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Introduction

Reforming reactions of biogas, arising from anaerobic digestion of organic waste and typically consisting of methane (50–75%), carbon dioxide (25–50%) and smaller amounts of nitrogen (2–8%), are presently a desirable route in the circular economy strategy reducing the environmental impact of greenhouse gas emissions. The catalytic conversion of biogas into syngas by **Dry Reforming (DR)**, $\text{CO}_2 + \text{CH}_4 \rightarrow 2\text{CO} + 2\text{H}_2$, $\Delta H_{298\text{K}} = 247 \text{ kJ/mol}$ is ideal for its further transformation into fuels and oxygenates thanks to optimal H₂/CO ratio.

The Ni/Al₂O₃ industrial catalysts adopted for syngas production by **CH₄ Steam Reforming (SR)** suffer from deactivation problems when applied with dry feed, due to sintering and coking phenomena. The variable composition of biogas, having generally CH₄/CO₂ ≥ 1 depending on the different waste adopted for its obtainment, prompts to find robust catalysts that are able to completely convert CH₄ by addition of wet air. In this complex feed (CH₄+CO₂+O₂+H₂O), a **CH₄ Tri-Reforming process (TR)** might occur consisting of concomitant **Partial Oxidation (PO)**, $\text{CH}_4 + 1/2\text{O}_2 \rightarrow 2\text{CO} + 2\text{H}_2$ by O₂, SR by H₂O, and DR by CO₂ reactions.

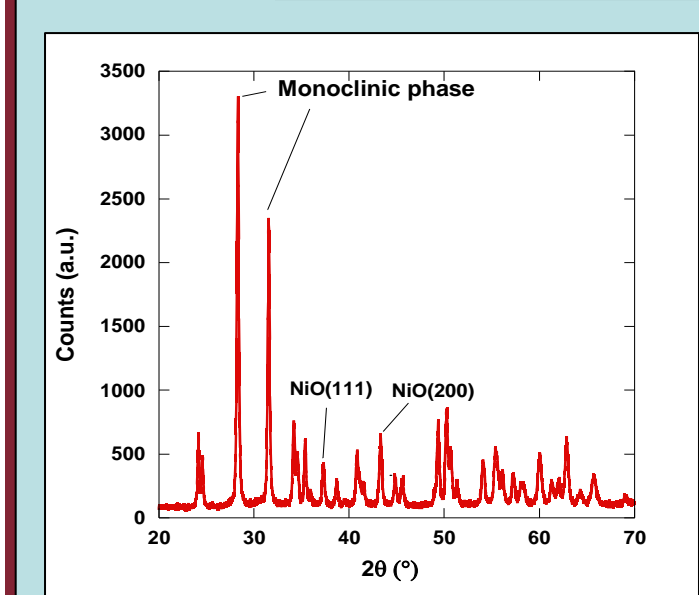
In this work the CH₄-TR performances of a supported Ni/ZrO₂ catalyst, resistant to sintering and carbon deposition in the CH₄-PO [1], are compared with those of a NiCo alloy supported on Al₂O₃, very active as magnetic catalyst for CH₄-SR [2].

Characterization

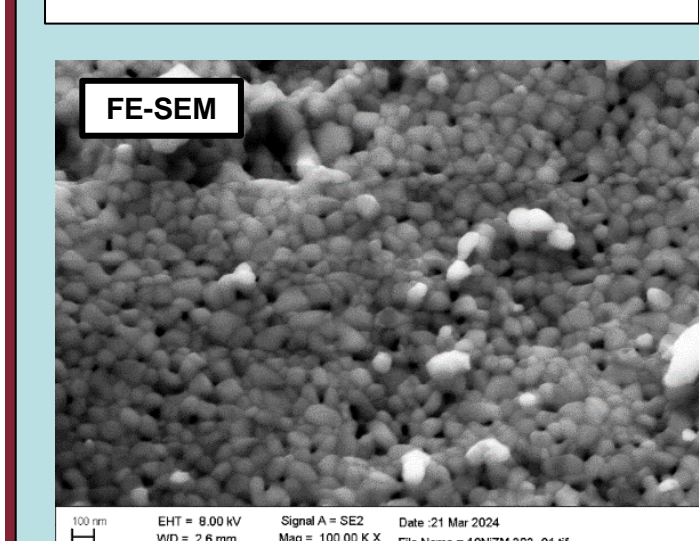
XRD and FE-SEM of fresh samples...

10.6NiO/Zm

Calcined precursor



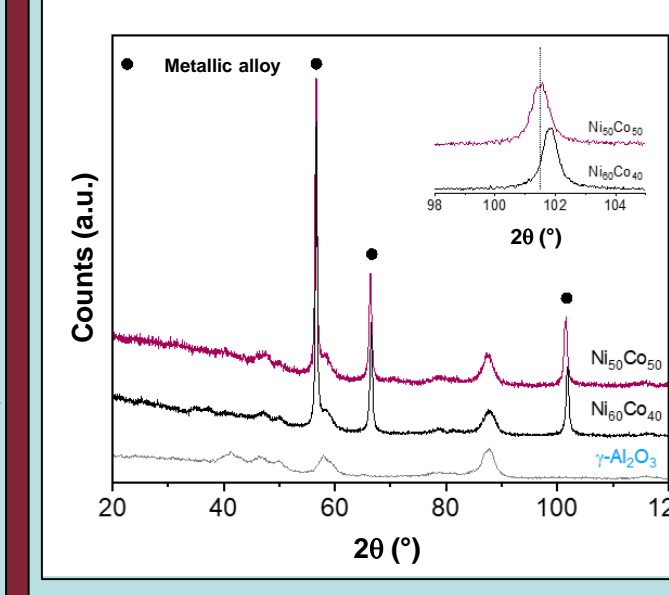
In XRD spectrum of calcined precursor
 > reflections of monoclinic ZrO₂ and NiO phases are present
 > crystallites mean diameter is 45 nm for NiO and 50 nm for ZrO₂



