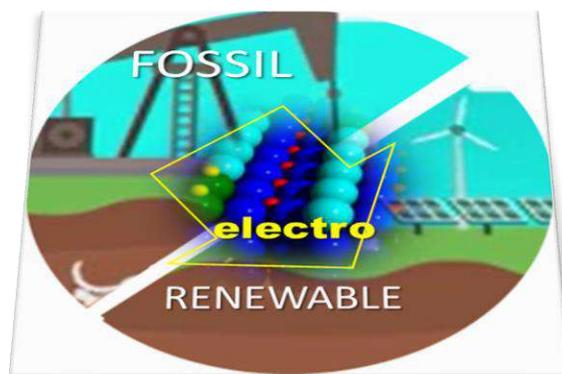


RETHINKING e-CATALYSYS TO ADDRESS DEFOSSILIZATION OF CHEMICAL AND ENERGY PRODUCTION



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ERC Synergy Grant



Outline

- **Background and Landscape**
 - From linear to a cyclic (NZE) society
 - Replacing Fossil Fuels: A System Change
 - Close the C-cycle in Energy Intensive Industries
- **e-Catalysis**
 - Opportunities, Prospects & Challenges
 - Electrocatalysis: a Paradigm Shift
 - eNH₃: a case study
 - From electro to photo-electro catalysis
- **Conclusions**



SUMMARY

Q&A

From linear to circular C economy

need of dedicated technologies to close the cycle

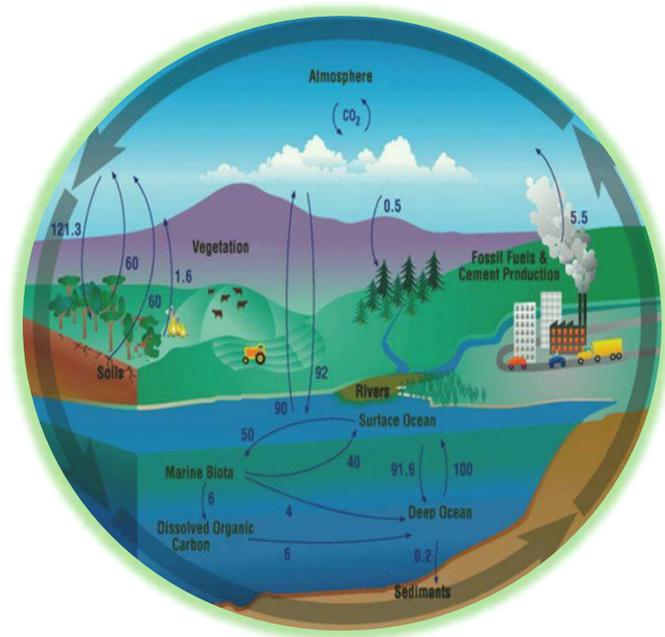
*carbon in nature is circular,
but mechanisms are
complex, fragile and slow*

emissions



*we have altered this mechanism with an
intensive use of fossils and emissions of
GHG (CO₂ & others) - a **linear C**
economy based on fossils as convenient
energy vector*

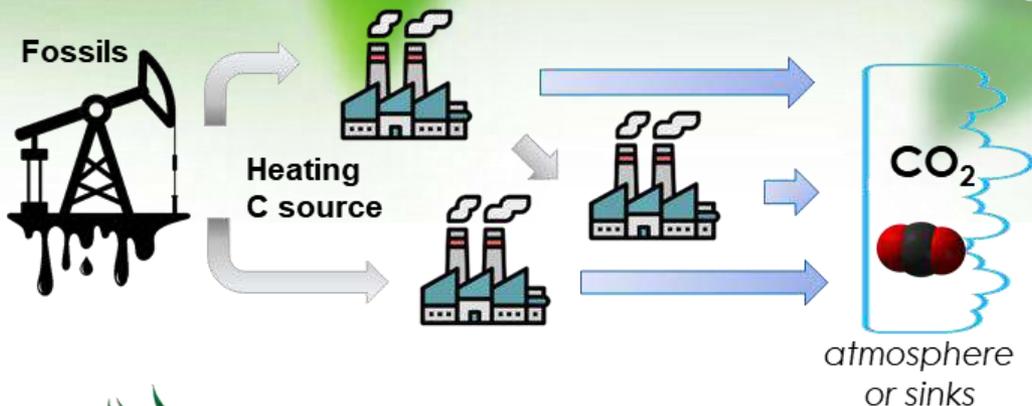
*carbon neutrality → a **circular** approach,
substituting fossils with equivalent energy
vectors based on renewables (*solar fuels*),
not maintain a linear model with
enhanced sinks*



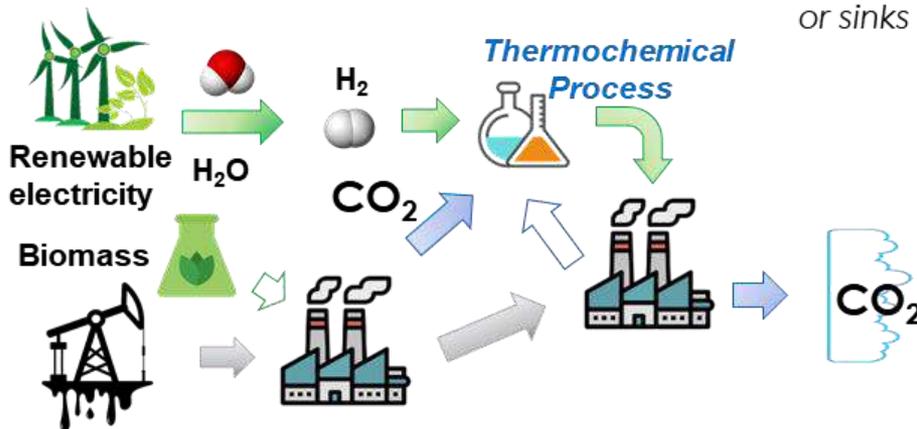
need of dedicated technologies & a new systemic approach

From linear to circular economy

a linear model

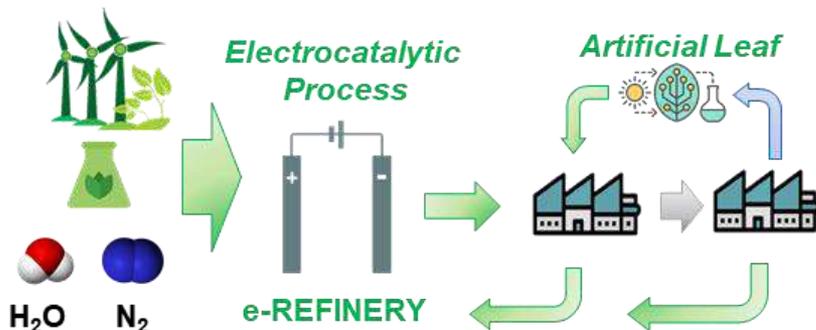


indirect circular model

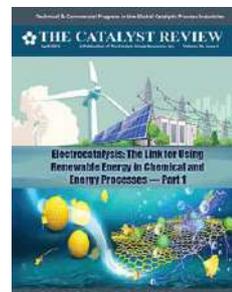


direct & full circular economy

SMART & digitally interconnected



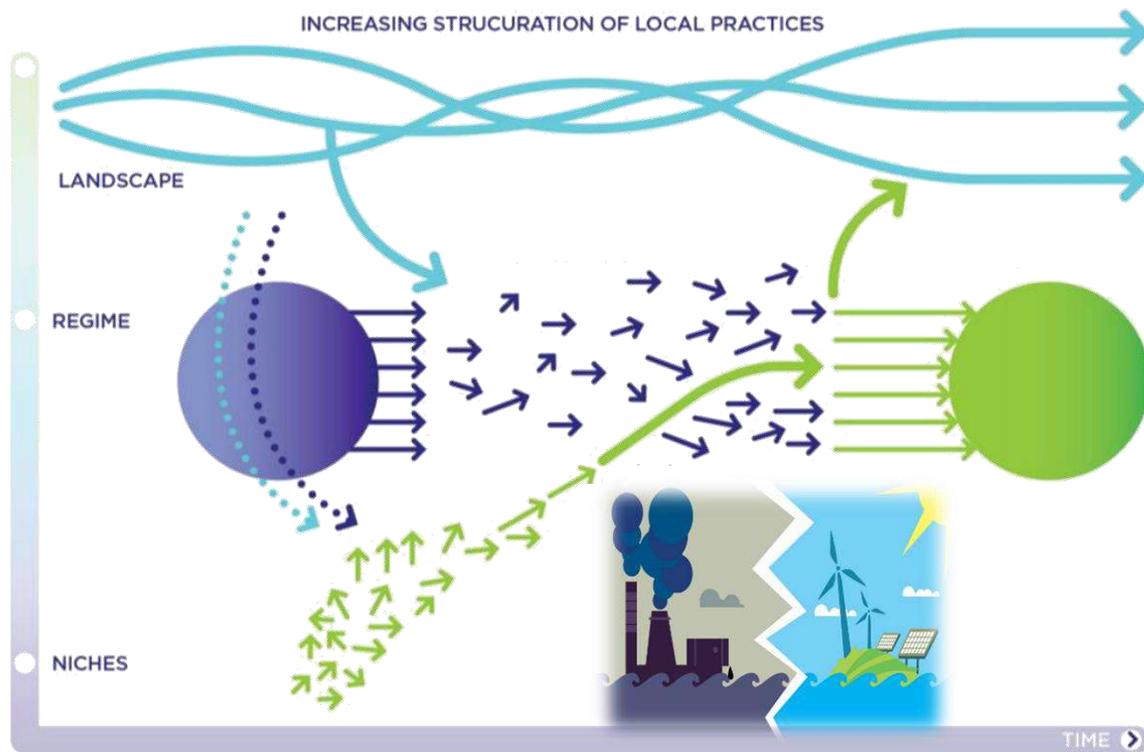
A net-zero emission (NZE) society





A (radical) System Change

- A **radical** system transition to a **new** energy & chemistry system in terms of raw materials, technologies, infrastructure, etc.
 - a **Deep Transition** involving a full economical, social, scientific and technological modification \Rightarrow **catalysis** should **evolve** accordingly also in terms of **fundamental aspects** to maintain its **crucial role**



New technologies and their role cannot be assessed properly out of the context of this in deep transition

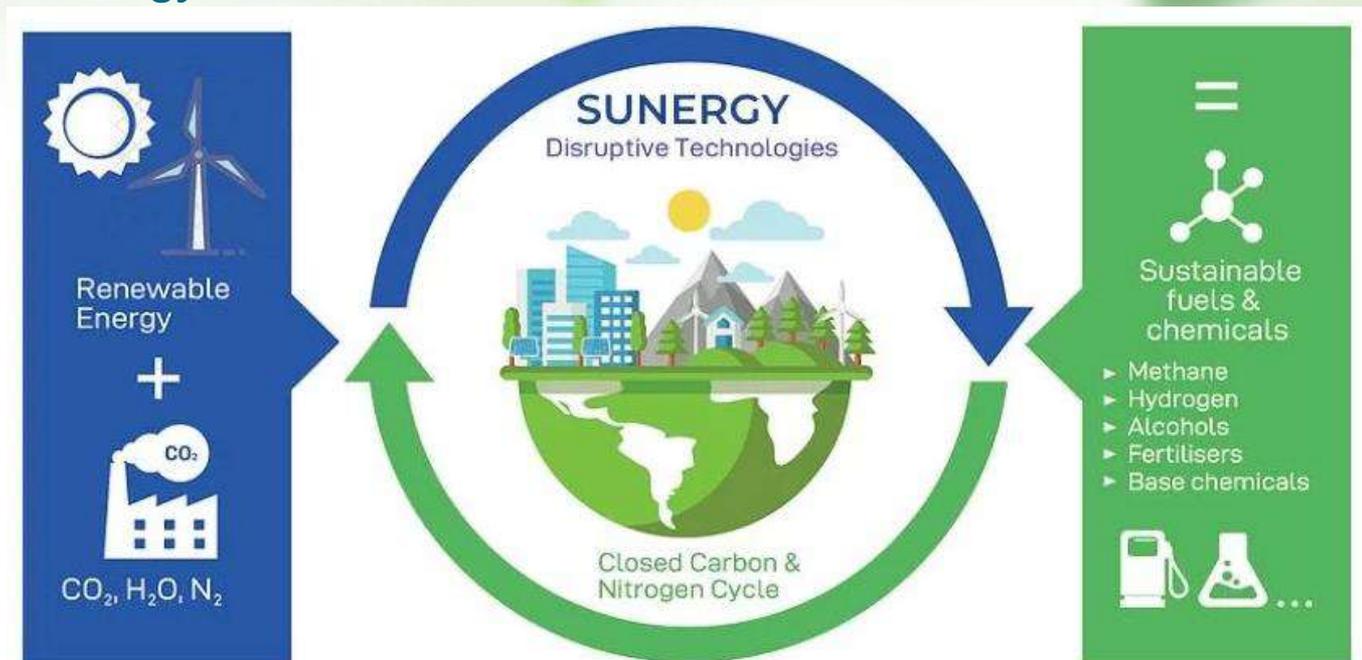




SUNERGY

Unlocking the renewable energy future

<https://www.sunergy-initiative.eu/>

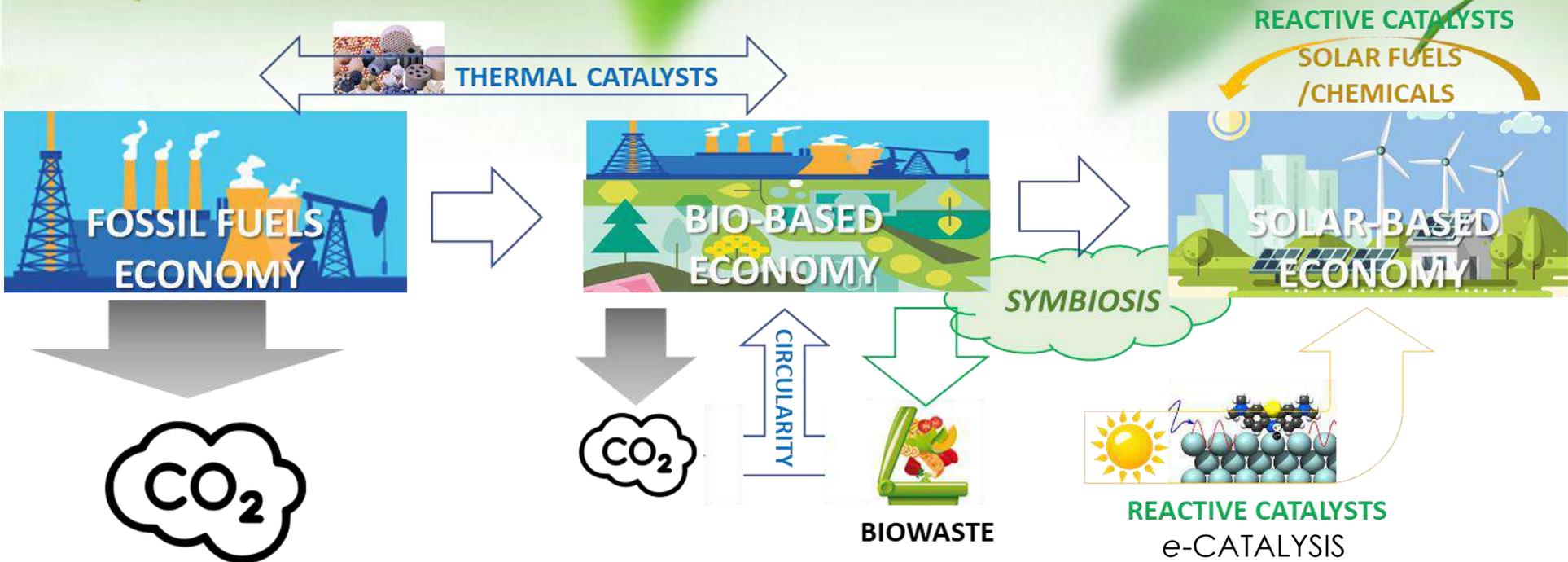


Disruptive Technologies

By using energy from renewable sources (sunlight, wind) and abundant small molecules (CO_2 , H_2O , N_2), **e-fuels** and **-chemicals** as backbone to **NZE**:

- Storage of renewable energy as liquid fuels
- Production of fossil-free base chemicals for industry and agriculture
- Technologies with a negative CO_2 footprint
- Close the C-cycle in Ells

The on-going transformation



The **initial** transition from a fossil fuel to a *mixed fossil and bio-based economy*, driven from the need of reducing the carbon footprint, has been accomplished mainly by **adapting thermal** catalysts. The **next step** of transformation to a **solar-based economy**, based on renewable energy (produce locally or remotely, transporting them via solar fuels/chemicals) in **symbiosis** with bio-based economy to use its CO₂ and biowaste emissions as carbon-source alternative to fossil fuels, requires the development of **conceptually new catalysts**, indicated as **reactive** catalysts.



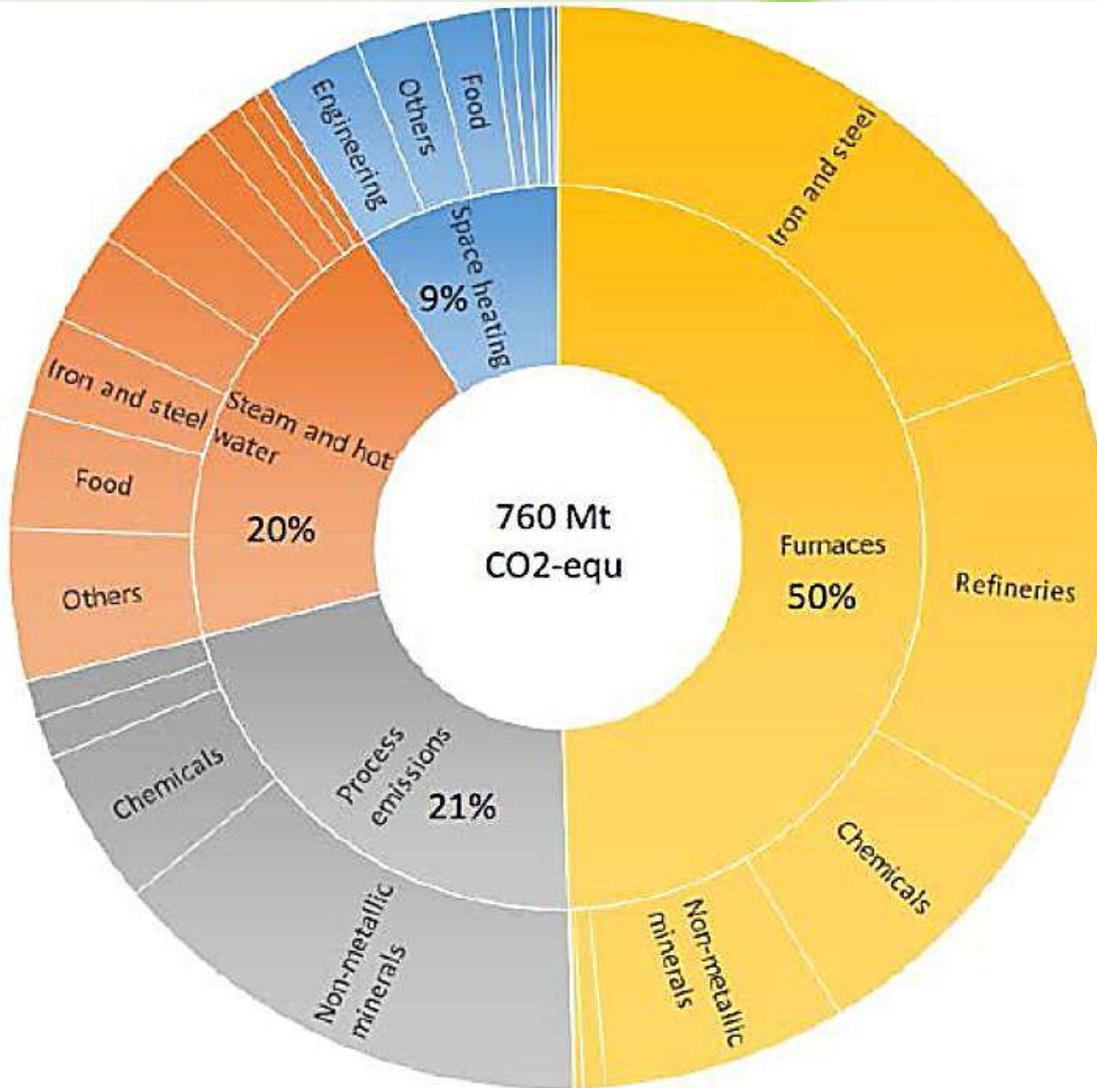
Thermal vs. reactive (e^-) catalysis

- In "reactive" catalysis, differently from "conventional" (thermal) catalysis, **very reactive species** are generated
 - either by application of a potential and electrical current or by light absorption and creation of charge separation, or by activation of reactant molecules when generating a (non-thermal) plasma, which consist of radicals, excited species, ions, photons and electrons → *photo-, electro- and plasma-catalysis*
- **Thermal** catalysis
 - the rate limiting step is the adsorption/transformation of reactant molecules (usually), with the temperature of reaction necessary to overcome the energy barrier of this rate-limiting step.
- **Reactive (e^-)** catalysis
 - issue is instead to control the path of transformation of these reactive species along the target one.

