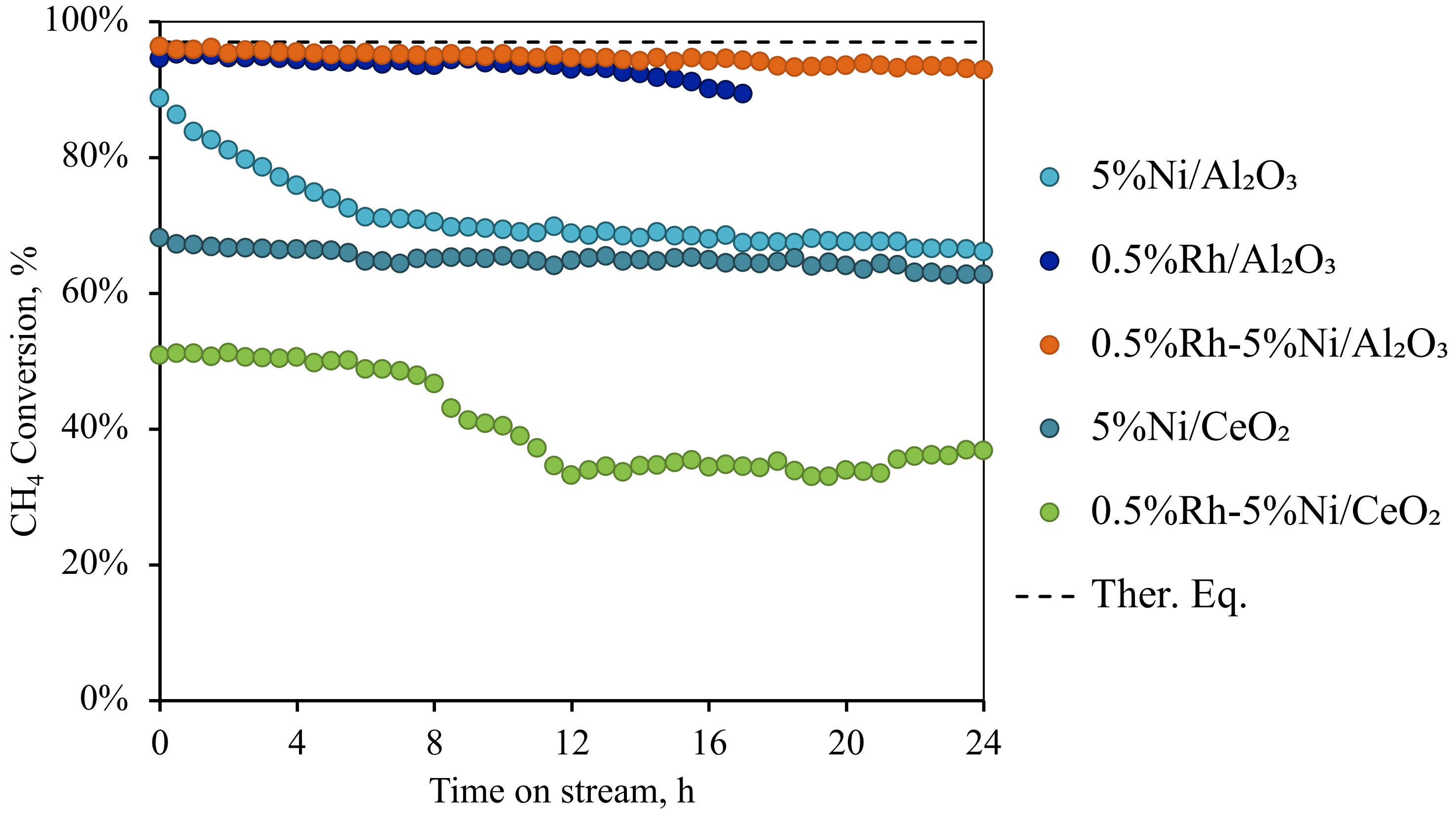
