Noble metals-based catalysts for hydrogen production via bioethanol reforming in a fluidized bed reactor

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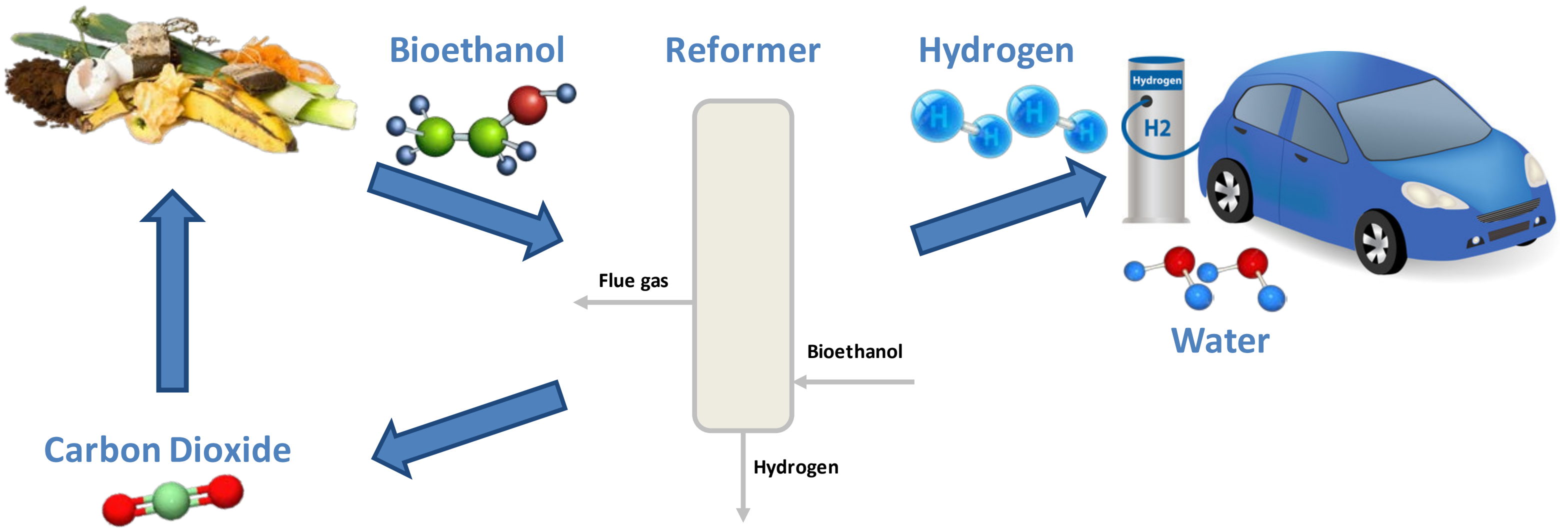
BIOETHANOL AS H_2 SOURCE



BIOETHANOL Typical composition: 12-15 wt% ethanol[1]

