Syngas economy with **green hydrogen** for rapid decarbonization of fuels and chemicals

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KAUST RESEARCH CONFERENCE
Hydrogen-Based Mobility and Power
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جامعة الملك عبدالله
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King Abdullah University of
Science and Technology

CCRC Clean Combustion Research Center

Active coal power plants (2022):

1. China 1,118 (+96 under construction)
2. India 285 (+23 under construction)
3. USA 225
4. Japan 92 (+6 under construction)
5. Indonesia 87 (+25 under construction)

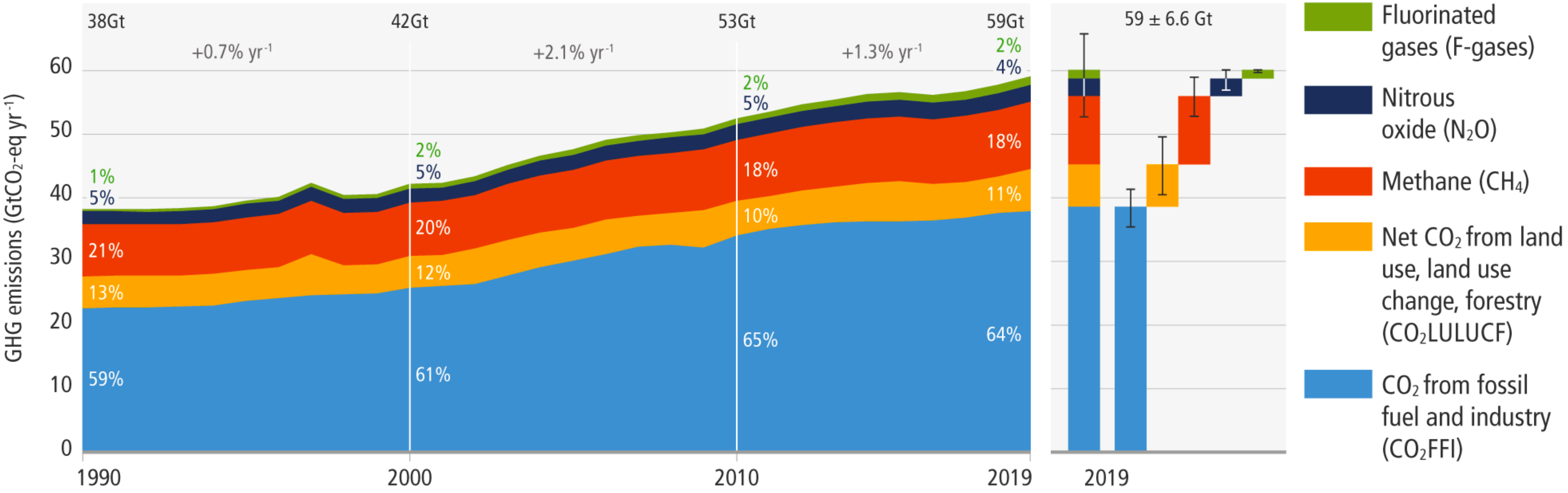
..

13. Korea 23 (+2 under construction)

Total: 2,439 (+ 187 under construction)
10.1 Gt/year CO_2 emissions

Sources: BP, Statista, IEA, GlobalEnergyMonitor

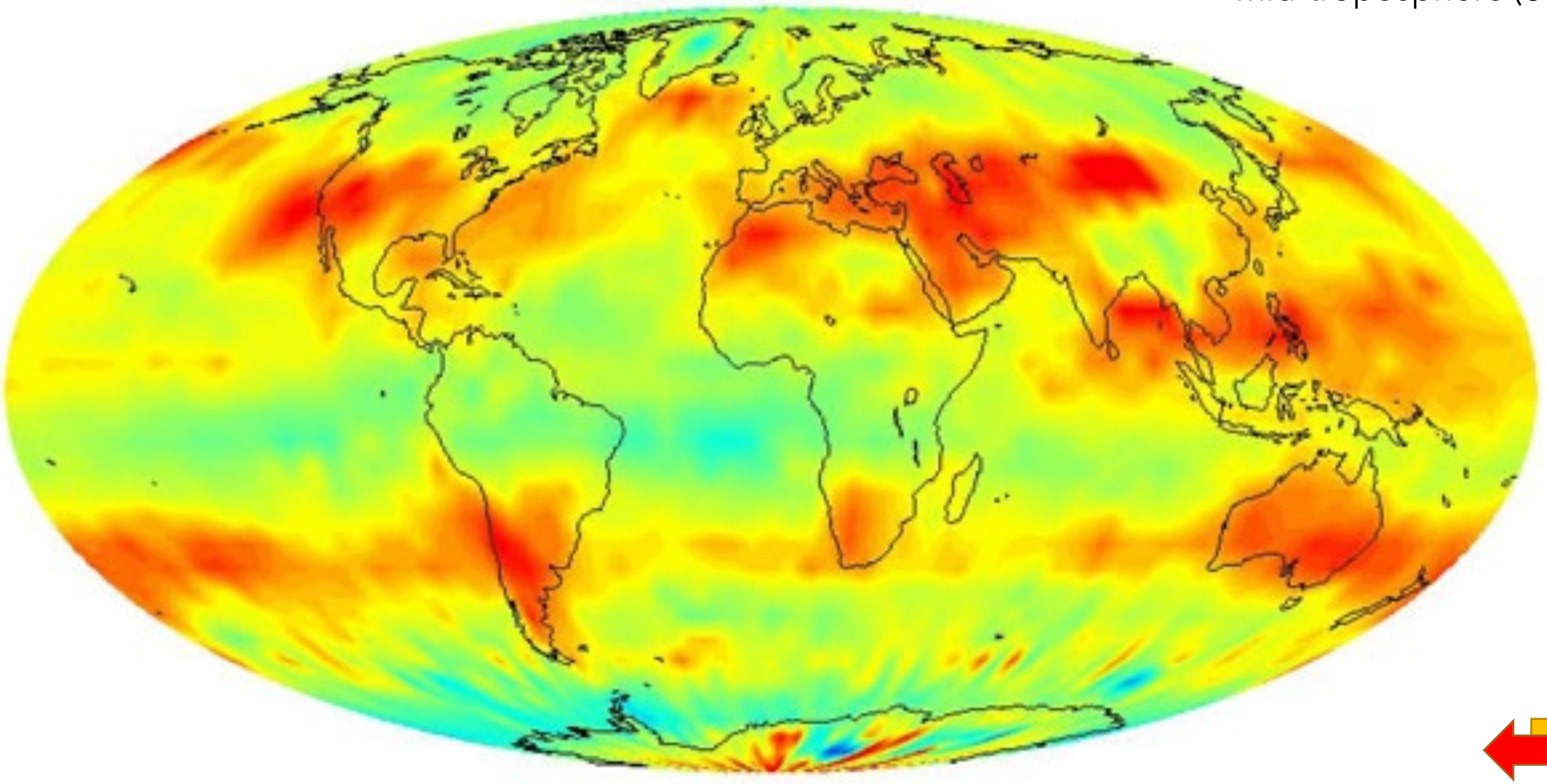
How much Greenhouse Gases are there?



IPCC, 2022: *Climate Change 2022: Mitigation of Climate Change. Contribution of Working Group III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change* [P.R. Shukla, J. Skea, R. Slade, A. Al Khourdajie, R. van Diemen, D. McCollum, M. Pathak, S. Some, P. Vyas, R. Fradera, M. Belkacemi, A. Hasija, G. Lisboa, S. Luz, J. Malley, (eds.)]. Cambridge University Press, Cambridge, UK and New York, NY, USA. DOI: 10.1017/9781009157926

Where is CO_2?

mid-troposphere (5 miles)



- The total mean mass of the atmosphere is 5.1480×10^{18} kg
- Current CO_2 (Sep 2022): **415.95 ppm (1 ppm = 5.148 Gt)**
- Total CO_2 in the atmosphere: 2141 Gt (yearly addition ~ 15 Gt)

Image Credit: NASA/JPL

What scale are we talking about?

Breathing out*
1 kg CO_2/day

Today's crowd
100 kg/day

8 billion people
8 billion kg/day
8 million ton/day
3 billion ton/year

0.1 billion ton/year

Total excess emissions:
43 billion tons/year
= $43 Trillion/yr

**Based on 15 breaths per minute (range: 12-20/min), 26 mL CO_2 (4% in 665 mL average breath, range 500-800mL), 1 atm, 35 °C*

GREENHOUSE GASES

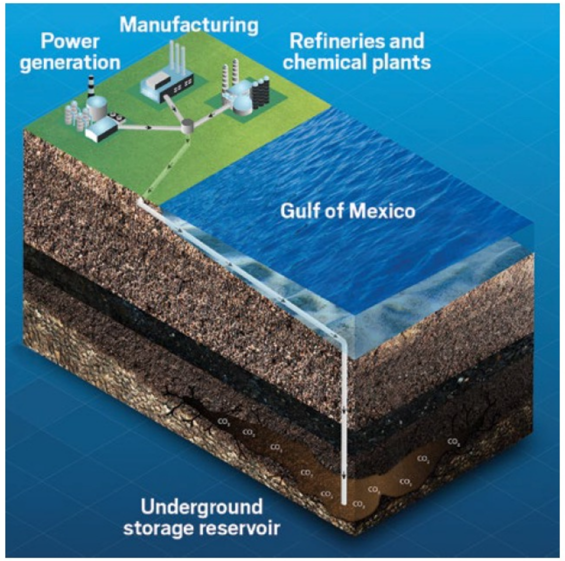
c&en
CHEMICAL & ENGINEERING NEWS

ExxonMobil proposes huge carbon capture hub

Houston project would store 100 million metric tons of CO_2 annually and cost $100 billion

Once resistant to carbon reduction initiatives, ExxonMobil has unveiled a plan to build one of the world's largest projects for carbon capture and storage (CCS) along the Houston Ship Channel in Texas. Said by some to be like dialysis for a planet, CCS involves stripping CO_2 from industrial plant emissions—or from the air—and storing it in a secure underground location to prevent the gas from contributing to global warming.