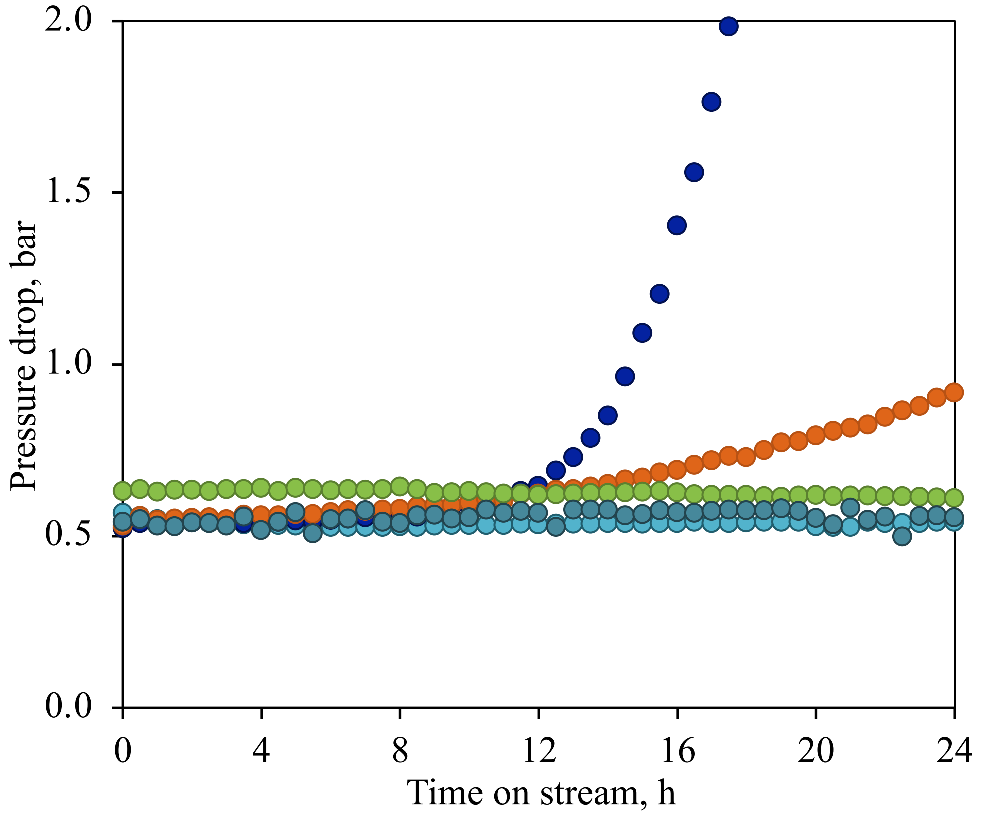
Stability tests (T = 750°C)