Impurities: few ppm to 1% of heavier alcohols, acids, aldehydes, esters

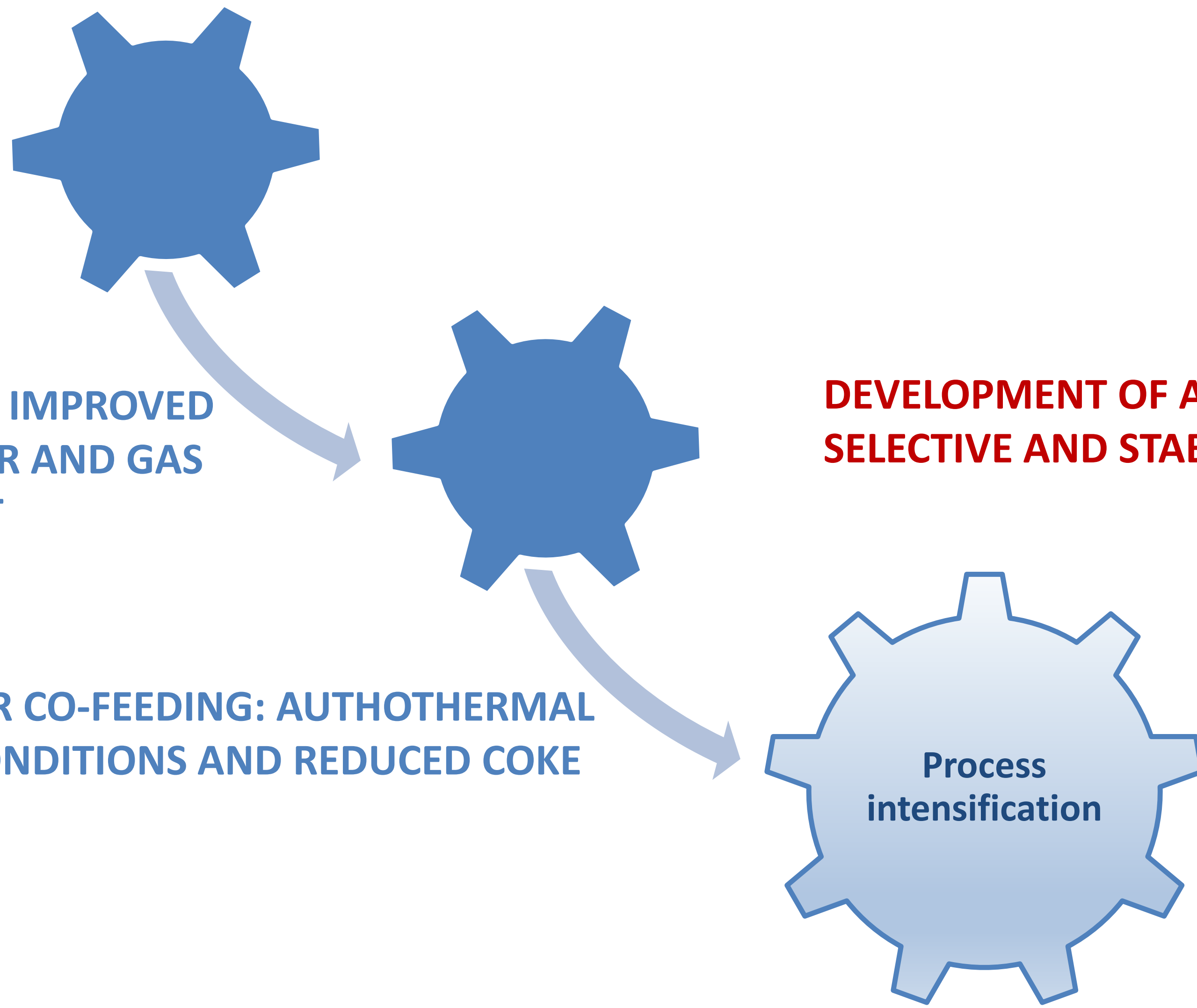
Expensive steps for bioethanol dehydration and purification

Direct use of raw bio-ethanol →

Rarely investigated for reforming: negative impact on the catalyst[2]