The proposed project would cost $100 billion and capture and store 100 million metric tons of CO_2 per year. The emissions saved would be equivalent to removing 1 in every 12 cars on US roads, the company says. ExxonMobil is proposing to build infrastructure to capture its own CO_2 emissions, as well as those from power plants, oil refineries, and chemical plants

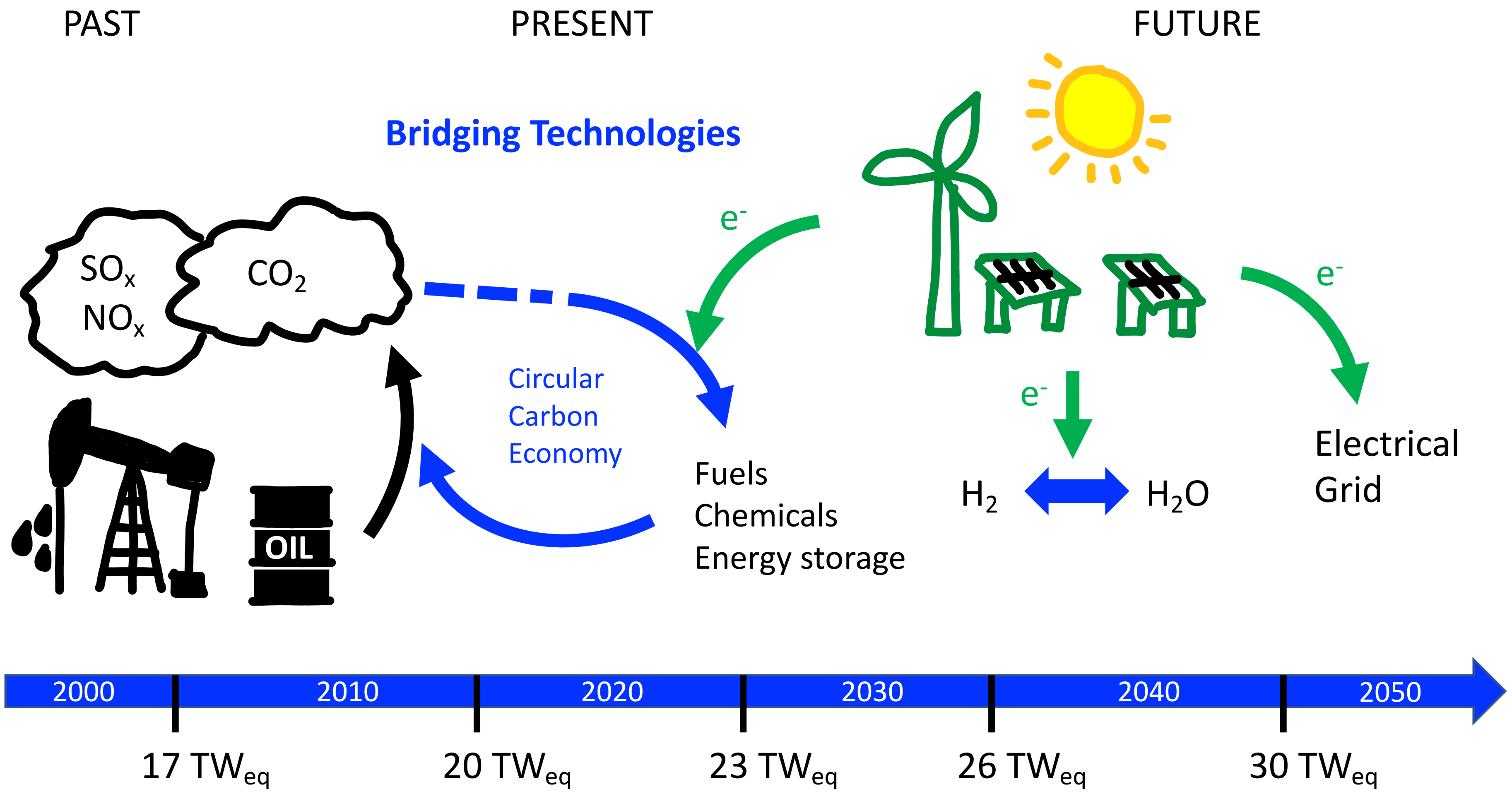


ExxonMobil proposes building a pipeline in the Houston Ship Channel region to gather CO_2 from industrial facilities including chemical plants and refineries. The CO_2 would be pumped into a reservoir thousands of meters below the seabed, where ExxonMobil claims it will be sealed by impermeable rock.

APRIL 26, 2021 | CEN.ACS.ORG | C&EN

Carbon Dioxide Capture Adsorbents: Chemistry and Methods, H. A. Patel, J. Byun, C. T. Yavuz*, ***ChemSusChem***, 2017, *10*, 1303-1317

Transition needed



How to reach carbon emission targets with technology and public awareness, C. T. Yavuz*, ***Matter***, 2022, *5*, 2566-2569

2030 target:

25 Gt CO_2e

To limit global warming to 1.5°C

Negative emissions of

10 Gt/y CO_2 by 2050

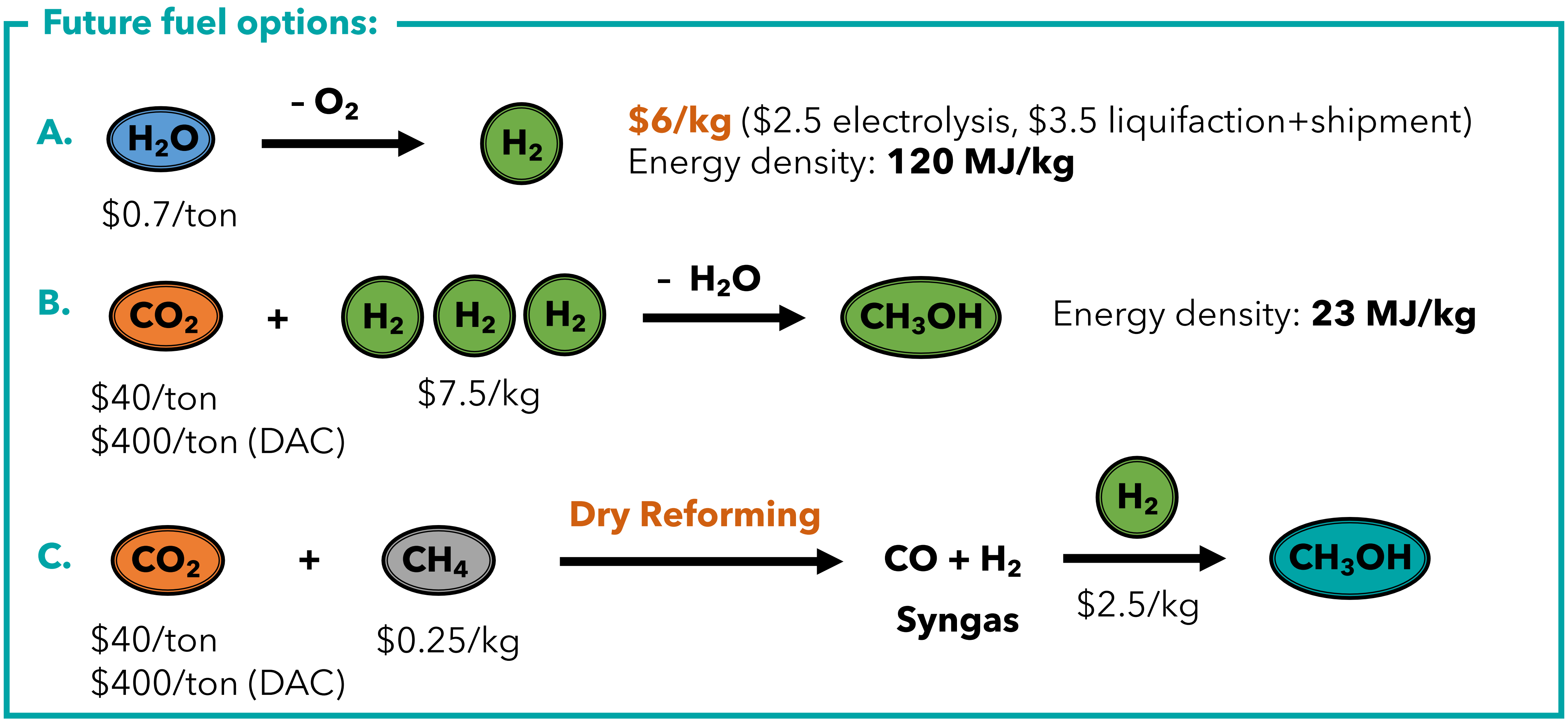
20 Gt/y CO_2 by 2100

UN Emissions Gap Report 2019
https://www.unenvironment.org/resources/emissions-gap-report-2019

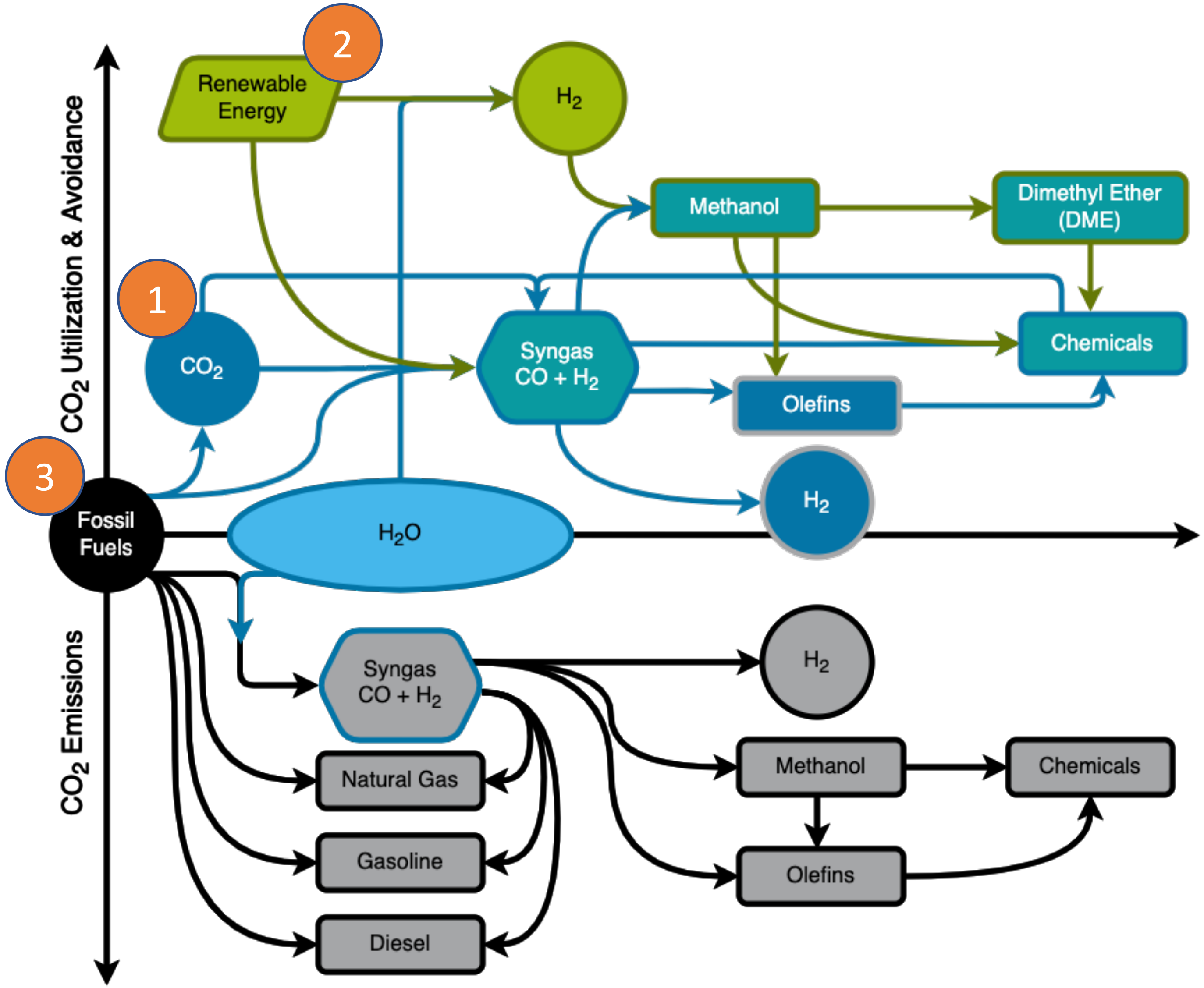
National Academies of Sciences, Engineering, and Medicine. 2019. ***Negative Emissions Technologies and Reliable Sequestration: A Research Agenda***. Washington, DC: The National Academies Press. DOI: https://doi.org/10.17226/25259

How to get rid of 10 Gt/yr CO_2?