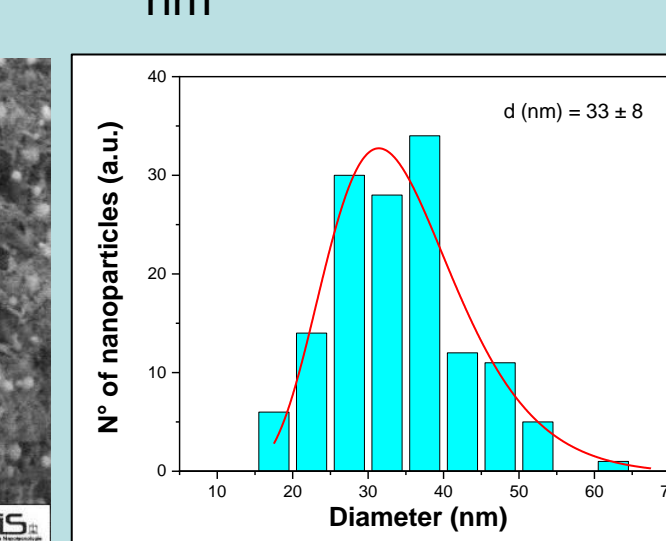
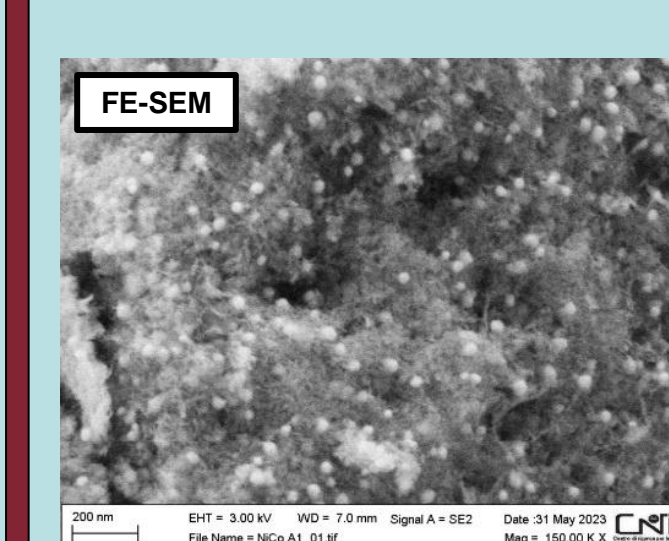
In FE-SEM images
 > NiO particles are not distinguished from those of ZrO₂ support, suggesting similar morphology and size