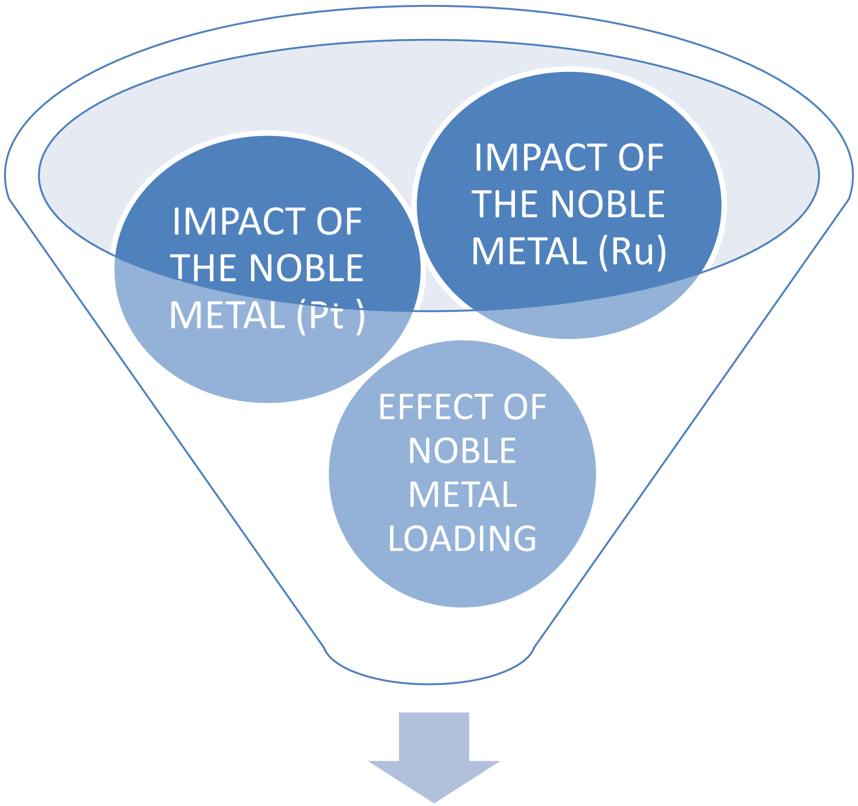
[1] Wang. W. et al., Int. J. Energy Res. 34 (2010) 1285-1290.
[2] Le Valant A. et al., Int J Hydrogen Energy 36 (2011) 311-318.

ETHANOL REFORMING: PROCESS INTENSIFICATION



AIMS OF THE WORK

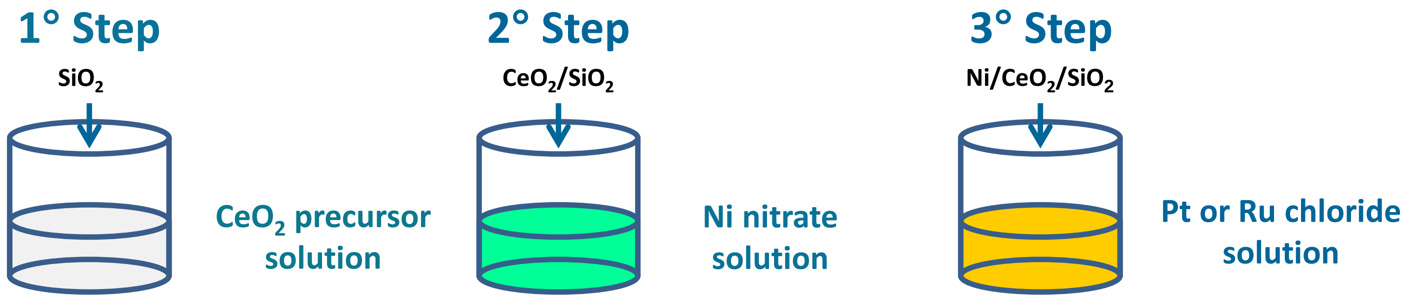
EVALUATION OF THE STABILITY OF BIMETALLIC CATALYSTS FOR OXIDATIVE STEAM REFORMING IN A FLUIDIZED BED