- **CO_2 market is too small:** Urea (0.15 Gt/yr), Food (0.05 Gt/yr), Methanol* (0.04 Gt/yr)
- **If avoidance impossible:** recycling back to fuel would be best



Our net zero vision: Syngas economy



Solving 3 major issues:

1. Over **10 gigatons** CO_2 utilization, essentially reaching Paris and COP26 targets
2. Elevating **renewable** industry to the **scale** they need
3. Bringing oil sector, waste recycling, biomass industry all into the same solution – creating a **unique cooperation** that will solve the problem quickly!

How to reach carbon emission targets with technology and public awareness, C. T. Yavuz*, ***Matter***, 2022, 5, 2566-2569

Syngas economy

Syngas Battery?

$$CH_4\ (g) + CO_2\ (g) \rightarrow 2CO\ (g) + 2H_2\ (g) \qquad \Delta H^o_{298K} = 247\ kJ\ mol^{-1} \qquad (1)$$

$$CH_4\ (g) + H_2O\ (g) \rightarrow CO\ (g) + 3H_2\ (g) \qquad \Delta H^o_{298K} = 206\ kJ\ mol^{-1} \qquad (2)$$

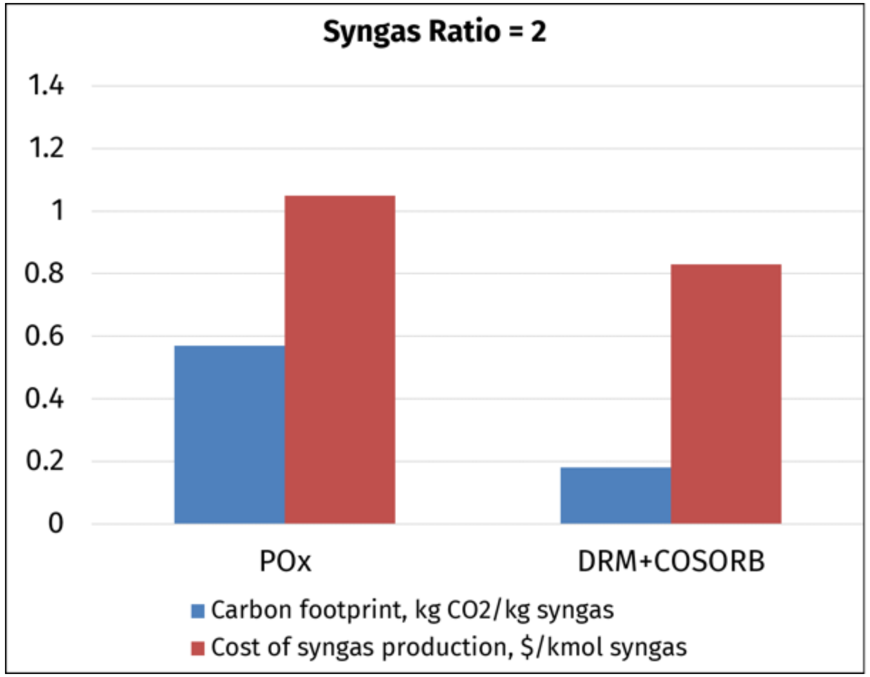
$$CO\ (g) + 2H_2\ (g) \rightarrow CH_3OH\ (g) \qquad \Delta H^o_{298K} = -91\ kJ\ mol^{-1} \qquad (3)$$

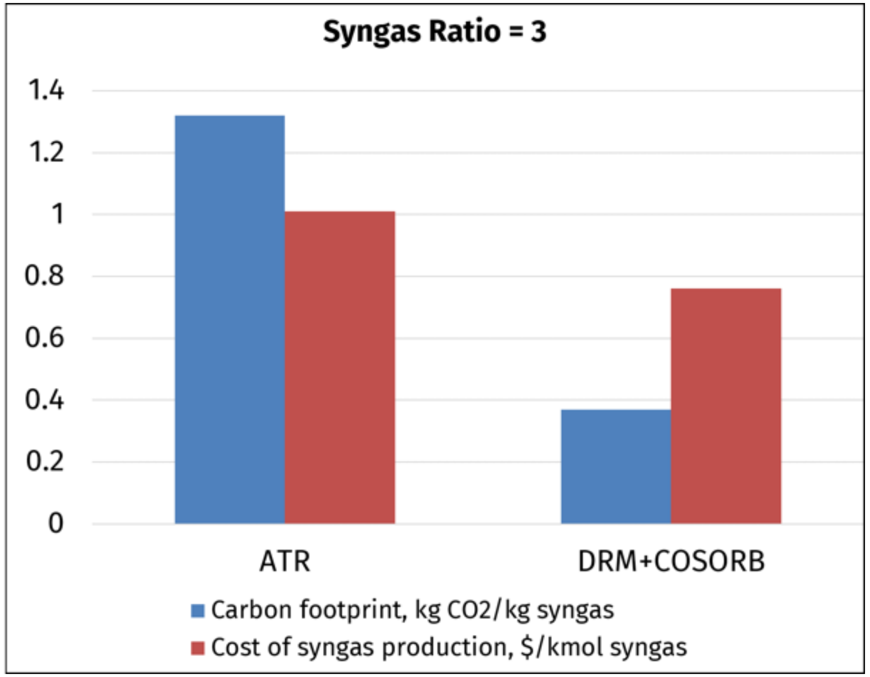
$$2CH_3OH\ (g) \rightarrow CH_3OCH_3\ (g) + H_2O\ (g) \qquad \Delta H^o_{298K} = -24\ kJ\ mol^{-1} \qquad (4)$$

$$3CH_4\ (g) + CO_2\ (g) \rightarrow 2CH_3OCH_3\ (g) \qquad \Delta H^o_{298K} = 250\ kJ\ mol^{-1} \qquad (5)$$

- For every syngas equivalent, approximately 0.4 CO_2 is used, after accounting for the heating the reactors. This amounts to **2 gigatons of CO_2** usage for all hydrogen needs in the world.
- For every dimethyl ether molecule 0.4 CO_2 is used. If vehicles/boilers were run on DME, approximately **10 gigatons of CO_2** would be used.

Dry reforming as a NET



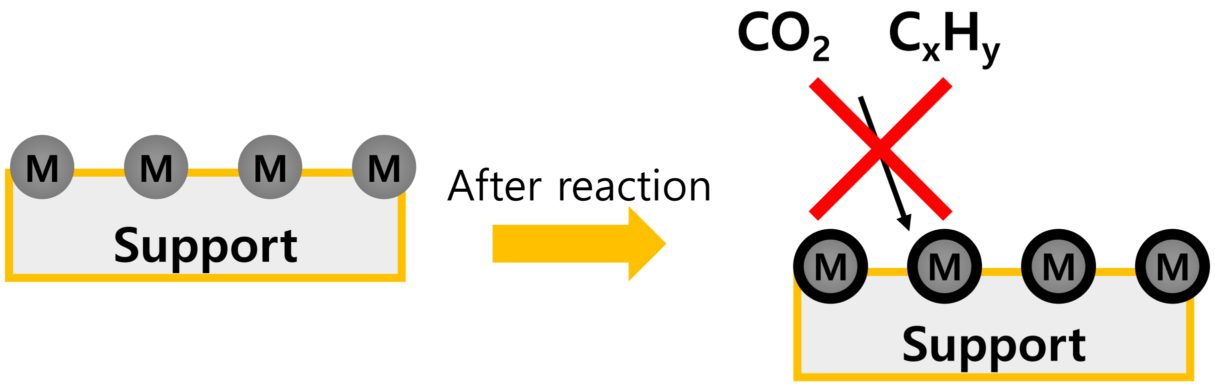


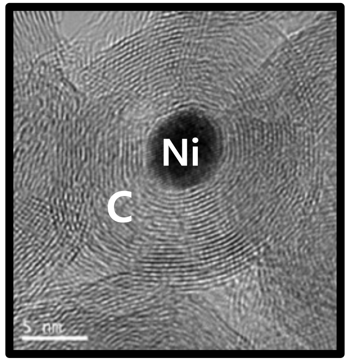
POx: Partial oxidation
ATR: Auto-thermal reformer
DRM: Dry refoming of methane
COSORB: CO absorption

Optimization Approach to the Reduction of CO_2 Emissions for Syngas Production Involving Dry Reforming
S. Afzal, D. Sengupta, A. Sarkar, M. El-Halwagi, N. Elbashir*, ***ACS Sustainable Chem. Eng.***, 2018, *6*, 7532-7544.

Main challenge is the deactivation of catalysts

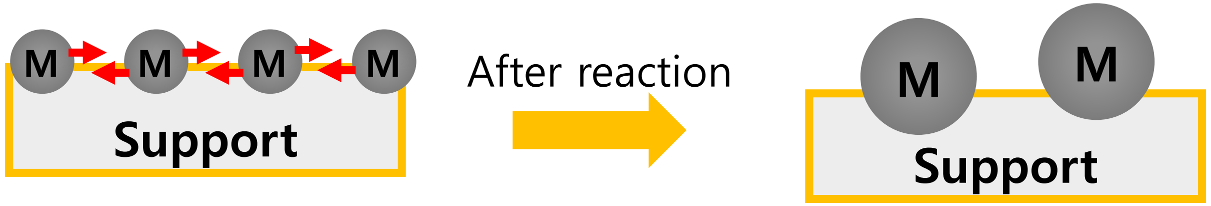
- **Coke formation: undesirable carbon formation on active surfaces**

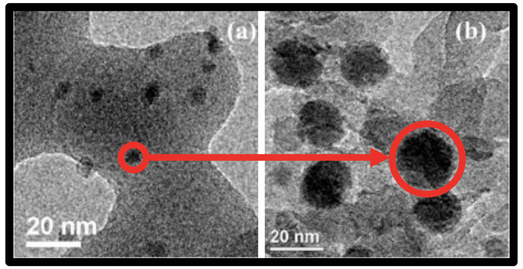




A. Serrano-Lotina et al. Appl. Catal., A 474 (2014) 107-113

- **Sintering: reduction of active surfaces**





R. Rinaldi et al. K. Mol. Catal. A: Chem. 301 (2009) 11-17

CAN SINGLE CRYSTALLINE SUPPORT SOLVE STABILITY ISSUES?