Ni₅₀Co₅₀/γ-Al₂O₃

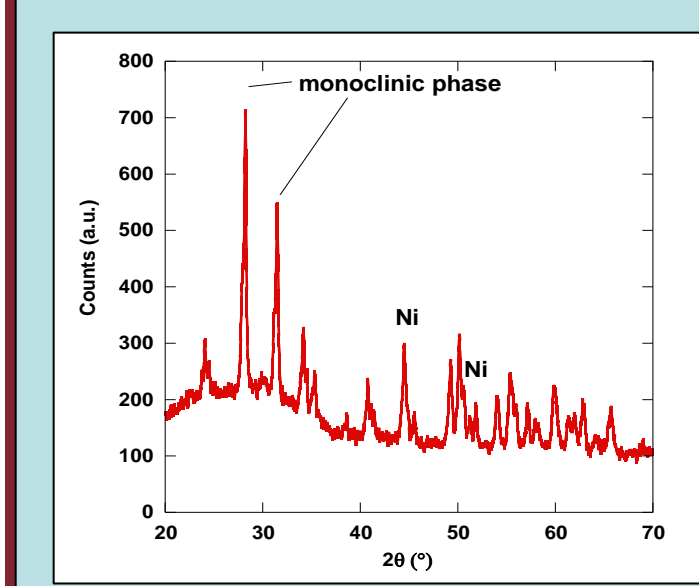
Reduced catalyst



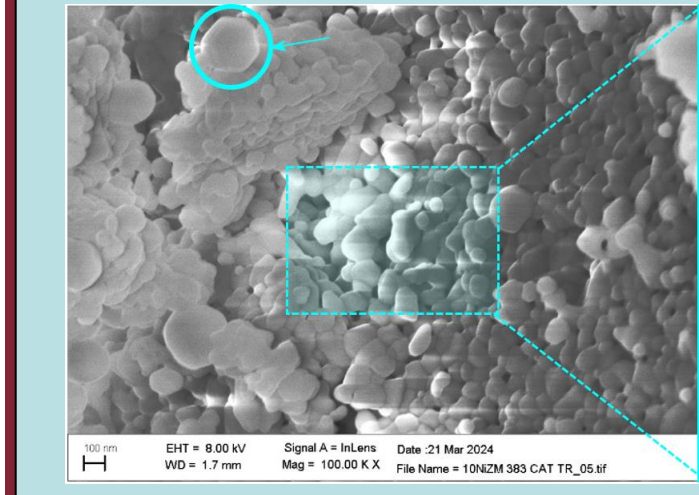
In XRD spectrum of reduced fresh catalyst
 > reflections of the metallic NiCo alloy and of γ-Al₂O₃ are present
 > mean diameter of NiCo nanoparticles is 33 nm, with a distribution of the sizes between 15 and 70 nm



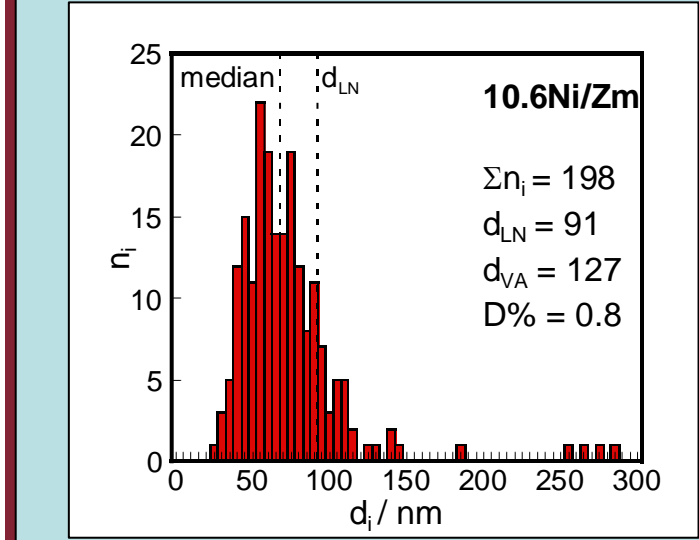
...and after TRI-REFORMING reaction



XRD spectra show signals of metallic Ni⁰. Monoclinic ZrO₂ signals remain unchanged.
 > Crystallites mean diameter of Ni is 45 nm, suggesting aggregation of Ni⁰ crystallites

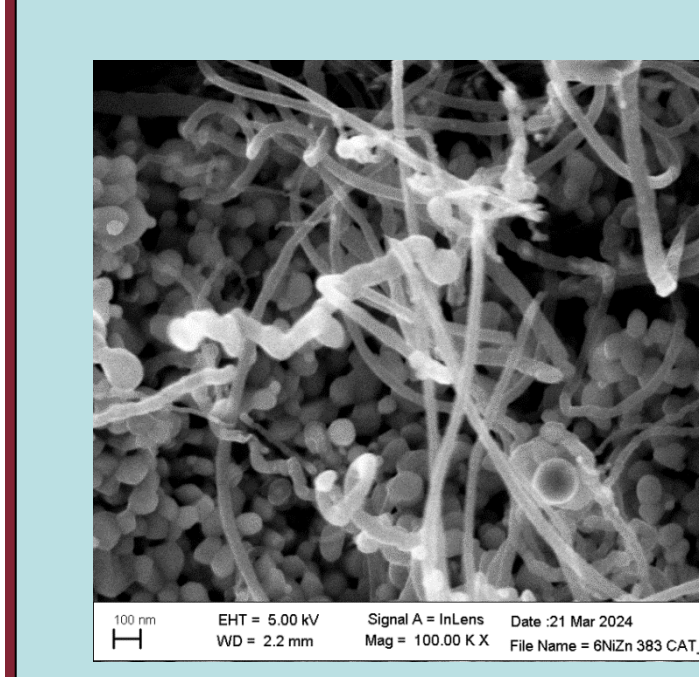


NiCo particles are somewhat larger than in fresh catalyst and reach size of 200 nm
 => some aggregation occurs also on Al₂O₃ support



particle size distribution, obtained by SEM images analysis, shows an increase of Ni nanoparticles mean size (about 90 nm) compared to NiO, confirming aggregation after the catalytic process