Why we need a shift to e-catalysis ?

Electrification chemical (EIs) industry

Energy Intensive Industry



- Half of all the emissions in the energy-intensive industries are being caused by heating fossil fuels in furnaces for high-temperature processes
- Other 20% for steam & hot water
- 21% process emissions



How to reduce CO₂ emissions in process industry

use FFs in process furnaces

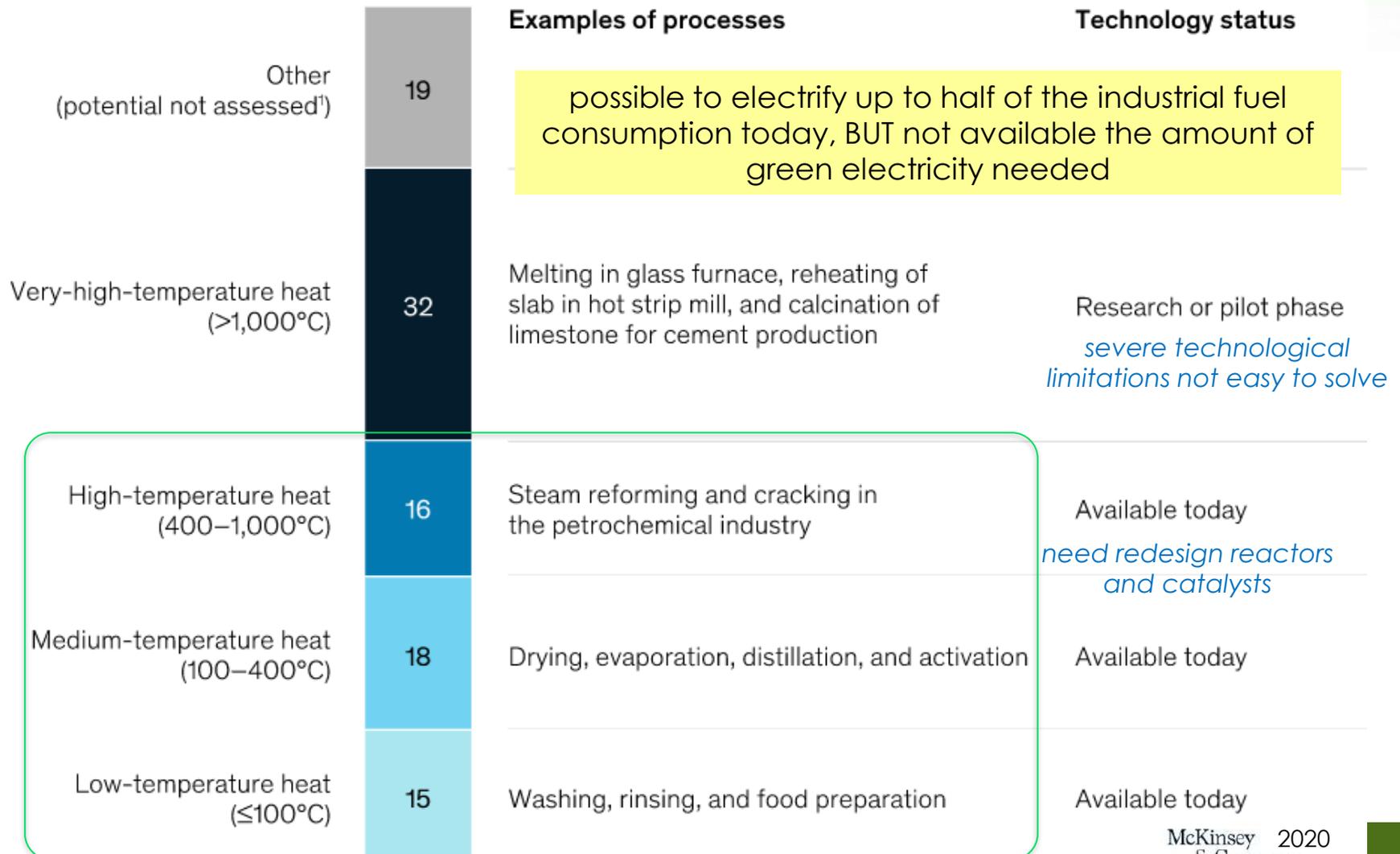
- Improve energy efficiency
 - already largely made in the past, further improvements limited
- Electrification, using electricity from RE sources
 - depends on applications, rebuild/redesign furnaces, needs green electricity 24h (avoiding natural fluctuations) in large amounts
 - green chemical energy vectors - CES (H₂, but not only) → transport/storage of CES → transport from remote areas (RE economy) → SFs
- Direct solar heating (concentrated solar power, CSP)
 - limited effective possibilities, large fluctuations
- Biobased fuels
 - transitional solution, limited carbon footprint reduction
- CCS (storage, in the different forms)
 - not a sustainable and cost-effective solution

→ CO₂ utilization

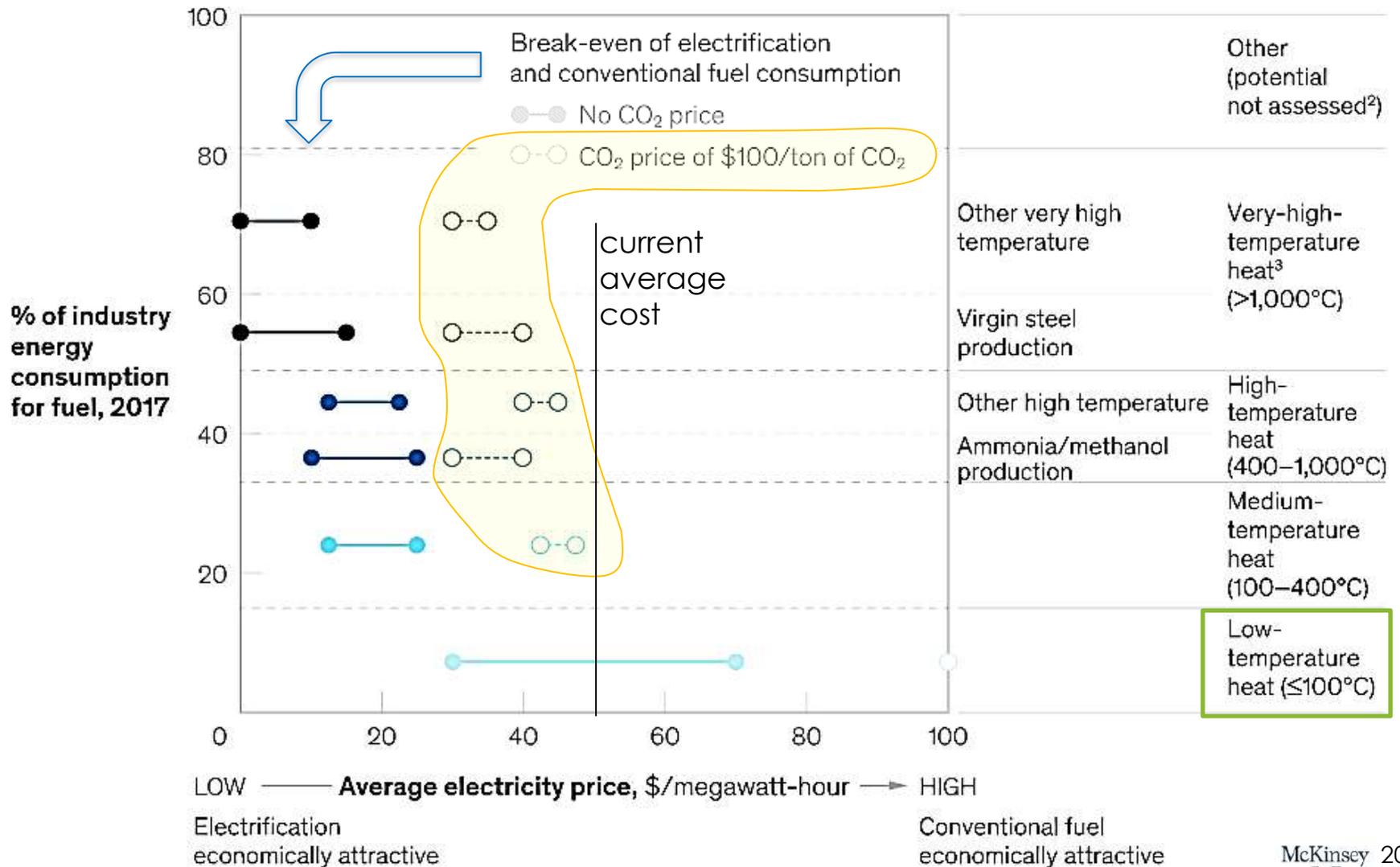
close the C cycle
→ substitute FFs

What electrification can do for industry

Share of total estimated fuel consumption for energy, 2017, %



When electrified furnaces are convenient

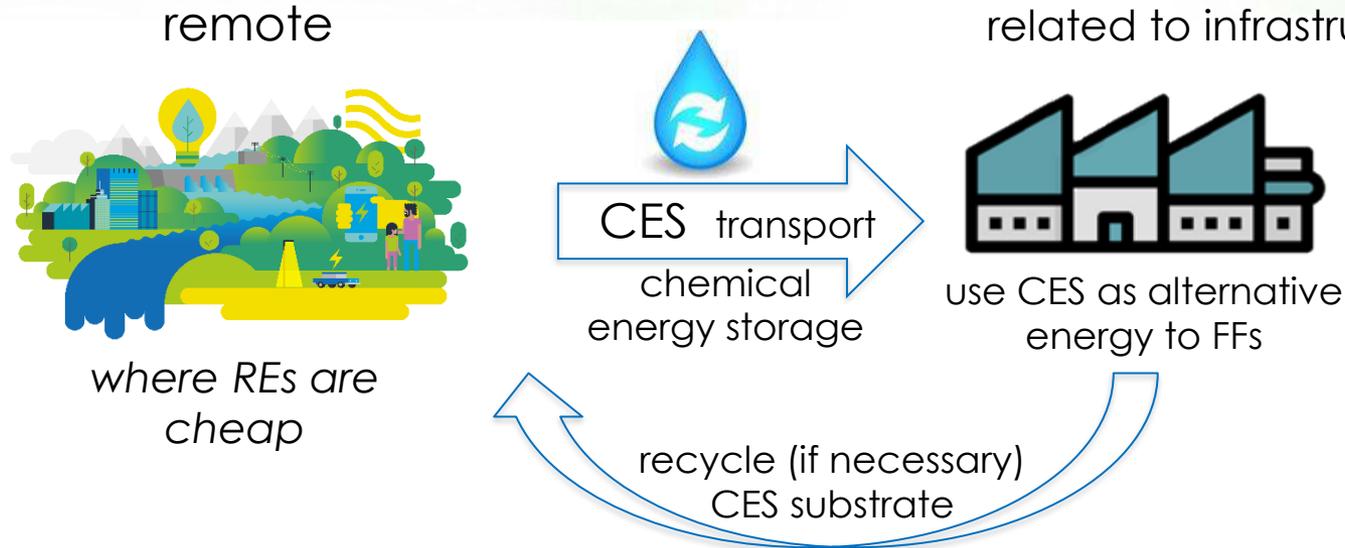


McKinsey 2020 & Company

Issues: cost but also availability (24h) of green electricity

Use CES produced remotely

overcome problem of fluctuation/availability (transport/storage) renewable electricity and reduces costs related to infrastructure changes



• CES vectors

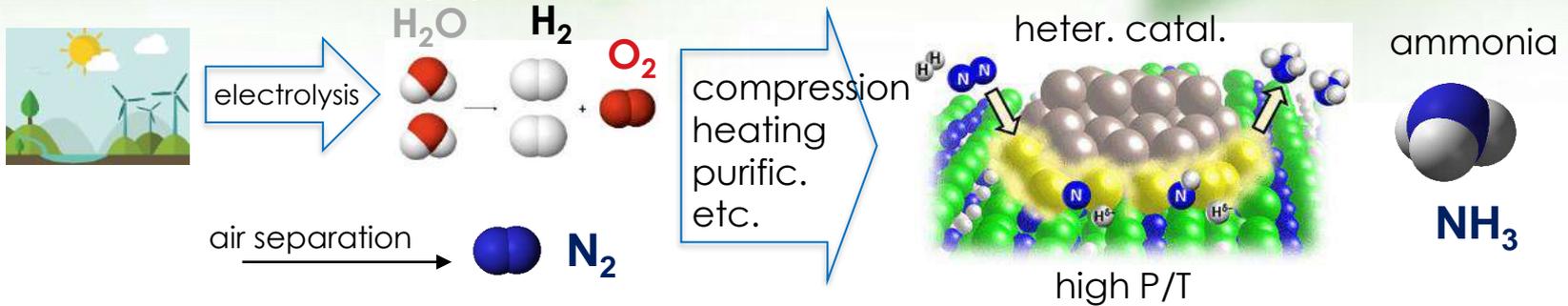
- green H₂ (transport → pipelines, but constrains)
- **hydrogen vectors** (NH₃, HCOOH, metal hydride, Liquid Organic Hydrogen Carriers - LOHC, etc.)
- **energy vectors** (CH₃OH, CH₄, hydrocarbons, etc.)

Green ammonia production

as an example

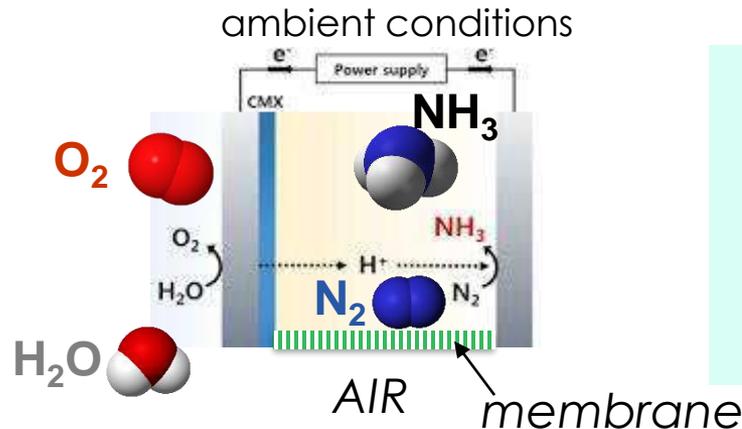
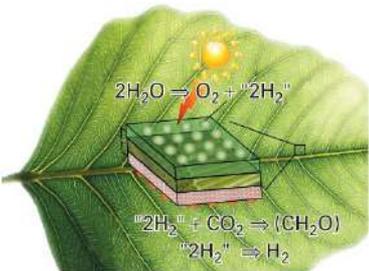
conventional NH₃ from FFs: average 2.6 ton CO₂ per ton_{NH₃}

current: a multi-step process



future: a direct, fully integrated, system (**artificial-leaf** type)

*better energy efficiency (avoid overpotentials), single step -
reduce costs, delocalized use, direct use solar energy*



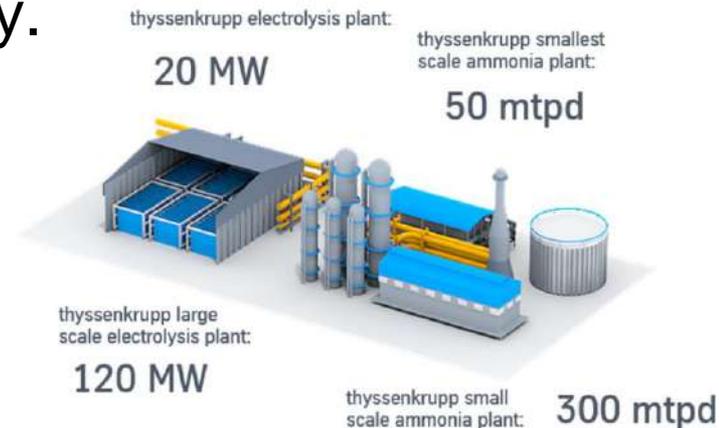
while starting activities with current generation, it is necessary to invest on the **next** generation technologies (the current **limiting** factor)



Green ammonia projects

some examples
>50% carbon footprint reduction
with respect conventional

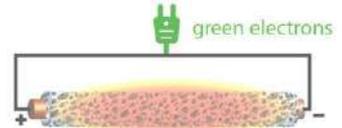
- Yara International, Statkraft and Aker Horizons partnership (Feb. 22, 2021): establish Europe's first large-scale green ammonia project in Porsgrunn, Norway.
- Thyssenkrupp/Uhde Chlorine Eng:
 - based on alkaline water electrolysis
- Haldor Topsoe and Air Products global alliance (May, 2020):
 - for large-scale green ammonia & other projects (NEOM facility in Saudi Arabia will use solar and wind power to create 3,500 tonnes of green ammonia per day by 2025).
- Australia
 - USD173 million Project for the world's largest green ammonia plant



Electrification Chemical Reactors

Reactor intensification, strong decarbonization

- Thermal energy transfer in electricity-based reactors (**Power-to-Heat**, applied mainly to boilers and heat pumps)
 - **Ohmic or Joule:** electric current passing through a resistive conductor produces heat \Rightarrow to maximize the effect a *specific design* of catalyst/reactor is necessary
 - **Induction heating:** rapidly alternating magnetic field either generates eddy currents in conducting materials resulting in the Joule heating of those materials or generates heat in ferro-/ferrimagnetic materials by the magnetic hysteresis losses
 - **Microwave/RF heating:** rapidly alternating electric field of the microwave generates heat by moving dipolar molecules or ions in liquids, or by getting absorbed in the so-called “dielectric lossy” solid non-magnetic materials
- Creating **directly** reactive species (change mechanism action) (**Power to Chem**) \Rightarrow Electro-, photo-, plasma-catal., sonochem.