Single crystal MgO production

2 Mg (s) + CO_2 (g) → 2 MgO (s) + C (s, graphene)

>1000°C

Batch process

Continuous flow

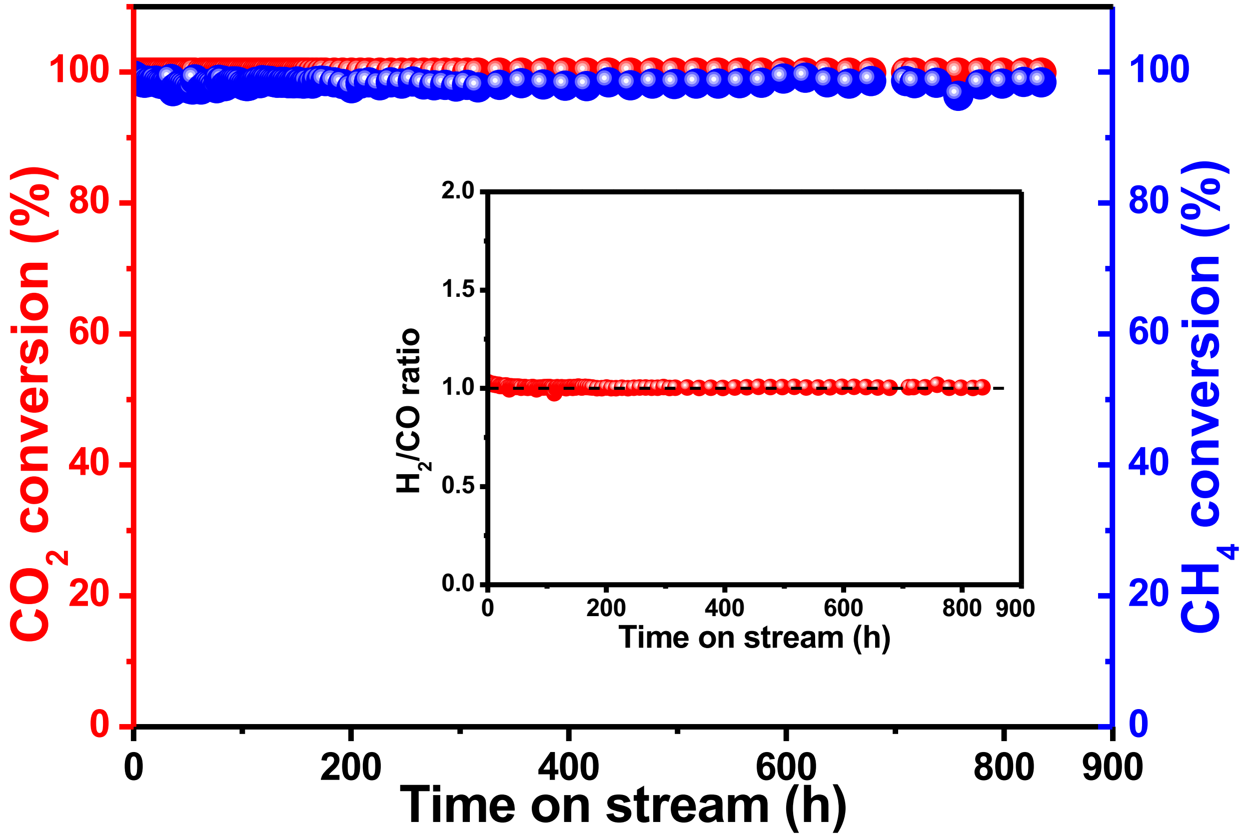
Videos courtesy of Dickinson Corporation, San Rafael, CA

NiMoCat synthesis

$$NiCl_2{\cdot}6H_2O\ (s) + (NH_4)_6Mo_7O_{24}{\cdot}4H_2O\ (s) + MgO\ (s) \xrightarrow[\text{Ethylene glycol, } 80^{o}C]{PVP,\ N_2H_4} \text{NiMoCat}\ (s)$$

Kilogram scale NiMoCat

850 hours (35 days) of continuous activity



Dry reforming of methane (DRM)

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

- Continuous DRM reaction with NiMoCat
- Deactivation did not occur for 35 days of reaction.
- H_2/CO ratio reached theoretical value of 1.

Conditions

T=800°C

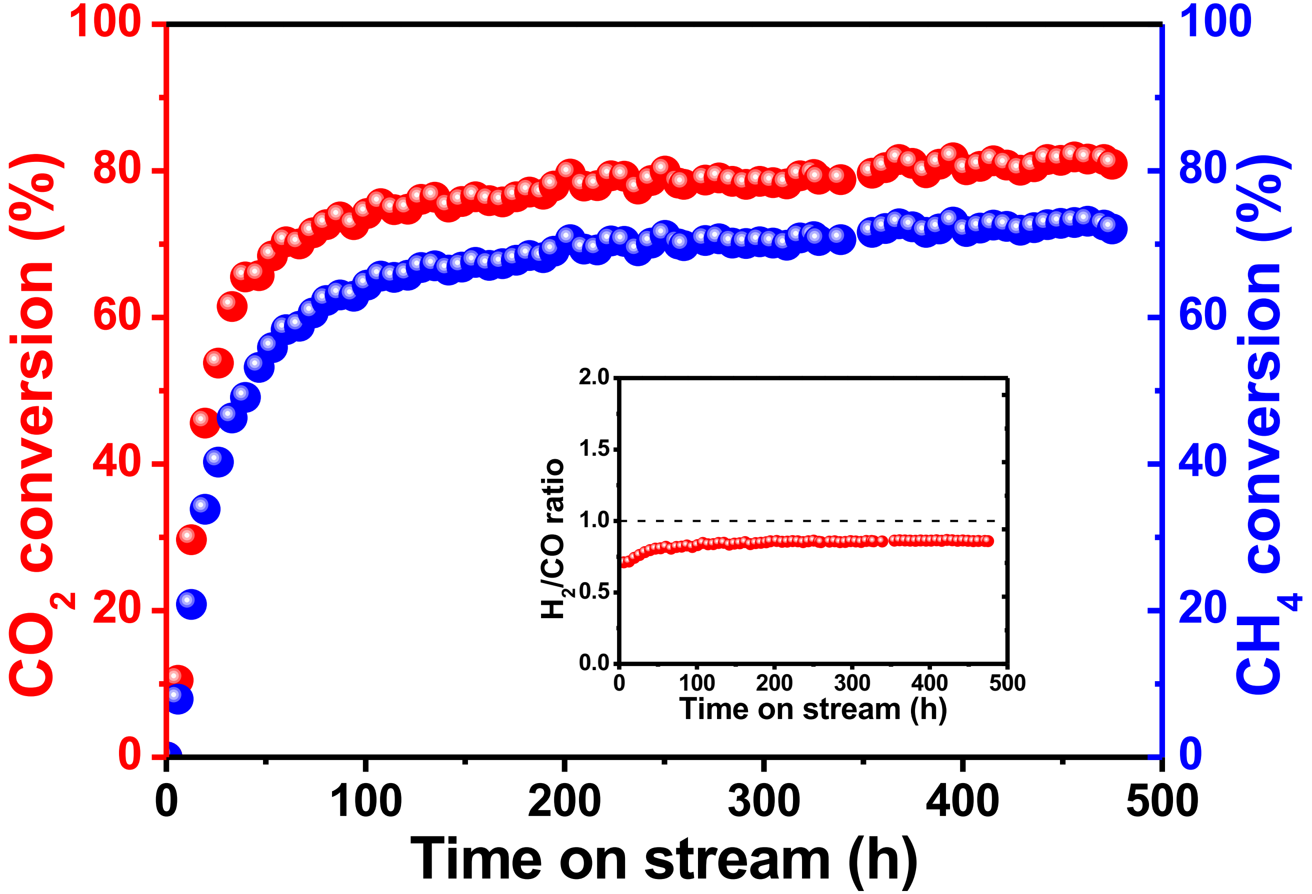
CO_2:CH_4:He=5:5:40 mL/min

50mg catalyst

(GHSV: 60 L/g_{cat}h)

Dry reforming of methane by stable Ni–Mo nanocatalysts on single-crystalline MgO, Y. Song, E. Ozdemir, S. Ramesh, A. Adishev, S. Subramanian, A. Harale, M. Albuali, B. A. Fadhel, A. Jamal, D. Moon, S. H. Choi, C. T. Yavuz*, ***Science***, 2020, *367*, 777-781

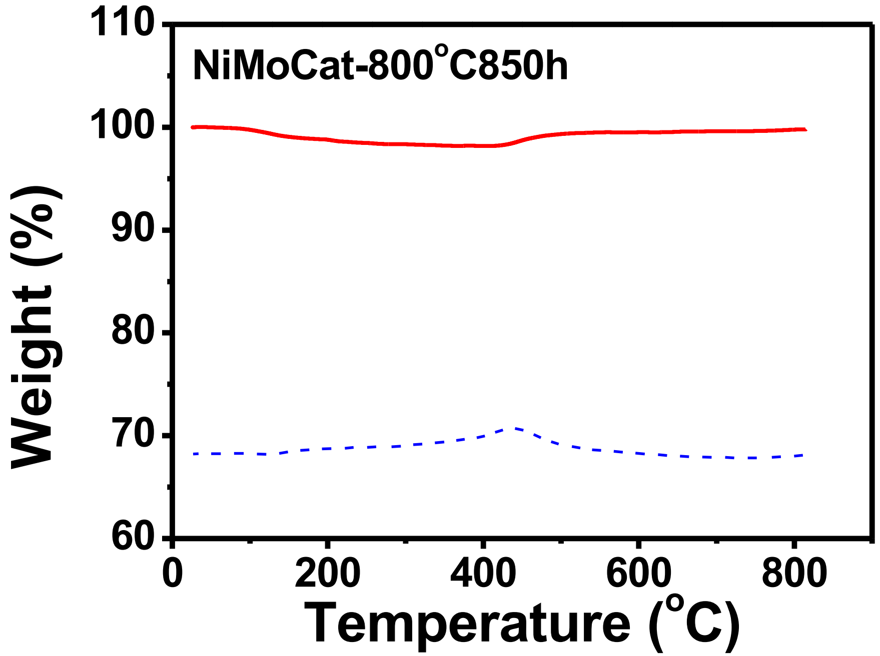
Higher Gas Hourly Space Velocity (GHSV)

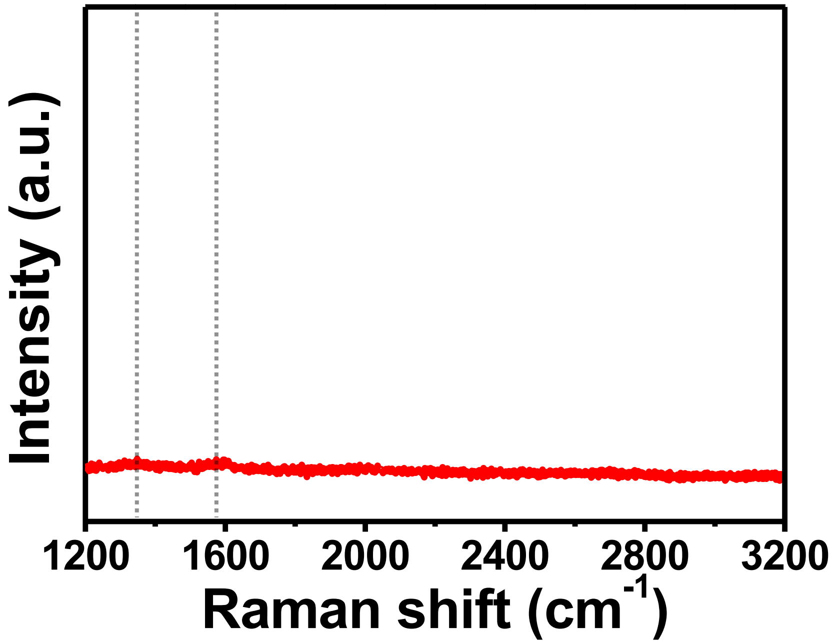


- Higher GHSV (300 L/g.h vs. 60 L/g.h) exhibits lower conversion as expected.
- No deactivation was observed for 500 hours.