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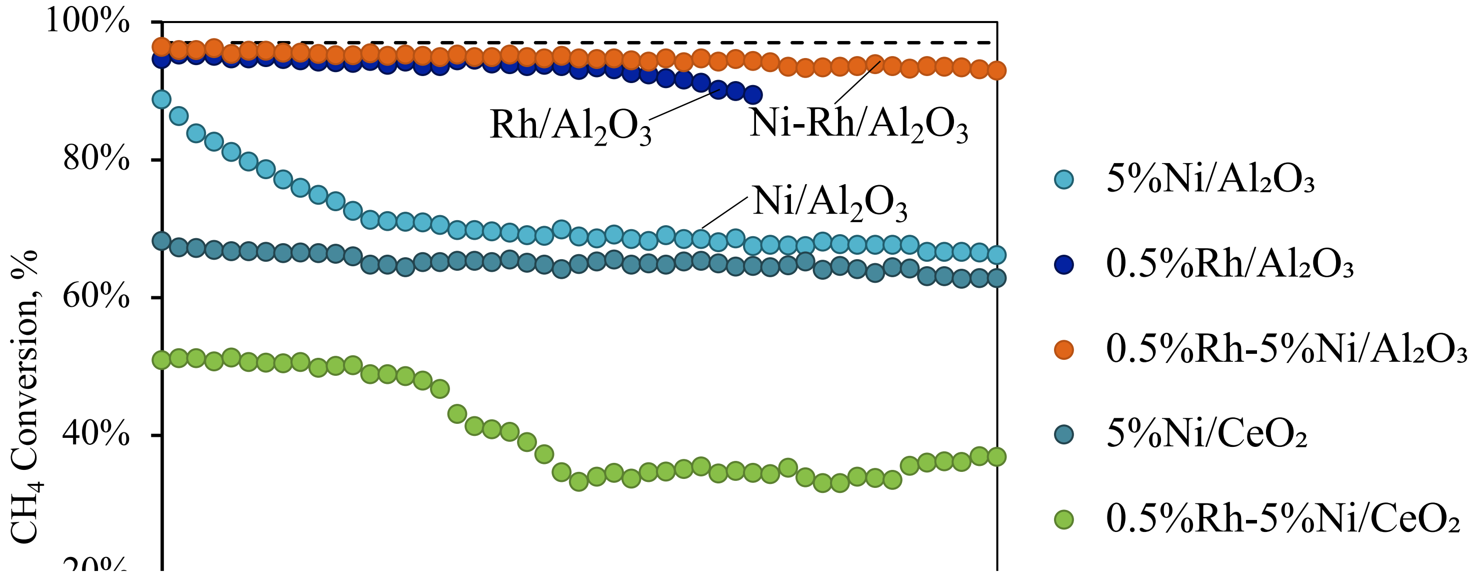
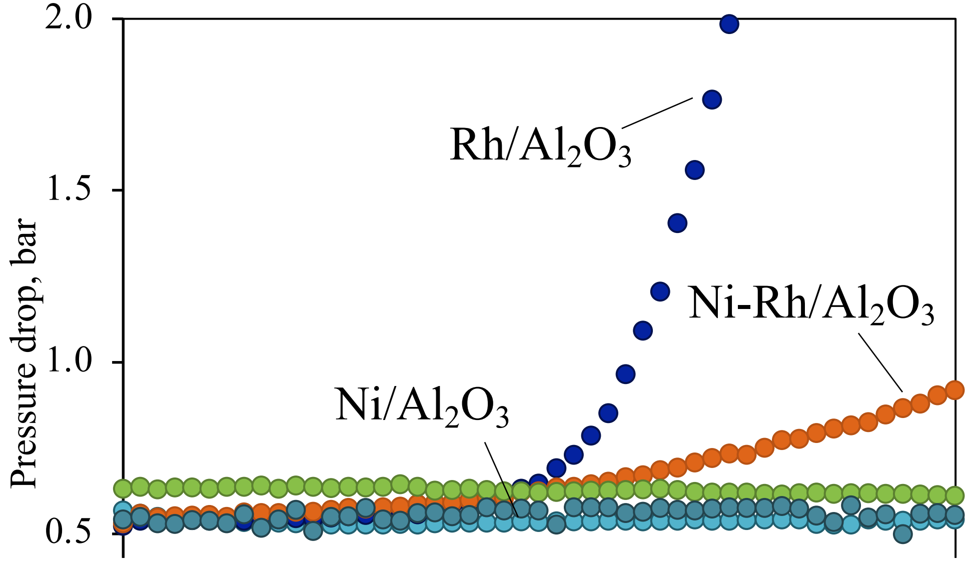


