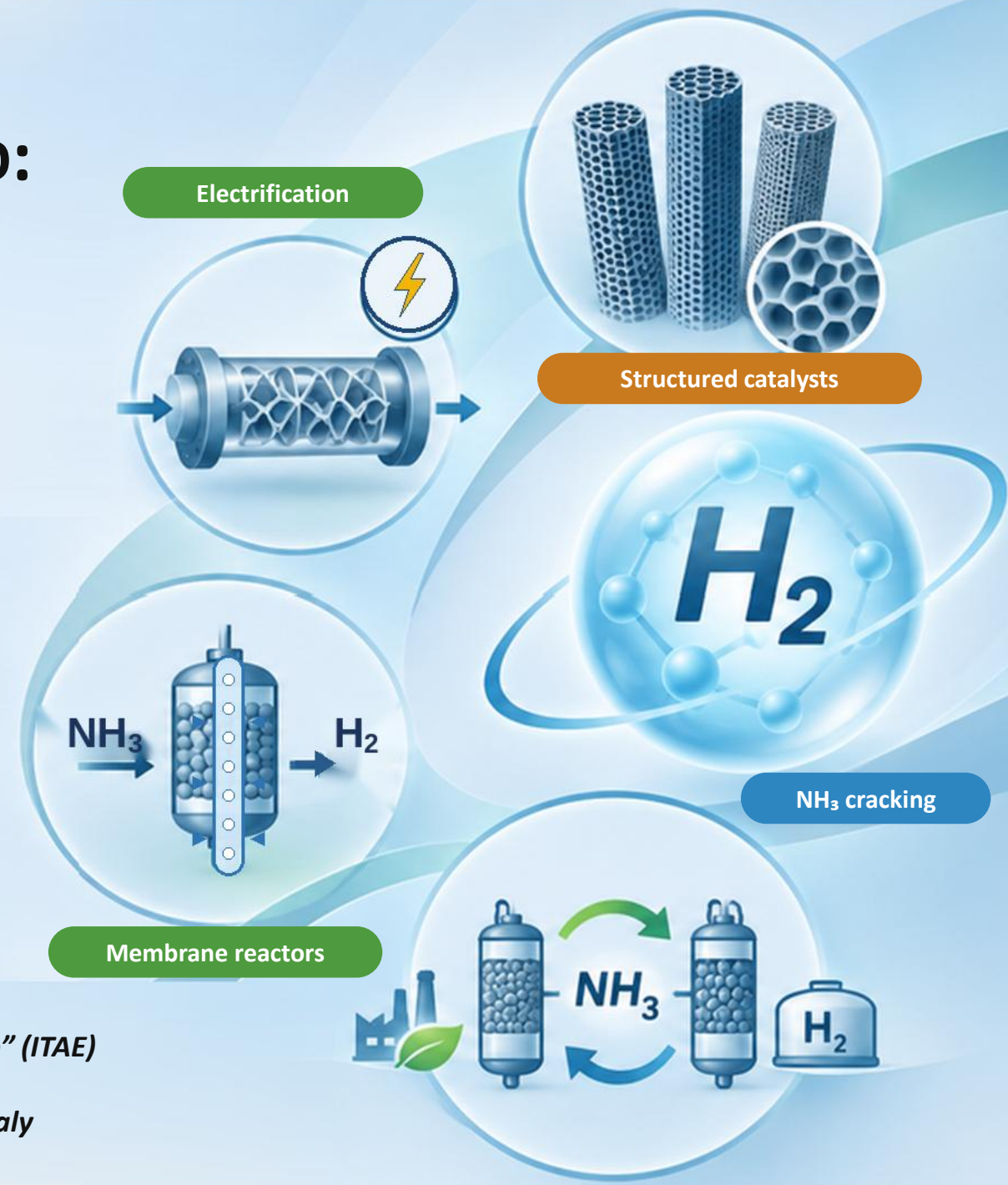
Nuove Frontiere dell'Idrogeno: Catalisi, Materiali e Intensificazione di Processo



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OUTLINE

1

Hydrogen & ammonia

Why hydrogen, why it must be stored, ammonia as a carbon-free carrier

2

Catalyst design & kinetics

Ni-perovskite catalysts, characterization, mechanism and kinetic modelling

3

Structured catalysts

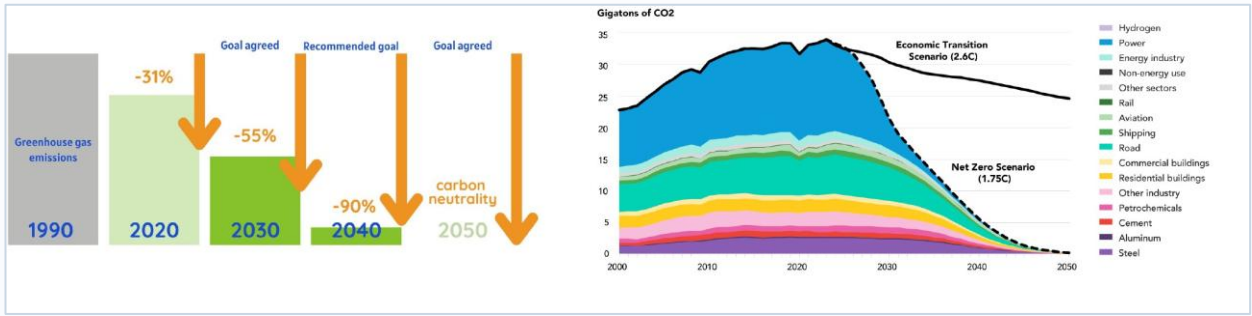
Cellular materials, coating and packing, 3D-printed supports, scale-up

4

Process intensification

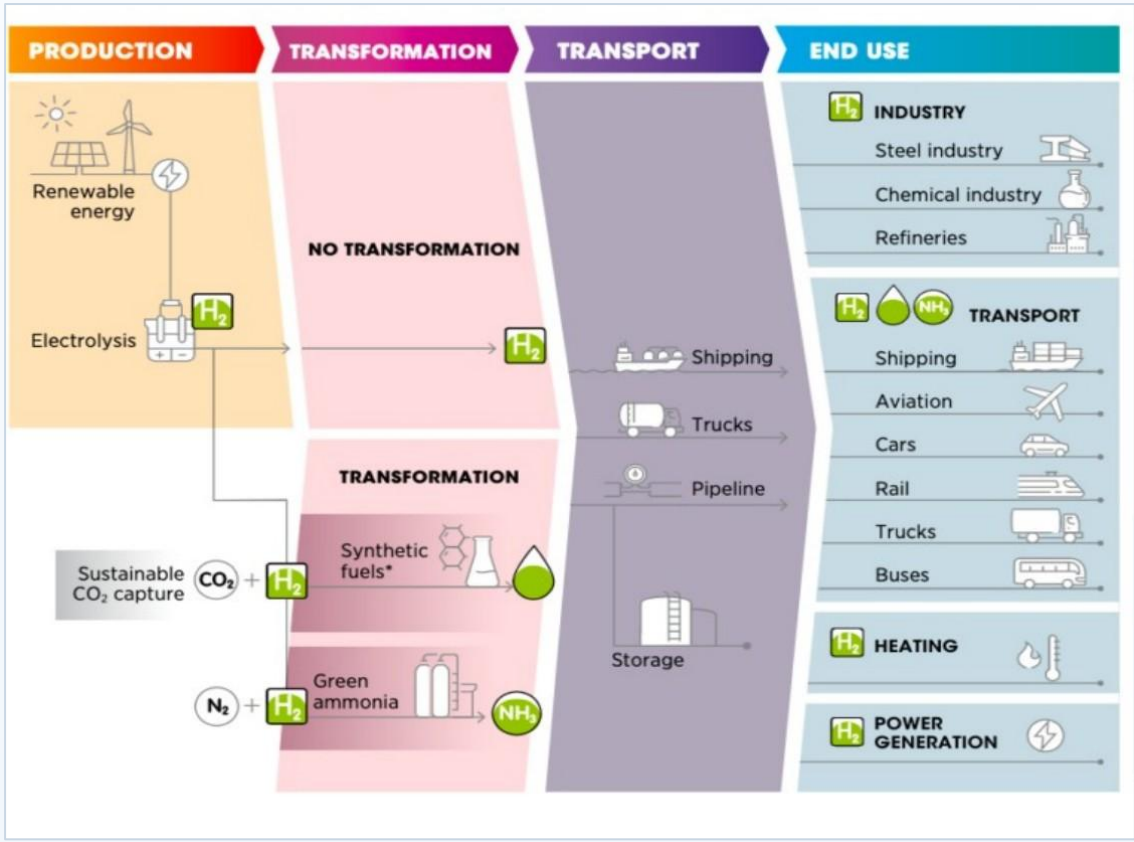
Electrified heating and membrane reactors: from thermal to electrochemical cracking

WHY HYDROGEN?



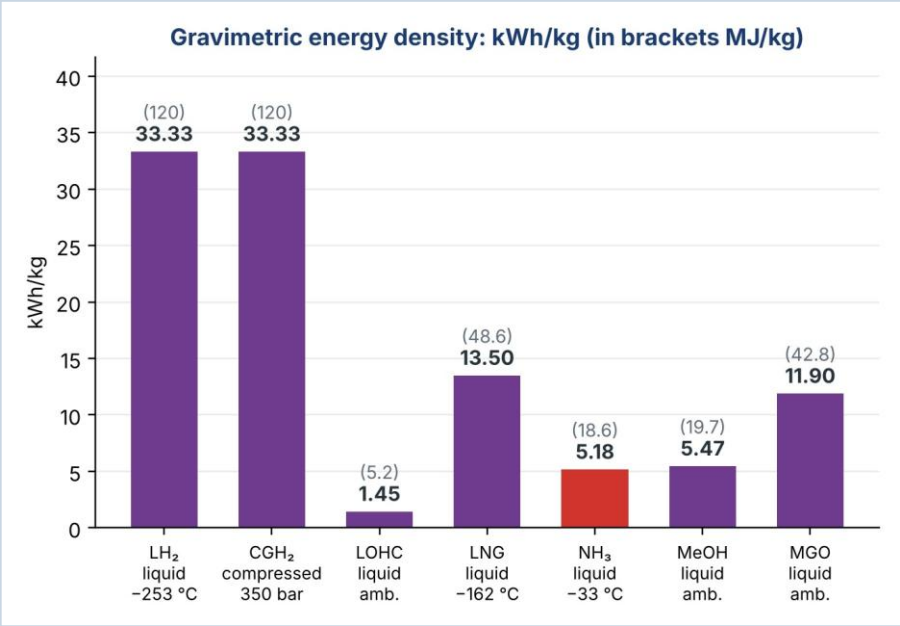
EU 2050 long-term strategy: emission-reduction pathway

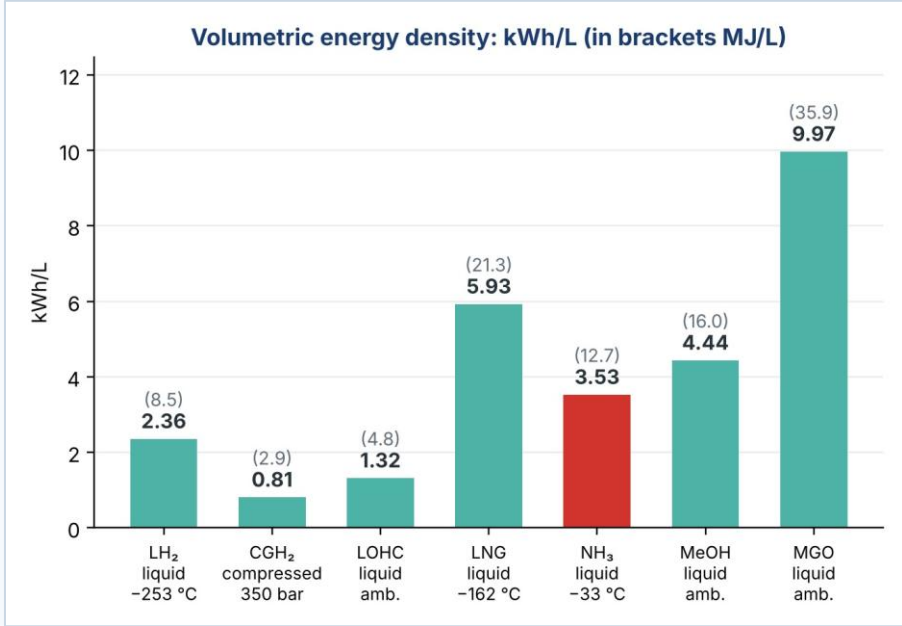
- **EU climate neutrality by 2050** is legally binding (European Climate Law); intermediate target **–55% GHG by 2030** vs 1990
- Renewables become the backbone of the energy system, but they are **variable and geographically distributed**
- Hydrogen connects renewable electricity to sectors that are **hard to electrify directly**: steel, chemicals, refining, heavy-duty transport, shipping, aviation



Hydrogen value chain: production → transformation → transport → end use

WHY DO WE NEED TO STORE HYDROGEN DIFFERENTLY?