Dry reforming of methane by stable Ni–Mo nanocatalysts on single-crystalline MgO, Y. Song, E. Ozdemir, S. Ramesh, A. Adishev, S. Subramanian, A. Harale, M. Albuali, B. A. Fadhel, A. Jamal, D. Moon, S. H. Choi, C. T. Yavuz*, ***Science***, 2020, *367*, 777-781

No coking





- Lack of weight loss in the spent catalyst (850 h) thermo gravimetric analysis (TGA, red line) under air atmosphere indicates no carbon deposition
- No spike in DTA (dotted line) indicates no exothermic carbon burning

- Raman spectra of the spent catalyst (850 h) shows no graphitic carbon deposition since there are no D (1350 cm^{-1}) or G (1580 cm^{-1}) bands, characteristic of coking behavior.

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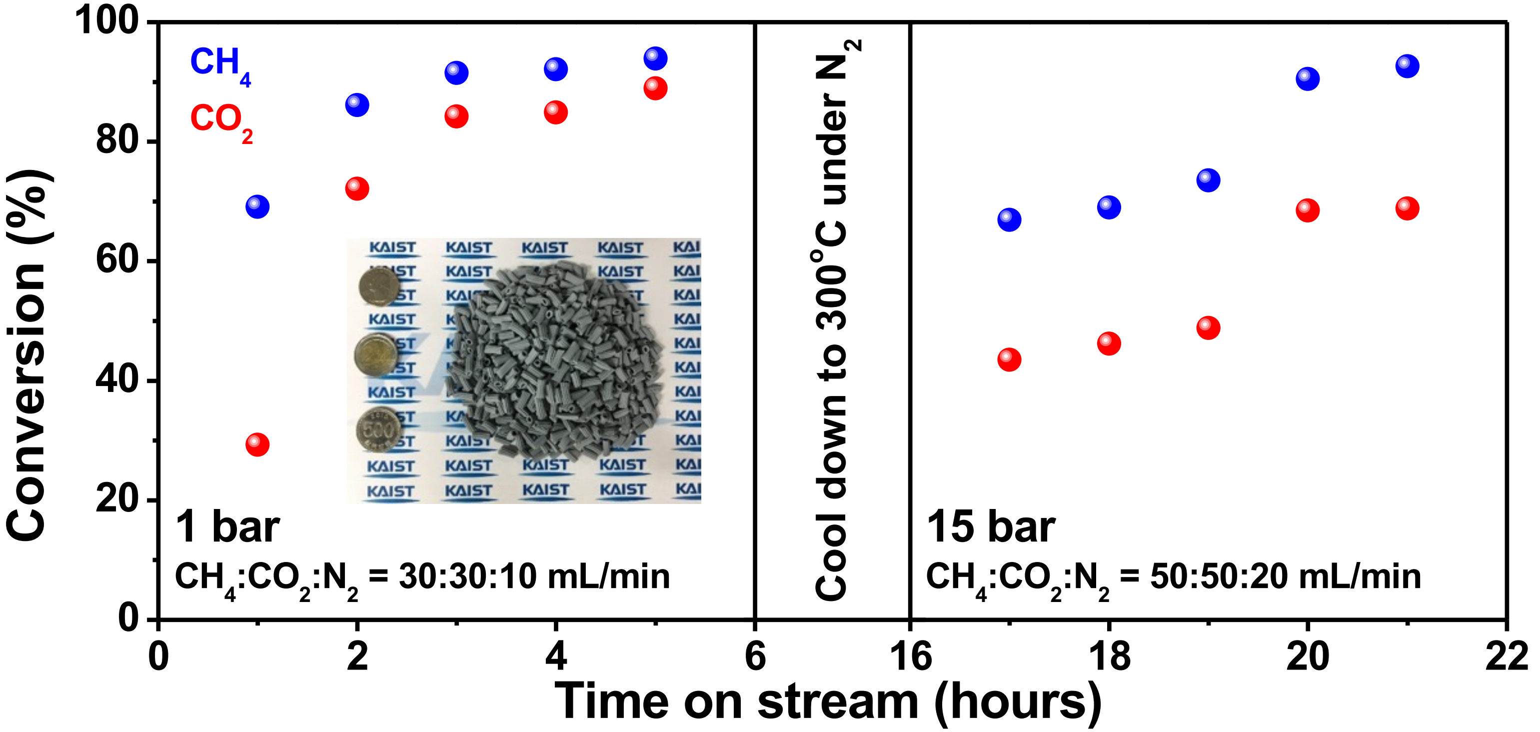
High pressure test at Saudi Aramco R&DC, Dhahran

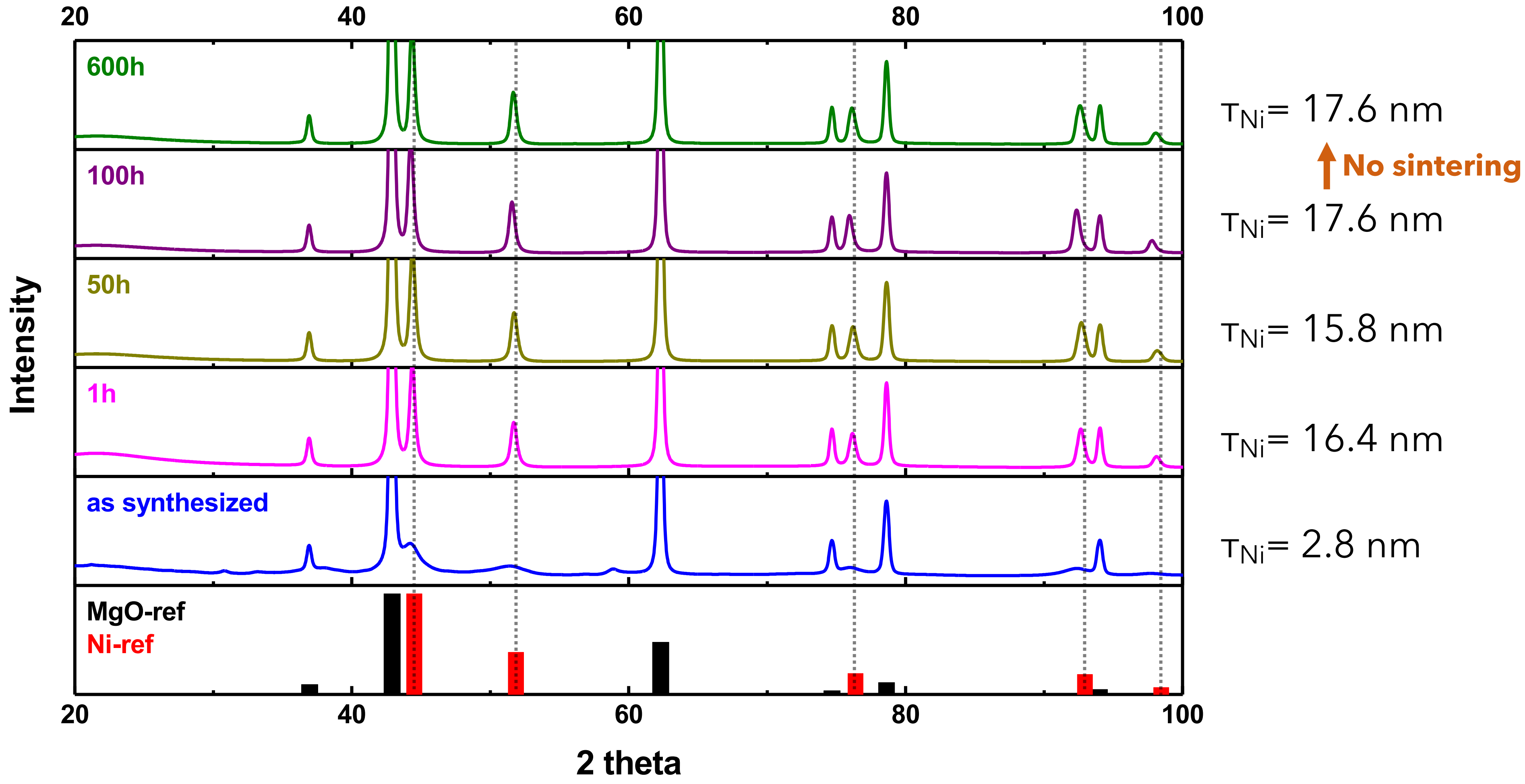


- Catalyst was pelletized and shipped to **Saudi Aramco R&DC** for high pressure test.
- Activity test was performed at 1 bar for activation and went up to 15 bar.

Dry reforming of methane by stable Ni–Mo nanocatalysts on single-crystalline MgO, Y. Song, E. Ozdemir, S. Ramesh, A. Adishev, S. Subramanian, A. Harale, M. Albuali, B. A. Fadhel, A. Jamal, D. Moon, S. H. Choi, C. T. Yavuz*, ***Science***, 2020, *367*, 777-781

So what's the trick?

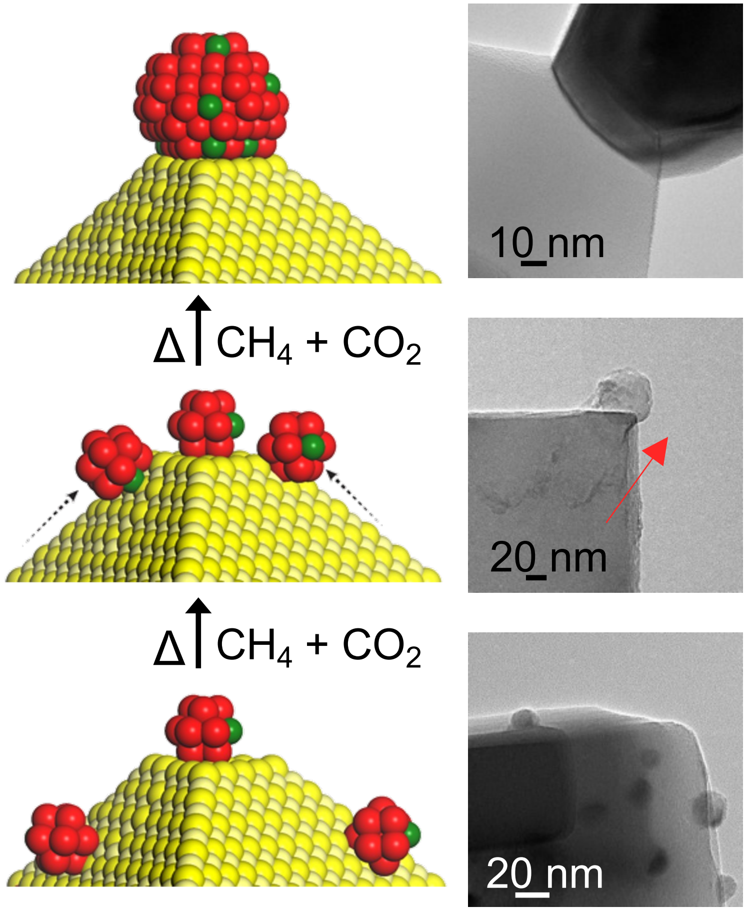
Sintering until activated but no more



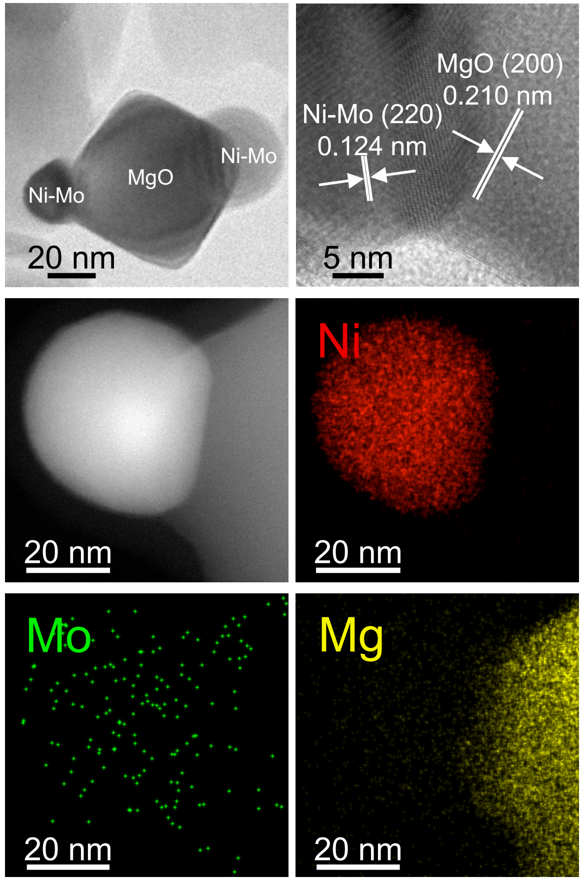
- Ni peaks evolve at 800°C, relative intensity of Ni increases
  → Higher crystallinity of Ni