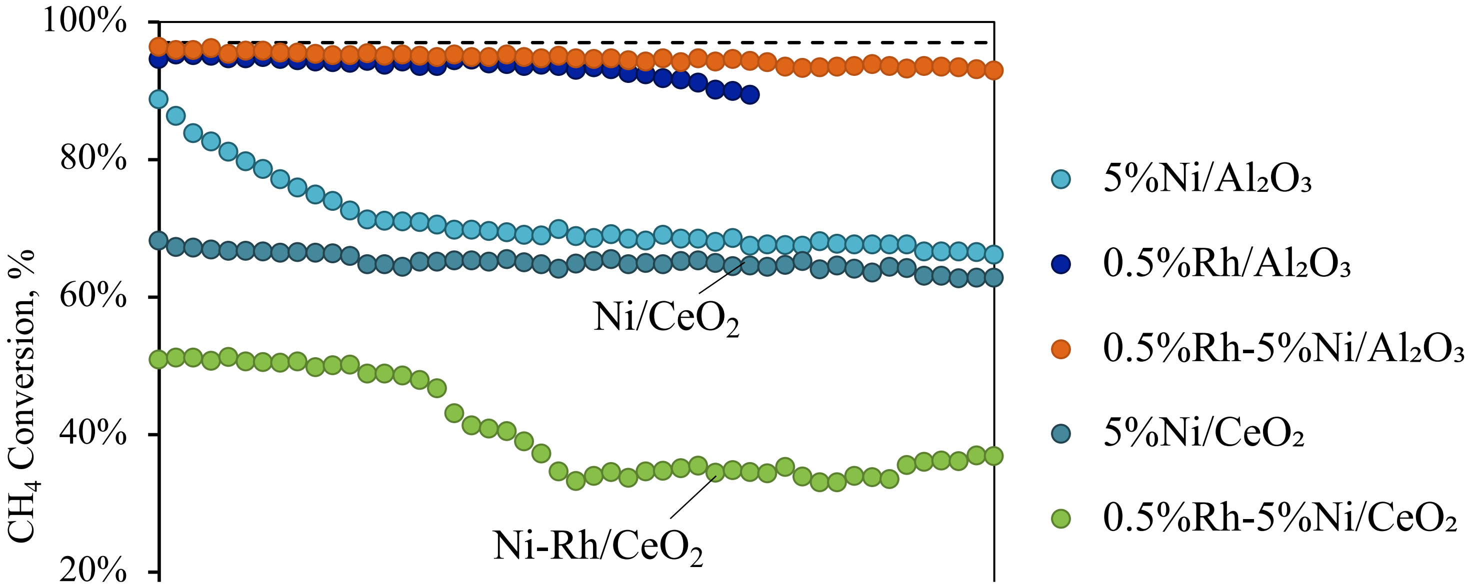


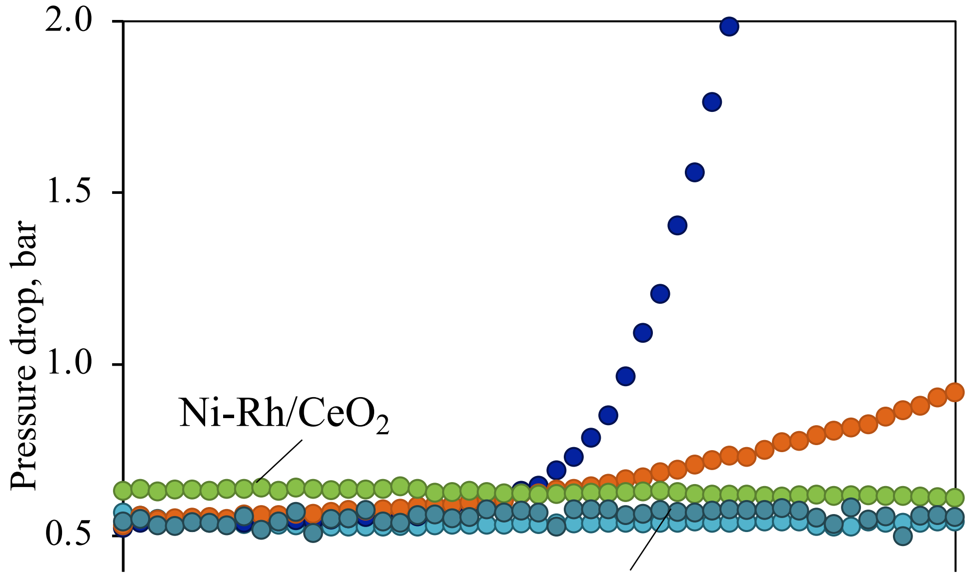
Rh
promotes coke deposition

Ni
suffers of sintering phenomenon

Rh + Ni
- **no sintering**
- **reduced coke deposition**

Stability tests (T = 750°C)