Lower heating values; 1 kWh = 3.6 MJ · LH_2 liquid H_2 · CGH_2 compressed H_2 · LOHC liquid organic H_2 carrier · LNG liquefied natural gas · MeOH methanol · MGO marine gas oil

≈ 120 MJ/kg

H_2 has the highest gravimetric energy density…

3–8 MJ/L

…but very low volumetric density (compressed at 350 bar ≈ 3 MJ/L; liquid at –253 °C ≈ 8 MJ/L)

Chemical carriers

NH_3, methanol, LOHC store H_2 in chemical bonds at mild T and P

HYDROGEN CARRIERS: WHY AMMONIA?

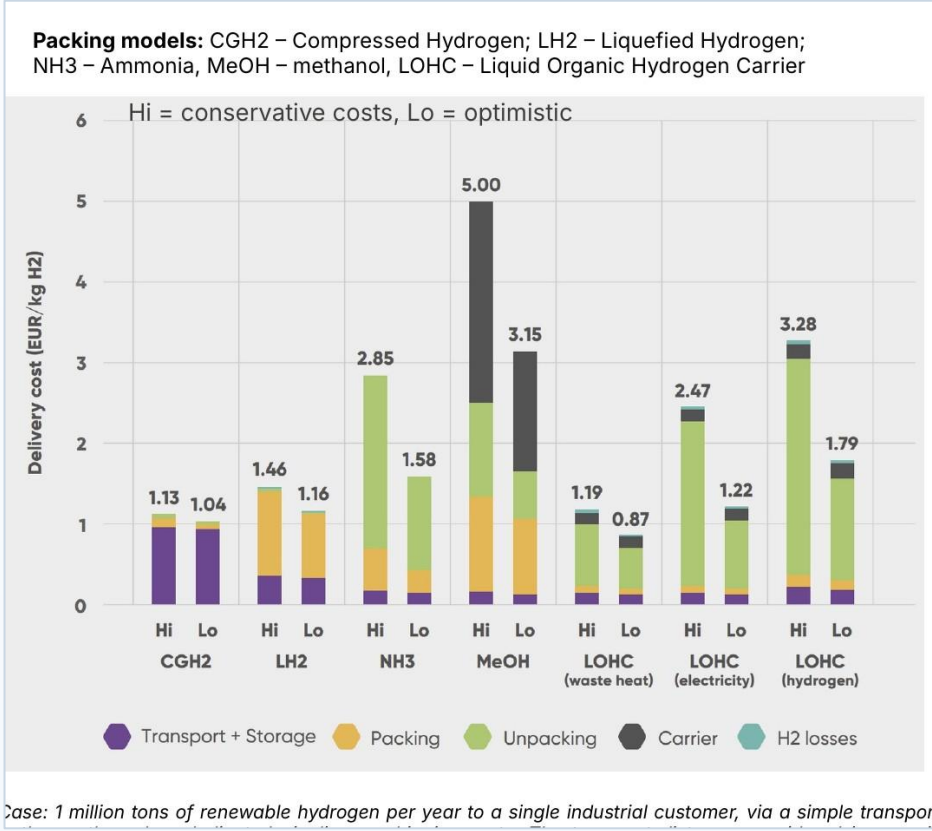
17.6 wt%
H_2 content, carbon-free

121 kg H_2/m^3
liquid NH_3 (vs 71 kg/m^3 liquid H_2)

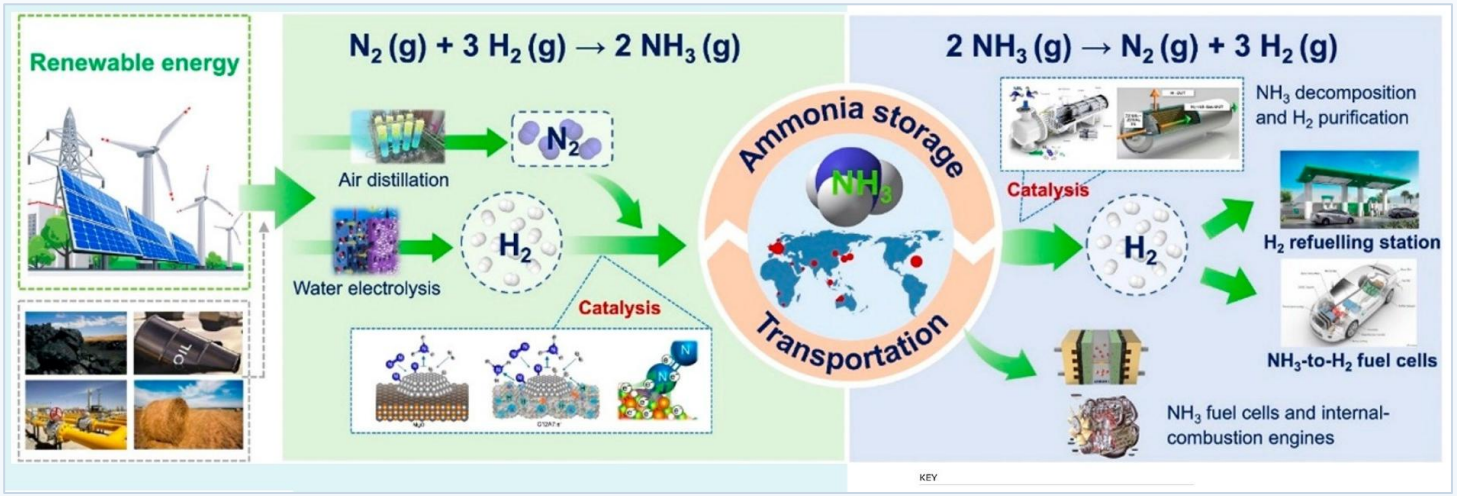
8.6 bar @ 25 °C
easy liquefaction (or –33 °C, 1 atm)

Existing infrastructure
production, shipping, port terminals

Shipping efficiency: MeOH 98.0% · **NH_3 97.4%** · LNG 96.2% · LH_2 89.1%



H_2 delivery cost by ship – 1 Mt H_2/y, ~2,500 km (Hi = conservative, Lo = optimistic)



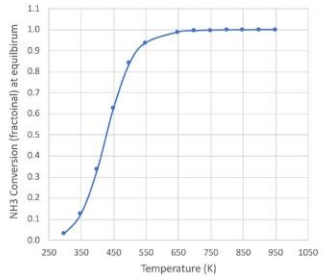
Ammonia cycle: synthesis → storage & transport → decomposition

NH_3 is dense, carbon-free and cheap to ship: its delivery cost is dominated by cracking (unpacking) → room for catalysis and process intensification

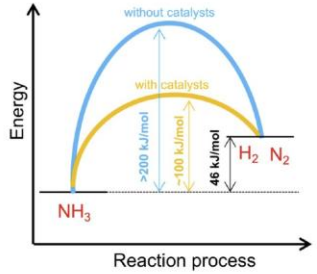
NH_3 DECOMPOSITION: THERMODYNAMICS VS KINETICS

Thermodynamics vs Kinetics

$$NH_3\,(g) \rightarrow \frac{1}{2}N_2\,(g) + \frac{3}{2}H_2\,(g)\;\Delta H = +46\ \text{kJ/mol}$$



Ammonia decomposition is endothermic and becomes thermodynamically favorable above approximately 450 K (at 10^5 Pa). Figure shows the equilibrium conversion over a wide temperature range at 10^5 Pa pressure for pure NH_3 feed, with complete conversion above 650 K.



The decomposition of ammonia can occur without a catalyst, but it requires high temperatures and pressures to proceed at a significant rate . The use of a catalyst accelerates the reaction by providing an alternative reaction pathway with lower activation energy.

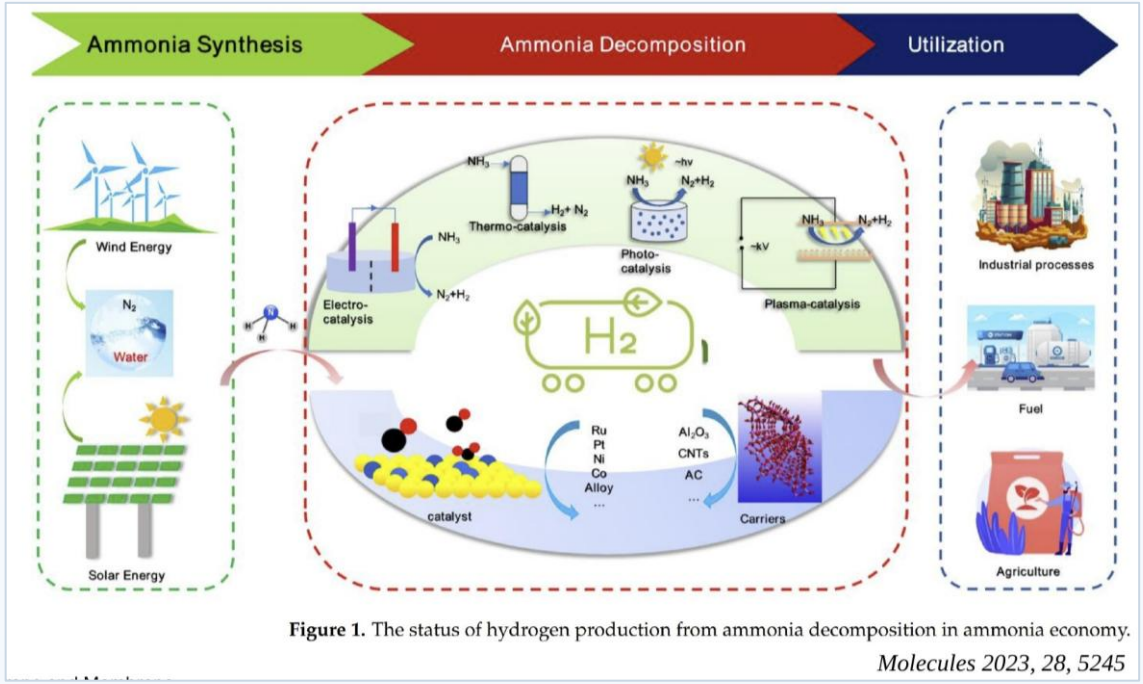


Figure 1. The status of hydrogen production from ammonia decomposition in ammonia economy.

