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SAPIENZA UNIVERSITÀ DI ROMA — Dipartimento di Chimica

Structured Co–Ni Catalysts Prepared by Additive Manufacturing for Induction-Heated Methane Bi-reforming

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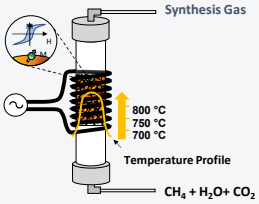
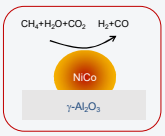
1 Why Induction Heating for Chemical Processes? Why additive manufacturing applied to catalysis ?

Methane reforming plays a key role in future sustainable energy systems. However, conventional externally heated reactors are affected by thermal inertia and heat transfer limitations. Induction heating enables direct catalyst heating through electromagnetic energy conversion, improving energy efficiency and allowing rapid start-up and shut-down. In parallel, additive manufacturing provides unprecedented control over catalyst architecture, making it possible to optimize heat and mass transfer phenomena. The combination of these two technologies offers a promising route toward process intensification and electrification of methane reforming processes.



2 The Scientific Challenge

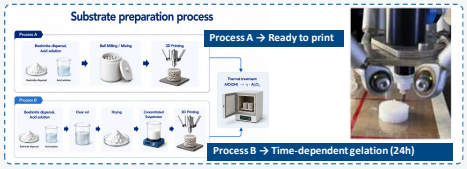
- Magnetic materials in a radiofrequency field convert electromagnetic energy into heat directly at the catalyst — contactless, rapid and localized.
- Combine, in a single material, the catalytic activity needed for methane reforming (T > 750 °C) with a magnetic response strong enough to reach that temperature.
- Ni is an excellent reforming catalyst, but its Curie temperature (350 °C) is far too low — above it, magnetic heating switches off.
- Co has a much higher Curie temperature (1200 °C) and, while a poorer reforming catalyst, promotes carbon gasification and improves stability.
- **Solution: bimetallic NiCo alloy nanoparticles supported on γ-Al_2O_3, combining catalysis and induction heating.**



3 Materials & Methods

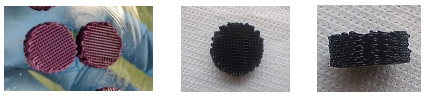
Structured substrates by Additive Manufacturing

- Aqueous boehmite paste (Disperal®, HNO_3-peptized, ~45 wt% solids), extruded layer-by-layer at room T using a Liquid Deposition Modeling (LDM) — WASP Delta 40100 Clay printer.
- Two paste routes compared: (A) ready-to-print; (B) time-dependent gelation, 24 h aging.
- Consolidation + calcination at 550 °C, 1 h — topotactic boehmite → γ-Al_2O_3 conversion.
- **Both approaches enabled successful fabrication of γ-Al_2O_3 lattice structures by Liquid Deposition Modelling**



NiCo Catalyst Synthesis

- Calcined γ-Al_2O_3 scaffolds loaded by wet impregnation with (1:1 by mol) Ni and Co nitrate precursors (4 M).
- Samples drying at 80 °C overnight.
- Calcination in air flow (600 °C, 1h) followed by reduction at 900 °C (H_2 3%vol atmosphere) → formation of the NiCo alloy phase.
- This procedure ensured homogeneous distribution of the active metallic phase throughout the structured support. Target metal loading ~10–12 wt%, near-equiatomic Ni:Co ratio.
- Monolithic supported catalysts (~5 g) assembled for reactor testing (3 discs).



Impregnated scaffolds (purple) and reduced catalysts (black)

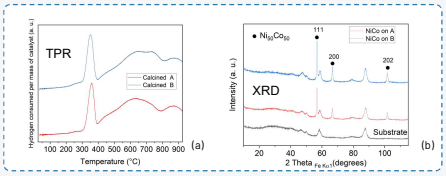
Characterization & Testing

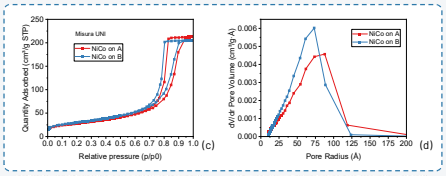
- Reducibility (H_2-Temperature Programmed Reduction-TPR)
- Structure / crystallite size: X-ray Diffraction Analysis XRD (Scherrer analysis).
- Texture: N_2 physisorption at 77 K — BET surface area, BJH pore-size distribution.
- Morphology: SEM particle-size distribution.
- Magnetic heating: Specific Absorption Rate (SAR) from temperature heating and cooling curves under an r.f. field (21–32 mT).
- Catalytic tests: custom induction-heated fixed-bed reactor, copper coil, feed CH_4:H_2O:CO_2 = 3:2:1 and 3:1:2

4 Substrate & Catalyst Characterization

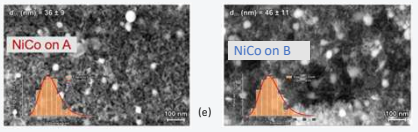
Printed γ-Al_2O_3 substrates exhibited excellent mechanical integrity together with high porosity and apparent density ~28% of the γ-Al_2O_3 theoretical value. After NiCo impregnation, calcination and reduction at 900 °C, Nitrogen adsorption measurements confirmed preservation of mesoporosity. The two substrate routes give measurably different nanoparticle sizes and textural properties: larger NiCo nanoparticles on substrate B (d_{in} = 46 nm vs 36 nm on A) cause a sharper surface-area loss vs the bare substrate (~40% for B, ~30% for A).