Ni/CeO_2
- **no sintering**
- **no coke deposition**

$Rh\text{-}Ni/CeO_2$
deactivates because of sintering

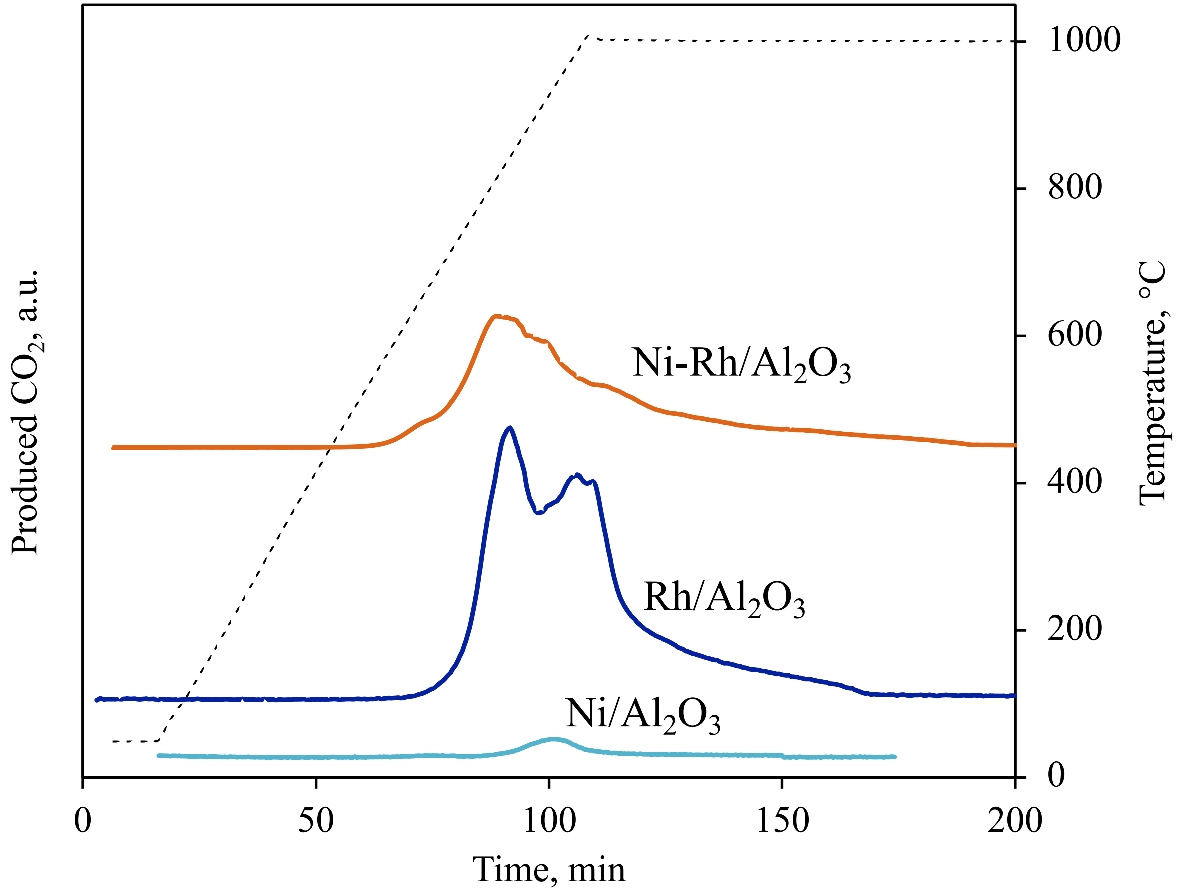
Stability tests (T = 750°C)