Direct use RE in chemical production

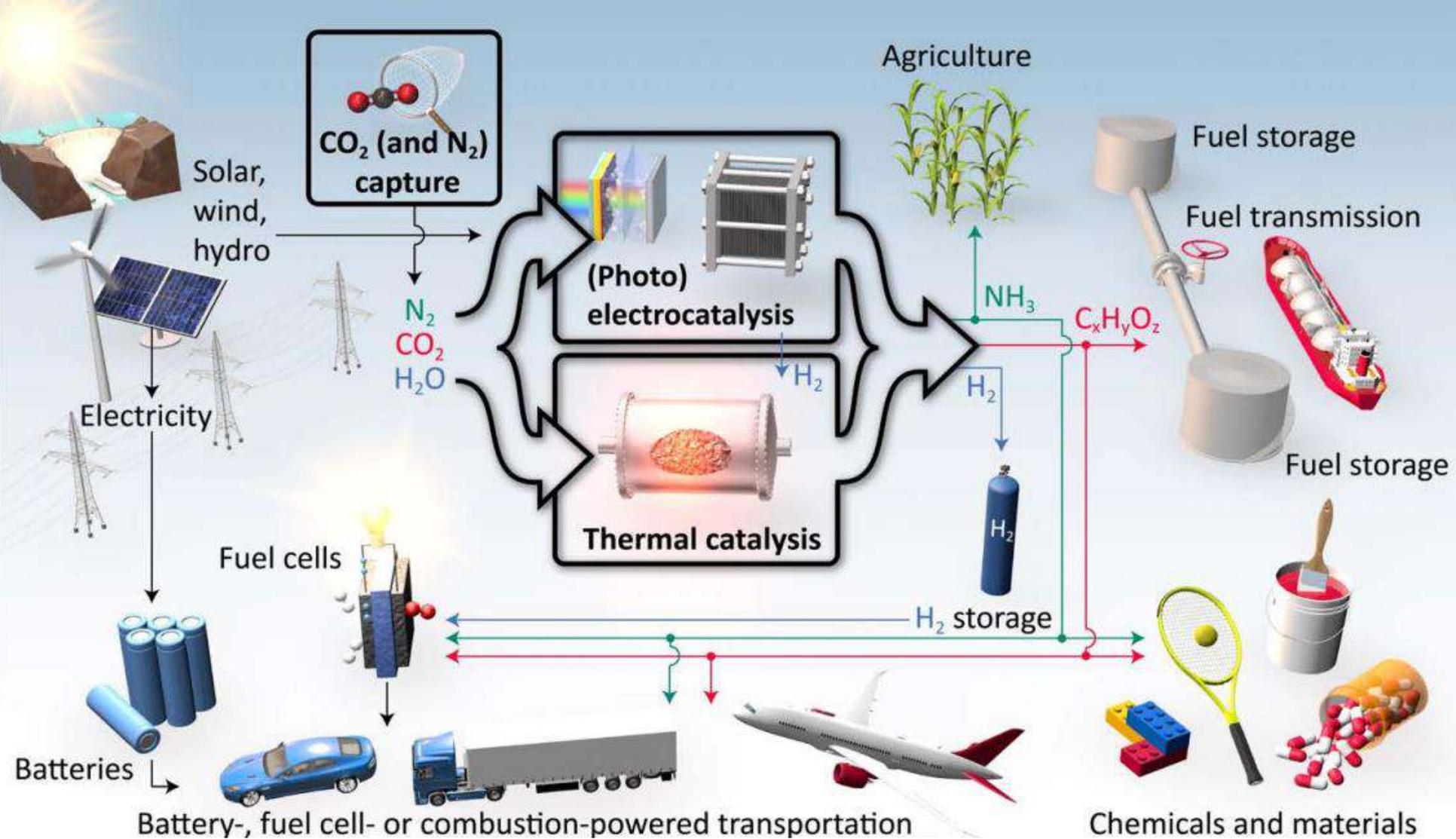
- Plasma (@catalysis)
- Microwave
- Photocatalysis
- Electrocatalysis (and photo-electro catalysis)

All these technologies are particularly suited for small-size (distributed) devices, i.e. systems which can be used up to a regional or district level, and for a circular economy

All above options are relevant to develop novel routes for a solar-driven chemistry, **electro-catalysis** is perhaps the **most advanced** presently for industrial implementations.

More advanced on crucial aspects such scalability to larger-size devices, which is actually the major limit of the other technologies.



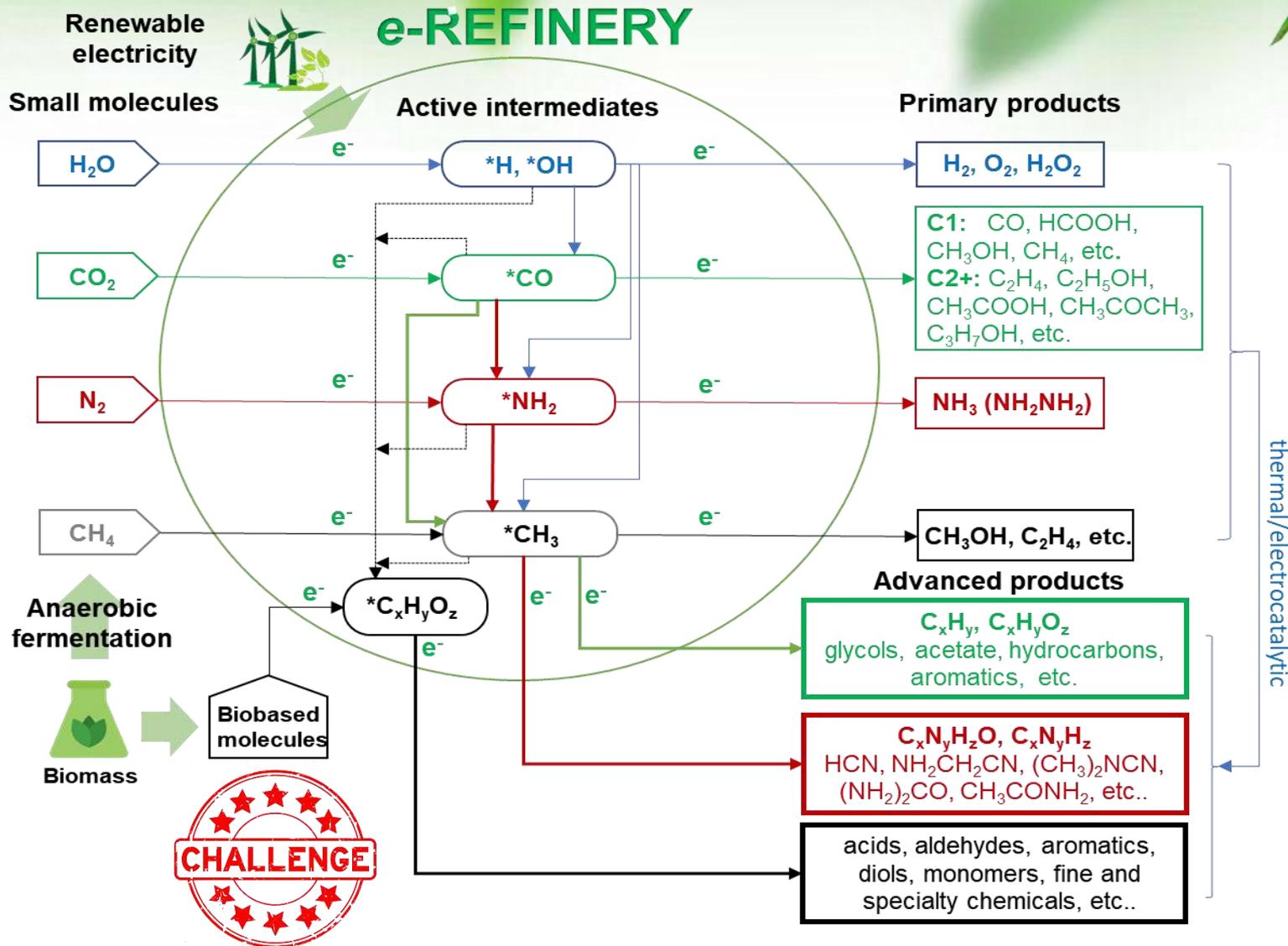


The vision on solar fuels: transforming small molecules (H_2O , CO_2 , N_2) through renewable energy to substitute the use of fossil fuels



e-Refinery

from small and biobased molecules to a framework of chemical production (e-chemistry) alternative to that based on fossil fuels (petrochemistry)





e-(bio)refinery

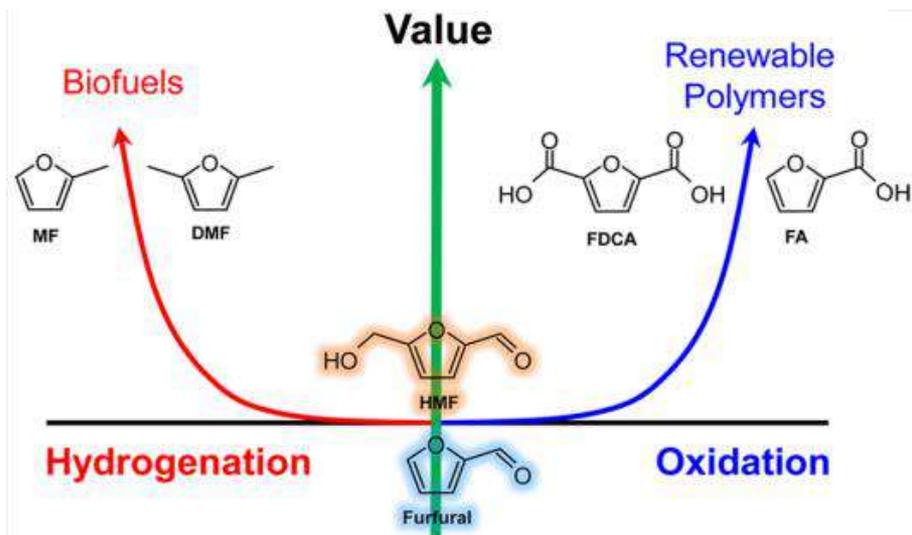
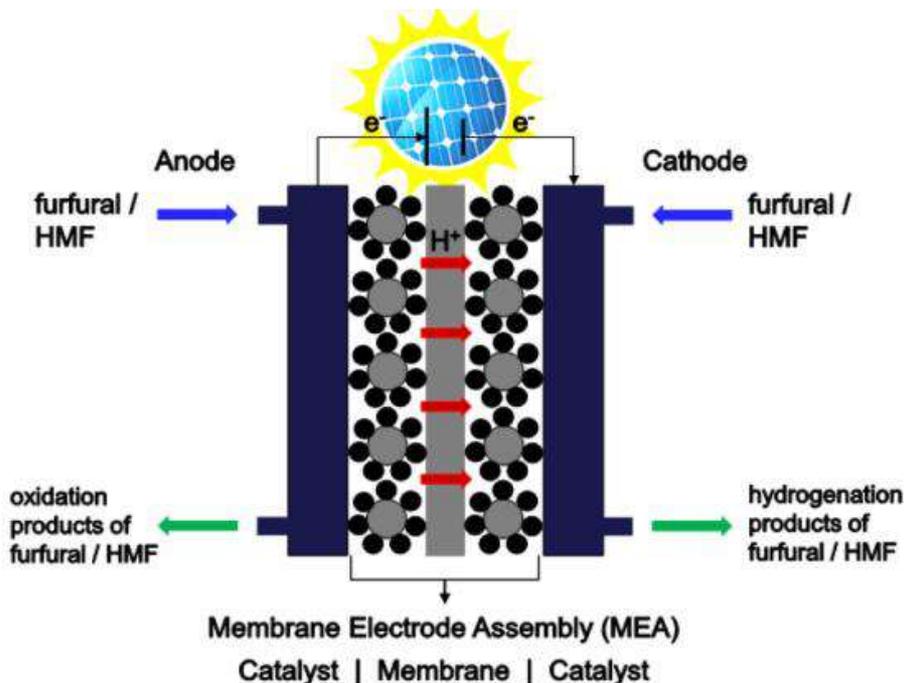


- Electrosynthesis is a promising method to convert large amounts of surplus electricity into chemicals.
 - **large amounts of electricity can be converted and stored as chemical energy.** Moreover, the capacity is not limited to its size and energy density, as is the case with batteries.
 - There have also been a few larger scale applications for organic electrosynthesis such as the Kolbe reaction (oxidative decarboxylation resulting in dimer formation) and the electrohydrodimerization of acrylonitrile
- **modular nature** of electrochemical reactors \Rightarrow fitting a variety of production scales.
- **Integrating** electrochemistry in a biorefinery \Rightarrow advantages such as heat integration as well as waste reduction.
 - various product streams are present in a biorefinery \rightarrow **new opportunities** for combining an oxidation with a reduction step in a single electrochemical reactor, thereby increasing the overall energy efficiency.

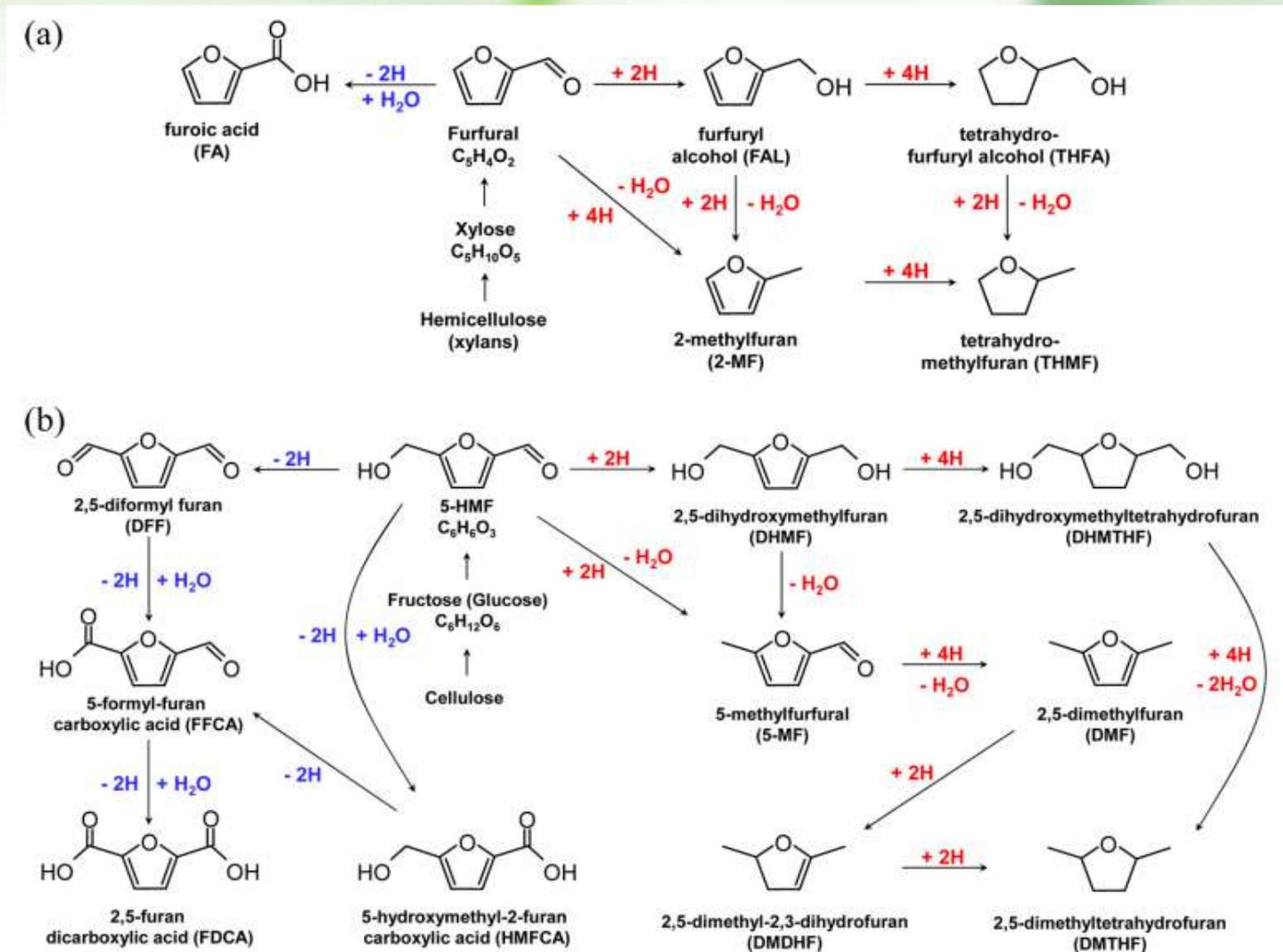
Tandem electrocatalytic processes

potential advantages of electrocatalytic furanic synthesis over other conventional methods:

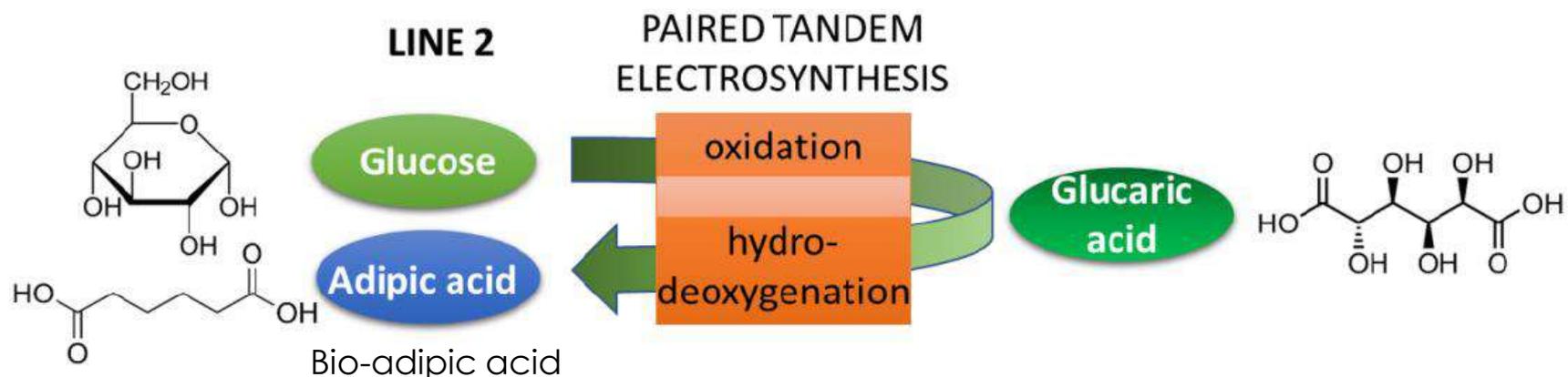
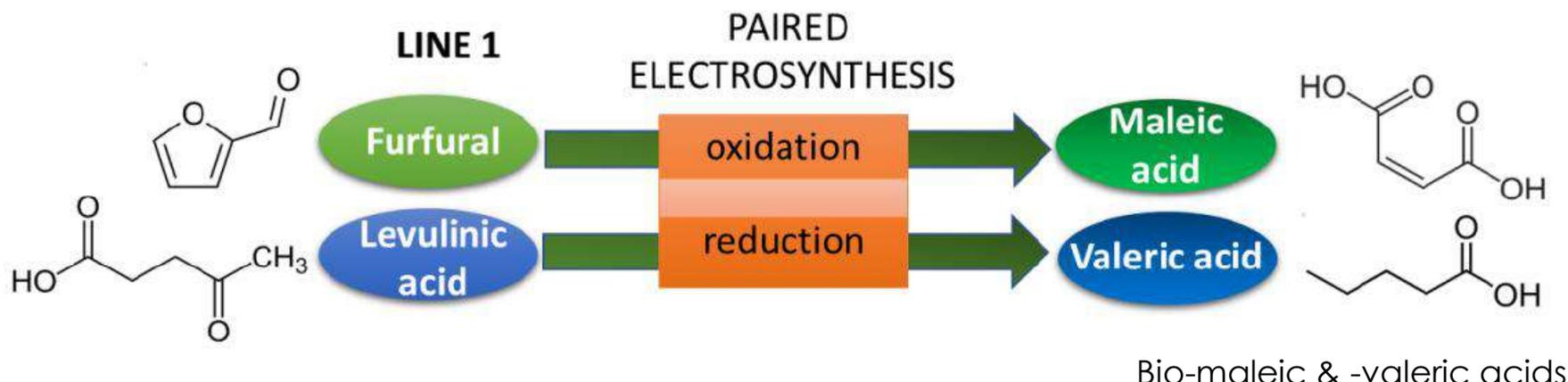
1. H_2O as the proton source instead of high-cost H_2 gas
2. low operating temperatures and pressures
3. precise control of the reaction rate and product selectivity by applying carefully chosen potential or current
4. easy study of the reactivity of the molecules of interest by simple and quick voltammetric techniques, i.e. cyclic voltammetry (CV)
5. simultaneous production of oxidation and hydrogenation products in a continuous membrane reactor (i.e., paired electrolysis).