Sample	SSA (m^2/g)	Pore vol. (cc/g)	Me (wt%)	Ni/Co	d_{in} (SEM) (nm)	d_{ex} (SEM) (nm)	d (XRD) (nm)
γ-Al_2O_3 A	200±10	0.46	—	—	—	—	—
γ-Al_2O_3 B	220±10	0.45	—	—	—	—	—
NiCo on A	144±7	0.37	12±0.6	1.17	36±9	41±9	39
NiCo on B	130±7	0.38	12±0.6	1.02	46±10	51±11	43



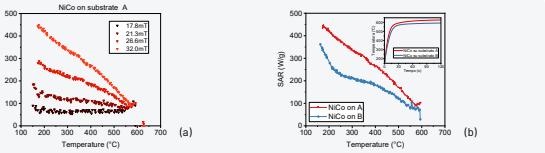


(a) Temperature Programmed reduction profiles of calcined substrates. Both samples show similar reduction profiles. The first peak is associated to Co^{+3} to Co^{+2} reduction. The following peaks are associated to formation of metallic alloy; **(b)** XRD profiles of NiCo catalyst and the bare substrate thermally treated at 900°C. NiCo alloy is the only observed phase other than the substrate; **(c, d)** N_2 adsorption/desorption isotherms & BJH pore-size distribution; **(e)** SEM images showing NiCo nanoparticles dispersed on substrate A and B and the particle size distribution (calculated from multiple images).



5 Magnetic Heating Performance (SAR)

- Specific Absorption Rate (SAR) determined from the heating/cooling-rate difference, normalized to the mass of the magnetic phase.
- NiCo on substrate A shows SAR up to ~450 W g^{-1} at 32.0 mT and ~280 W g^{-1} at 26.8 mT at low temperature, converging to ~80–100 W g^{-1} near 550–600 °C as the Curie transition is approached.
- NiCo on substrate B dissipates consistently less heat at every field, consistent with its larger nanoparticles (46 nm vs 36 nm) which reduce magnetization-reversal efficiency.
- Both catalysts reach thermal equilibrium in under 2 minutes — high SAR at only ~10–12 wt% metal loading confirms efficient field coupling for high-T induction catalysis.

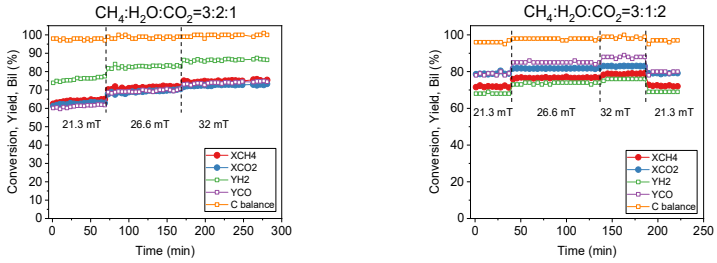


(a) SAR vs temperature at different applied fields for NiCo on substrate A — **(b)** NiCo on substrate A vs NiCo on substrate B at 32 mT. In the inset the temperature profile vs time for both samples.

6 Catalytic Performance under Induction Heating

700–735 °C
catalyst surface temperature reached by induction

- Catalytic performance is reported for NiCo on substrate A that reached idoneous temperatures for reforming reactions. ~5 g of monolithic NiCo/γ-Al_2O_3 catalyst (three stacked monoliths).
- Bi-reforming feed CH_4:H_2O:CO_2 = 3:2:1 and CH_4:H_2O:CO_2 = 3:1:2 GHSV ~10000 h^{-1} [CH_4] = 25%v/v (N_2 as balance)
- CH_4 conversion is function of the applied rf field (higher field produce higher temperatures) and largely insensitive to feed-composition changes.
- A higher CO_2 fraction in the feed improves CO_2 conversion, shifting syngas production from steam- toward dry-reforming and lowering the H_2/CO ratio.
- Conversion values are in line with expectations from conventional (non-inductive) heating at the same temperature.



CH_4 and CO_2 conversion, H_2 and CO yield vs magnetic field for two inlet mixture composition on NiCo on substrate A

Conclusions & Outlook

- Mechanically stable γ-Al_2O_3 lattice substrates were successfully 3D-printed by LDM from water-based boehmite pastes.
- Substrates were homogeneously loaded with catalytically active, magnetically responsive NiCo nanoparticles.
- Induction-heated NiCo/γ-Al_2O_3 catalysts reach reforming-relevant temperatures (700–735 °C) with conversions matching conventional heating; substrate A outperforms B thanks to smaller, more efficient nanoparticles.
- Next steps: tune metal–support interaction to control particle growth on B; increase metal loading to reach higher operating temperatures.

References

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[2] Scarfiello et al., Supported catalysts for induction-heated steam reforming of methane, Int. J. Hydrogen Energy 46 (2021) 134–145.
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Acknowledgments

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