...or after DRY-REFORMING reaction



Formation of C nanotubes under DR reaction, whereas they don't form under TR

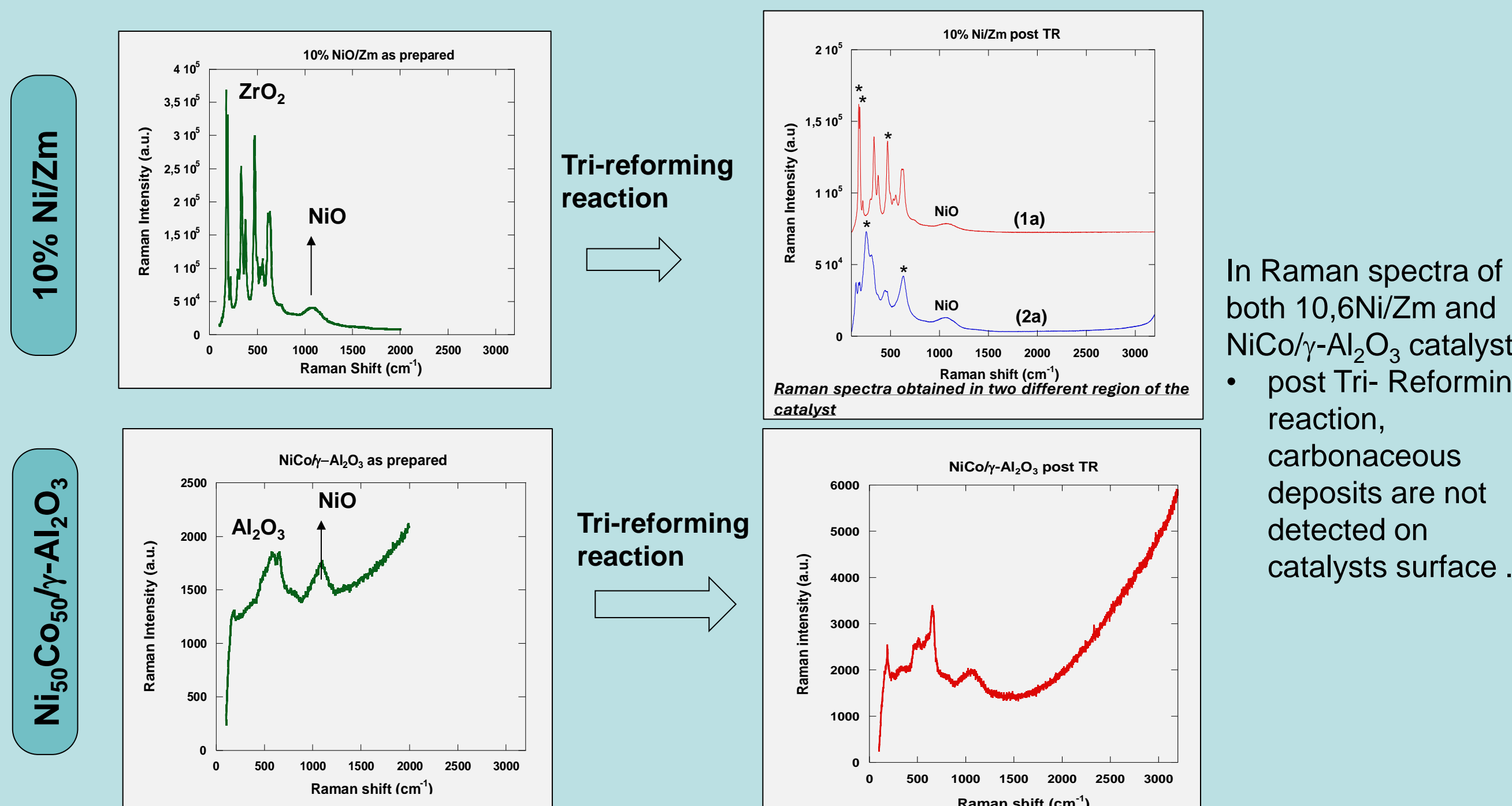
Catalysts	S.A. (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)
Zm	5.6	0.041
10.6NiO/Zm fresh	4.5	0.039
γ-Al ₂ O ₃	250	0.843
Ni ₅₀ Co ₅₀ /γ-Al ₂ O ₃ fresh	140	0.503

XRD analysis before and after catalysis shows that NiO is completely reduced during activation and remains reduced throughout the catalytic processes.

Despite the markedly lower specific surface area of ZrO₂ compared to γ-Al₂O₃ (45 vs 150 m²g⁻¹), the metallic nanoparticles reached dimensions little different in the two catalysts (up to 280 nm on ZrO₂ vs 200 nm on Al₂O₃), thus suggesting a quite similar interaction between metals and the two supports.

The formation of carbon nanotubes mainly depends from the specific catalytic reaction, suggesting that an higher concentration of oxidants in TR condition (CO₂+O₂+H₂O) avoids the formation on carbonaceous deposits on catalyst's surface.

Raman Spectroscopy



Experimental

Materials

Precursor → **Monoclinic NiO/ZrO₂ (NiO/Zm)** with Ni content about 10 wt%

> obtained by dry-impregnation of high surface area **Zr-oxhydroxide (Z_{hy}, 360 m² g⁻¹)** with Ni(NO₃)₂(aq) solution, drying at 110 °C and calcining at 900 °C (5 h) with a **slow heating rate** (0.25 °C/min).

Catalysts → **Monoclinic Ni/ZrO₂ (Ni/Zm)**

> obtained by *in situ*-reduction of NiO/Zm precursors in H₂/He flow up to 800 °C.

Precursor → **NiO-CoO/γ-Al₂O₃** with about 12.5% Ni and 12.5% Co

> Obtained by dehydration of γ-Al₂O₃ a 450 °C; co-equilibrium absorption of Ni(NO₃)₂*6H₂O and Co(NO₃)₂*6H₂O aqueous solution, overnight under **constant** magnetic agitation at T=25°C; filtration, drying at 120 °C (12 h) and calcination at 600 °C (1h) with a heating rate of 10°C/min.

Catalysts → **NiCo/γ-Al₂O₃ (Ni₅₀Co₅₀)**

> obtained by *in situ*-reduction of precursors in H₂/Ar flow for 5h at 900 °C.