Oxidation (Blue) and Hydrogenation (Red) Pathways of (a) Furfural and (b) HMF



A platform of options (PERFORM project)

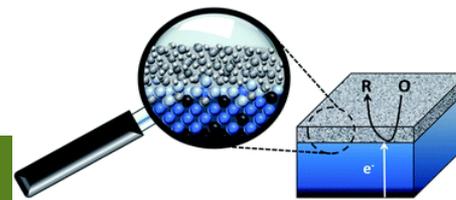




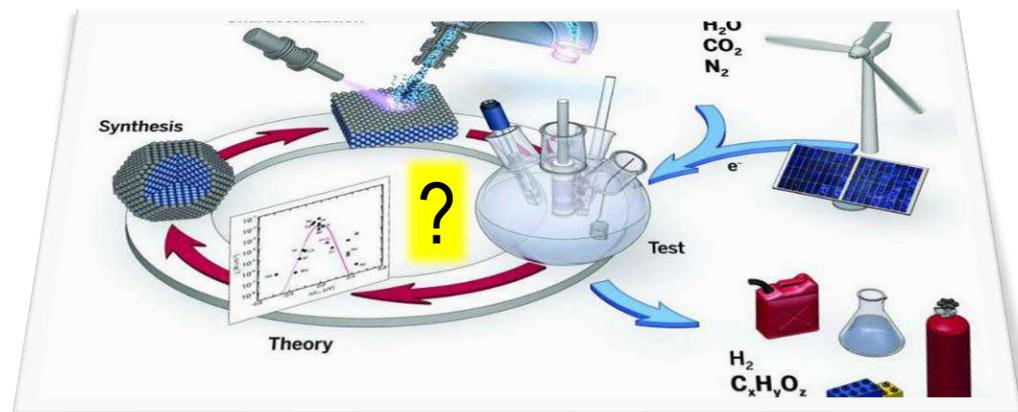
Electrocatalysis



- To explore **new complex reactions**
 - the approach often used is to utilize catalysts which are active in the thermal conditions for a similar reaction, but deposited over an electroconductive substrate → typically unsuccessful
 - a rational basis for the design of electrocatalysts, or at least guidelines as those available for several thermal catalytic reactions, are not (yet) available.
- *theory of electrochemistry* → (yet) not able to provide bases to control the selectivity.
 - computational approaches → not able to describe properly the complex phenomena and dynamics present at a charged interface
- need to develop a novel theoretical framework for electrocatalyst design strategies, particularly in complex reactions



Changing Catalysis Paradigms

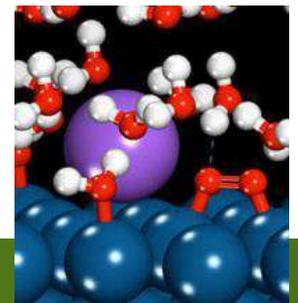


CATALYSIS IN THE PRESENCE OF CHARGED SPECIES (photo- or electro-induced) requires to change catalysis paradigms

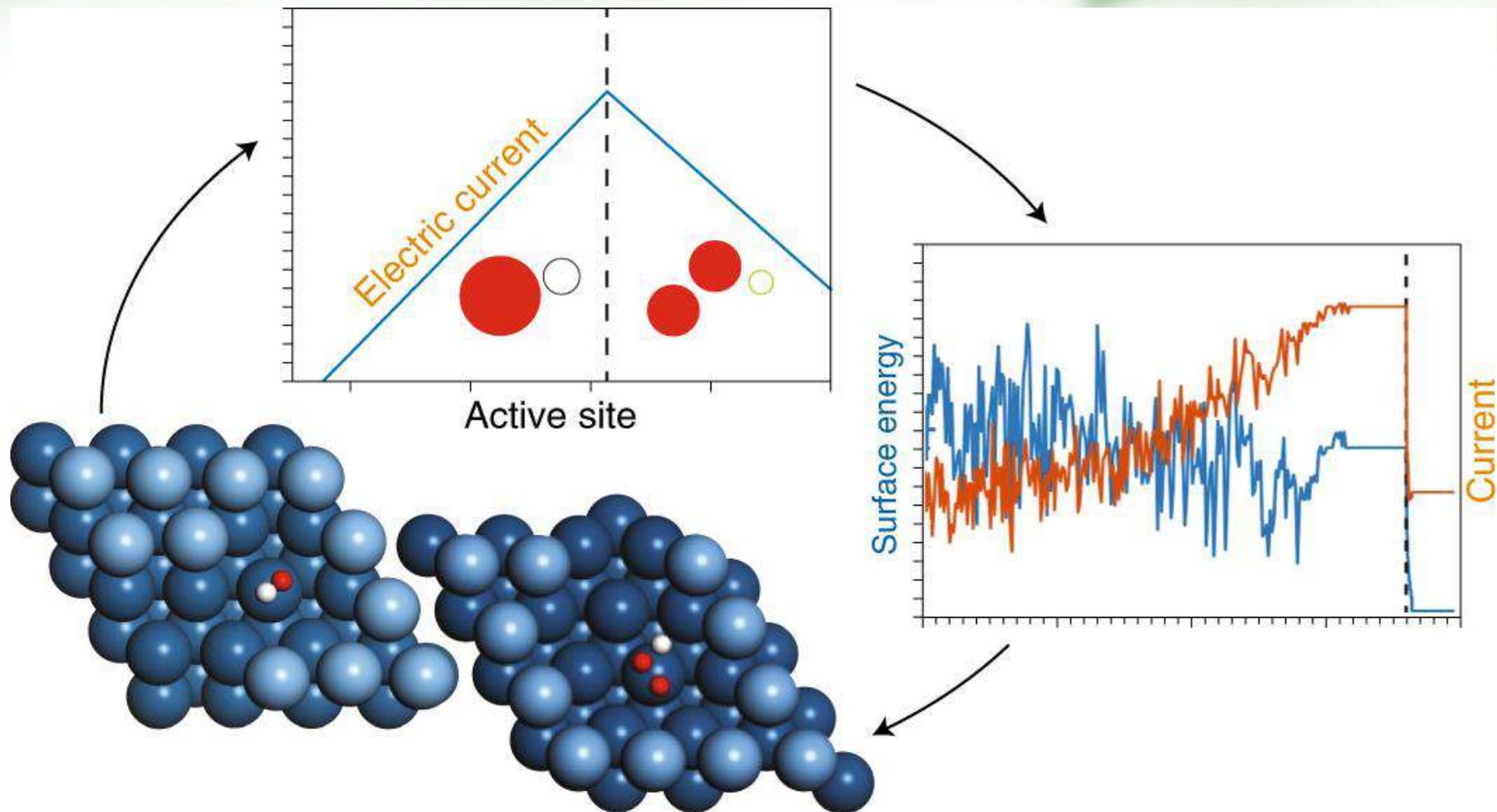
Electrocatalysis vs. electrochemistry

- An electrocatalyst is *not just* a catalyst participating in electrochemical reactions (the common definition), but rather a possibility to **go beyond electrochemistry through catalysis**.
 - *electrocatalysis lies at the heart of the chemical phenomena that take place at electrochemical interfaces. In the future it will be the key to driving technological innovations that are urgently needed to deliver reliable, affordable and environmentally friendly energy.*

N. M. Markovic, *Nature Materials*, 12 (2013) 101

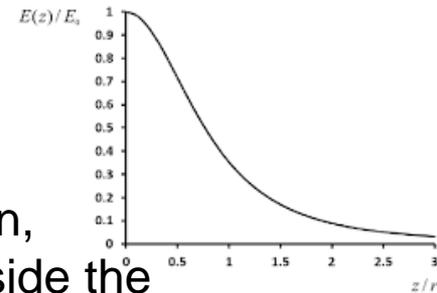


Induced surface reconstruction by application of an electrical current



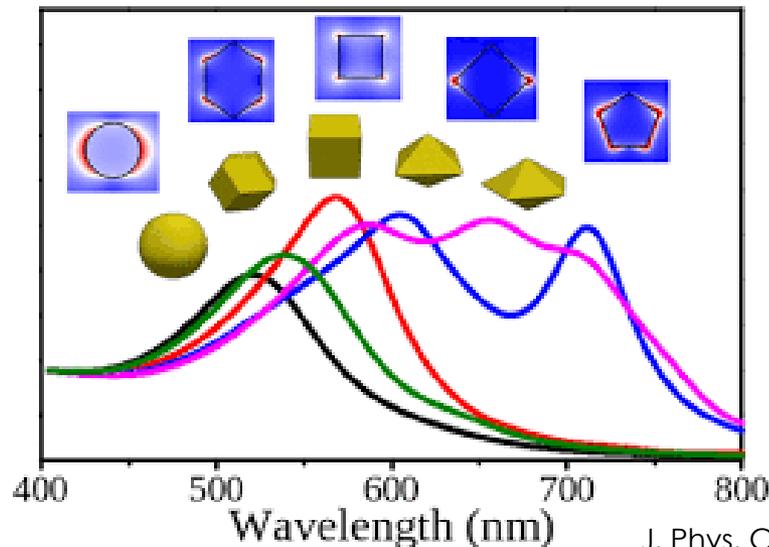
Nanoparticle Near-Surface Electric Field

- Surface reconstruction in some crystals involves splitting the surface atomic layer into two sublayers consisting of atoms with only positive or only negative effective electric charges.
- In a macroscopic crystal, the electric field induced by such a surface-dipole is practically totally concentrated between the sublayers. However, when the material has nanodimension, **an electric field of a significant magnitude** can be induced outside the sublayers as well and its features depends on the nanoshape.



Nanoscale Res Lett. 2016; 11: 48

*localizing
electric field at
and near the
surface.*

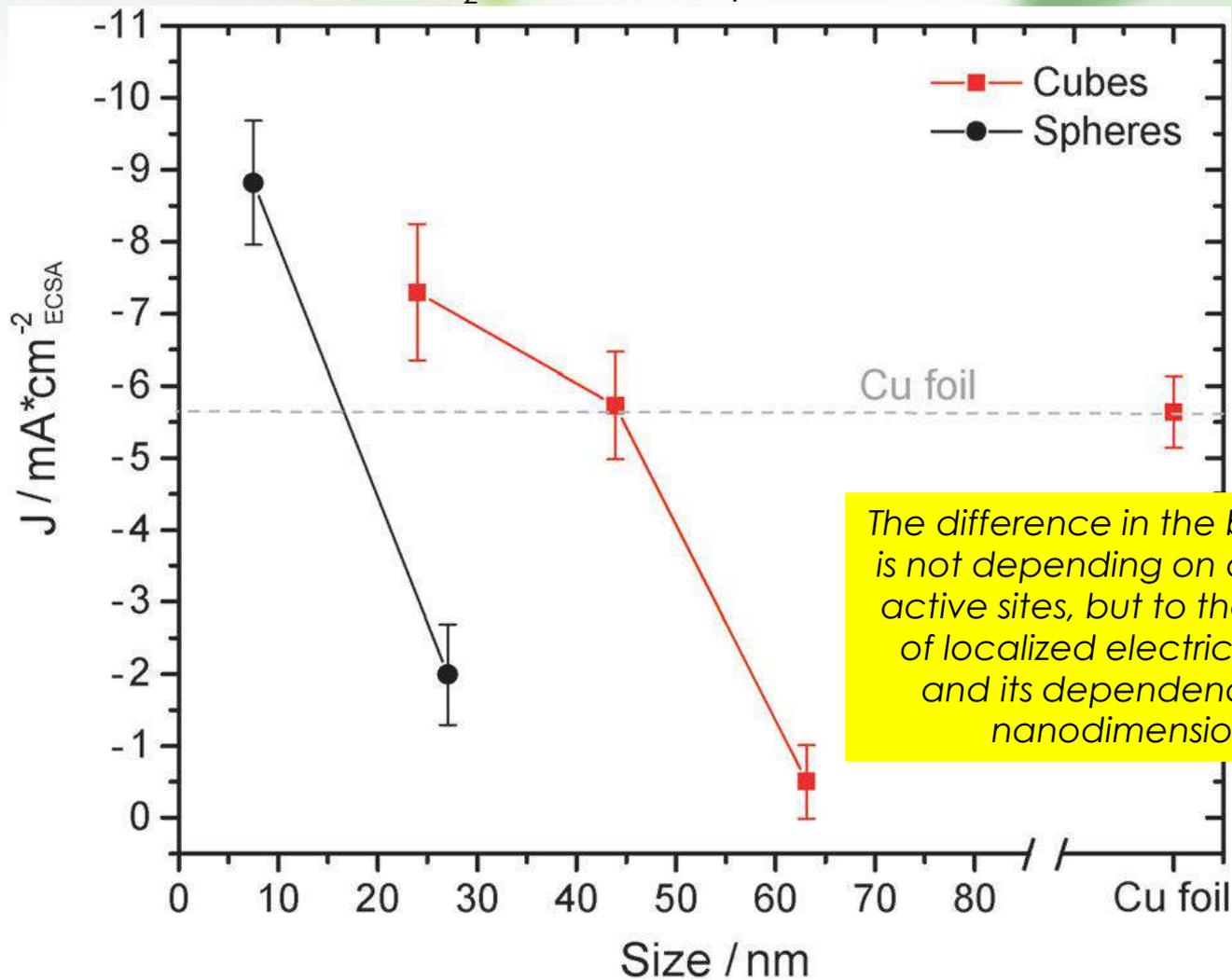


*The effect can be magnified
by application of a surface
potential (charge)*

J. Phys. Chem. C 2019, 123, 18, 11833

Cube-shaped copper nanocrystals on glassy carbon

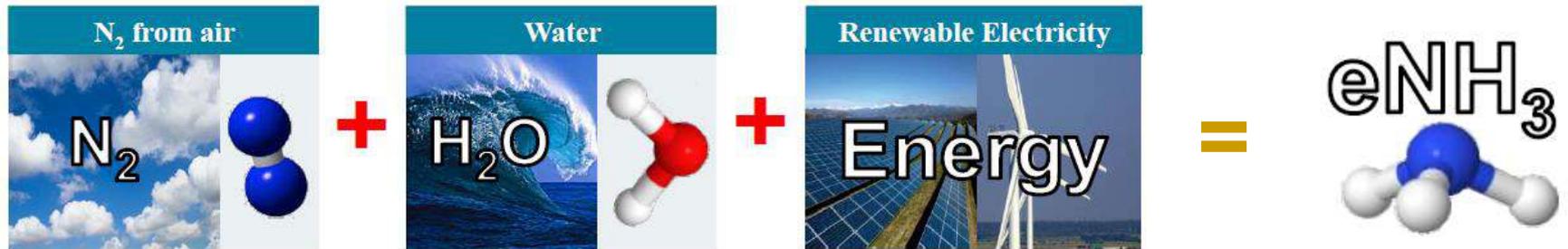
CO₂ electrocatalytic reduction



The difference in the behavior is not depending on different active sites, but to the effect of localized electrical field and its dependence on nanodimension

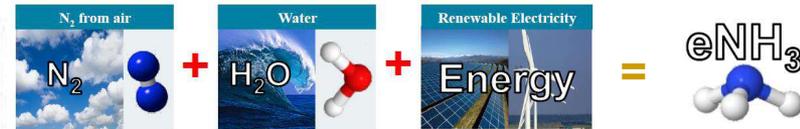
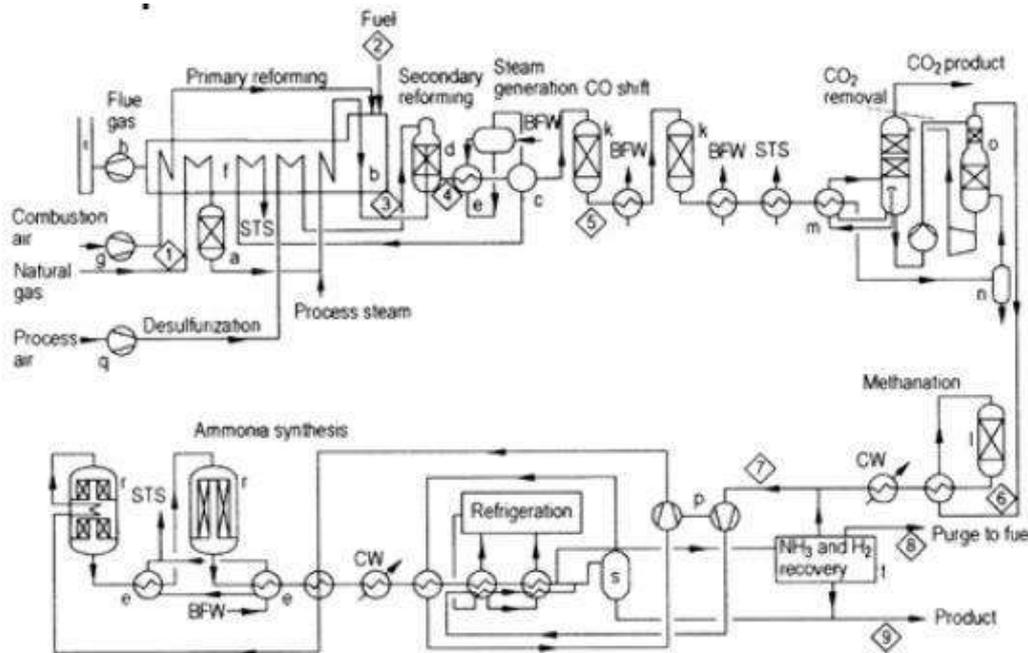
A case example

e-ammonia



Case study: direct NH₃ synthesis from N₂ (NRR)

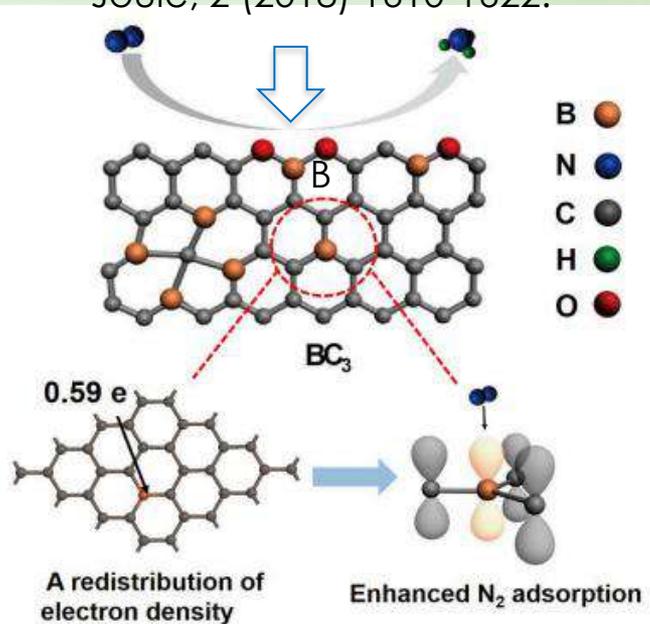
Production	Description
Actual industrial	Multistep and high pressure/temperature process, starting from natural gas. <i>Steps:</i> purification, steam reforming, air reforming, shift converter, CO ₂ removal, methanation, compression/cooling, NH ₃ synthesis, cooling/decompression. Efficient only in large-scale (transport, impact).
Direct electro-catalytic	One-single device (suited for <u>distributed</u> production). Start from N ₂ , H ₂ O and renewable energy, nearly room temperature and ambient pressure.



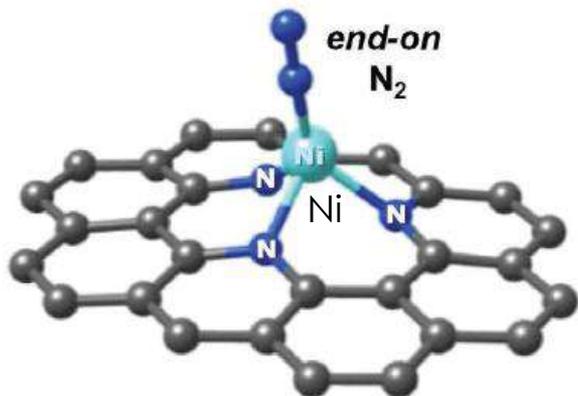
93% the carbon footprint (e.g. CO₂ emissions) from 1.83 t_{CO2}/t_{NH3} in the actual ammonia production scheme to 0.12 t_{CO2eq}/t_{NH3} in the direct synthesis

NRR mechanisms

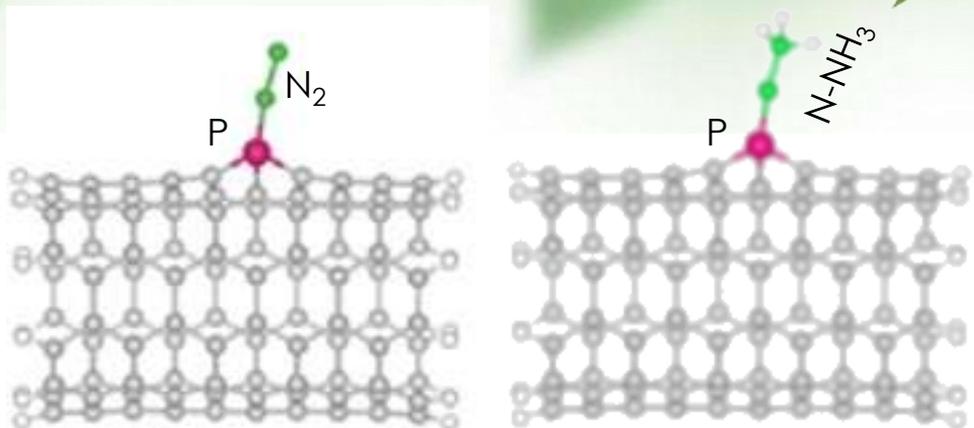
Joule, 2 (2018) 1610-1622.