Molecules 2023, 28, 5245

Technical routes – Huang et al., Molecules 2023, 28, 5245

- Endothermic (**ΔH = +46 kJ/mol NH_3**): equilibrium conversion is almost complete above ~650 K at 1 bar, but the reaction is **kinetically limited**
- Commercial crackers: **800–900 °C, 1–5 bar, Ni/Al_2O_3** → high energy demand, part of the H_2/NH_3 burnt to supply heat
- Our goal: active and stable catalysts at **400–500 °C** with **low or no Ru**, in compact, intensified and electrified reactors

OUR RESEARCH APPROACH

FROM CATALYST TO REACTOR: HOW WE RUN A STUDY

1 **Catalyst design & synthesis** — TRL 1–3
active phase · support · promoters; sol-gel combustion, SCS, co-precipitation, impregnation

2 **Characterization** — TRL 1–3
XRD, BET, H_2-TPR, CO chemisorption, CO_2/NH_3-TPD, XPS, TEM

3 **Kinetic study** — TRL 2–3
intrinsic rates, power-law & mechanistic models, E_a, rate-determining step

4 **Structured catalyst & scale-up** — TRL 3–4
foams, monoliths, 3D-printed POCS/TPMS; washcoating or packing

5 **Process intensification** — TRL 4–5
electrified heating (Joule, induction, plasma), membrane reactors



CATALYST DESIGN: FROM RU TO NI-PEROVSKITE PRECURSORS

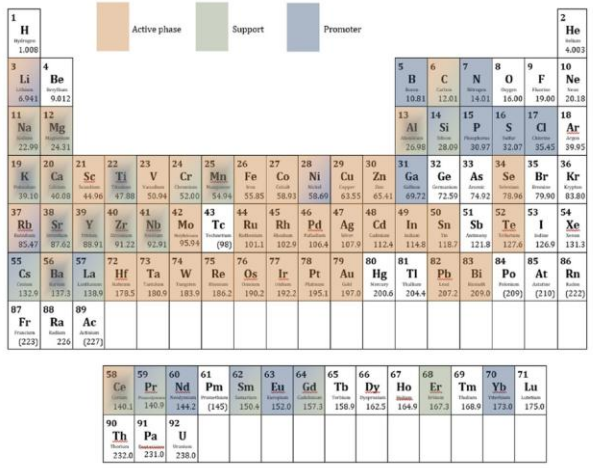


Figure 4. Simplified periodic table of the elements used in the formulation of catalysts for the decomposition of ammonia.

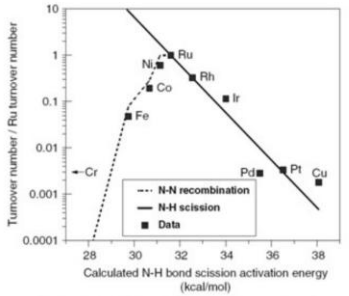
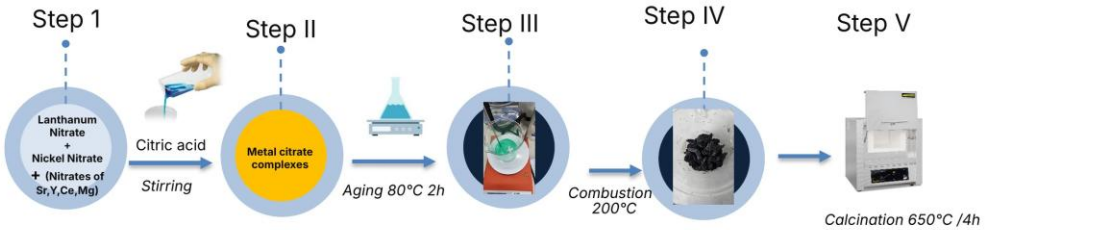


Figure 5 - Correlation between rate of ammonia decomposition and rate of N–H bond scission and N–N recombination

Ind. Eng. Chem. Res. 2021, 60, 18560

Elements in NH_3 decomposition catalysts and activity trend vs N–H scission energy



Sr Precursor	Y Precursor	Mg Precursor	Ce Precursor	Liquid medium	Fuel
$Sr(NO_3)_2$ Strontium nitrate	$Y(NO_3)_3$ Yttrium nitrate	$Mg(NO_3)_2$ Magnesium nitrate	$Ce(NO_3)_2$ Cerium Nitrate	water	Citric acid

Sol-gel (self-)combustion synthesis of doped $LaNiO_3$ perovskites

Our choice: **$La_{1-x}A_xNiO_3$** precursors (A = Mg, Ce, Y, Sr) by sol-gel combustion

1 · Ru vs Ni

- **Ru**: most active at low T, but scarce and costly → limited scalability
- **Ni**: cost-effective, high conversion only **> 650 °C**
- Strong **Ni–N binding** hinders N_2 recombinative desorption at low T

2 · Perovskite precursors (ABO_3)

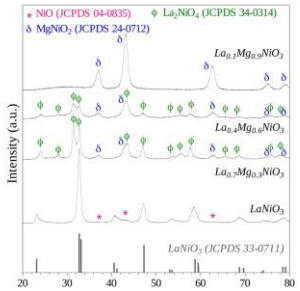
- A = lanthanide / alkaline-earth; B = transition metal (**$LaNiO_3$**)
- Under H_2, **Ni exsolution** → highly dispersed Ni nanoparticles anchored to the oxide
- Structure-sensitive reaction: particle size matters (mesoporous $LaNiO_3$: **89% at 550 °C, stable 72 h** – Gamez et al.)

3 · Doping and basicity

- A/B substitution → lattice distortion, O vacancies; tunes redox, acid–base, electronic properties
- Alkali / alkaline-earth = **e^- donors** → weaker Ni–N bond, faster N_2 desorption (often the RDS)
- **MgO**: cheap, stable, basic O^{2-} sites, H spillover; Mg-doped $LaNiO_3$ the best (Pinzón et al.)

PHYSICO-CHEMICAL CHARACTERIZATION: A FLASH

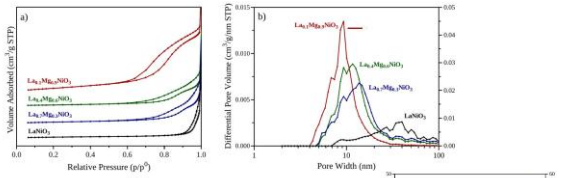
XRD



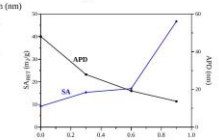
Sample	S-Q (wt.%)			
	$LaNiO_3$ (33-0711)	La_2NiO_4 (34-0314)	$MgNiO_2$ (24-0712)	NiO (04-0835)
$LaNiO_3$	99.3	-	-	0.7
$La_{0.7}Mg_{0.3}NiO_3$	-	89.0	11.0	-
$La_{0.4}Mg_{0.6}NiO_3$	-	72.2	27.8	-
$La_{0.1}Mg_{0.9}NiO_3$	-	-	100	-

Mg substitution: $LaNiO_3$ → La_2NiO_4 + $MgNiO_2$; x = 0.9 → 100% $MgNiO_2$ solid solution

N_2 physisorption

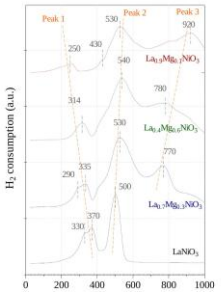


Sample	SA_{BET} (m^2/g)	PV_{BJH} (cm^3/g)	APD (nm)
$LaNiO_3$	9.19	0.1104	48.1
$La_{0.7}Mg_{0.3}NiO_3$	15.35	0.1072	27.9
$La_{0.4}Mg_{0.6}NiO_3$	17.00	0.0814	19.2
$La_{0.1}Mg_{0.9}NiO_3$	46.71	0.1598	13.7



Surface area grows with Mg: 9 → 47 $m^2\ g^{-1}$; pore diameter 48 → 14 nm

H_2-TPR

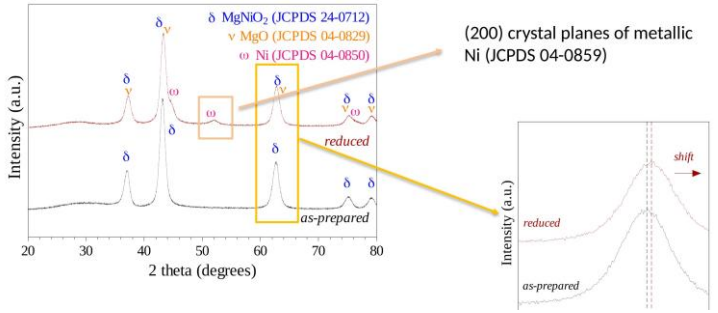


Sample	Hydrogen consumption (mmol/g)			
	Peak 1	Peak 2 (up to 600°C)	Total	Reducibility[a] (%)
$LaNiO_3$	2.83	3.26	6.09	98.9
$La_{0.7}Mg_{0.3}NiO_3$	0.54	2.36	2.90	91.2
$La_{0.4}Mg_{0.6}NiO_3$	0.48	2.73	3.21	75.9
$La_{0.1}Mg_{0.9}NiO_3$	0.39	2.31	2.60	31.1

[a]Calculated on the basis of XRD composition.

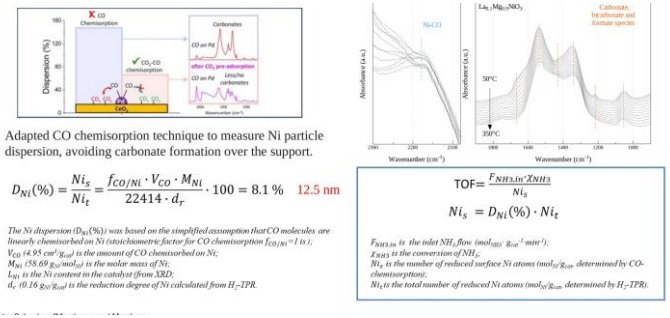
Reducibility 98.9% → 31.1%: strong Ni–Mg interaction

XRD after reduction



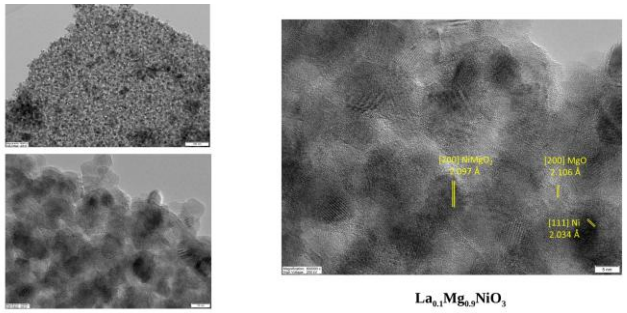
Partial reduction of $MgNiO_2$ → exsolved metallic Ni (≈ 7.6 nm)