Characterization and reactivity studies

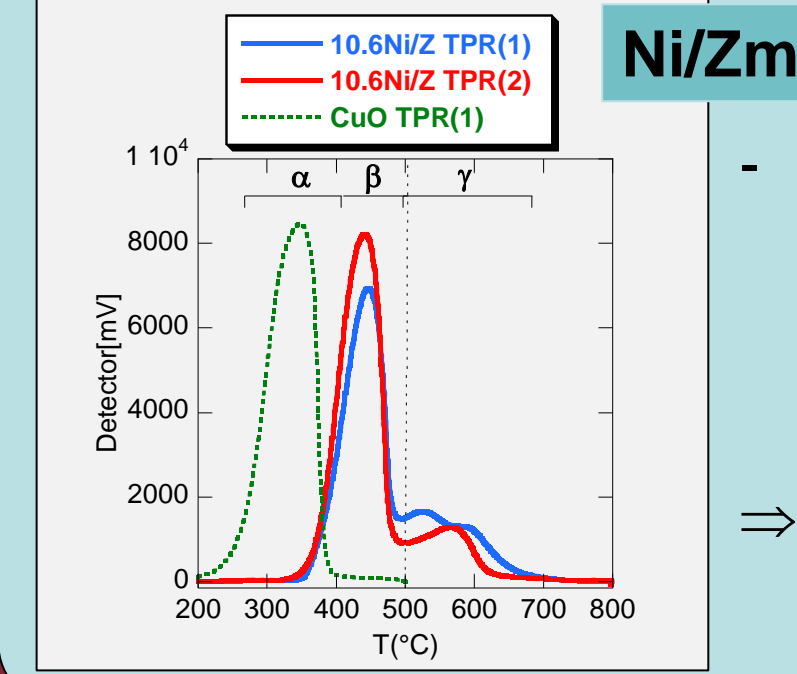
- **Chemical analysis** → Atomic Absorption Spectroscopy
- **N₂ adsorption/desorption at 77 K** → BET isotherm and BJH method for surface area and porosity
- **XRD characterisation** → Cu Kα (Ni-filtered) radiation
- **Raman scattering** → backscattering geometry, λ= 488.0 nm (Ar⁺ ion laser)
- **FE-SEM** → Field emission scanning electron microscopy with EDXS analysis
- **H₂-TPR and TPO analysis** → Three steps: TPR₁ + TPO+ TPR₂

Catalytic activity measurements

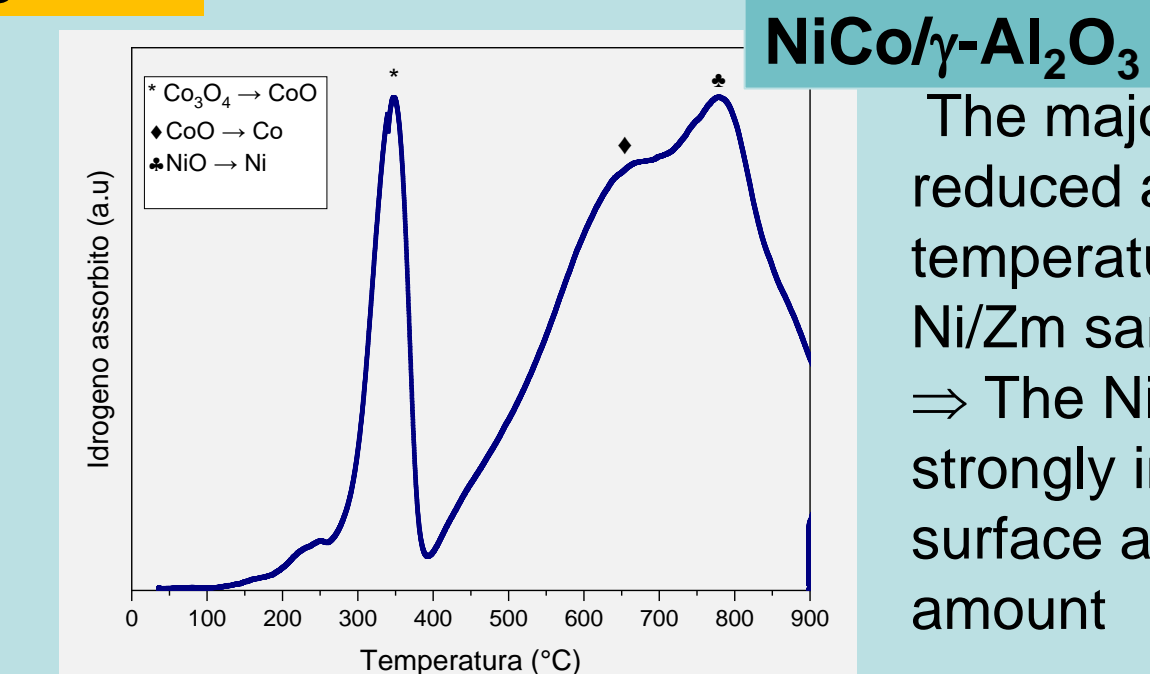
- at steady-state;
- 25 mg of catalyst; GHSV = 360 000 NL kg⁻¹ h⁻¹; F_{tot} = 150 cc/min
- plug flow reactor at atmospheric pressure;
- Micro-GC reactants and products analyses

- **Dry-reforming (DR, CH₄+CO₂)**
- **Oxy-Dry-reforming (ODR, CH₄+CO₂+O₂)**
- **Bi-reforming (BR, CH₄+CO₂+H₂O)**
- **Tri-reforming (TR, CH₄+CO₂+O₂+H₂O)**

TPR analysis



Ni/Zm
 - In TPR(2) profile the amount of NiO-γ species, strongly interacting with the surface, are little lower than in TPR(1), while new NiO-β species, less interacting with the surface, formed.
 => during TPR(1) only a small fraction of the NiO suffers disanchoring and little sintering.