SELECTION OF DURABLE CATALYSTS TO TEST UNDER RAW BIOETHANOL

CATALYST PREPARATION & CHARACTERZATION

Mesoporous SiO_2 gel

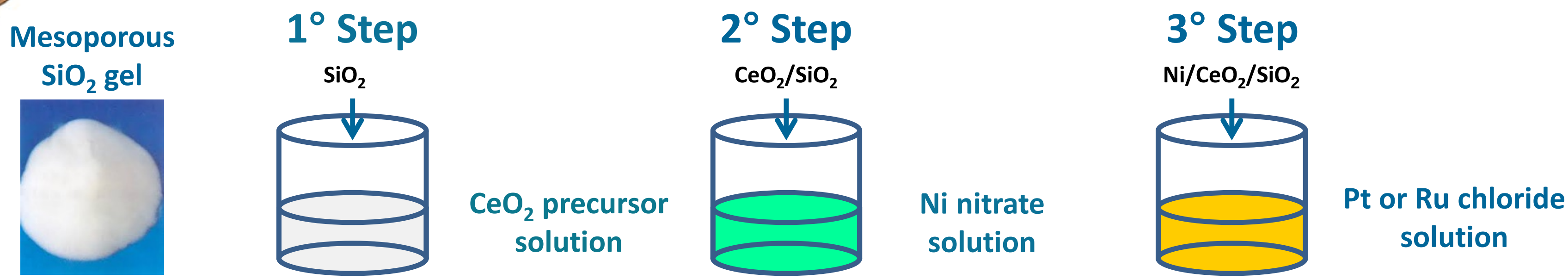


- $10Ni/CeO_2$-SiO_2
- $0.5Pt$-$10Ni/CeO_2$-SiO_2
- $1Pt$-$10Ni/CeO_2$-SiO_2
- $2Pt$-$10Ni/CeO_2$-SiO_2
- $3Pt$-$10Ni/CeO_2$-SiO_2
- $0.5Ru$-$10Ni/CeO_2$-SiO_2
- $1Ru$-$10Ni/CeO_2$-SiO_2
- $2Ru$-$10Ni/CeO_2$-SiO_2
- $3Ru$-$10Ni/CeO_2$-SiO_2

Impregnation order (Ni earlier than Pt), Ni (10 wt%) and Pt/Ru (3 wt%) loadings as well as CeO_2/SiO_2 ratio (30 wt%) previously optimized

Palma V. et al., Int. J. Hydrogen Energ., 42, 2017, 1598-1608.

CATALYST PREPARATION & CHARACTERZATION



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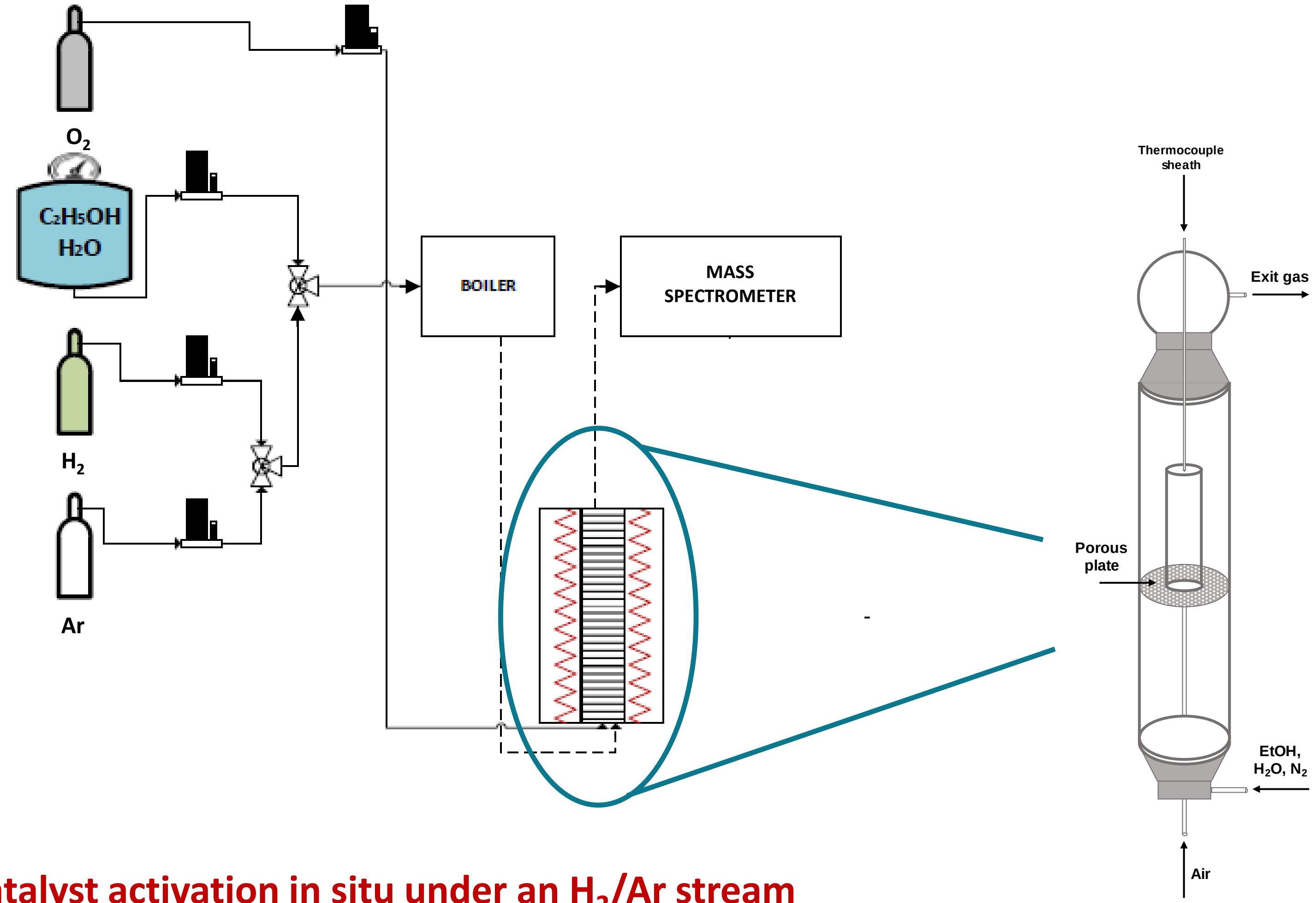
- $2Ru$-$10Ni/CeO_2$-SiO_2
- $3Ru$-$10Ni/CeO_2$-SiO_2