CO chemisorption



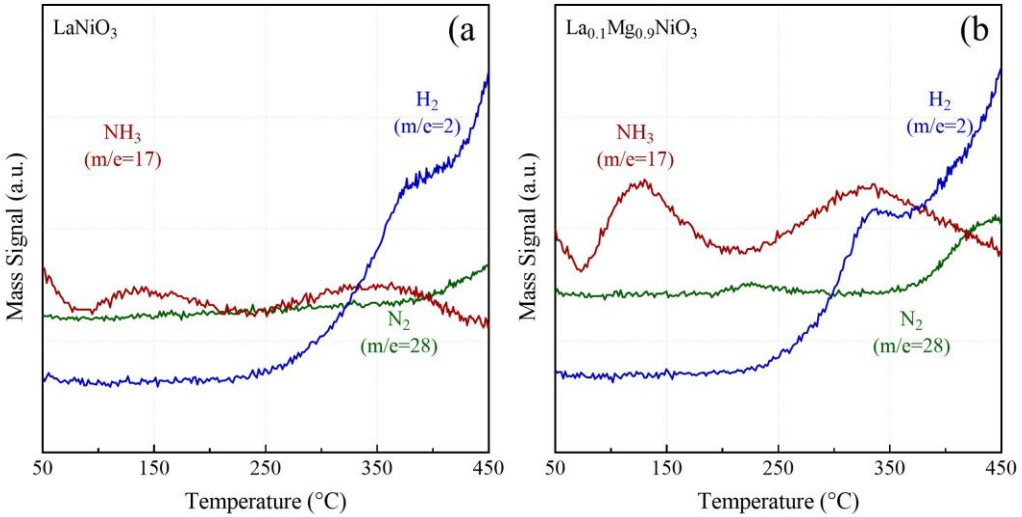
Ni dispersion 8.1%, particle size 12.5 nm (adapted method, no carbonates)

HR-TEM



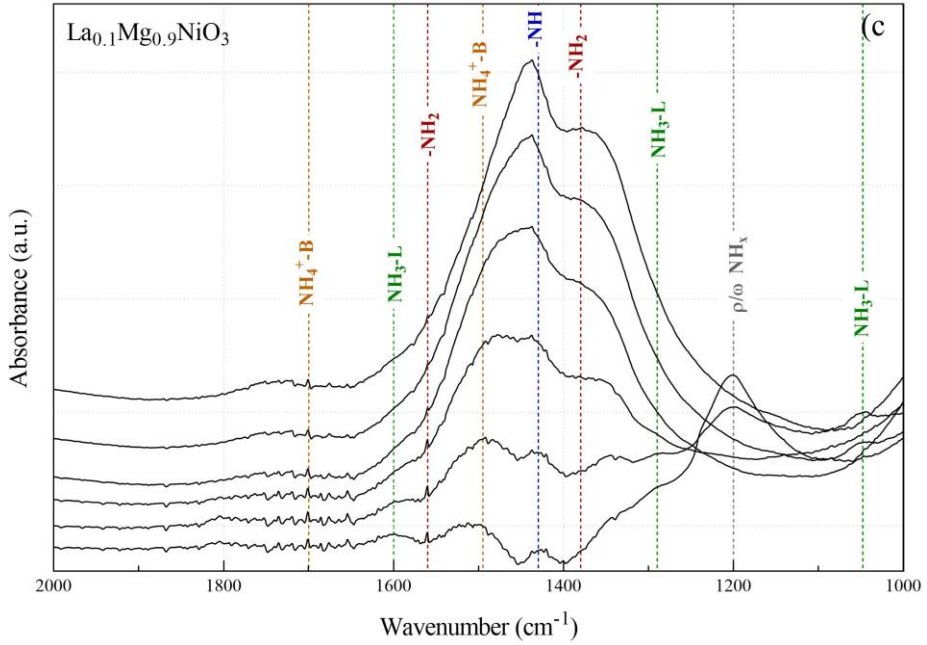
Ni(111), MgO and $MgNiO_2$ planes: small Ni particles anchored to the oxide

REACTION MECHANISM: NH_3-TPD-MS AND IN SITU DRIFTS



NH_3-TPD-MS on reduced $LaNiO_3$ (a) and $La_{0.1}Mg_{0.9}NiO_3$ (b)

- **$LaNiO_3$**: H_2 evolves from ~250 °C, N_2 only above 350 °C and not complete → N recombination is the demanding step
- **Mg addition** shifts H_2 and N_2 desorption to lower T → easier N_2/H_2 recombination, higher activity



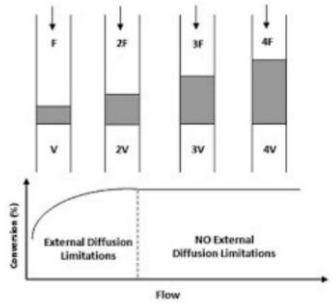
In situ DRIFTS of NH_3 decomposition on $La_{0.1}Mg_{0.9}NiO_3$ (increasing T)

- NH_3 on Lewis sites reacts faster than NH_4^+ on Brønsted sites
- **$–NH_2$ / –NH** intermediates already at low T → N–H scission is easy, not the RDS

Dehydrogenation is fast, while adsorbed N atoms (N*) accumulate and N_2 is released late → this suggests recombinative N_2 desorption as the rate-determining step

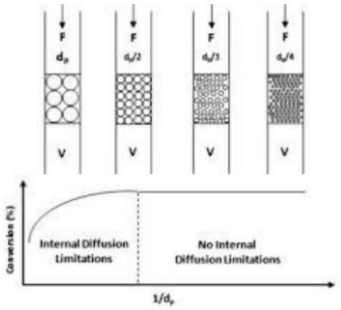
KINETIC STUDY: WORKING IN THE INTRINSIC KINETIC REGIME

External (film) diffusion

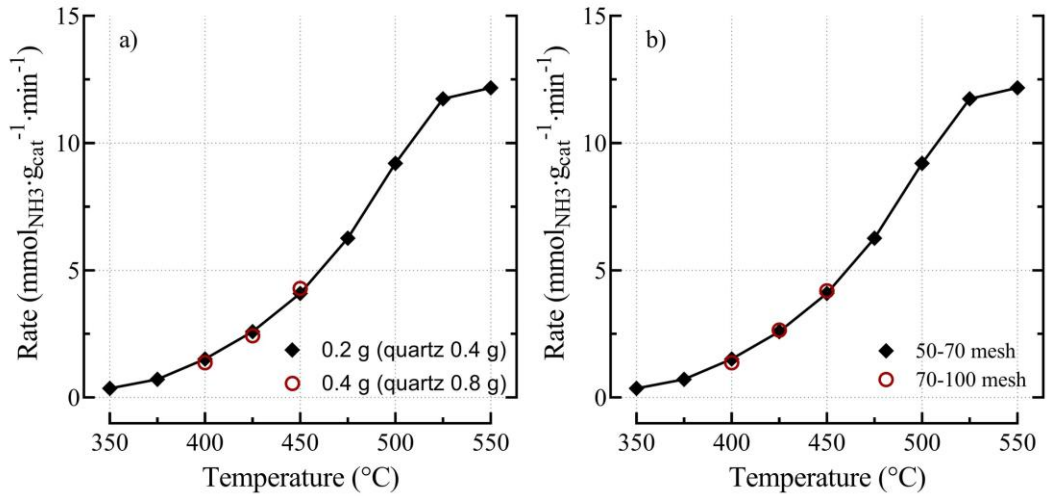


- Reactants must cross the gas film around the particle
- **Test**: increase catalyst mass and flow together (constant GHSV)
- Same rate → **no external limitation**

Internal (pore) diffusion



- Reactants must diffuse inside the pores of the particle
- **Test**: reduce particle size at constant GHSV
- Same rate → **no internal limitation**



a) catalyst mass doubled at constant GHSV · b) particle size 50–70 vs 70–100 mesh

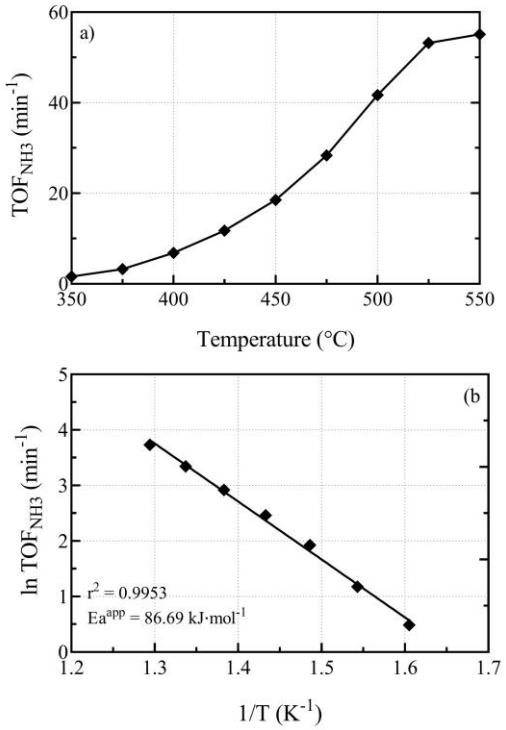
Selected conditions

GHSV 60,000 mL g^{-1} h^{-1} · catalyst:quartz 1:2 · 50–70 mesh

25 vol.% NH_3/He · 1 atm · isothermal, diluted bed

Only rates free from mass- and heat-transfer limitations give meaningful kinetic parameters

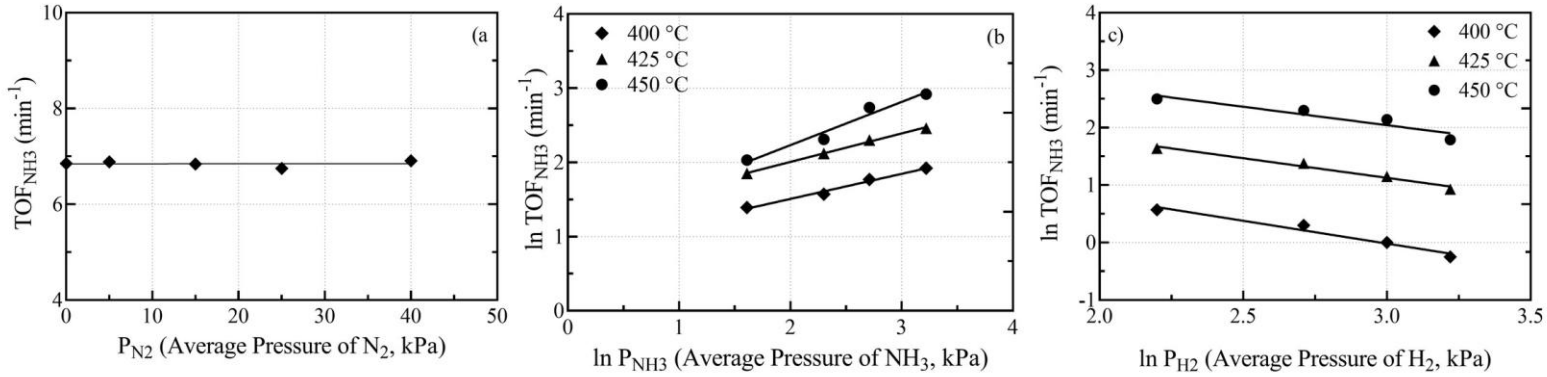
APPARENT ACTIVATION ENERGY AND POWER-LAW KINETICS



a) TOF vs T · b) Arrhenius plot

TOF = A·exp(−E_a,app / RT)

E_a,app = 86.7 kJ mol^{-1} (r^2 = 0.995)



Effect of N_2 (a, 400 °C), NH_3 (b) and H_2 (c) partial pressure on TOF

$r_{NH3} = k \cdot P_{NH3}^{a} \cdot P_{H2}^{b} \cdot P_{N2}^{c}$ TOF = r / Ni_s (Ni_s = 0.221 mmol g^{-1}, CO chemisorption)

Order	400 °C	425 °C	450 °C
a (NH_3)	+0.34	+0.39	+0.59
b (H_2)	−0.80	−0.69	−0.65
c (N_2)	≈ 0	–	–