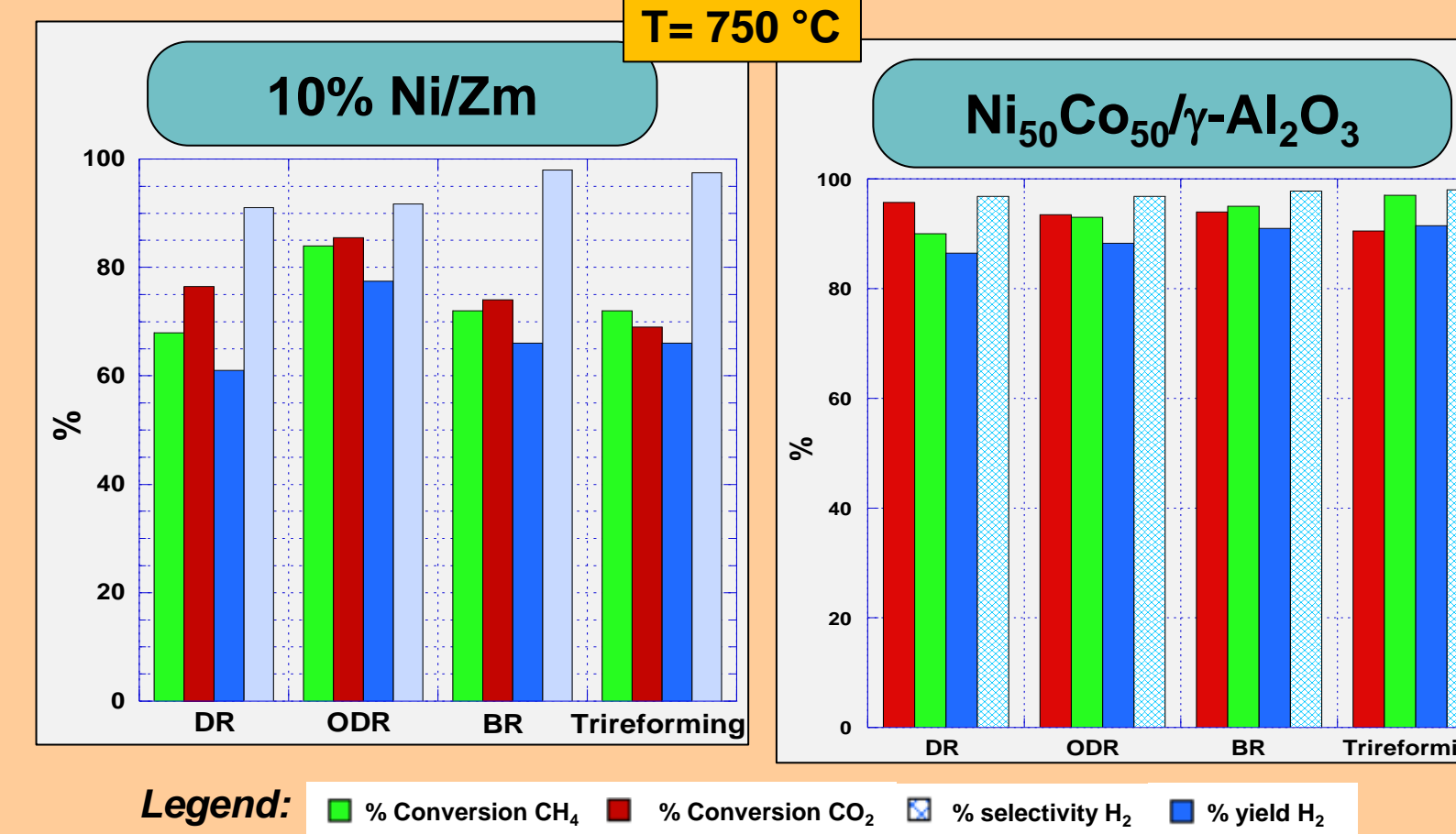


NiCo/γ-Al₂O₃
 The major amount of NiO reduced at higher temperature compared to Ni/Zm sample
 => The NiO species strongly interacting with the surface are in higher amount

Catalytic activity

CO₂ valorization in various mixtures

Reactants concentration:
 [CH₄]=CO₂ = 6%, [H₂O]=0.6%, [O₂]=0.3%.



The two catalysts show high catalytic activity for the H₂ production through reforming of CO₂ with methane by all processes (Dry-, Oxy-Dry-, Bi- e Tri-reforming) with Ni₅₀Co₅₀/γ-Al₂O₃ a little more active than 10.6Ni/Zm:
 • CO₂ conversion was always ~ 95%.