Characterization: Surface Area Measurements (BET) on fresh and spent catalysts
Thermogravimetric (TGA) Analysis on Spent Catalysts

Carbon formation rate measurements from TGA data $CFR = \frac{mass_{coke}}{mass_{catalyst} \cdot mass_{carbon,fed} \cdot time}$

Palma V. et al., Int. J. Hydrogen Energ., 42, 2017, 1598-1608.

LABORATORY APPARATUS & PROCEDURE



- Catalyst activation in situ under an H_2/Ar stream
- Stability test at H_2O/C_2H_5OH (r.a.) ratio of 4 and O_2/C_2H_5OH (r.o.) of 0.5

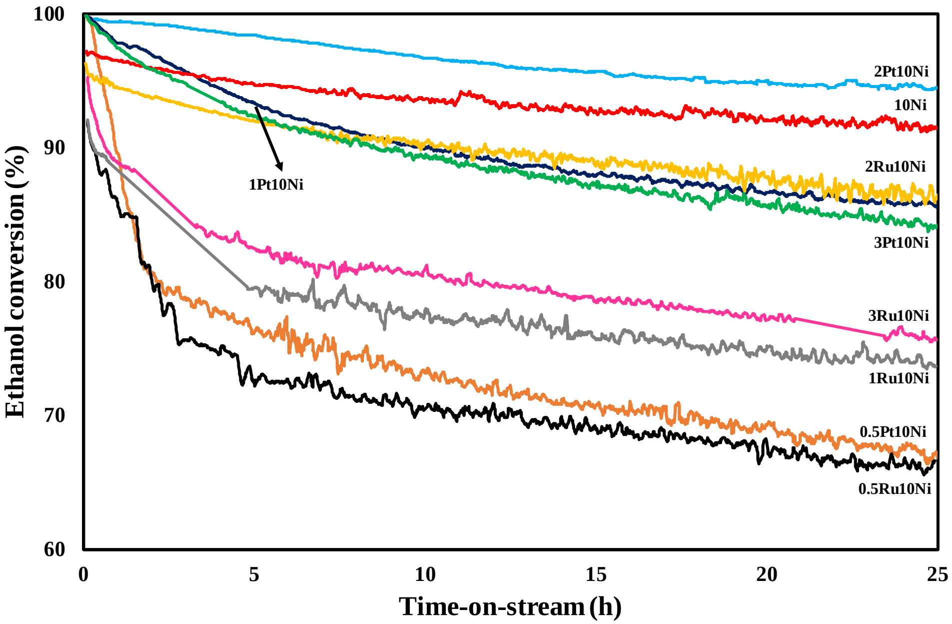
WHSV (ethanol mass flow rate/catalytic mass) = 61.7 h^{-1} T=500°C