- **a > 0**, increasing with T
- **b < 0**: strong H_2 inhibition (H* competes for sites)
- **c ≈ 0**: N_2 does not inhibit the reaction

MECHANISTIC MODEL: N_2 RECOMBINATIVE DESORPTION AS RDS

Proposed mechanism (Bradford-type)

$NH_3 + * \rightleftharpoons N^* + 3/2\ H_2$ quasi-equilibrium (K_9)

$2\ N^* \rightarrow N_2 + 2\ *$ **rate-determining step**

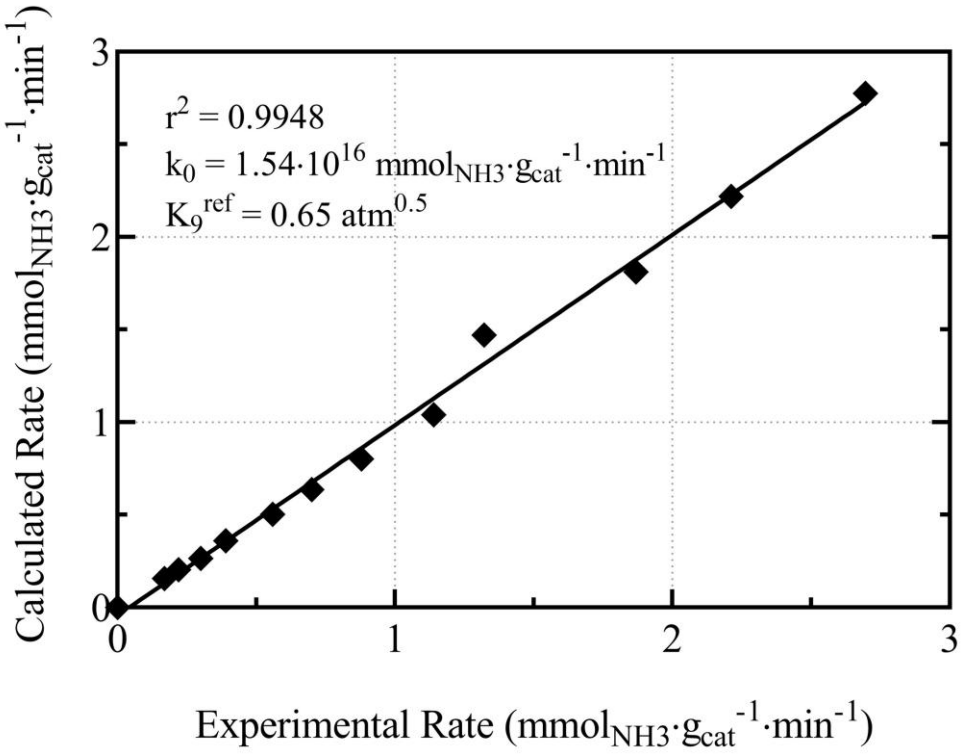
Fast N–H scission; N is the most abundant surface intermediate*

$$r_{NH3} = k \cdot P_{NH3}^{2} / (P_{H2}^{1.5} + K_9 \cdot P_{NH3})^2$$

$$k = k_0 \cdot \exp(-E_a / RT)$$

$$K_9 = K_{9,ref} \cdot \exp[-\Delta H_9/R \cdot (1/T - 1/T_{ref})], \quad T_{ref} = 400\ °C$$

Parameter	Value	Unit
k_0	$1.54 \cdot 10^{16}$	$mmol_{NH3}\ atm\ g_{cat}^{-1}\ min^{-1}$
E_a	217	$kJ\ mol^{-1}$
$K_{9,ref}$ (400 °C)	0.65	$atm^{0.5}$
ΔH_9	+29.7	$kJ\ mol^{-1}$



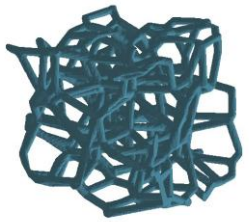
Parity plot: calculated vs experimental rate (400–450 °C, H_2 effect)

$r^2 = 0.995$: N* recombinative desorption is the RDS, consistent with MS and DRIFTS

STRUCTURED CATALYSTS: CLASSIFICATION OF CELLULAR MATERIALS

Cellular materials as catalyst supports

Stochastic

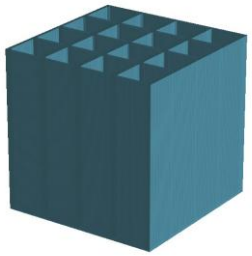


Open-cell foams

- Random cell size and shape
- High porosity (80–95%)
- Low ΔP, good mixing
- Limited control of geometry

Replica / sponge method

Periodic 2D

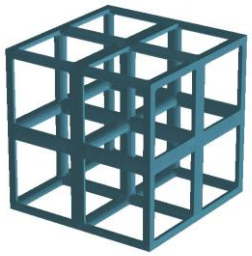


Honeycomb monoliths

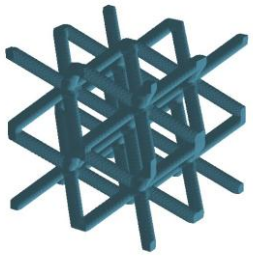
- Straight parallel channels
- Very low ΔP
- Laminar flow, no radial mixing
- Poor radial heat transfer

Extrusion

Periodic 3D · strut-based (POCS)



Cubic

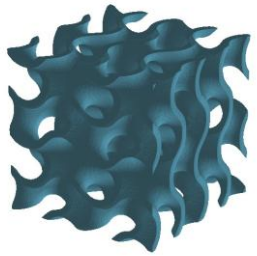


BCC / Kelvin

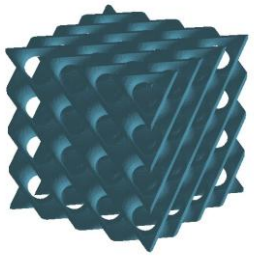
- Unit cell repeated in space
- Tunable cell size, strut Ø, porosity
- Enhanced radial heat & mass transfer

Additive manufacturing

Periodic 3D · sheet-based (TPMS)



Gyroid



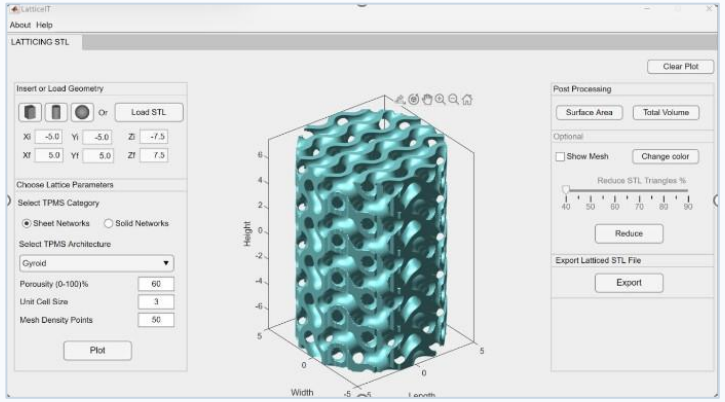
Diamond

- Smooth, continuous minimal surfaces
- High surface-to-volume ratio
- Two interpenetrating channel networks

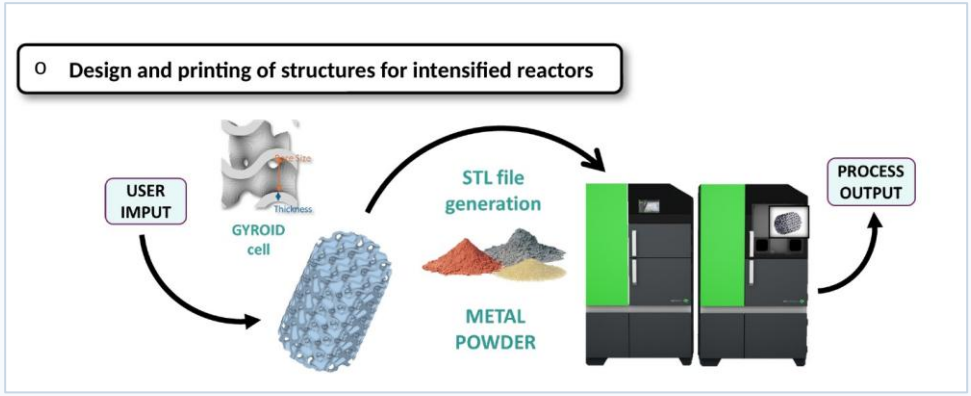
Additive manufacturing

How we prepare structured catalysts

① Design and 3D printing of the support



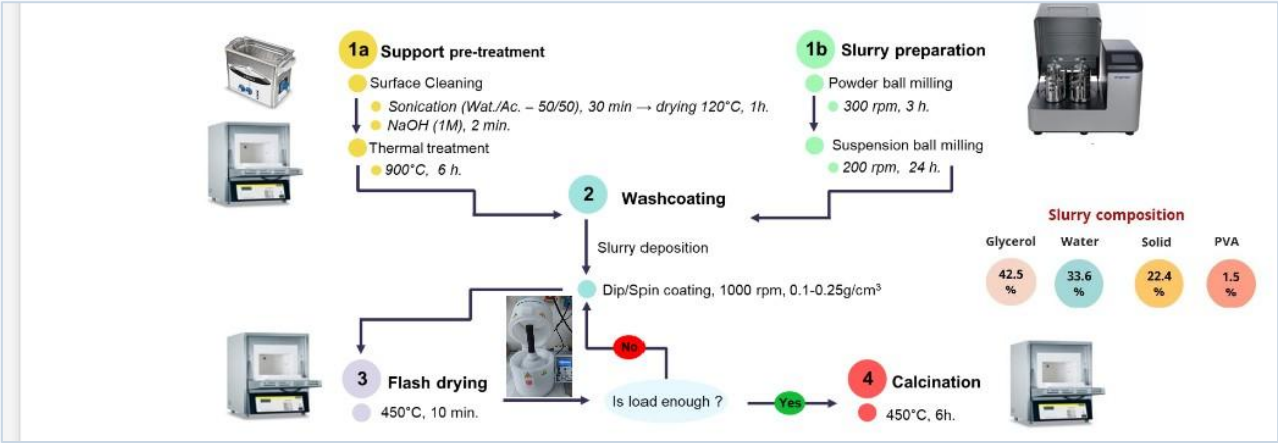
TPMS design: cell type, cell size, porosity



CAD → STL → laser powder bed fusion (Inconel)

- Geometry designed **a priori**: cell 2–4 mm, porosity 50–90%
- **LPBF** of metal alloys (Inconel) → conductive, robust supports

② Catalyst activation: dip/spin washcoating



1a **Pre-treatment:** sonication, NaOH etching, oxidation at 900 °C → rough oxide layer for anchoring