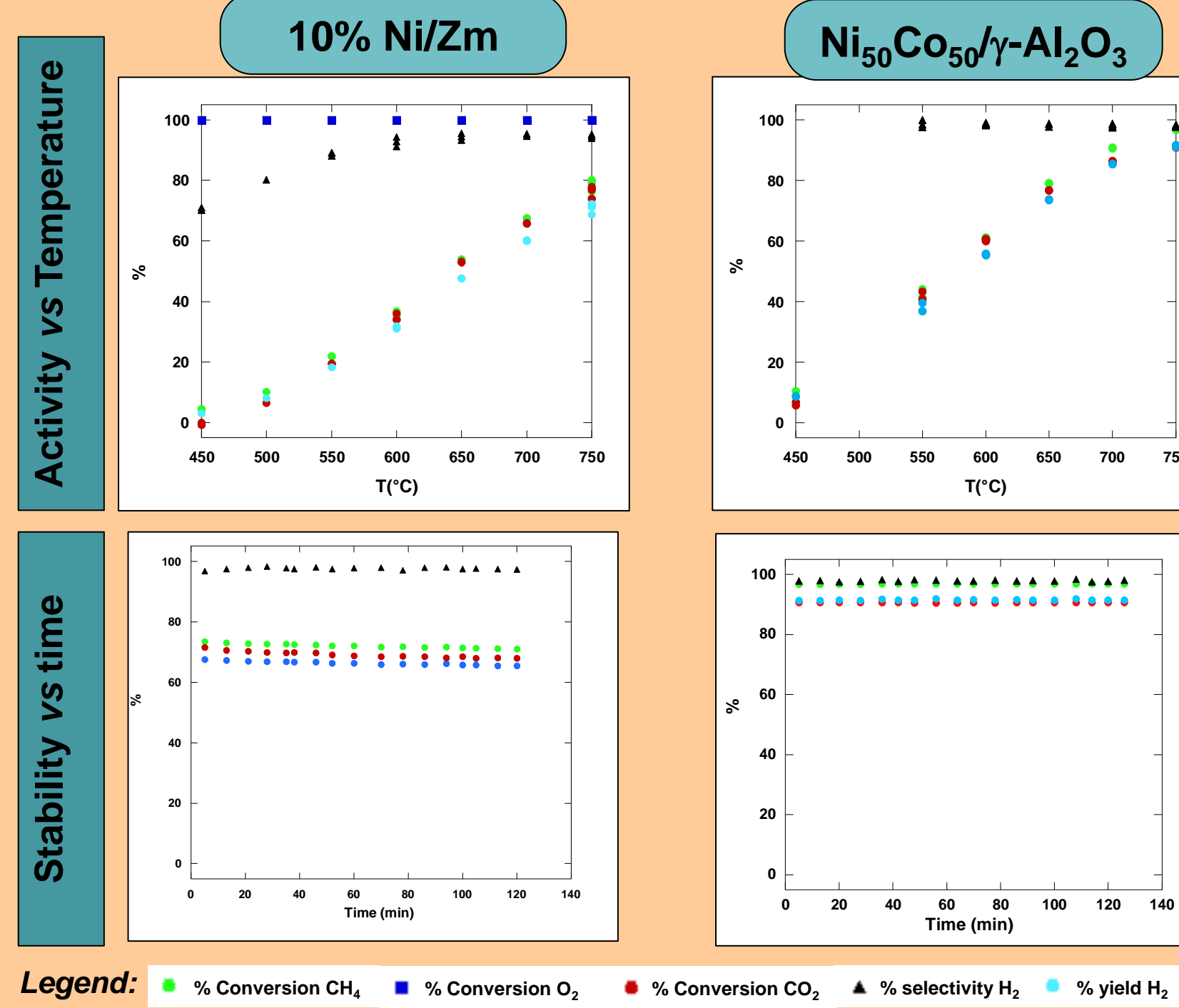
for Ni₅₀Co₅₀/γ-Al₂O₃ the selectivity was always ~ 98%, while reached this value only in the Bi- and Tri-Reforming for 10.6Ni/Zm.

The presence of O₂ and H₂O in the reaction mixture doesn't implicate substantial variation of activity, especially for Ni₅₀Co₅₀/γ-Al₂O₃.

> **good performances with few changes in the feed composition**
 => **versatile catalysts**

Tri-reforming process

CH₄+CO₂+O₂+H₂O feed



In both 10.6Ni/Zm e Ni₅₀Co₅₀/γ-Al₂O₃,
 • the H₂/CO ratio remain nearly 1, indicating that also in presence of O₂ and H₂O the **main reaction is the Dry Reforming** CO₂+CH₄→2CO+2H₂;
 => side reactions (Water Gas Shift) doesn't occur;
 • The activity is quite stable during time on stream, with just a little decrease for 10.6Ni/Zm, indicating the absence of important deactivation phenomena.