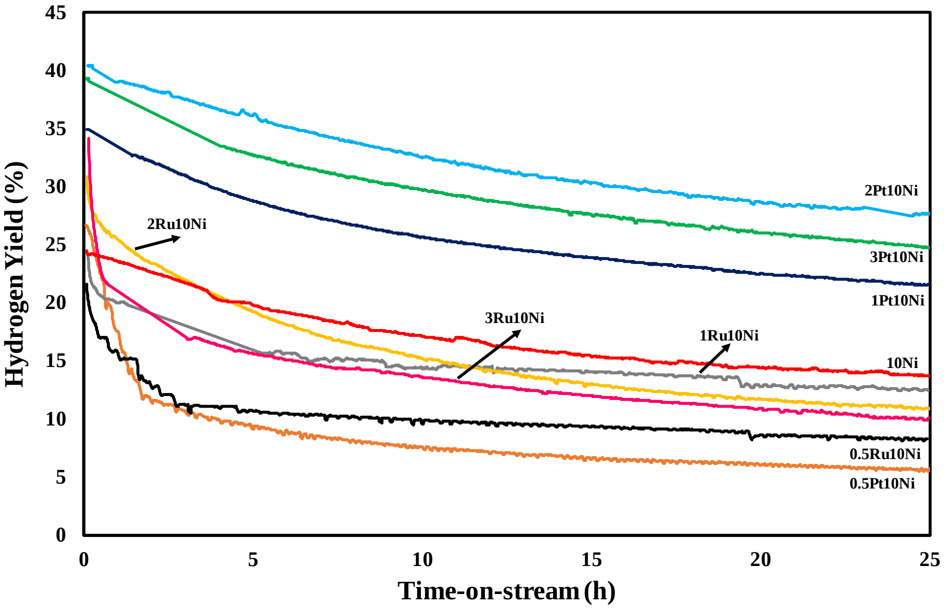
Palma V. et al., Int. J. Hydrogen Energ., 42, 2017, 1598-1608.

RESULTS OF STABILITY TESTS

EFFECT OF CATALYTIC FORMULATION: Ru-Ni and Pt-Ni SAMPLES

T=500°C $H_2O/C_2H_5OH=4$ $O_2/C_2H_5OH=0.5$ WHSV=61.7 h^{-1}





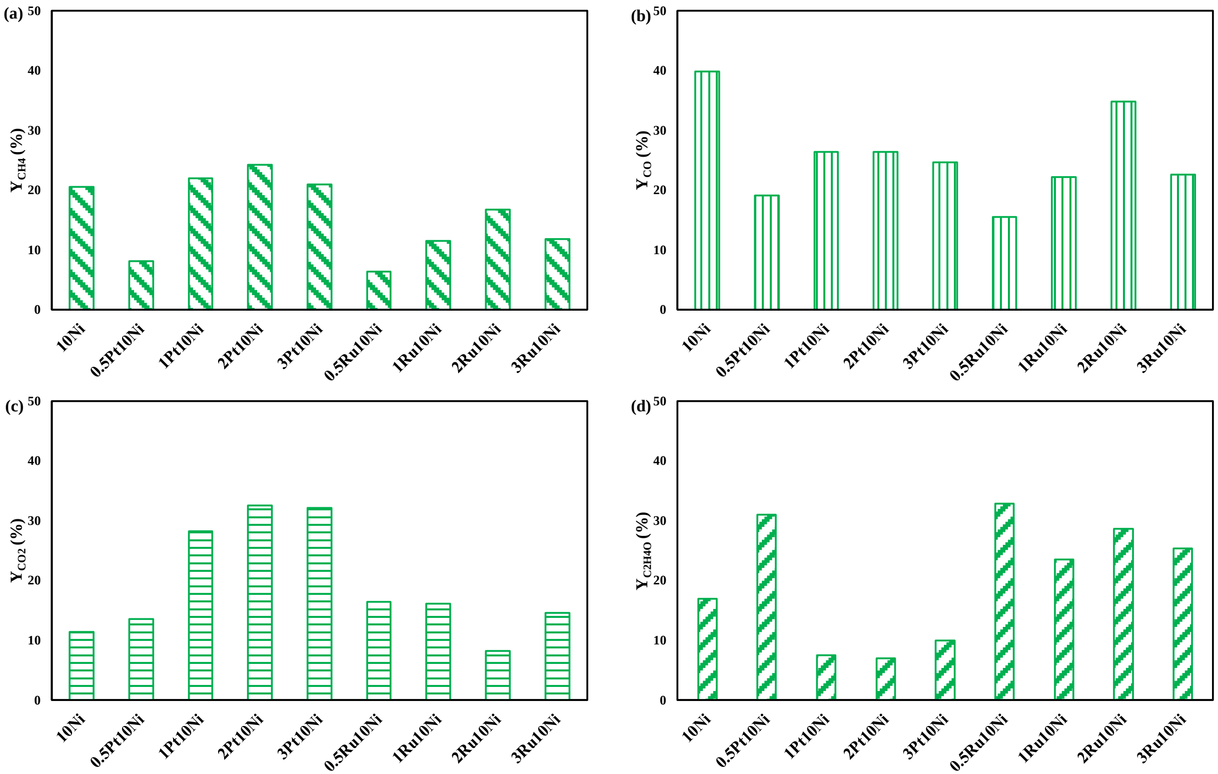
HIGEST DURABILITY FOR THE 2Pt10Ni SAMPLE