Coke yield $$Y_C = \frac{mol_C}{mol_{C,fed}}$$

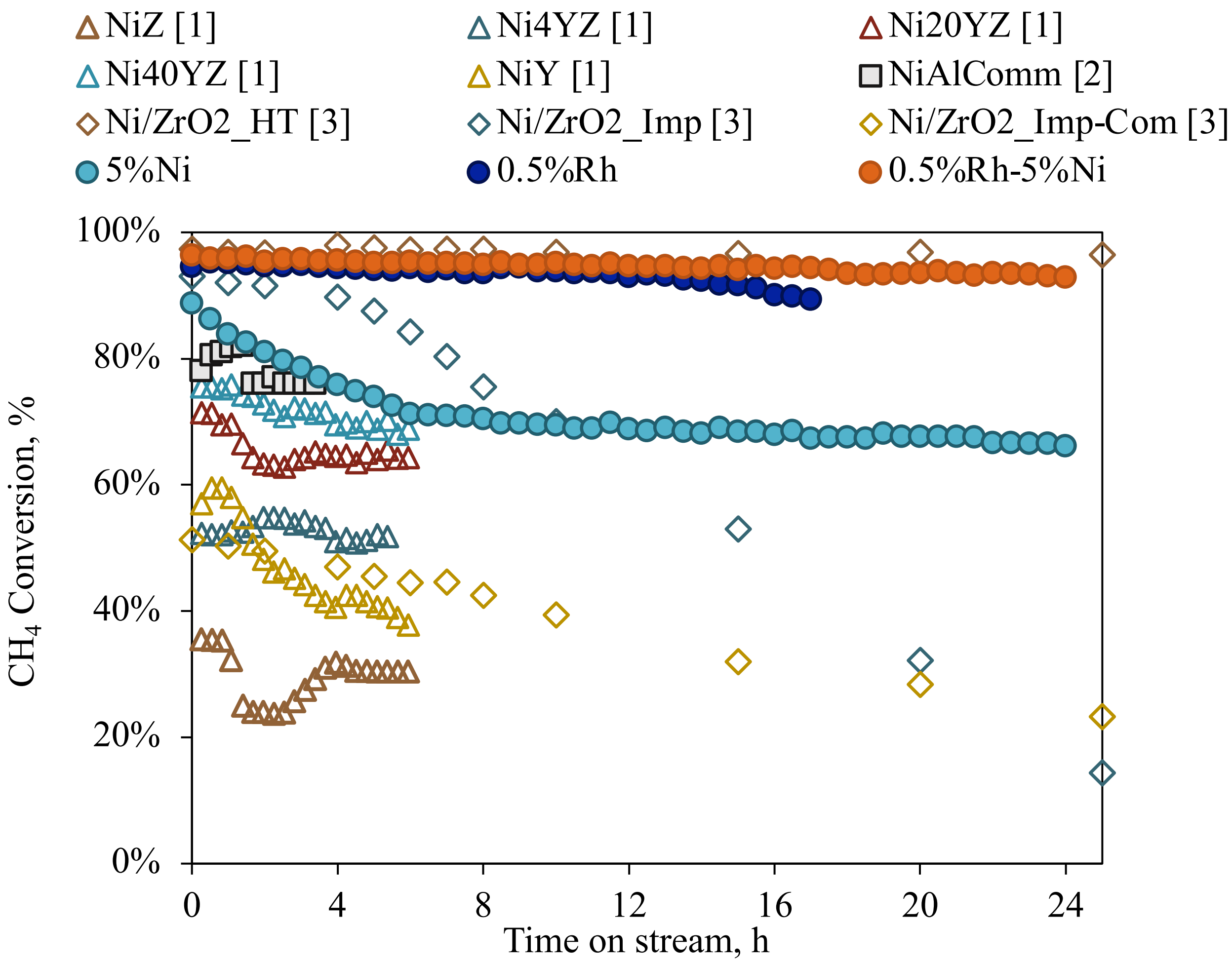
Carbon formation rate $$CFR = \frac{mass_{coke}}{mass_{catalyst} \cdot mass_{C,fed} \cdot time} \cdot 100$$

Sample	Y_C (%)	CFR ($mg_{coke}/g_{cat} \cdot g_{C,fed} \cdot h$)
5%Ni/Al_2O_3	0.010	0.0046
0.5%Rh/Al_2O_3	0.230	0.2629
0.5%Rh-5%Ni/Al_2O_3	0.095	0.0793
5%Ni/CeO_2	-	-
0.5%Rh-5%Ni/CeO_2	-	-