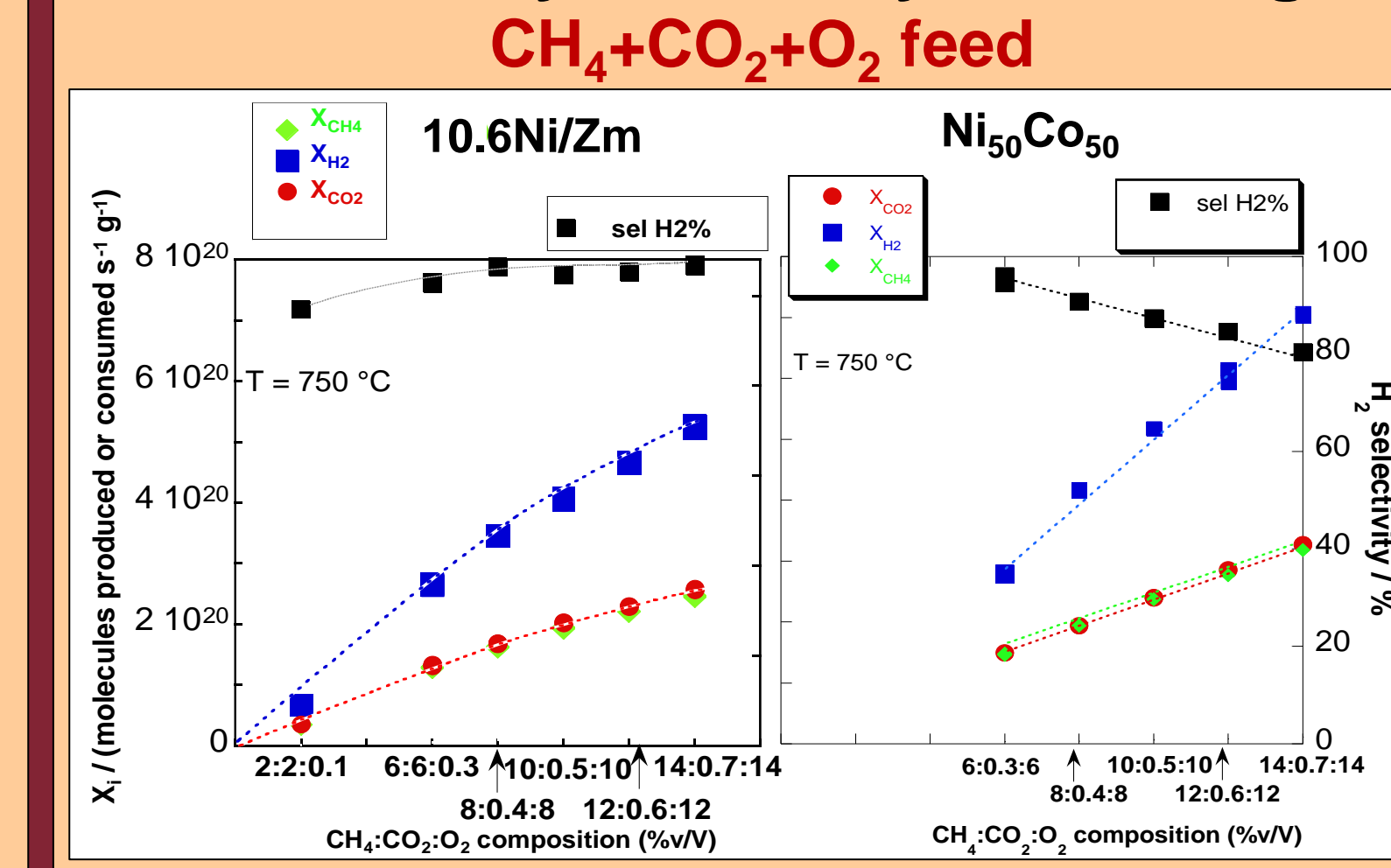
References

1. V. Poletto Dotsenko, M. Bellusci, A. Masi, D. Pietrogioiacomi, F. Varsano, Catal. Today 418, 2023, 114049
2. Campa, M.C., Pettiti, I., Tuti, S., Luccisano, G., Ardemani, L., Luisetto, I., Gazzoli, D., Pietrogioiacomi, D. Materials 2021, 14, 2495.

Productivity at increasing feed concentration

in the Oxydry-reforming

CH₄+CO₂+O₂ feed



For both catalysts, increasing [reactants] nearly up to industrial tail-gases composition and maintaining the same reactant ratio CH₄/CO₂=1
 - **CO₂ specific consumption per unit time** and **H₂ specific production per unit time** increased almost linearly,
 - H₂ selectivity almost constant or little decreasing: limited H₂O formation by Reverse Water Gas Shift

Concluding remarks

- Ni⁰ particle supported on monoclinic ZrO₂ or γ-Al₂O₃ are heterogeneous in terms of size and of their interaction-strength with the support surface.
 - Ni/ZrO₂ and NiCo/γ-Al₂O₃ catalysts are highly active and selective for syngas production by reforming of CH₄ with CO₂ in feeds with [CH₄]/[CO₂]=1.
 - A limited amount of co-fed oxidants O₂ and H₂O nearly unchanged syngas yields.
 - The quite similar activity of the two systems suggests that Ni⁰ active sites are a small fraction of exposed ones; they are possibly those at the boundary of metal particles.
- => All the results make the two systems interesting for CO₂ valorization in tail gases of industrial plants.