Low hydrogen yield over the 0.5Ru10Ni and 0.5Pt10Ni catalysts, previously identified as the most active samples

Ruocco C. et al., Top. Catal. 62, 2019, 1-12.

RESULTS OF STABILITY TESTS

REACTION PRODUCTS YIELD



High C_2H_4O production and low CH_4 yield over Ru series and 0.5Pt10Ni catalyst: occurrence of methane decomposition and coke formation

Ozkan G. et al., Int. J. Hydrogen Energ., 44, 2019, 9823-9829.

SPENT CATALYSTS CHARACTERIZATION

BET Analysis and CFR

Sample	BET Fresh Sample ($m^2 \cdot g^{-1}$)	BET Spent Sample ($m^2 \cdot g^{-1}$)	CFR ($g_{coke} \cdot g_{catalyst}^{-1} \cdot g_{carbon,fed}^{-1} \cdot h^{-1}$)
10Ni	230	182	$3.9 \cdot 10^{-6}$
0.5Pt10Ni	213	145	$8.4 \cdot 10^{-6}$
1Pt10Ni	214	179	$2.4 \cdot 10^{-6}$
2Pt10Ni	226	191	$1.5 \cdot 10^{-6}$
3Pt10Ni	227	186	$2 \cdot 10^{-6}$
0.5Ru10Ni	212	142	$7.9 \cdot 10^{-6}$
1Ru10Ni	208	143	$5.1 \cdot 10^{-6}$
2Ru10Ni	210	145	$5.8 \cdot 10^{-6}$
3Ru10Ni	218	149	$6.3 \cdot 10^{-6}$

Pronounced area reduction over the Ru series and the low-loaded samples due to carbonaceous deposits accumulation

CONCLUSIONS & FUTURE ACTIVITIES

Stability of Pt-Ni/CeO_2-SiO_2 and Ru-Ni catalysts for oxidative reforming of ethanol in a fluidized bed reactor

- ✓ Highest ethanol conversion and hydrogen yield over the 2Pt10Ni catalyst and good performance of the noble metals-free sample
- ✓ Worst durability for the 0.5Pt10Ni and 0.5Ru10Ni
- ✓ Increase of C_2H_4O selectivity over the Ru series
- ✓ Decrease of the carbon formation rate in the order 2Pt10Ni<3Pt10Ni<1Pt10Ni<10Ni

FUTURE ACTIVITIES: EVALUATION OF 2Pt-10Ni/CeO_2-SiO_2 CATALYST DURABILITY UNDER RAW BIOETHANOL FEEDING

THANK YOU FOR YOUR ATTENTION

ACKNOWLEDGEMENTS

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