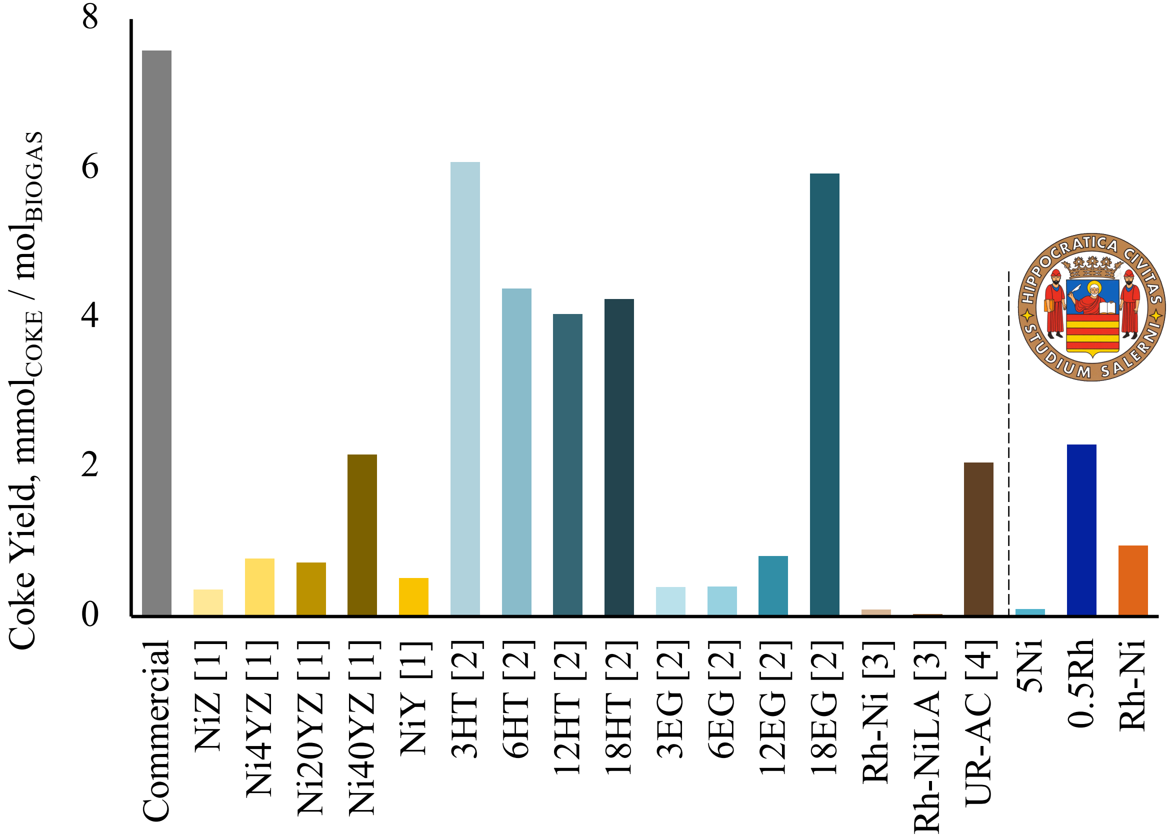
Temperature programmed oxidation



Comparison with literature



[1] Y.J.O. Asencios et al. Applied Catalysis B: Environmental 132– 133 (2013) 1– 12
[2] Y.J.O. Asencios et al. Applied Surface Science 317 (2014) 350–359
[3] R.K. Singha et al. Applied Energy 178 (2016) 110–125



[1] Y.J.O. Asencios et al. Applied Catalysis B: Environmental 132– 133 (2013) 1– 12
[2] P. Djinovi´c et al. Catalysis Today 253 (2015) 155–162
[3] A.F. Lucrédio et al. Fuel Processing Technology 102 (2012) 124–131
[4] C. Italiano et al., International Journal of Hydrogen Energy (2015)

Conclusions

Background

Biogas can be considered as an alternative to natural gas in hydrogen production

Catalysts for biogas reforming suffers of deactivation mainly because of sintering and coke deposition

This work

High metal dispersion ensure higher activity towards BOSR

Ni-Al_2O_3 interactions are not sufficient to ensure the thermal stability of the catalyst

Ni-Rh-Al_2O_3 interactions allow the active species stabilization and resistence to sintering and reduce coke deposition on Rh sites

Ni-CeO_2 interactions ensure the catalyst thermal stability and **CeO_2 avoid coke deposition**, but the activity is lowered by the worse metal dispersion

Al_2O_3-based formulations offered promising performances if compared to other results in literature

Thank you for your kind attention!

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