Small Methods 2020, 4, 1900821

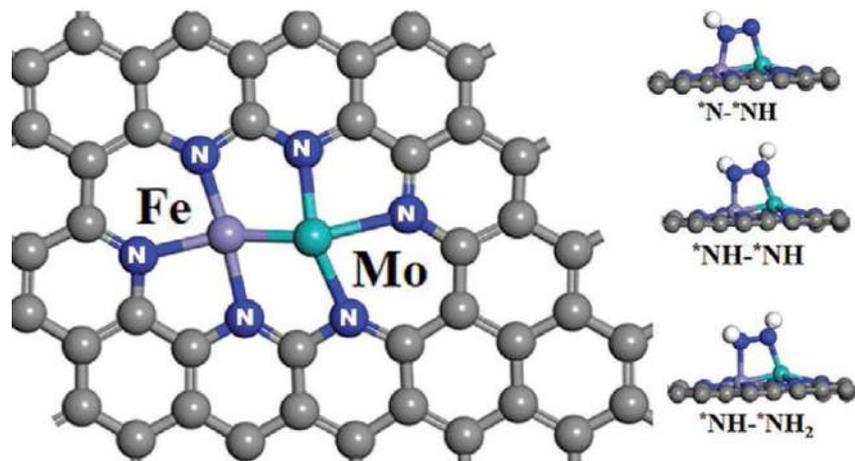


On homogeneous set of nanocarbon-based electrodes

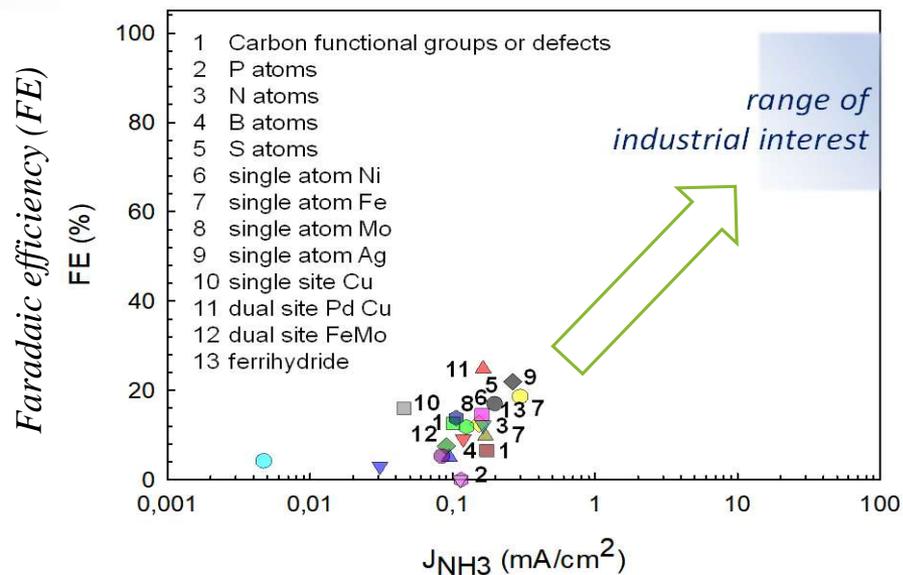


Nano Res., 13 (2020) 1376-1382.

ACS Cent. Sci., 6 (2020) 1762-1771.



Electrocatalysts for NRR



Specific current density of ammonia formation (J_{NH_3})

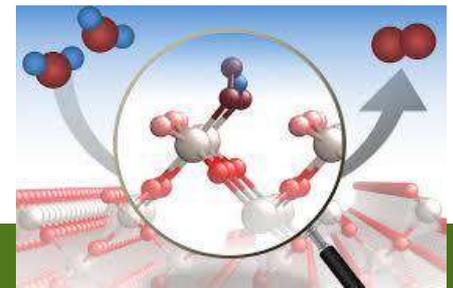
Electrocatalyst	Proposed NRR mechanism
Defective C-doped B-nitride nanosheets	Defect sites
N-doped porous carbons	Pyridinic and pyrrolic N
O-doped graphene	Presence of C=O and O-C=O groups
P-doped CNT	P atoms (substituting C) able to coordinate N_2
B-doped graphene	Electron-deficient environment at B-sites
B-doped C_2N	B substituting an edge N atom in C_2N
B2@ C_2N	Double boron atom species in defect cavities
Fe_2O_3/CNT	γ - $Fe_2O_3/FeOOH$ stabilized at CNT defect sites
FePc grafted on O-MWCNT	Isolated Fe atom
Pyrolysis of a ZIF-8 precursors	Atomically dispersed Ni sites in carbon matrix
FeMo/ γ - C_3N_4	Heteronuclear dual-atom catalytic sites
NiCo ₂ O ₄ on hollow N-carbon polyhedra	Oxygen vacancies in NiCo ₂ O ₄
Cu/activated carbon	Copper sites

based typically on DFT methods

Limits in modelling electrocatalysis

- In **electrocatalysis**,
 - **i)** a potential is applied, which can induce a **dynamic reconstruction of the catalyst**, **ii) interfaces and heterojunctions** are necessary to stabilize reactive charged species (electron, holes) regarding side reactions, **iii)** an uniform charge distributed over the catalyst surface is not present, but likely a **non-uniform** situation depending on the nanostructure, which can largely influence the effective (local) rate of charge transfer to the incoming molecules (and thus reaction rate), **iv)** the **asymmetric charge distribution** creates likely a reorganization of the adsorbed layer on the surface and impact also the double layer (when present) at the interface,
 - which in turn **influences the reactivity of the molecules** itself, for example water molecules regarding their splitting

Although in catalysis a localized approach is used (active site), the **thermal** effect (not accounted) averages the situation and avoids a great dependence from local effects, which instead are maximized in reactive catalysis (operating in mild conditions)



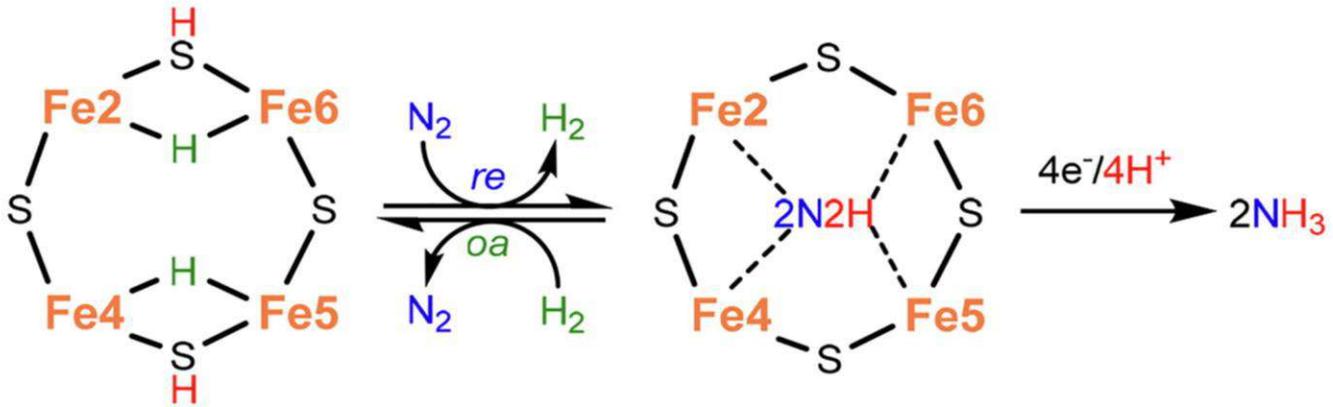


How to proceed? Rethink electrocatalysis

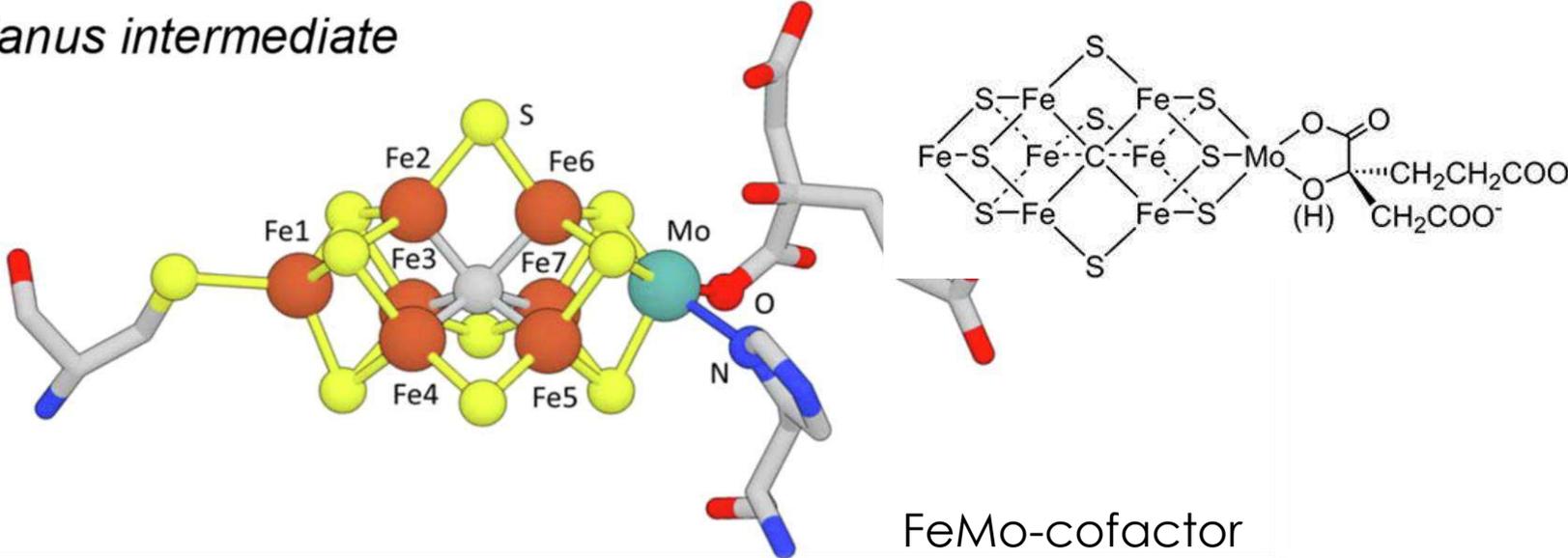
one of the possibilities

- biomimetic catalysis is popular, BUT not often properly addressed → case of NRR (*Nitrogenase*)
 - *Nitrogenase* is a unique system able to convert N_2 to NH_3 . Three classes of Nitrogenase, differ for the heteroatom present (Mo, V or Fe) → Mo-dependent nitrogenase is the most important
 - It contains two metallo-components, dinitrogenase [molybdenum–iron (MoFe) protein] and dinitrogenase reductase (Fe protein), which associate and dissociate in a catalytic cycle also requiring a reducing source and MgATP.
 - The MoFe protein contains two metal clusters: the iron–molybdenum cofactor (FeMo-co), which provides the active site for substrate binding and reduction, and P-cluster, involved in electron transfer from the Fe protein to FeMo-co.
 - **The FeMo-cofactor is thus the key element for the mechanism of N_2 fixation.**

Nitrogenase mechanism



Janus intermediate



FeMo-cofactor

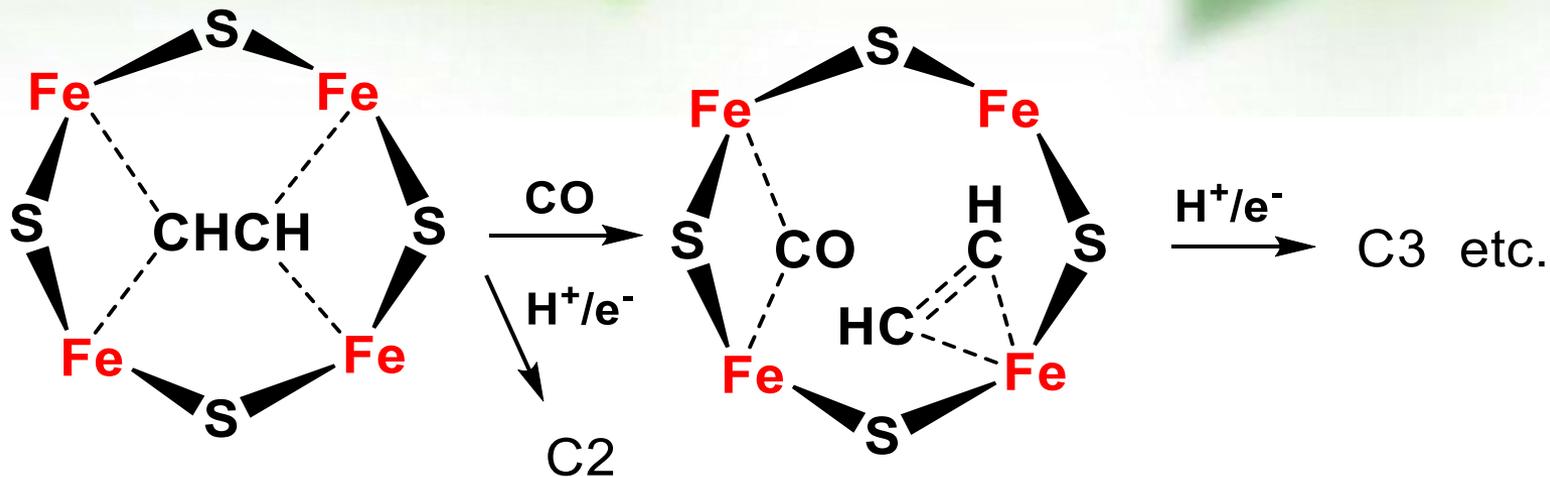


Key features of *Nitrogenase* mechanism



- A specific binding site for N_2 able to first accept four electrons/protons to form two [Fe–H–Fe] bridging **hydrides**,
- Coordination of N_2 on **two iron atoms** with simultaneous reductive elimination of H_2 ,
- **Multi**-electron/proton transfer to a coordinated undissociated N_2 molecule to form a N_2H_2 molecule **stabilized** by interaction with two iron atoms,
- Further **multi** H^+/e^- transfer to form an *end-on* N_2H_4 coordinated molecule,
- Further steps of H^+/e^- transfer with stepwise release of ammonia.

Nitrogenase in CO₂ reduction

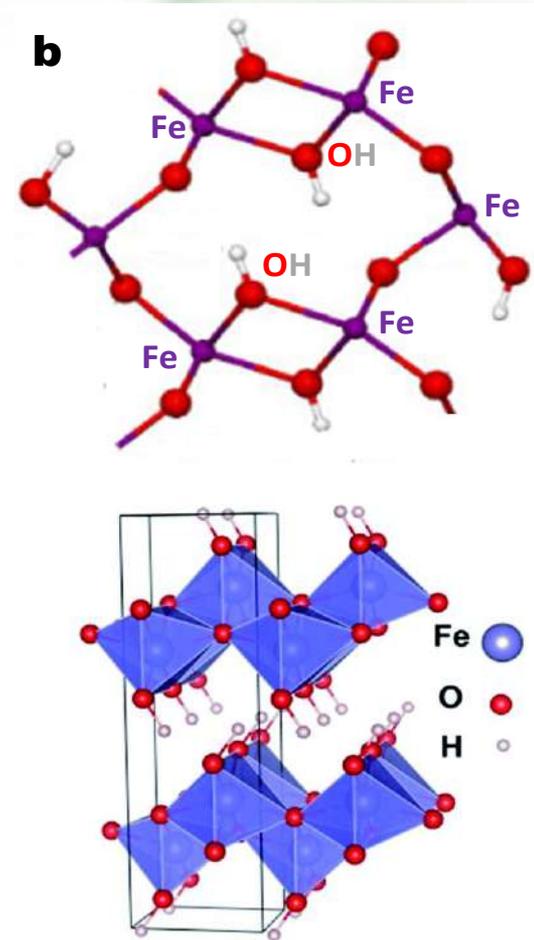
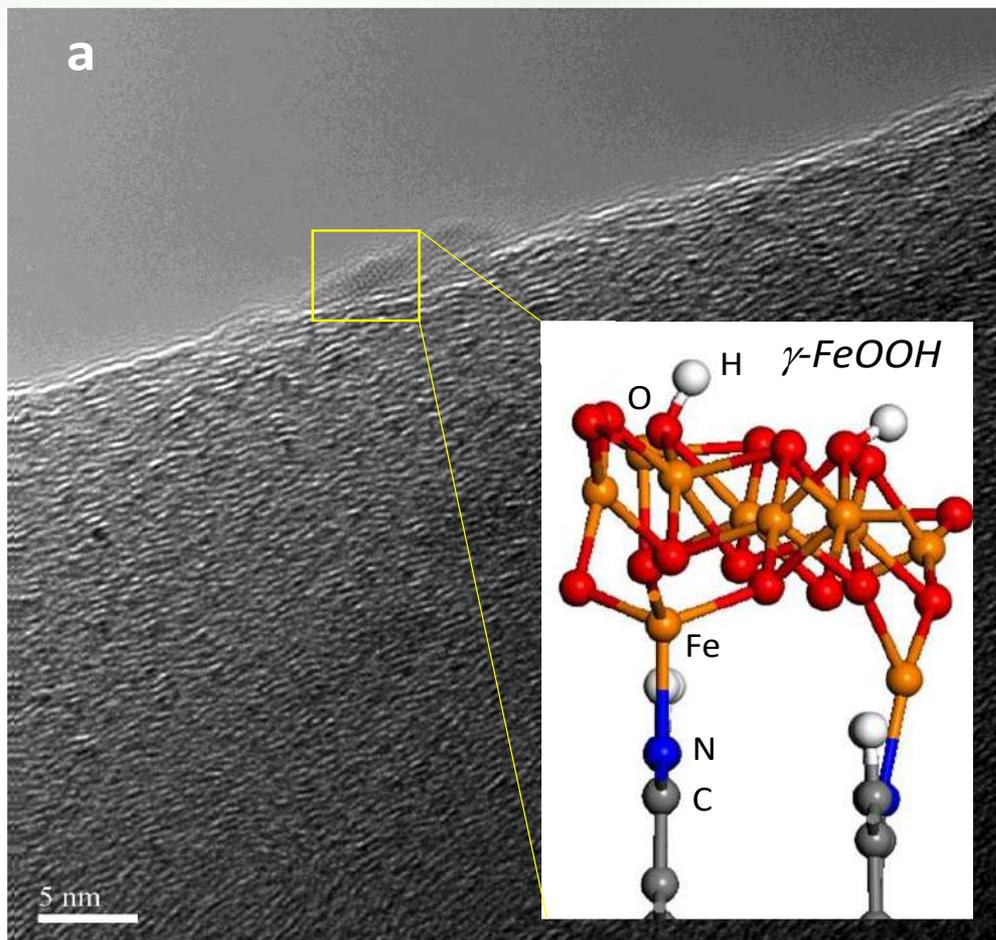


- Nitrogenase can also catalyse the reductive carbon–carbon coupling of CO_x into hydrocarbon products
 - *Janus intermediate* reacts with two CO molecules (produced on the Fe protein) to form an ethyne like intermediate → hydrogenated to ethylene or could react further to form a ferracycle leaving other Fe free to form other Fe-hydride species and further coordinate CO → C₂ → C₃ product

an effective biomimetic electrocatalyst should reproduce all features (multi H⁺/e⁻, hydride, multi-atom binding intermediate, forming C₂+ from CO₂)