$\lambda_{synchrotron}$ = 0.9 Å
$\lambda_{Cu\ K\alpha}$ = 1.54 Å

Mechanism of stability



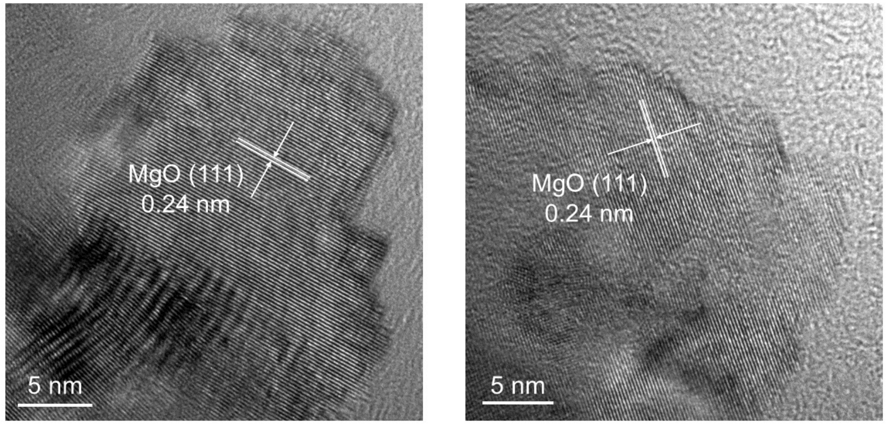
- Dispersion of Mo is concentrated in Ni: evidence of Ni-Mo alloy formation
- No MgO-NiO solid solution observed
- Ni was completely reduced (clear separation of Ni and MgO region).
- No carbon (neither graphitic layers nor CNT) was observed.
- Mo largely spreads in Ni rather than in MgO.



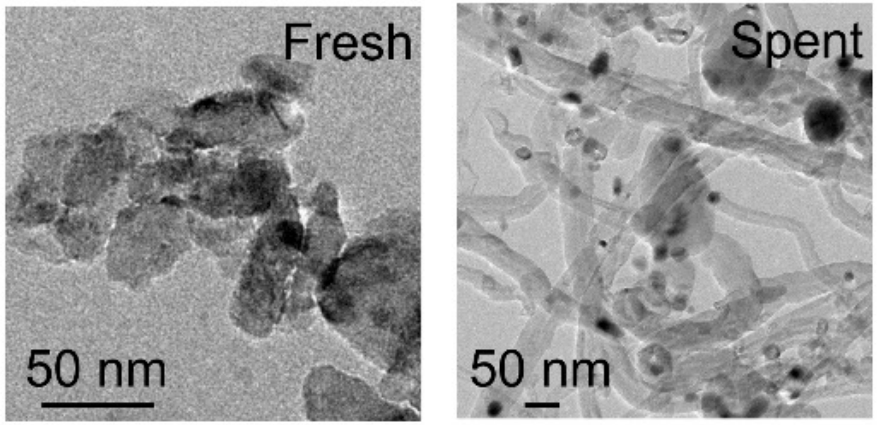
Nanocatalysts On Single Crystal Edges (NOSCE)

Ball milling to destroy NOSCE

Ground NiMoCat



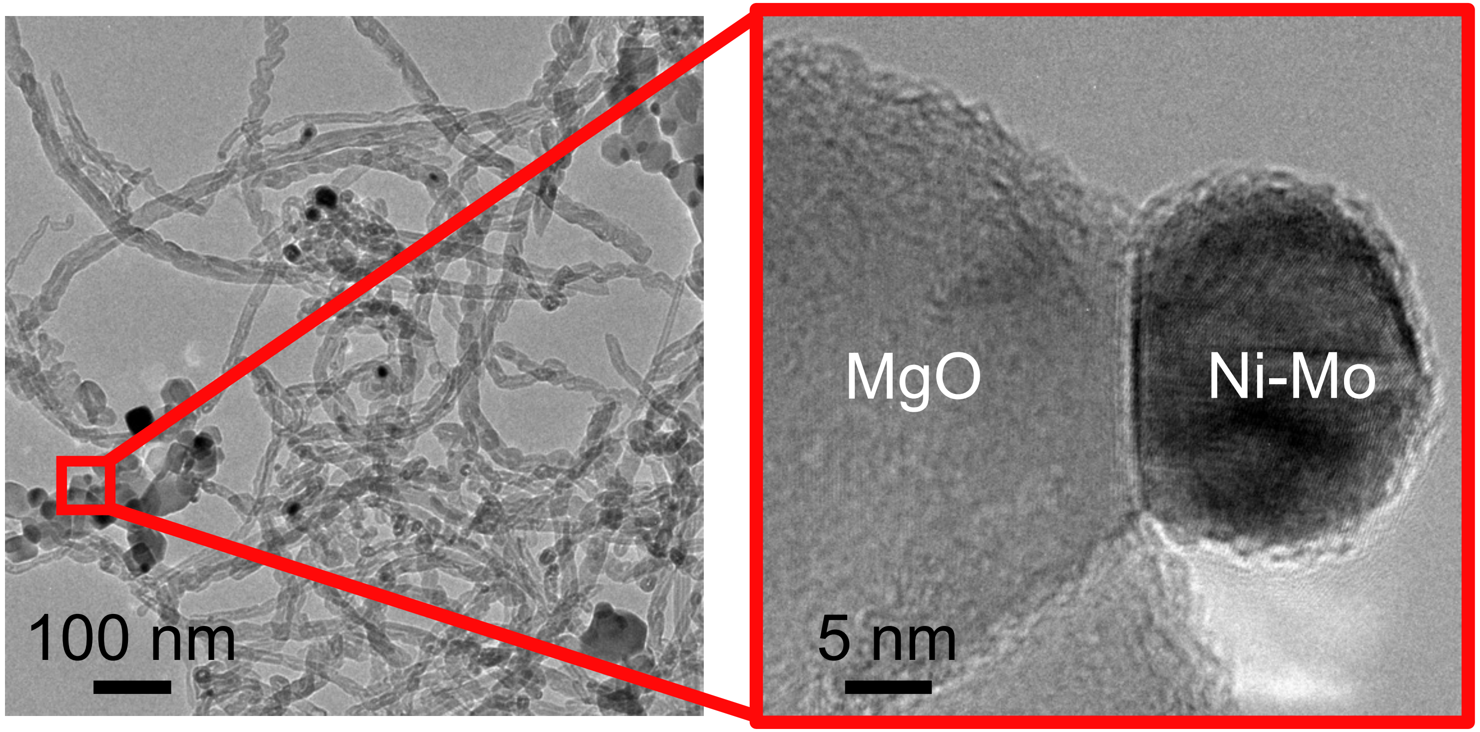
Analyzed for DRM



- Activated NiMoCat was ground with ball milling technique, which clearly shows step edges not covered with Ni-Mo particles.
- Ground NiMoCat was tested under the same conditions of the original catalyst, but this time severe coking observed.

Dry reforming of methane by stable Ni–Mo nanocatalysts on single-crystalline MgO, Y. Song, E. Ozdemir, S. Ramesh, A. Adishev, S. Subramanian, A. Harale, M. Albuali, B. A. Fadhel, A. Jamal, D. Moon, S. H. Choi, C. T. Yavuz*, ***Science***, 2020, *367*, 777-781

Conventional wet impregnation



- A control catalyst prepared through conventional wet impregnation method
- Severe coking was observed at 800 °C in just 80 hours.
- Ni-Mo particles on *NOSCE* positions are coke resistant.

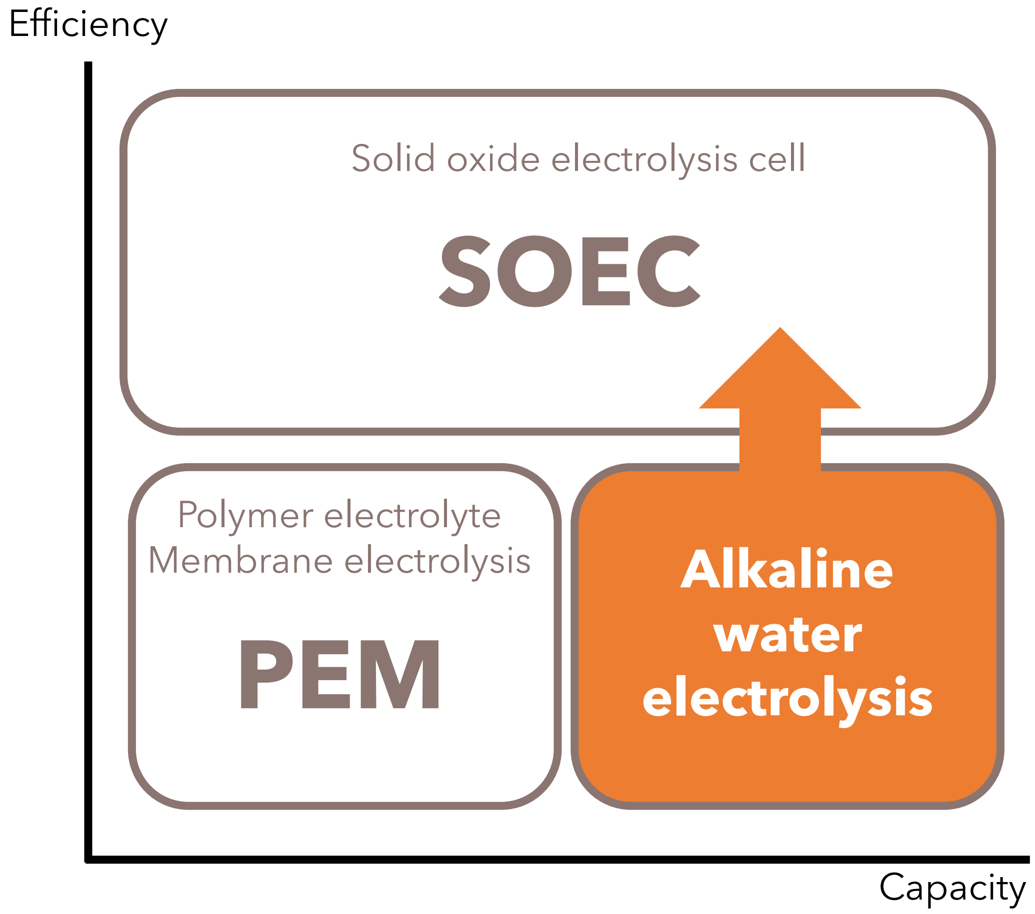
Dry reforming of methane by stable Ni–Mo nanocatalysts on single-crystalline MgO, Y. Song, E. Ozdemir, S. Ramesh, A. Adishev, S. Subramanian, A. Harale, M. Albuali, B. A. Fadhel, A. Jamal, D. Moon, S. H. Choi, C. T. Yavuz*, ***Science***, 2020, *367*, 777-781