1b **Slurry:** ball-milled catalyst (22.4%) in glycerol / water / PVA

2 **Dip/spin coating:** 1000 rpm removes the excess, homogeneous film

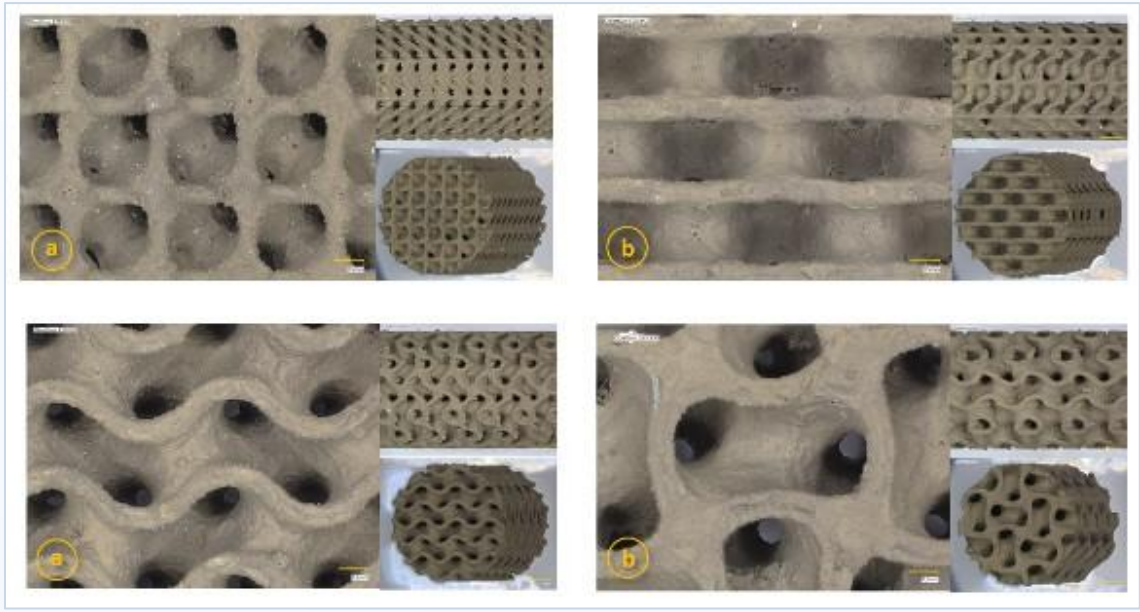
3 **Flash drying:** 450 °C, 10 min · repeat until target load

4 **Calcination:** 450 °C, 6 h

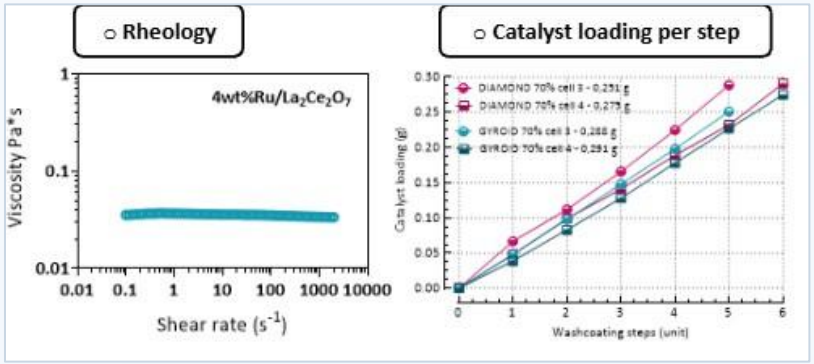
COATING EXAMPLE: GYROID VS DIAMOND TPMS

TPMS	Cell size	Sheet size	Solid Vol.	Fluid Vol.	Porosity (ε)	Pore size	Mesh	Surface Area	Specific S.A.
(Type)	(mm)	(mm)	(mm^3)	(mm^3)	(%)	(mm)		(mm^2)	(mm^2/mm^3)
DIAMOND	3	0.23	368	809	70	1.27	50[d]	3246[d]	8.81[d]
	(3)[a]	(0.28)[a]	(535)[b]	(642)[c]	(54.53)[c]	(1.22)[c]	-	-	-
DIAMOND	4	0.31	369	809	70	1.69	50[d]	2495[d]	6.77[d]
	(4.01)[a]	(0.3)[a]	(491)[b]	(686)[c]	(58.28)[c]	(1.71)[c]	-	-	-
GYROID	3	0.23	366	811	70	1.27	50[d]	2619[d]	7.15[d]
	(3)[a]	(0.32)[a]	(489)[b]	(689)[c]	(58.51)[c]	(1.18)[c]	-	-	-
GYROID	4	0.31	370	808	70	1.69	50[d]	2022[d]	5.47[d]
	(4)[a]	(0.38)[a]	(449)[b]	(729)[c]	(61.90)[c]	(1.62)[c]	-	-	-

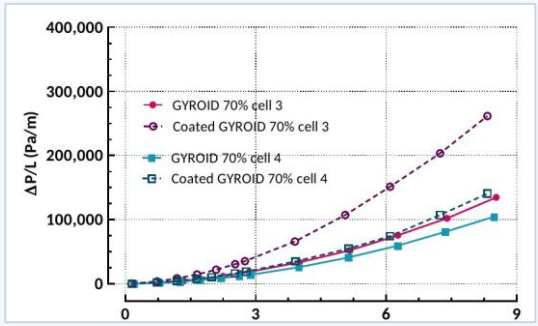
Bare TPMS supports (Inconel, ε = 70%, cell 3–4 mm)



Optical microscopy after washcoating: Diamond (top) and Gyroid (bottom)



Newtonian slurry · linear loading per step



ΔP/L vs u, Gyroid bare/coated

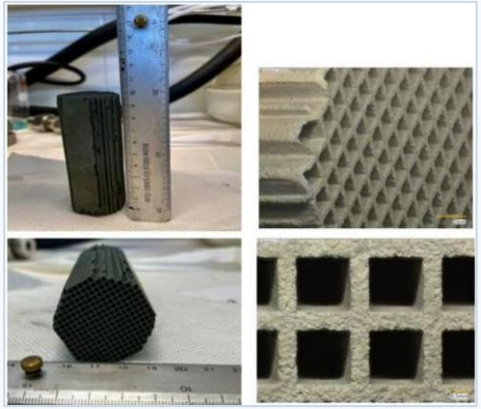
- Same porosity, different **geometry and cell size**
- Catalyst load **0.1–0.2 g/cm³** (layer **50–100 µm**)
- Homogeneous, well-anchored coating
- Coating raises ΔP; **smaller cells → higher ΔP**

SCALE-UP OF COATED STRUCTURES AND PACKING AS AN ALTERNATIVE

Washcoating: scale-up



SiC foams 40 PPI: 1.17 → 15 → 114 cm³ (×100 in volume)

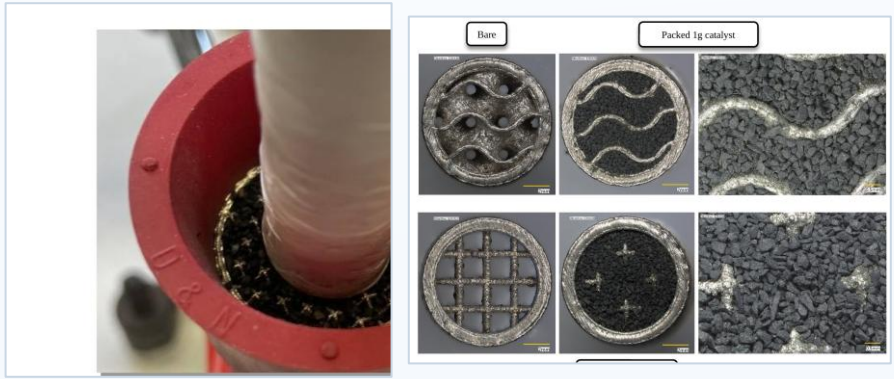


SiC monolith Ø 3.5 × 10.5 cm

0.1–0.2 g/cm³
coated catalyst (50–100 µm layer)

- Load constant over ×100 volume
- Same slurry and dip/spin sequence
- Slurry powder 5 g → 35 g
- Best heat transfer, low ΔP

Packing: alternative route



Pellets loaded step-wise in the cells · bare vs packed

≈ 1 g/cm³
packed catalyst (5–10× higher inventory)

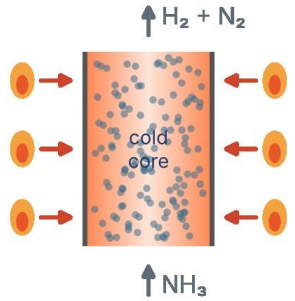
Conductive skeleton · higher ΔP than coated

Coating for heat transfer and low ΔP · packing for catalyst inventory: the choice depends on the reaction

ELECTRIFIED HEATING: HOW TO SUPPLY HEAT TO THE REACTION

NH_3 cracking is endothermic (+46 kJ/mol): the reactor is limited by **heat transfer**. Intensification = generate heat **where the catalyst is**, fast and from renewable electricity.

Conventional (fired)

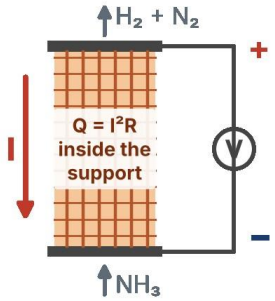


Working principle

1. Fuel is burnt **outside** the reactor tubes
2. Heat crosses the **wall**, then the **bed**
3. The wall is hot, the **core stays colder**

+ Mature, large scale
− Radial gradients, slow
− CO_2 / NH_3 burnt for heat

Joule (resistive)

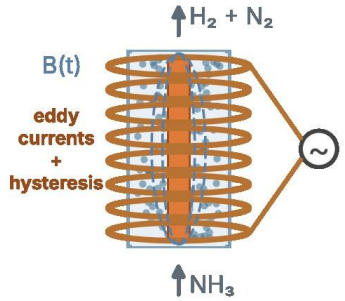


Working principle

1. **Current I** flows through a conductive support
2. The support is a **resistance R**
3. Heat **Q = I²R** released **inside**

+ Uniform, efficient
+ Compact, fast
− Conductive support
− Electrical contacts

Induction

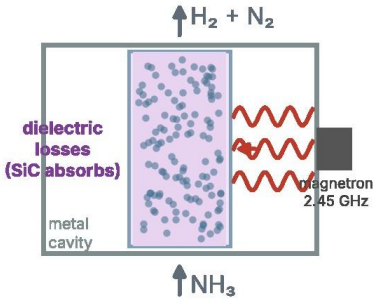


Working principle

1. **AC coil** creates an alternating **magnetic field**
2. **Eddy currents + hysteresis** in a magnetic material
3. Heats **without contact**

+ Heats in seconds
+ Self-limiting at Curie T
− Coil design
− Magnetic stability

Microwave

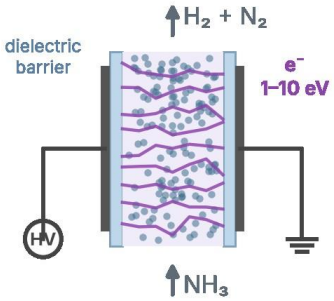


Working principle

1. **Magnetron** emits 2.45 GHz waves in a cavity
2. A **dielectric** (SiC, oxides) absorbs the field
3. Heat generated **in the volume**

+ Volumetric, selective
+ Fast start-up
− Non-uniform field, hot spots
− Complex equipment

Non-thermal plasma (DBD)



Working principle

1. **High voltage** across a **dielectric barrier**
2. **Micro-discharges** → energetic electrons
3. Electrons **break NH_3 bonds**, gas stays cold

+ Low bulk T
+ Instant on/off
− Low energy efficiency
− Scale-up open

PLUG-IN – INTENSIFIED ELECTRIFIED REFORMING FOR LOW-CARBON H_2

PRIN 2020 (MUR) · Prot. 2020N38E75 · 36 months · ≈ 1.1 M€ · PI: PoliMI (E. Tronconi) · Partners: UniSA, CNR (ITAE, STEMS, ITM) · **TRL 2 → 4**

Abstract

Blue and green H_2 from natural gas / biogas by **electrified steam reforming** on **thermally conductive structured catalysts** (SiC open-cell foams). Heat is supplied by **microwave, resistive (Joule) or induction** heating, and the reformer is combined with an **H_2-selective membrane** or a **CO_2 sorbent** in a single multifunctional unit.