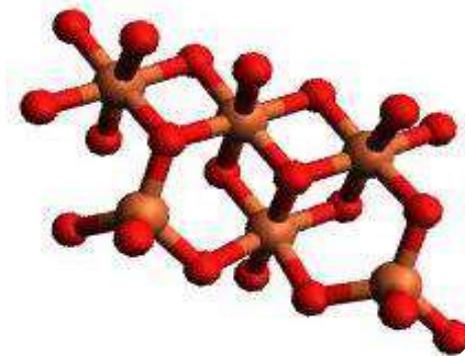
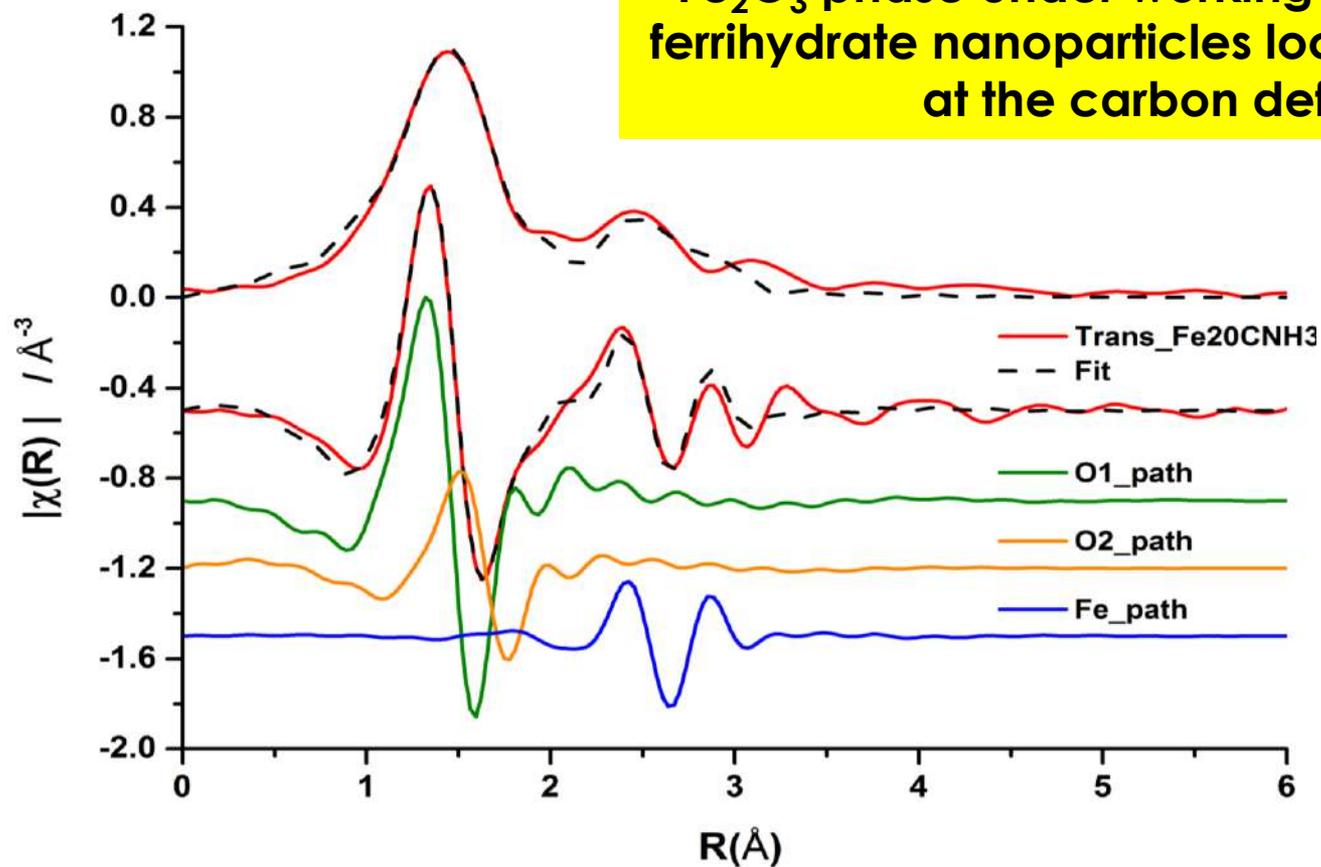


Ferrihydrite (on CNTs) for NRR and CO₂ to C₂+ conversion



Nature of iron species (Operando EXAFS)

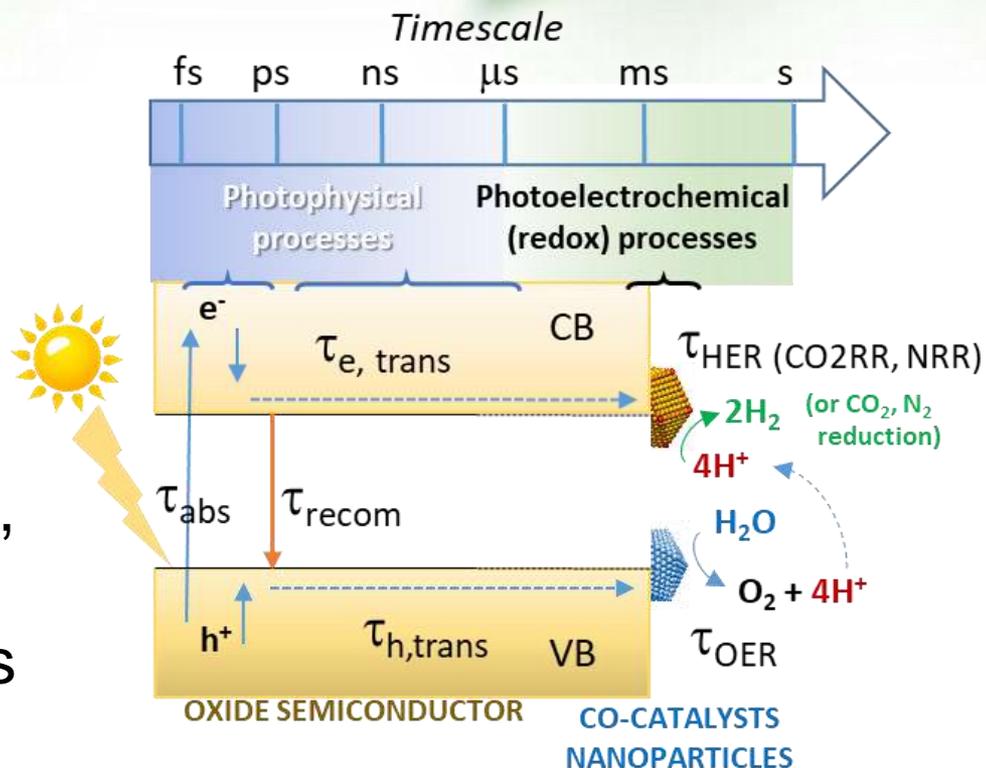
A ferrihydrate (FeOOH) is present rather than a Fe_2O_3 phase under working conditions, with the ferrihydrate nanoparticles located predominantly at the carbon defect sites.



Are we addressing the right problems?

photocatalysis

- photocatalysis → light harvesting and charge separation (fast processes) → slow step is the redox
- *co-catalysts*: phase boundaries/heterojunctions, etc. → trap charges, rather than accelerate the process



Focus should be on the **true catalytic effect**, rather than trapping (in cocatalyst nanoparticles)

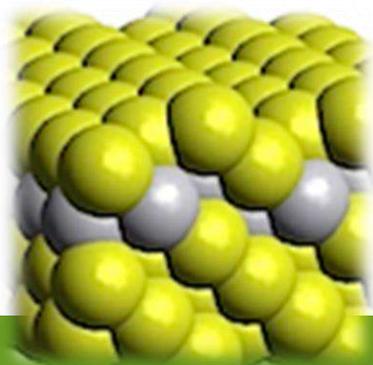


Conclusions



2/2

- Catalysis will remain a key technology in the future panorama, but its capability to **accelerate** the transition, and **not** being one of the limiting (technological) factors delaying the transition depends on its **capability**, as science and technology, to **rethink** its background fundamentals to address more properly the difference between conventional (thermal) catalysis and reactive catalysts, comprising the latter photo- and electro-catalysis and plasma-catalysis as main areas.



**Take
home message*

Conclusions

- The on-going transition in energy and chemistry will lead to a **system change**, associated with the progressive substitution of fossil fuels.
 - This *system change* cannot occur with *just* the implementation of current methodologies and way of thinking; the development of **radical new approaches** is necessary (incl. in electrocatalysis)
 - Electrocatalytic technologies play a **key role** in enabling this transition and providing the necessary technologies, but should address the **complexity** required to address the challenge
 - An **acceleration** in the development of electrocatalysis requires a strong community which operate in synergy; build and strength this community is the aim of SUNERGY initiative.
 - Need of **new paradigms** in electrocatalysis.

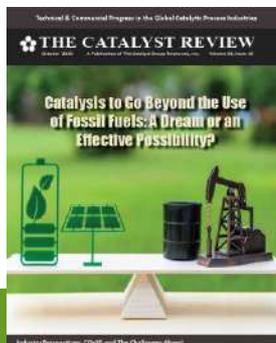
CHANGE



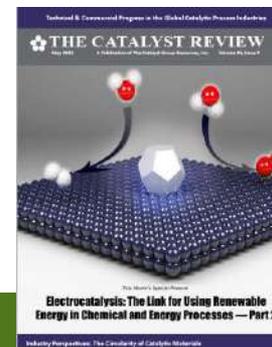
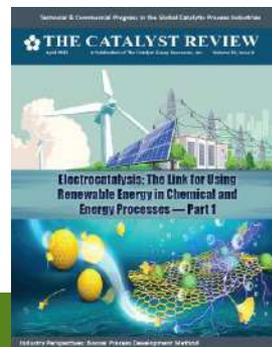
Further discussions (reviews)

- Redesign chemical processes to substitute the use of fossil fuels: A viewpoint of the implications on catalysis, G Centi, S Perathoner, *Catal. Today* 2021, DOI: 10.1016/j.cattod.2021.03.007
- Reuse of CO₂ in energy intensive process industries, S Perathoner, KM Van Geem, GB Marin, G Centi, *Chem. Comm.* 2021, DOI: 10.1039/D1CC03154F
- Nanocarbon for Energy Material Applications: N₂ Reduction Reaction, G Centi, S Perathoner, *Small* 2021, 2007055. DOI: 10.1002/sml.202007055
- Chemistry and energy beyond fossil fuels. A perspective view on the role of syngas from waste sources G Centi, S Perathoner, *Catal. Today* 2020, 342, 4-12
- Chemical engineering role in the use of renewable energy and alternative carbon sources in chemical production, G Centi, G Iaquaniello, S Perathoner, *BMC Chem. Eng.* 2019, 1 (1), 1-16
- Catalysis for solar-driven chemistry: the role of electrocatalysis, S Perathoner, G Centi, *Cataly. Today* 2019, 330, 157-170
- Needs and gaps for catalysis in addressing transitions in chemistry and energy from a sustainability perspective, G Centi, J Čejka, *ChemSusChem* 2019, 12 (3), 621-632
- 2D oxide nanomaterials to address the energy transition and catalysis, CJ Heard, J Čejka, M Opanasenko, P Nachtigall, G Centi, S Perathoner, *Adv. Materials* 2019, 31 (3), 1801712
- New catalytic materials for energy and chemistry in transition, J Čejka, P Nachtigall, G Centi, *Chem. Soc. Rev.* 2018, 47, 8066 - 8071

The Catalyst Rev., Oct. 2020



The Catalyst Rev, April & May 2021





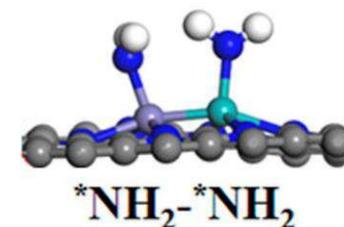
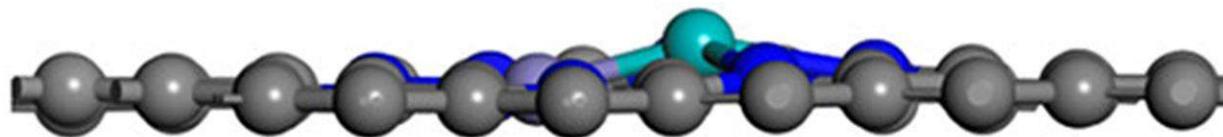
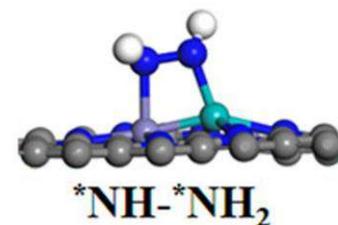
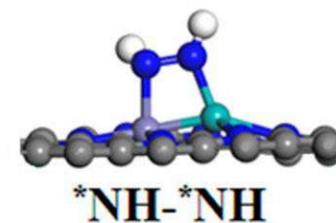
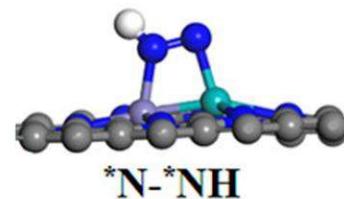
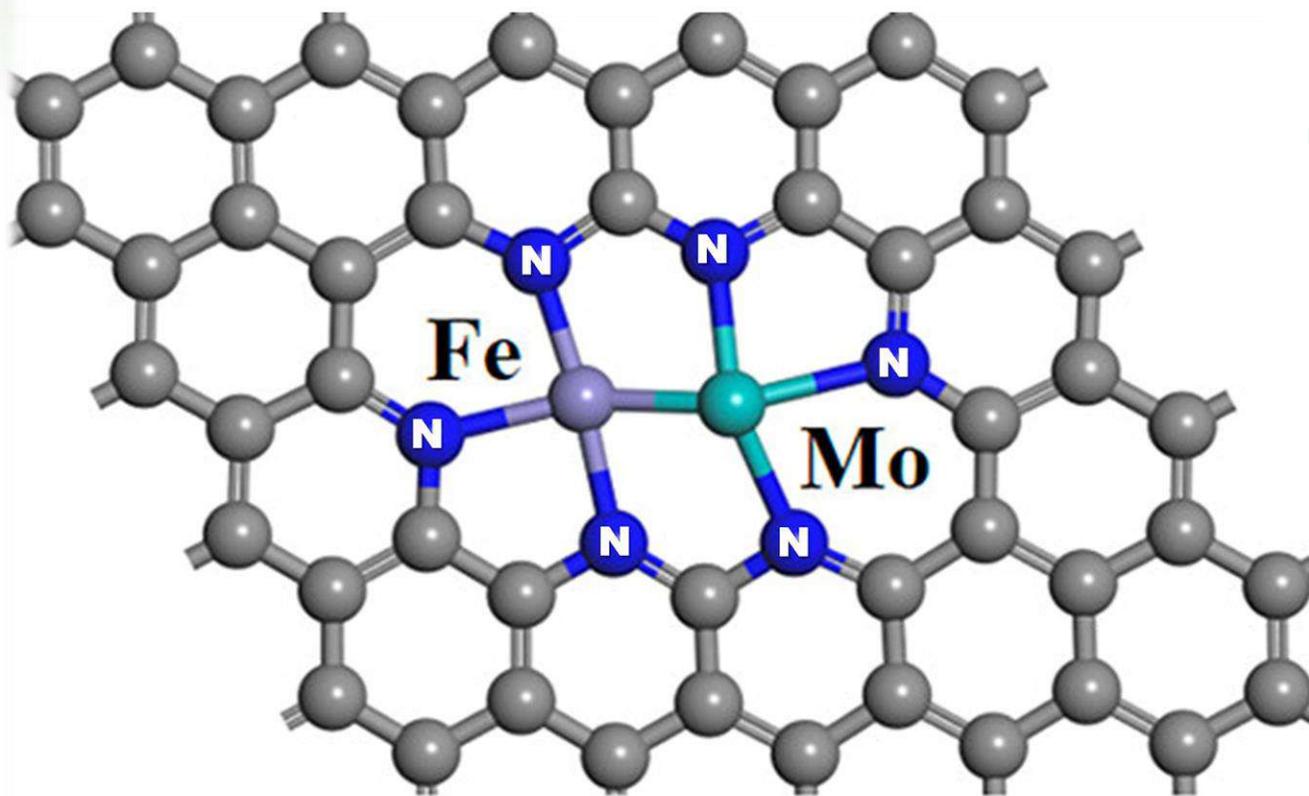
BACKUP SLIDES

Conclusions

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 - This transition could be **faster** than expected and only companies having prepared **business changes** associated to this transition in time, will effectively survive.
 - However, it is advisable to take a holistic view of the system transition (a system approach, rather than focused on specific processes), which impact aspects such as the ways to **assess feasibility** (from an engineering perspective), but also **technological** aspects such as how catalysts fundamentals should be rethought to face properly with this challenge.

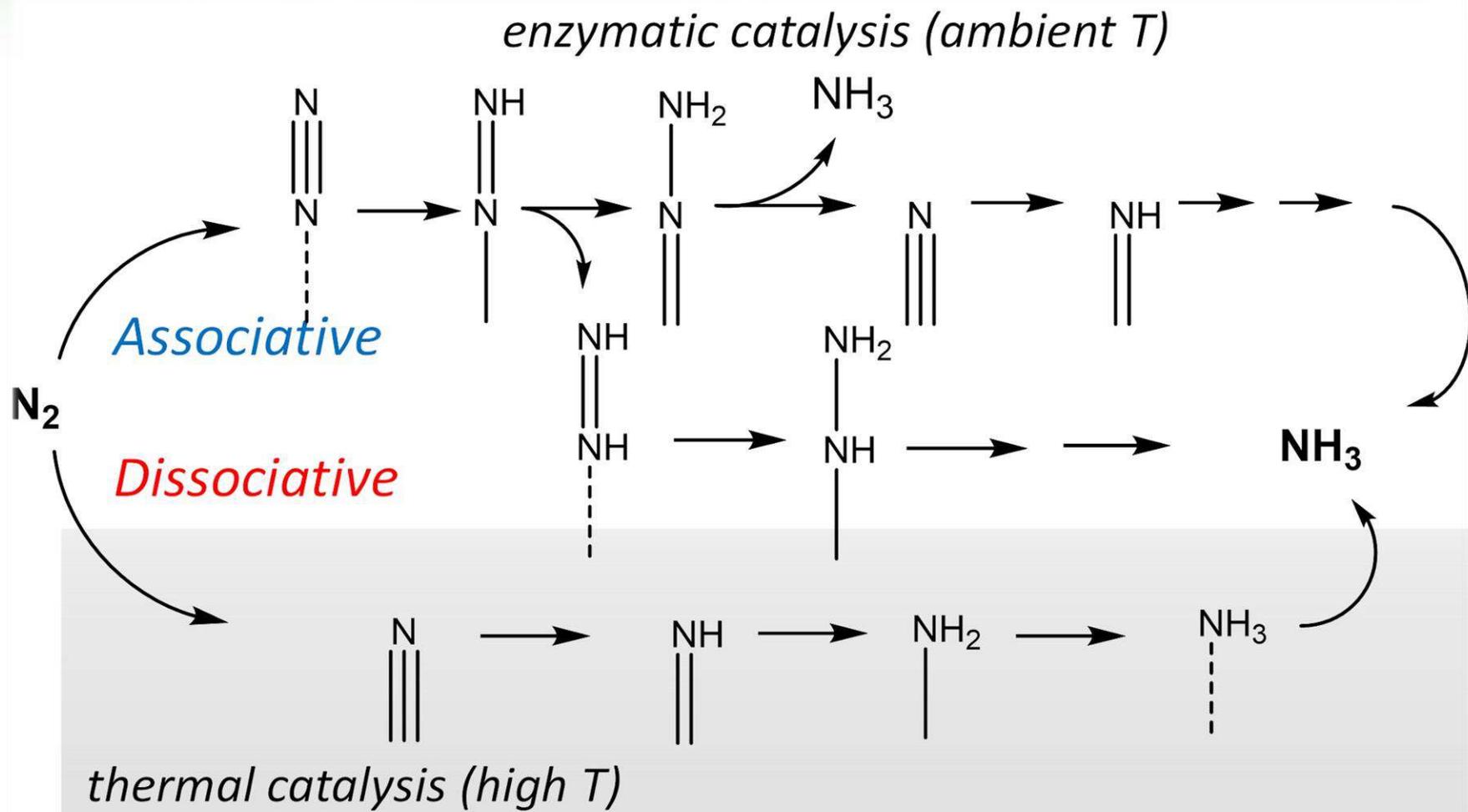


An example of proposed NRR mechanisms





Difference enzymatic & (thermal) catalytic mechanisms



Challenges and opportunities

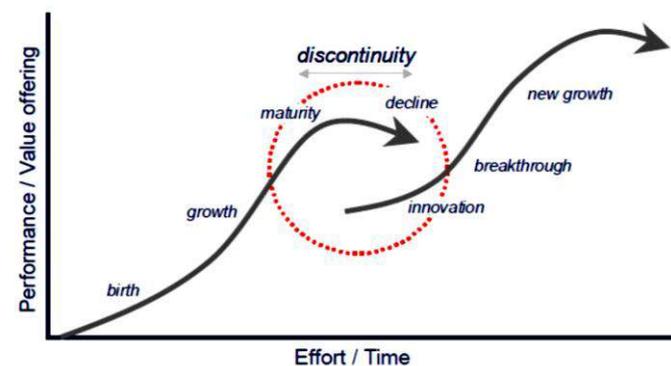
for electrocatalysis

- Identify **disruptive** processes for the new solar-driven chemistry scenario
- Creating an **innovative** landscape
- Pushing development of **ground-breaking** catalysts and catalysis **concepts**
- Process **Intensification** by electrocatalysis
- Opening of **new value chains**
- **New reaction paths** for the electrocatalytic conversion