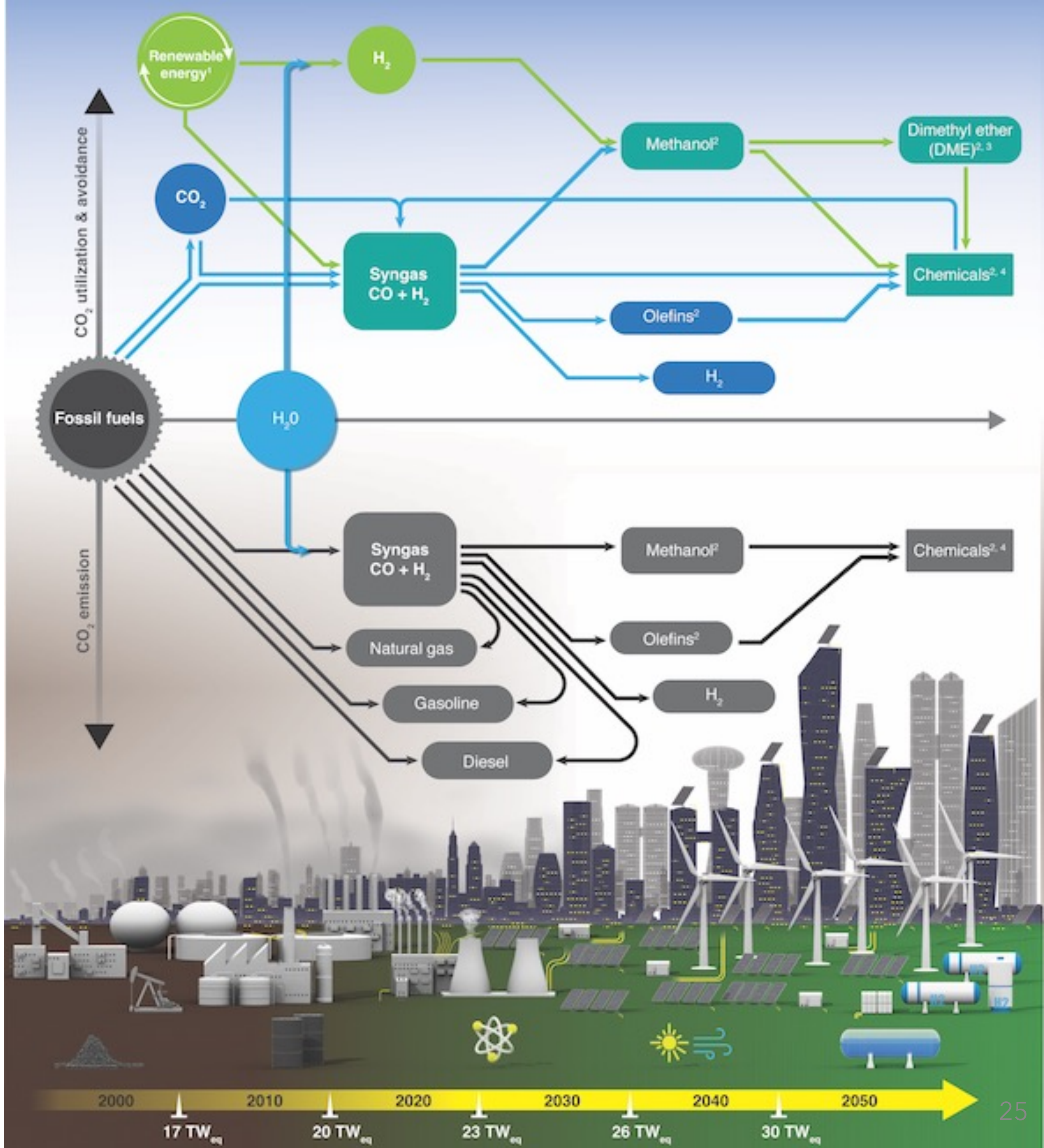
Comparisons with top Ni catalysts

Catalyst	Temperature	Accumulated Volume of Reactants (L/g_{cat})	H_2/CO Ratio	Catalytic Activity	Reference
Ni@Mo_2C	800°C	420 L/g_{cat}	-	CO_2 Conv.: 90% → 50% CH_4 Conv.: 80% → 50% (in 30 h)	Catalysis Today (2015)
NiMo_2C@La_2O_3	800°C	600 L/g_{cat}	-	CO_2 Conv.: 70% → 80% CH_4 Conv.: 50% → 65% (in 50 h)	Catalysis Today (2015)
Ni@SBA-15	750°C	180 L/g_{cat}	1.05 → 1.0 (in 20h)	CO_2 Conv.: 45% CH_4 Conv.: 35%	Chem. Commun (2014)
NiCe@SBA-16	700°C	3000 L/g_{cat}	0.7	CH_4 Conv. 72% → 68% (in 100 h)	ACS Catal. (2013)
Ni@SiO_2	750°C	300 L/g_{cat}	0.7	CO_2 Conv.: 71.2% → 65.6% CH_4 Conv.: 58.4% → 54.1% (in 24.5 h)	Applied Catalysis B: Environmental (2015)
NiMoCat (This work)	800 °C	10,200 L/g_{cat}	1.0	CO_2 Conv.: 99.9% CH_4 Conv.: 98.0% No sintering No coke formation (in 850 h)	Science (2020)

Dry reforming of methane by stable Ni–Mo nanocatalysts on single-crystalline MgO, Y. Song, E. Ozdemir, S. Ramesh, A. Adishev, S. Subramanian, A. Harale, M. Albuali, B. A. Fadhel, A. Jamal, D. Moon, S. H. Choi, C. T. Yavuz*, ***Science***, 2020, *367*, 777-781

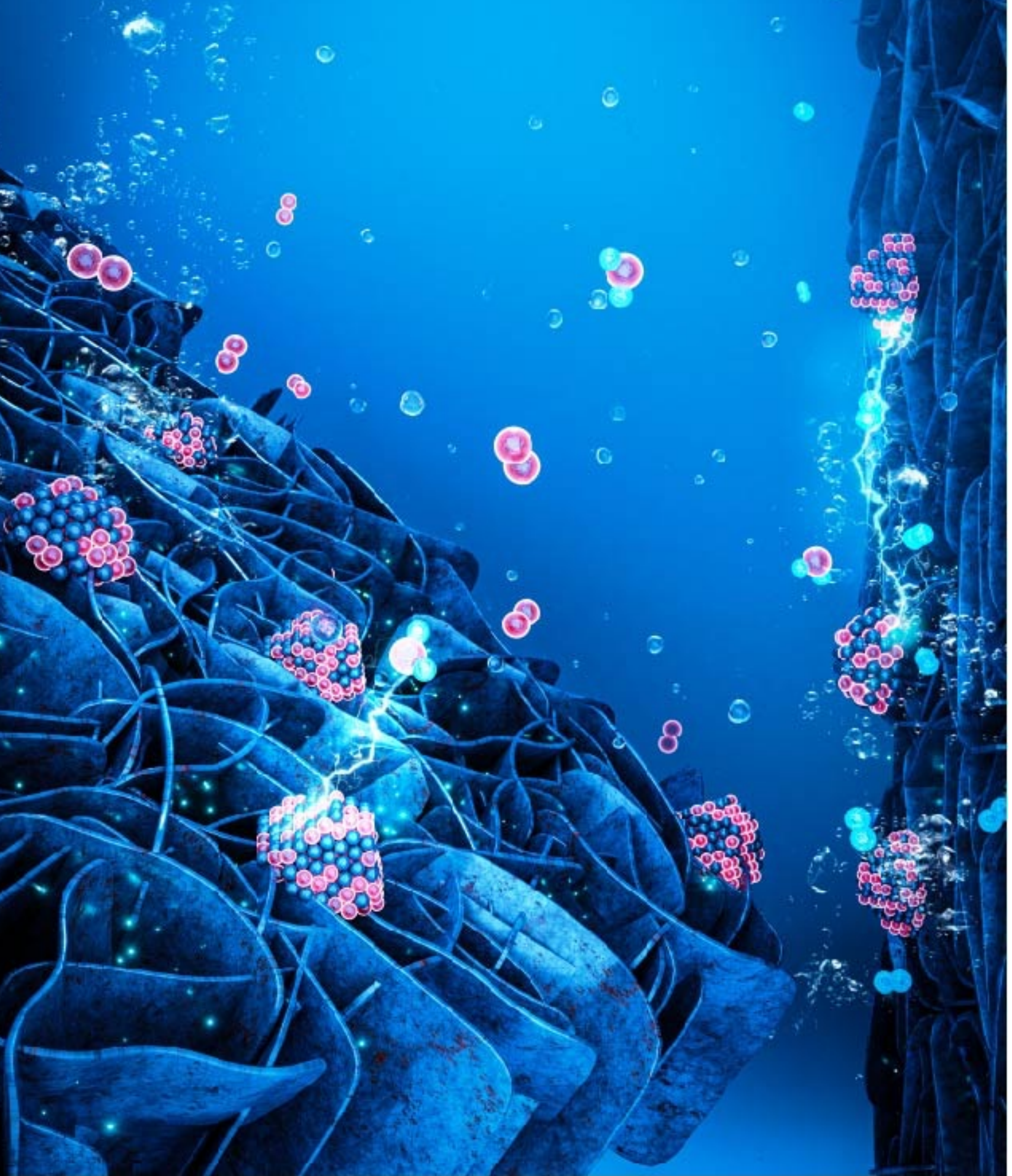
Green hydrogen?