Objectives

> 95%	> 99%	–95%	–20%
fuel conversion (TRL 2–4)	H_2 purity (membrane reactor)	CO_2 vs grey H_2	H_2 cost vs blue H_2

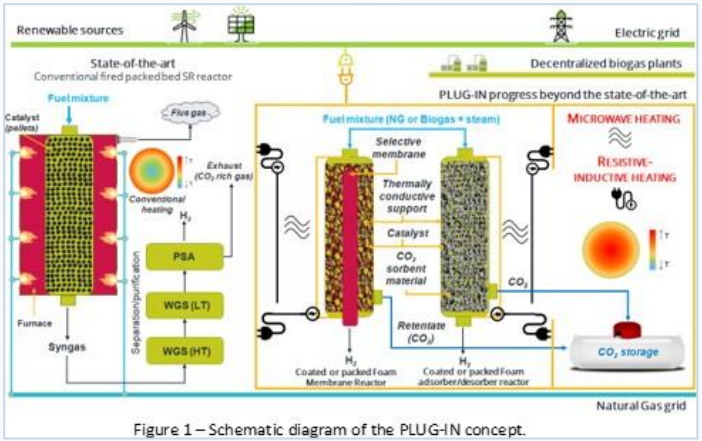
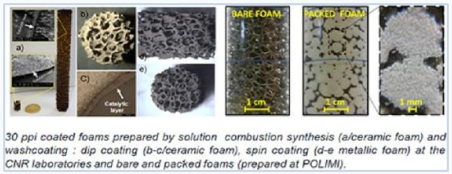


Figure 1 – Schematic diagram of the PLUG-IN concept.

PLUG-IN concept: electrified membrane / sorption-enhanced reformers



30 ppi coated foams prepared by solution combustion synthesis (a/ceramic foam) and washcoating : dip coating (b-c/ceramic foam), spin coating (d-e metallic foam) at the CNR laboratories and bare and packed foams (prepared at POLIMI).

SiC foams coated at CNR (SCS, dip/spin) and packed foams

What CNR-ITAE does (WP1 – Catalytic materials, WP2 – Testing)

- **Activation of SiC open-cell foams**: spray-, dip-, spin- and dip/spin-coating; in situ **solution combustion synthesis**
- **Packed foams**: catalyst micro-particles in the cells for higher H_2 productivity
- **Scale-up** of structured catalysts for bench tests with membranes and sorbents
- Tests under **microwave, resistive and induction** heating; slurry and Joule-heating conditions optimised with UniSA

REBEL – ELECTRIFIED CATALYTIC REACTOR FOR BIOFUELS FROM BIOGAS

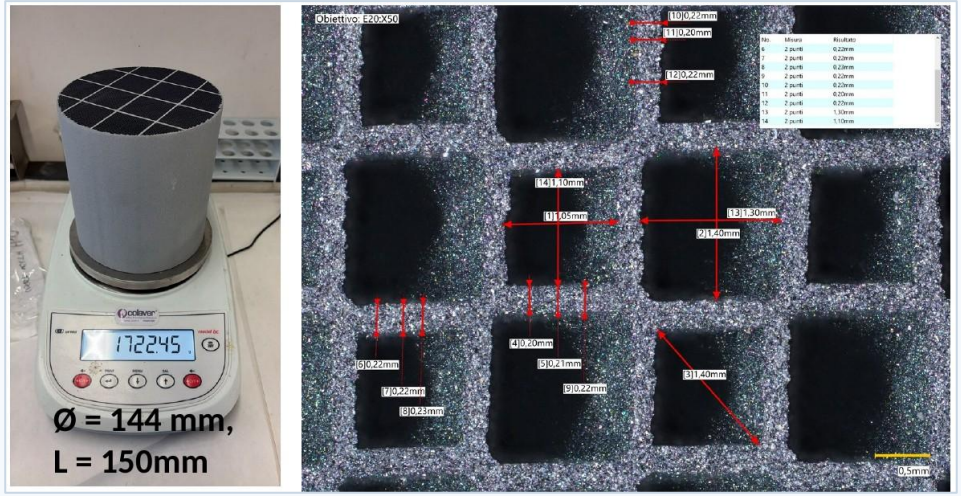
Mission Innovation (MASE) · MI_BIO_00285 · 18 months · ≈ 4.2 M€ · Lead: NEXTCHEM · Partners: UniSA, CNR-ITAE · **TRL 4 → 7**

Abstract

Biogas is converted to syngas in an **electrified reformer**, then to biofuels (Fischer–Tropsch SAF, bio-methanol). Heat is supplied by **resistive (Joule) heating elements integrated in structured catalysts**, close to the catalyst, instead of burning gas. The CO_2 of biogas is converted directly (dry reforming).

Objectives

TRL 7	~20 kW	10 Nm³/h	> 90%
pilot reformer	electrical input	biogas feed	thermal efficiency



Washcoated SiC monolith for the pilot (Ø 144 × 150 mm) and channel/wall measurement

TRL 4 (NEXTCHEM–UniSA): 200 h at 800 °C · thermal efficiency > 90% (vs 80–85%)

What CNR-ITAE does (WP2 – Optimisation and scale-up of the electrified structured catalyst, with UniSA)

- **Coating protocol** for SiC / Si-SiC foams and monoliths: slurry formulation, dip/spin coating, adhesion (< 5% loss)
- **Industrialisation** of the washcoating procedure (Milestone 3)
- **Scale-up**: structured catalysts for the pilot, **20–40 L** with **2–4 kg** of washcoat and catalyst
- **Post-mortem analysis** of the pilot catalyst: deactivation, sintering, coke

AMPERE – ELECTRIFIED PLATFORM FOR CO_2 VALORISATION

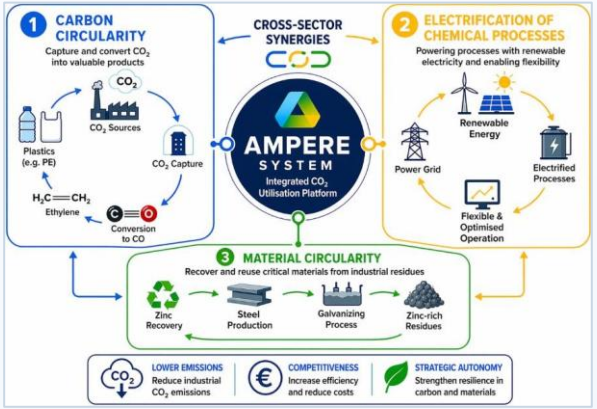
Horizon Europe CL4 (2026, proposal) · No. 101345828 · 48 months · ≈ 7 M€ · Coordinator: ZEFIRA · **CNR: sorbent & catalyst leader (WP2)** · TRL 6

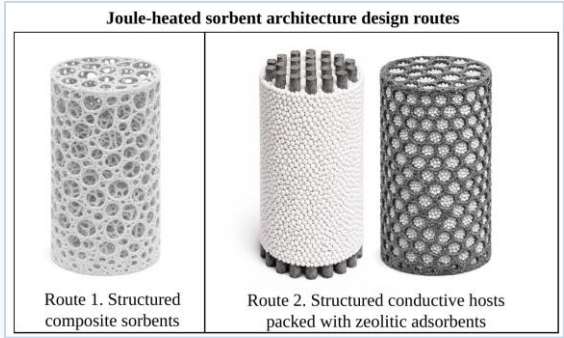
Abstract

Two-stage electrified platform converting CO_2 from refinery flue gas into **ethylene**. Stage 1 offers two routes: a **plasma–membrane reactor** or a **Joule-heated RWGS reactor**, both with integrated **CO_2 sorbents** (capture + conversion). Stage 2 is a water-selective membrane reactor. Demo at the TUPRAS refinery, 2 × 500 h.

Objectives

< 0.8 kg	< 25 kWh	< 1,300 €/t	1,000 h
CO_2-eq / kg C_2H_4 (−55%)	per kg C_2H_4	levelised cost	TRL 6 demo

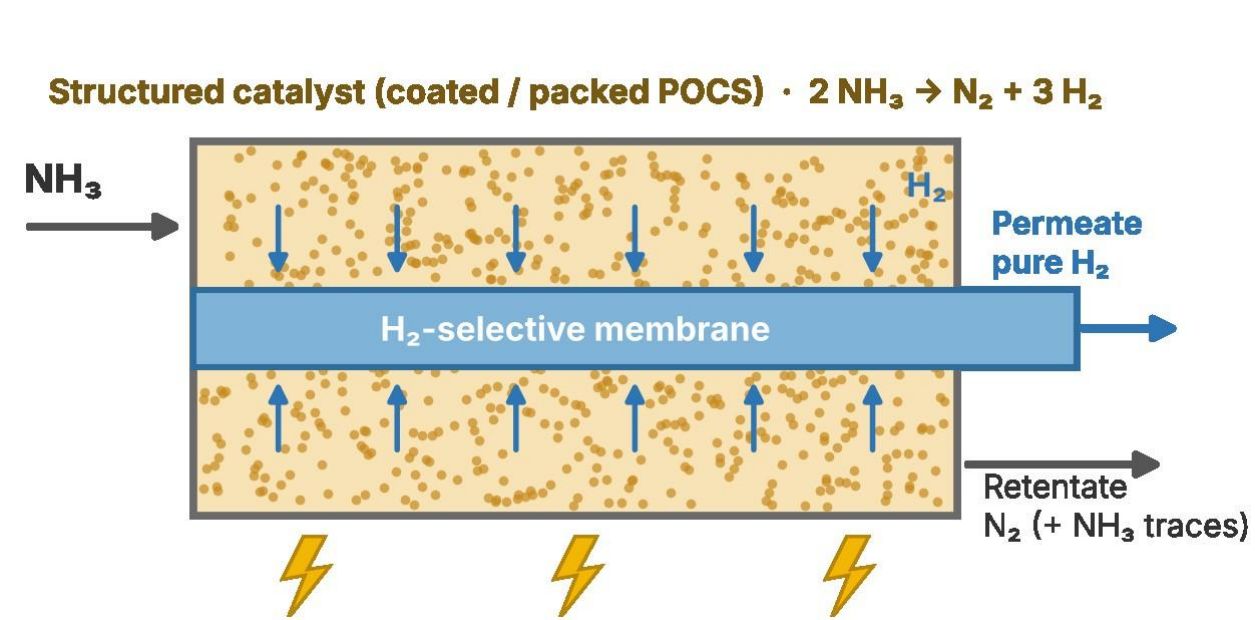




What CNR-ITAE does

- **CO_2 sorbents** (lead, T2.1): ceria/zeolite sorbents for plasma; **electrically regenerable** structured sorbents for Joule heating
- **Ru-free RWGS catalysts** (T2.2): Cu, Ni, Mo, Co on CeO_2, ZrO_2, Al_2O_3
- **Joule-heated sorbent routes**: structured composite sorbents, or conductive hosts packed with zeolites
- **Scale-up** of sorbent and catalyst to the prototype (lead, T4.1)

MEMBRANE REACTORS: REACTION AND SEPARATION IN ONE UNIT



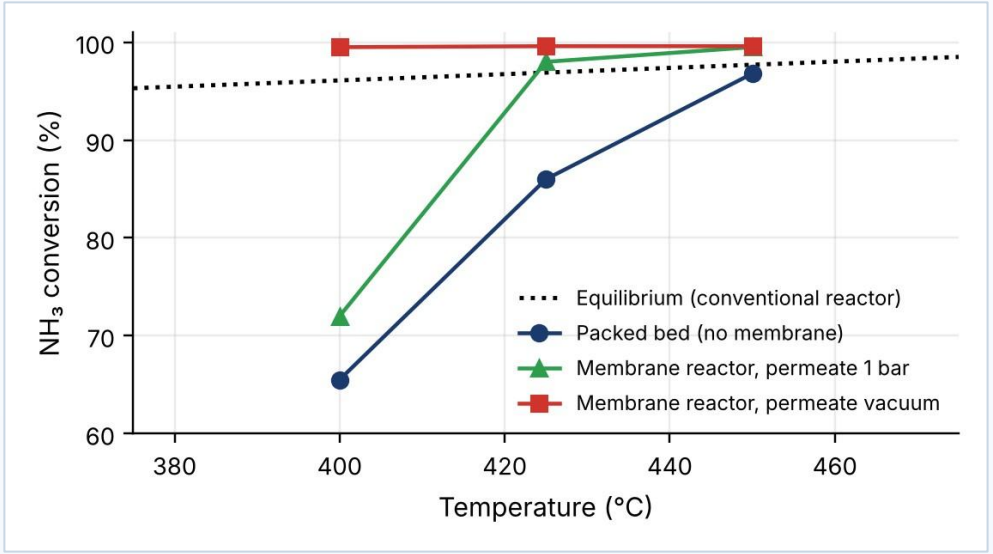
Catalytic membrane reactor: reaction and H_2 separation in one unit, with electrified heating

Why a membrane reactor?