Considerations on NRR approaches

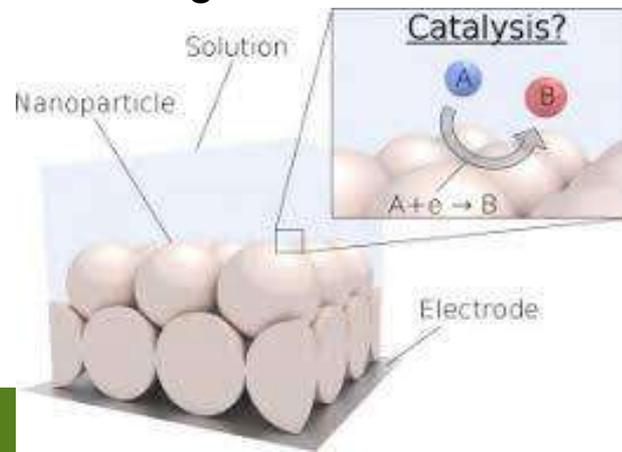
- A **different** approach would be likely necessary to make a step-forward.
 - current approaches, which are mostly the extension to electrocatalysis of the approaches used in conventional (thermal) catalysis, fail in catching the essence of the issues to design breakthrough (electro)catalysts for NRR
- Capability of the **current** approaches for mechanistic studies, particularly by theoretical methods, to correctly describe the true mechanism of reaction.
 - there are more complex phenomena dominating the behaviour of reactive catalysts still **not** correctly depicted in the current methods



Limits in modelling electrocatalysis

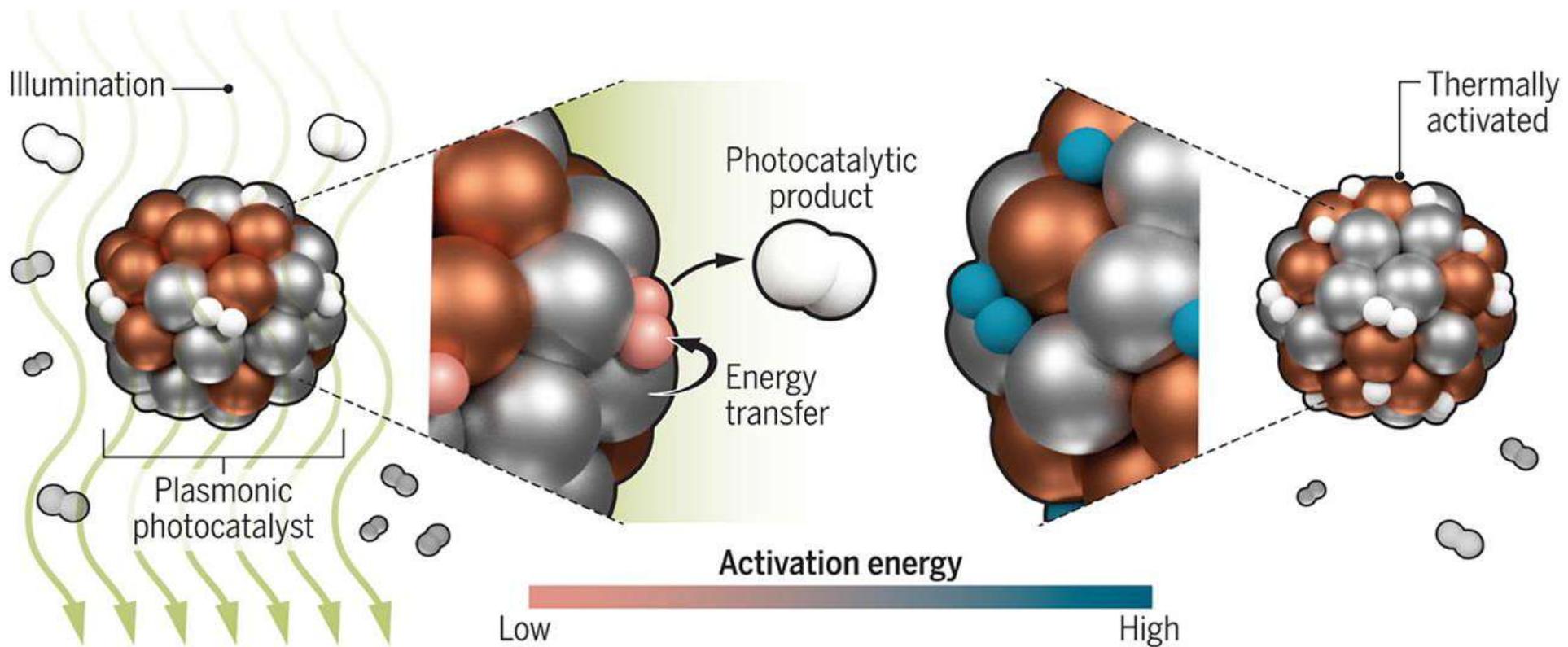
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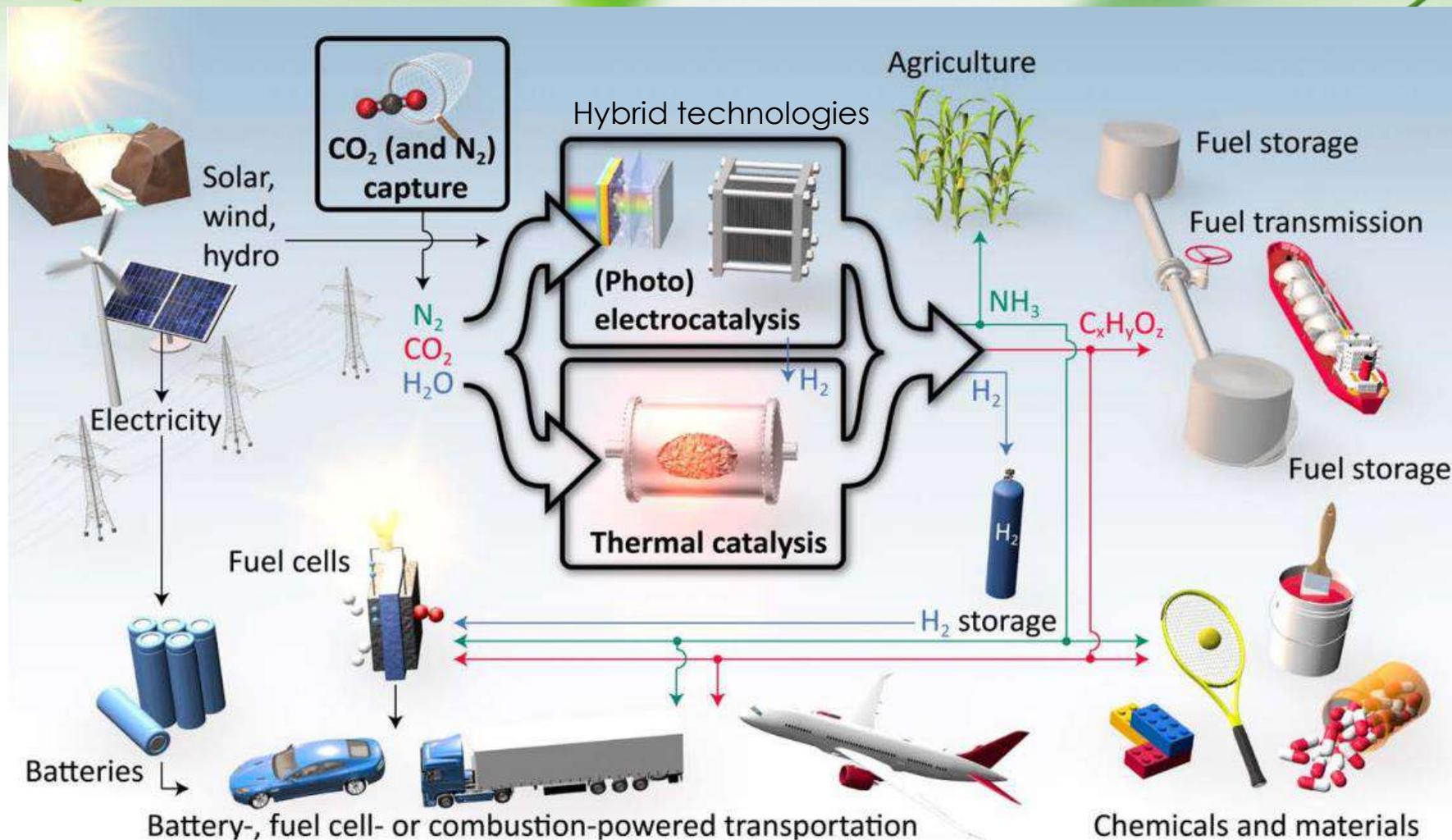
- the method proposed is largely based on reproducing for electrocatalysts the *approach used for thermal catalysis*
 - a localized interaction of a single molecule with the active site.
 - The presence of
 - i) many **adsorbed** species, which alter the properties of the solid and may even lead to **adsorbate-induced reconstruction**, ii) the aspects related to the **dynamics of gas-solid** interaction, iii) the deviation from ideality of many practical catalysts with the **presence of defects, interfaces, amorphous phases, dopants**, etc., iv) the presence of **localized charges** deriving from redox reactions, v) the presence of **strains and other deviations** from a crystalline arrangement,
 - are some aspects **rarely** accounted in current modelling approaches, but which are crucial for the catalytic behavior.



Plasmonic (photo)catalysis

By illuminating a plasmonic metal nanoparticle, the resulting hot-carriers that are produced can **reduce the activation barrier** of a chemical reaction by exciting the adsorbed molecules, either electronically or vibrationally





Electrocatalysis is at the core of SUNERGY initiative and actions



A *Paradigm* Shift in the Development of Catalysts

- **heterogeneous catalysis**

- reactants chemisorb and follow some surface mediated reaction paths that ultimately determine the types and rates of products formed. Typically, different paths involve different active sites or their combination, thus the design of the catalyst is essentially to **maximize the relevant active sites** and sometimes also the modalities of adsorption of the reactants/intermediates

- **reactive catalysis**

- plasmacatalysis: how to control the interaction of the catalyst with this mix of very reactive, highly energetic, and often short-living species without simply quenching them → **how to create a selective path of transformation with these reactive species**
- In electro- and photo-catalysts (EPC): share common aspects

- **Conceptual mechanism** of operation and control of yield and selectivity is different



Challenges and opportunities

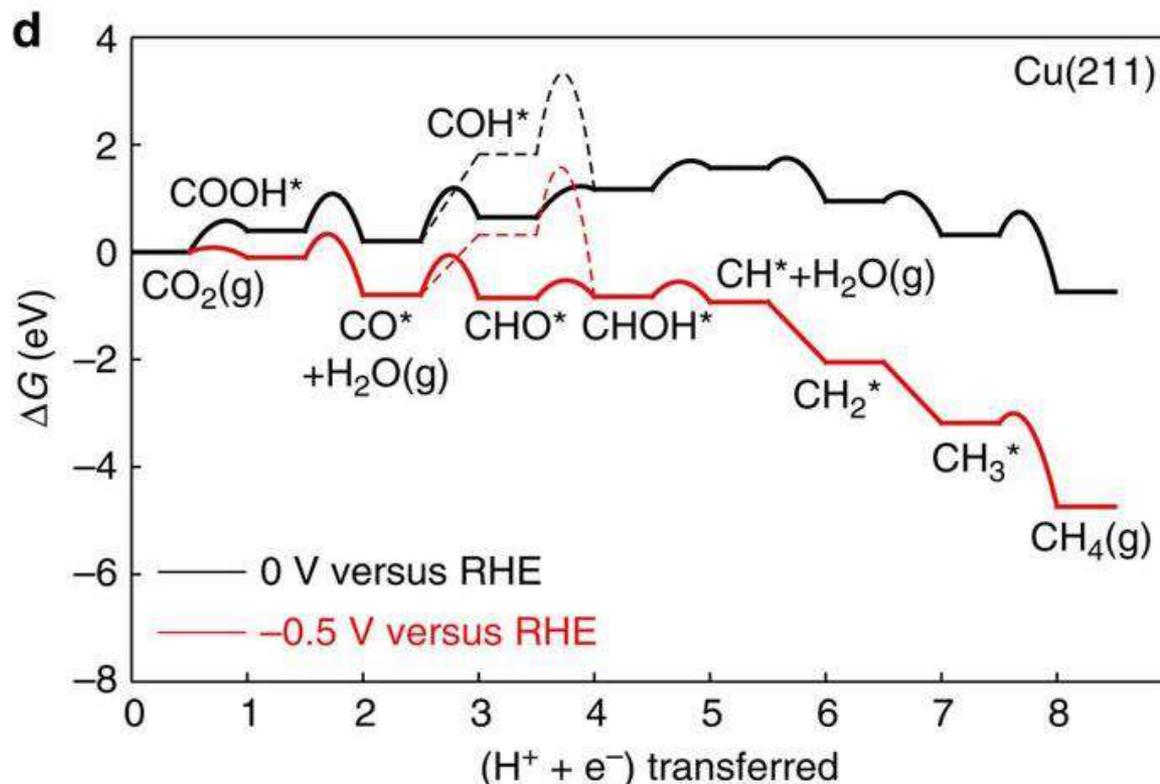
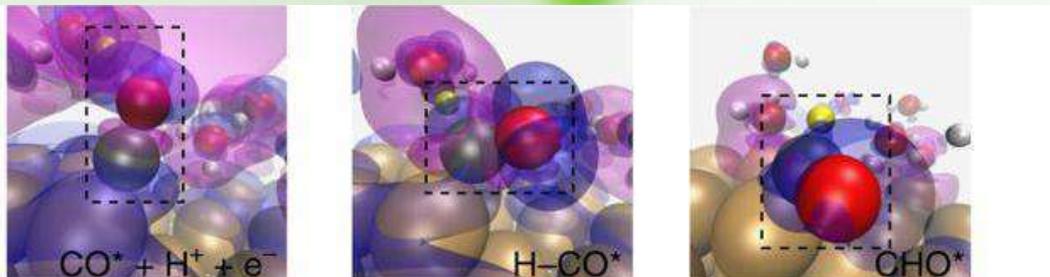
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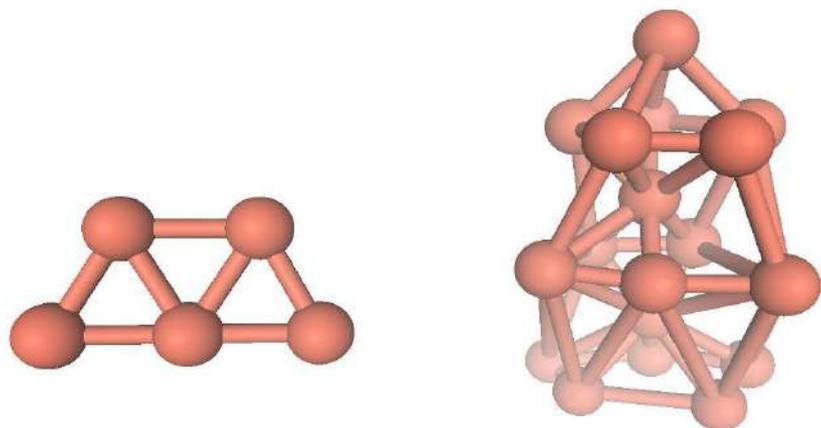


Change of reaction path upon application of a surface potential



free energy diagram for the reduction of CO₂ to CH₄ on Cu(211) at 0 V and -0.5 V versus RHE

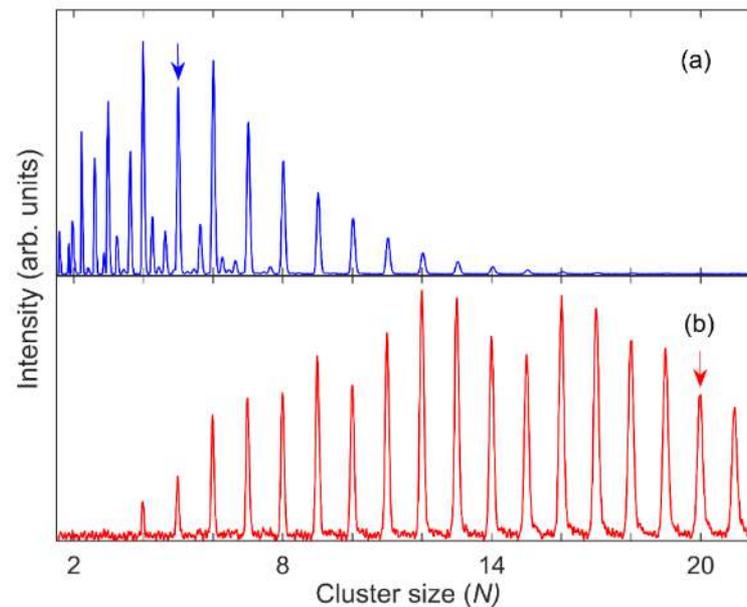
Catalysis at sub-nano (naked) clusters



Cu_5 *Cu nano-cluster* Cu_{20}

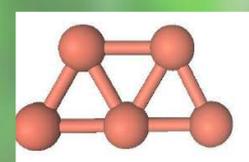
The number of atoms in the deposited clusters is precisely controlled using a combination of gas-phase cluster ion sources, mass spectrometry, and soft-landing techniques.