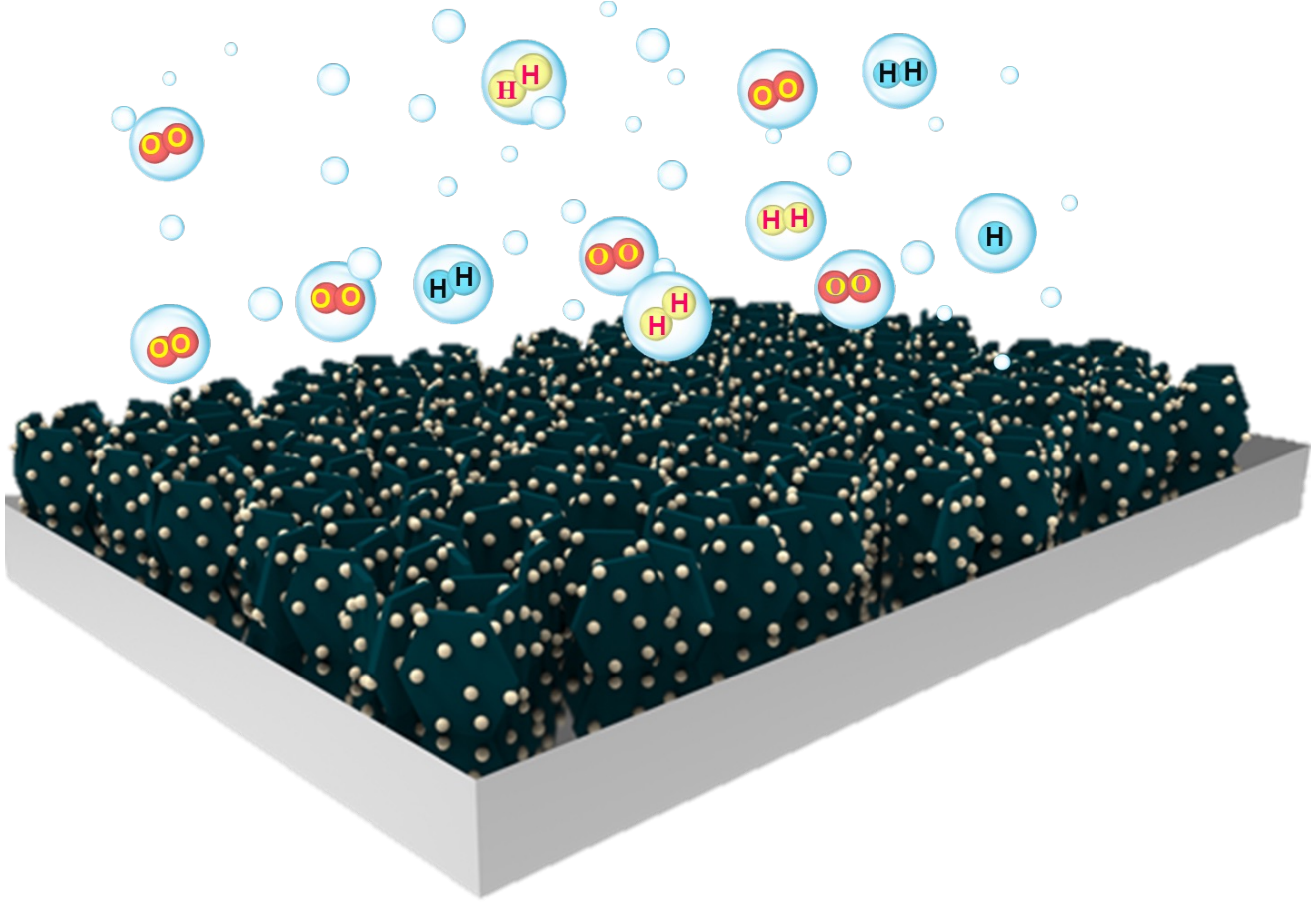




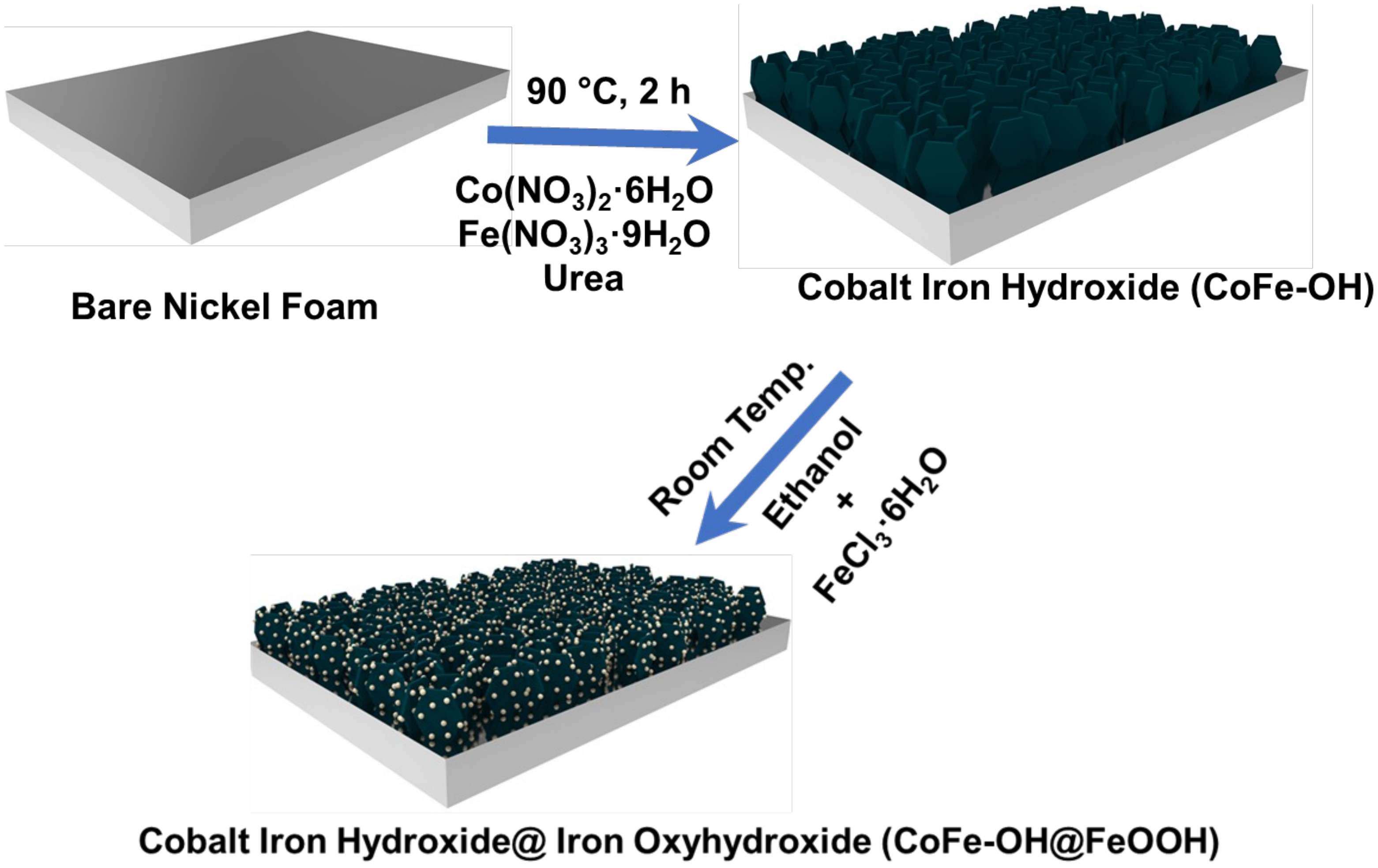
- Large scale: Alkaline water electrolysis
- Mobile applications: PEM

Earth abundant: Ni foam with Co-Fe hydroxides





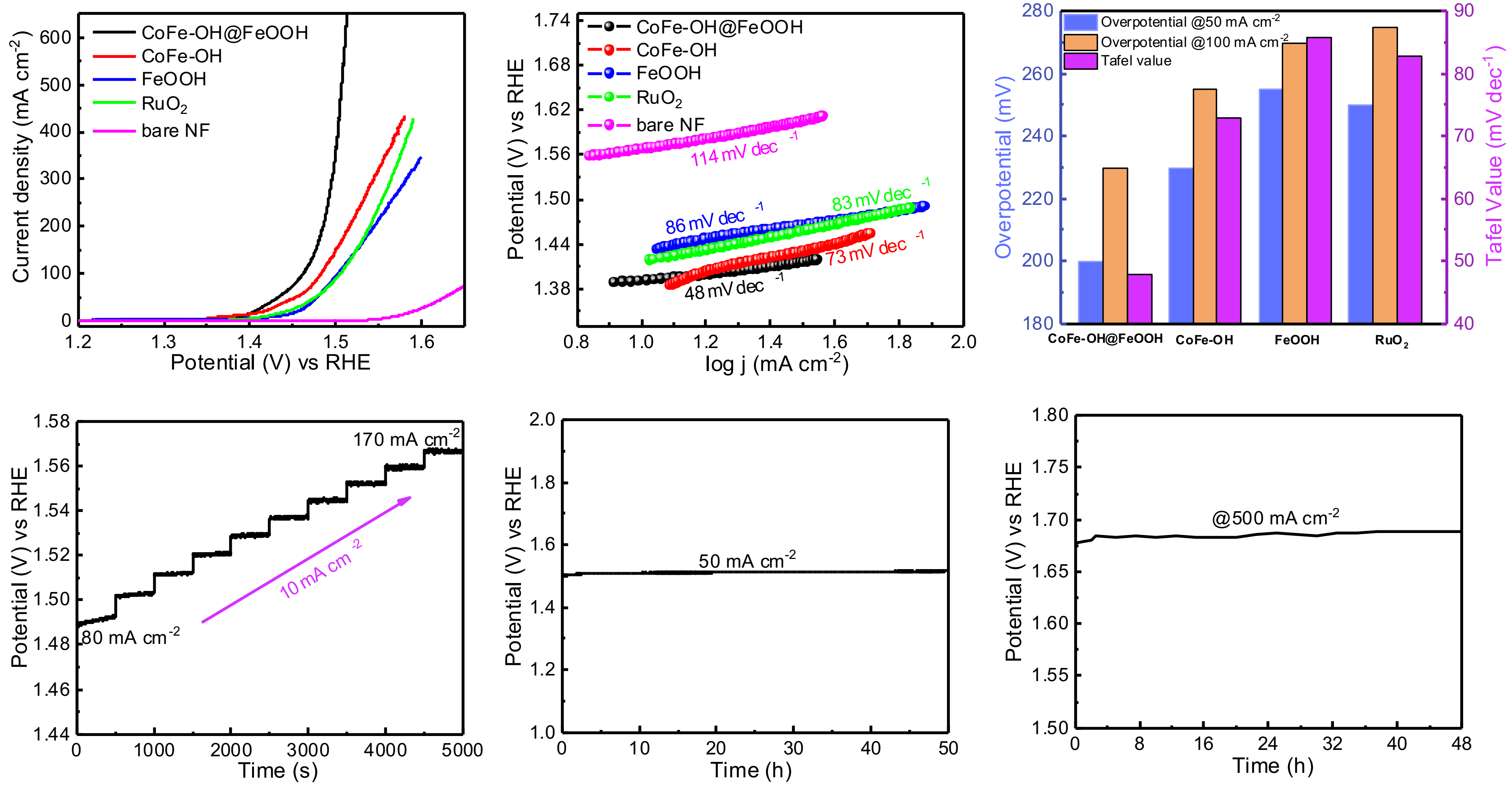
Easy fabrication



- ✓ Simple
- ✓ Scalable
- ✓ Cost Effective
- ✓ Binder Free

Low-overpotential overall water splitting by a cooperative interface of cobalt-iron hydroxide and iron oxyhydroxide
P. Babar, K. Patil, J. Mahmood, S. Kim, J. H. Kim*, C. T. Yavuz*, ***Cell Reports Physical Science***, 2022, 3, 100762.

Synergistic interface



- Efficient CoFe-OH@FeOOH electrocatalyst for overall water splitting.
- Interface coupling tailors electronic structure.
- CoFe-OH@FeOOH delivers a cell voltage of 1.56 V for overall water splitting.

Low-overpotential overall water splitting by a cooperative interface of cobalt-iron hydroxide and iron oxyhydroxide
P. Babar, K. Patil, J. Mahmood, S. Kim, J. H. Kim*, C. T. Yavuz*, ***Cell Reports Physical Science***, 2022, *3*, 100762.

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