- **Le Chatelier**: H_2 removed in situ → equilibrium shifted → high conversion at **lower T**
- **Kinetics**: H_2 inhibits the rate (order ≈ −0.7) → removing it **speeds up** the reaction
- **Pure H_2** in the permeate → no downstream PSA, smaller plant



POCS with channels for membranes



NH_3 conversion: packed bed vs membrane reactor (permeate at 1 bar or vacuum)

Membrane	Mechanism	Pros / limits
Pd / Pd-Ag	dense metal, H atom diffusion	$H_2/N_2 \approx \infty$ · costly, embrittlement
Carbon molecular sieve	size exclusion in nanopores	cheap, $H_2/N_2 > 300$ · NH_3 stability
Proton-conducting ceramics	H^+ transport driven by a voltage	electrochemical pumping → RdS project

AMBHER – AMMONIA AND MOF-BASED HYDROGEN STORAGE FOR EUROPE

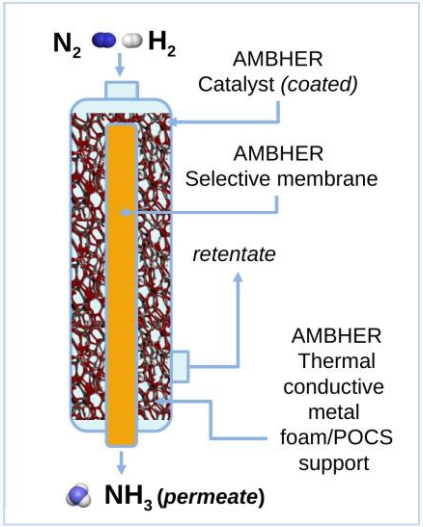
Horizon Europe (CL4) · GA 101058565 · 48 months · ≈ 5.9 M€ · Coordinator: TECNALIA · 16 partners, 7 countries · **CNR-ITAE: WP3 leader**

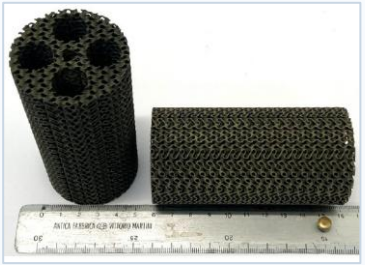
Abstract

Holistic approach to energy storage: **short-term** H_2 storage in 3D-printed **MOFs** in a conformable cryo-vessel, and **long-term** (seasonal) storage as **green NH_3**, produced in an intensified **catalytic membrane reactor** with thermally conductive **3D-printed POCS** and **NH_3-selective carbon molecular sieve membranes**.

Objectives (long-term storage)

< 20 bar	< 250 °C	> 8 mmol	TRL 5
vs 150–300 bar	low temperature	NH_3 g^{-1} h^{-1}	membrane reactor demo







Coated Gyroid / BCC POCS for the TRL 5 demonstrator

Membrane reactor vs no membrane (TU/e)

+83% H_2 conversion · **+77%** NH_3 rate

85% NH_3 recovered in the permeate

What CNR-ITAE does (WP3 – Key materials and components for long-term H_2 storage)

- **Activation of 3D-printed POCS / TPMS**: dip/spin washcoating and packing; slurry rheology and loading
- **Structured catalysts** for single membrane reactor (TRL 4), delivered to TU/e
- **Scale-up** to the demonstrator (TRL 5): Ø 51 × 200 mm POCS, up to ~60 g catalyst per structure
- **Catalyst scale-up** (50–100 g/run, TRL 4) with JM; reactor modelling with ENGIE and TU/e

ANDREAH – AMMONIA-BASED MEMBRANE REACTOR FOR GREEN H_2

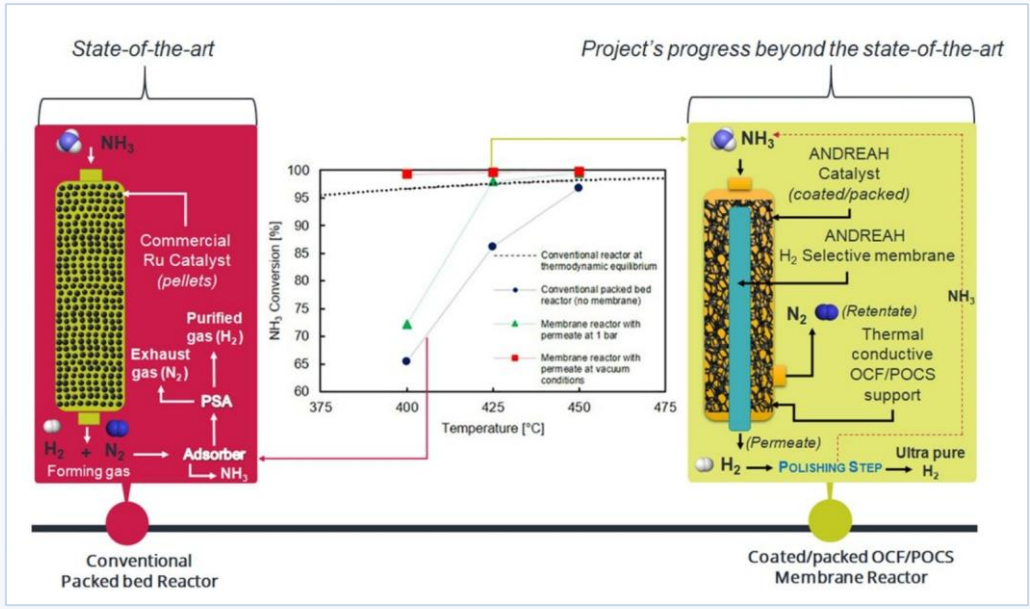
Clean Hydrogen Partnership (Horizon Europe) · GA 101112118 · 48 months · ≈ 3 M€ · Coordinator: TECNALIA · 9 partners · **CNR-ITAE: WP3 leader**

Abstract

Ammonia cracking is the missing link to use NH_3 as a hydrogen carrier. ANDREAH develops a **catalytic membrane reactor (CMR)** that combines low-CRM **structured catalysts**, **H_2-selective carbon molecular sieve membranes** and a sorbent-based **polishing** step, to produce fuel-cell-grade H_2 at lower temperature and cost.

Objectives

> 99.998%	400–450 °C	–80–90%	5.5 → 4.3 €/kg
H_2 purity	vs 800–900 °C	CRMs (< 1 wt% Ru)	H_2 cost (–22.5%)



What CNR-ITAE does (WP3 – Key component development and scale-up)

- **Catalysts (TRL 3)**: Ru, Ni and Ru–Ni on ABO_3 perovskites tuned by cation substitution → Ru-free **$La_{1-x}Mg_xNiO_3$**
- **Kinetics**: intrinsic rate laws for reactor modelling (D2.2) → N* recombinative desorption as RDS
- **Structured catalysts**: conductive OCF / 3D-printed POCS, coated (dip/spin, solution combustion) or packed
- **Scale-up**: 10–20 g → 50–100 g/run (TRL 4); structured catalysts delivered to TU/e for CMR tests (TRL 4–5)

RICERCA DI SISTEMA – ELECTROCHEMICAL MEMBRANE REACTOR FOR NH_3 CRACKING

Ricerca di Sistema PTR 2025–27 (MASE) · Macrotheme 2.D – NH_3 cracking for distributed H_2 · 3 years · CNR-ITAE + UniME · **TRL 1 → 3**

Abstract

A multifunctional **electrochemical membrane reactor (EMR)** decomposes NH_3 and separates **ultra-pure H_2** in one step: a porous **bifunctional anode** cracks NH_3, a dense **proton-conducting membrane** transports H^+ under an applied voltage, and a porous **cathode** evolves H_2. No PSA, no Pd, reduced use of critical raw materials.

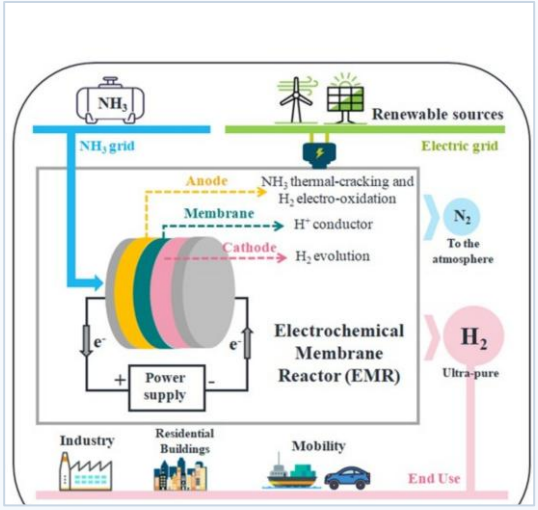
Objectives

Ultra-pure H_2
in one step

1 atm
400–750 °C

On-demand
voltage-controlled H_2 flux

Low CRM
Ni / perovskites



LA 2.11 · CNR
Anode catalyst + H^+ membrane

LA 2.12 · CNR
Cathode + EMR validation

LA 2.13 · UniME
Anode–membrane assembly

LA 2.14 · UniME
EMR cell & reactor design

Proof-of-concept EMR (TRL 3)

What CNR-ITAE does (scientific responsible: C. Italiano)

- **Anode**: Ni-perovskites (La–Mg–Ni) and Ru/pyrochlores with high proton conductivity; activity, H spill-over
- **Membrane**: dense $La_2Ce_2O_7$, La_2CeZrO_7 and catalytic $LaMgNiO_3$ discs by dry sintering
- **Cathode**: layered perovskites $A_{1-x}A'_xB_2O_{5-\delta}$ (e.g. NBSCF, Pechini) for H_2 evolution
- **EMR validation**: lab-scale tests (T, space velocity, voltage) vs packed-bed and thermal cracking

THANK YOU FOR YOUR ATTENTION

Take-home messages

1. NH_3 is a dense, carbon-free H_2 carrier: the bottleneck is efficient cracking
2. Ni-perovskites with Mg: Ru-free catalysts; N_2 recombinative desorption is the RDS
3. 3D-printed cellular supports, coated or packed, scaled up from lab to prototype
4. Electrified heating and membranes: compact reactors and ultra-pure H_2

Acknowledgements

ANDREAH (Clean Hydrogen Partnership) · **AMBHER** (Horizon Europe) · **REBEL** (Mission Innovation) · **PLUG-IN** (PRIN 2020) · **Ricerca di Sistema** (MASE)

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