These metal clusters do not contain organic ligands or capping agents



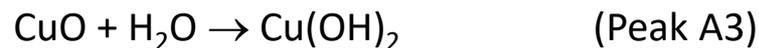
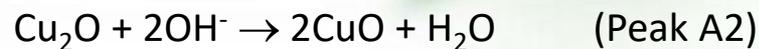
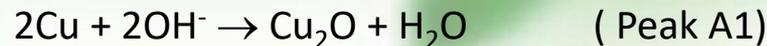
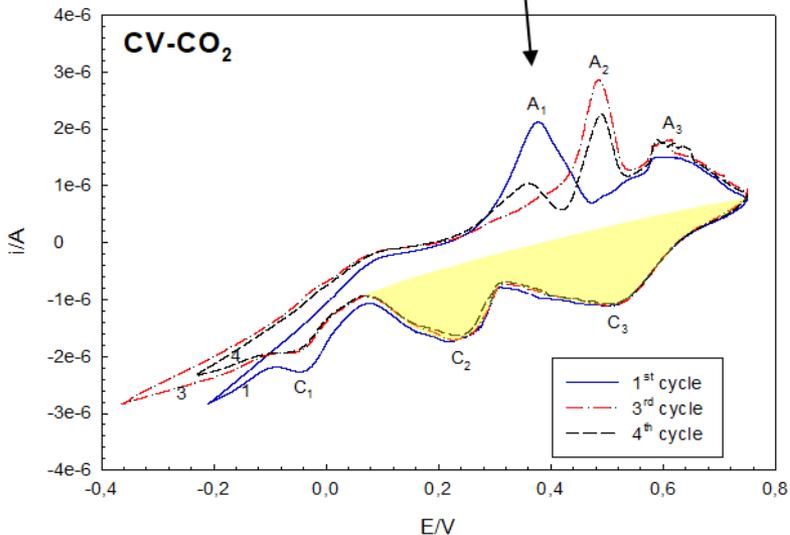
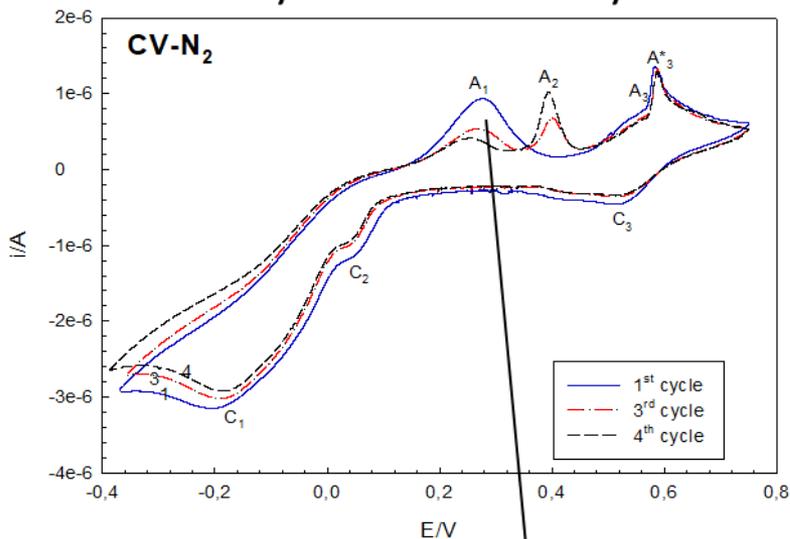


Electrochemical behavior

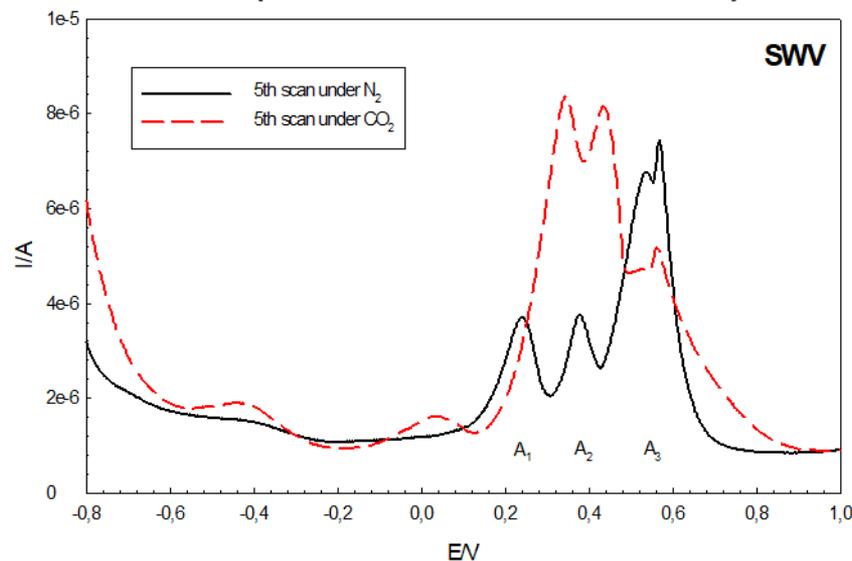


Cu₅ nano-cluster

Cyclic Voltammetry



Square Wave Voltammetry

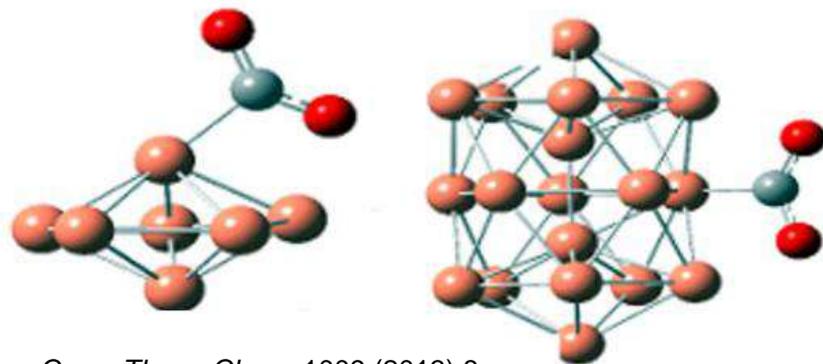


- CO₂ (HCO₃⁻) coordination modifies the redox chemistry of copper nano-clusters
- strong intensification of cathodic curve, due to CO₂ reduction

CO₂ electrocatalytic reduction at Cu nano-clusters

- Cu₂₀ nanoclusters show **enhanced redox** properties with respect to Cu₅ nanoclusters, but it is the ability of the copper nanocluster **in adsorption and activation of CO₂** (enhanced in Cu₅ nanocluster with respect to Cu₂₀ nanoclusters and Cu particles) which enables the possibility of low overpotential reduction of CO₂ during electrocatalytic conditions.

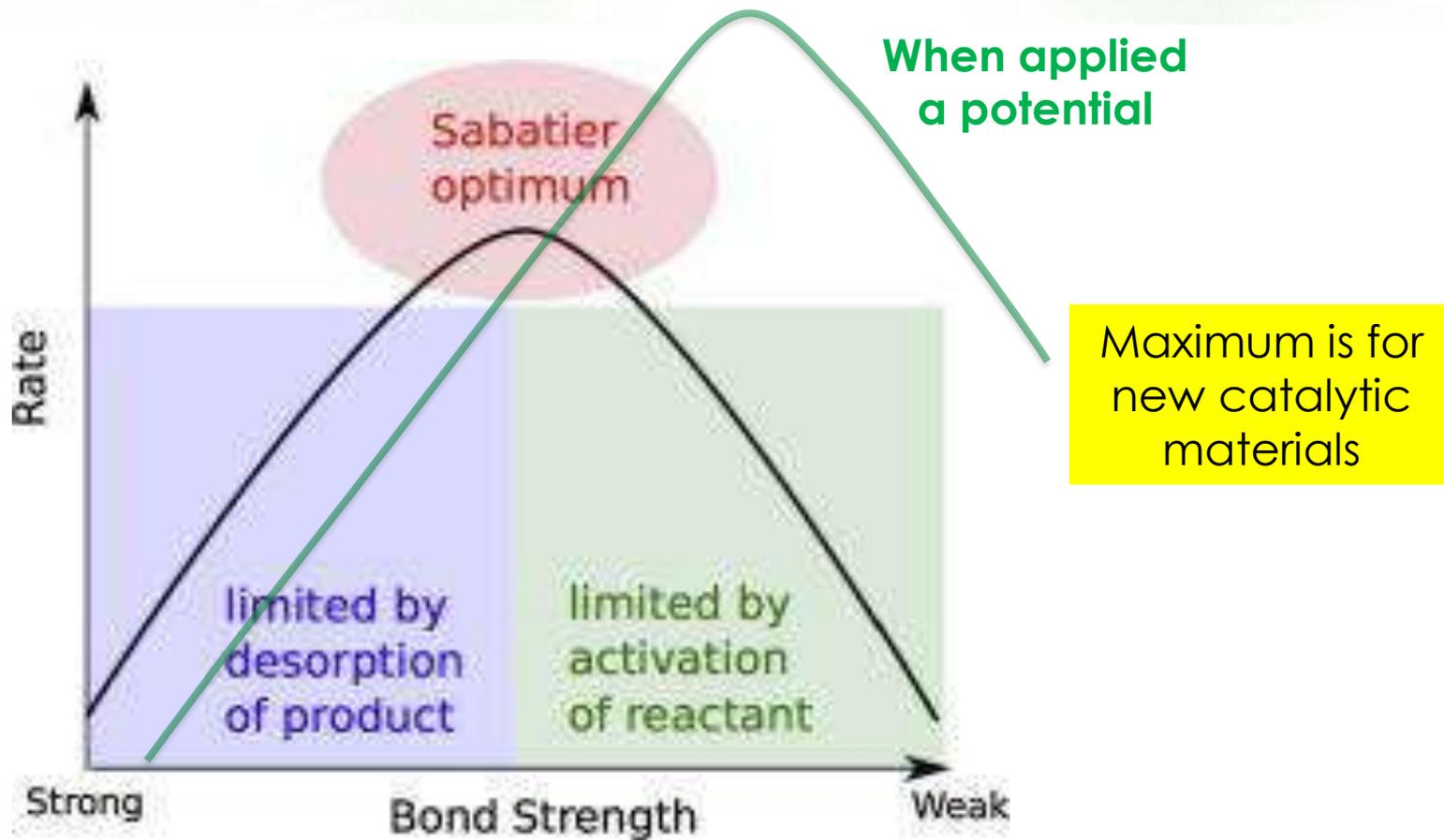
coord. CO₂ on Cu₇ and Cu₁₉



Comp.Theor. Chem. 1009 (2013) 8



Volcano plot

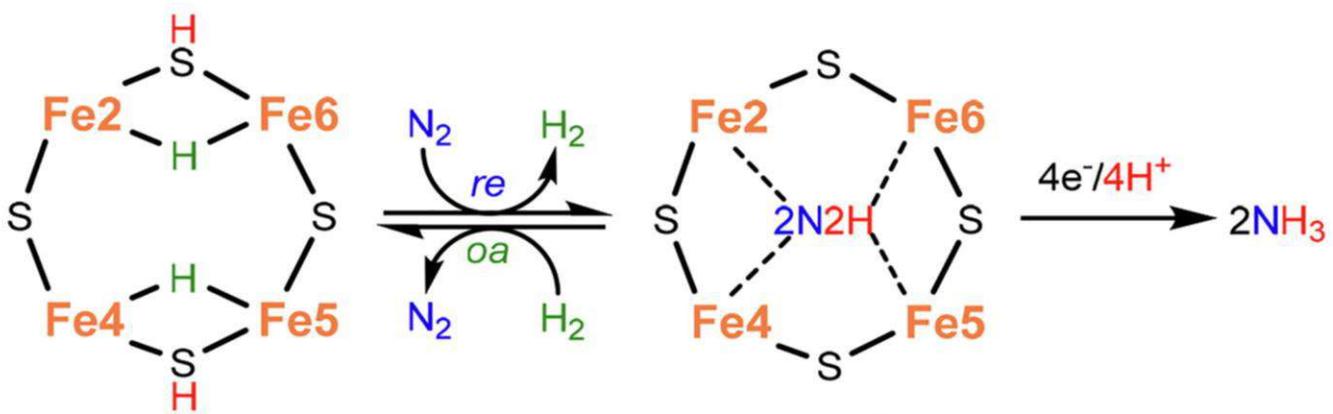




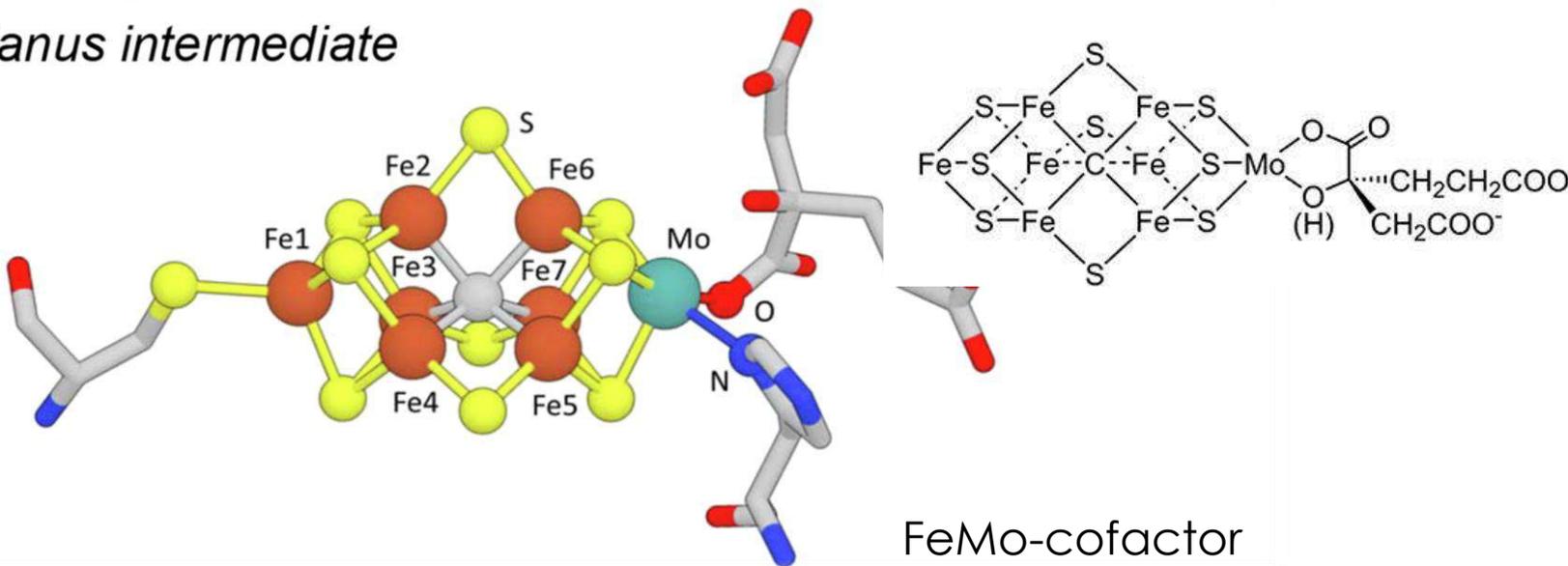
How to proceed? Rethink electrocatalysis

- biomimetic catalysis is popular, BUT not often properly addressed → case of NRR (*Nitrogenase*)
 - *Nitrogenase* is a unique system able to convert N_2 to NH_3 . Three classes of Nitrogenase, differ for the heteroatom present (Mo, V or Fe) → Mo-dependent nitrogenase is the most important
 - It contains two metallo-components, dinitrogenase [molybdenum–iron (MoFe) protein] and dinitrogenase reductase (Fe protein), which associate and dissociate in a catalytic cycle also requiring a reducing source and MgATP.
 - The MoFe protein contains two metal clusters: the iron–molybdenum cofactor (FeMo-co), which provides the active site for substrate binding and reduction, and P-cluster, involved in electron transfer from the Fe protein to FeMo-co.
 - **The FeMo-cofactor is thus the key element for the mechanism of N_2 fixation.**

Nitrogenase mechanism



Janus intermediate



FeMo-cofactor



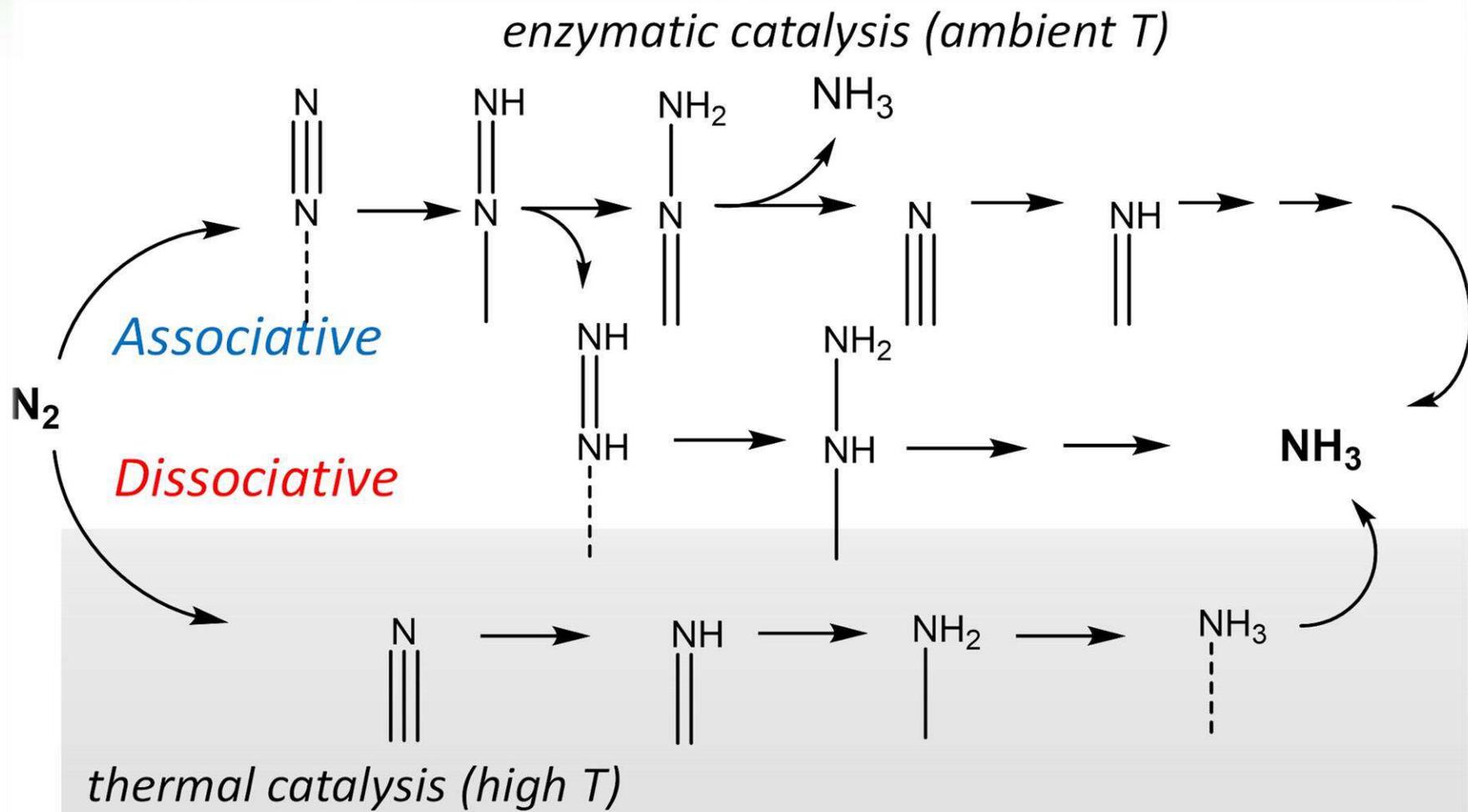
Key features of *Nitrogenase* mechanism



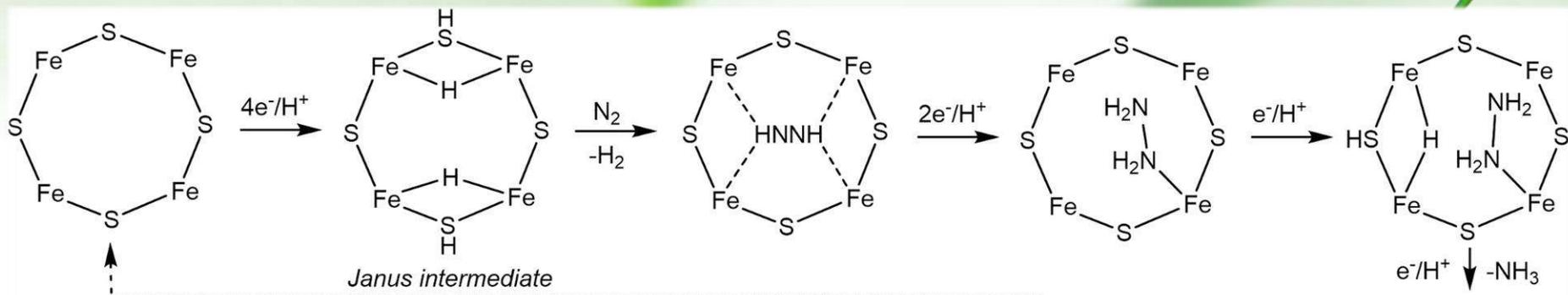
- A specific binding site for N_2 able to first accept four electrons/protons to form two [Fe–H–Fe] bridging **hydrides**,
- Coordination of N_2 on **two iron atoms** with simultaneous reductive elimination of H_2 ,
- **Multi**-electron/proton transfer to a coordinated undissociated N_2 molecule to form a N_2H_2 molecule **stabilized** by interaction with two iron atoms,
- Further **multi** H^+/e^- transfer to form an *end-on* N_2H_4 coordinated molecule,
- Further steps of H^+/e^- transfer with stepwise release of ammonia.



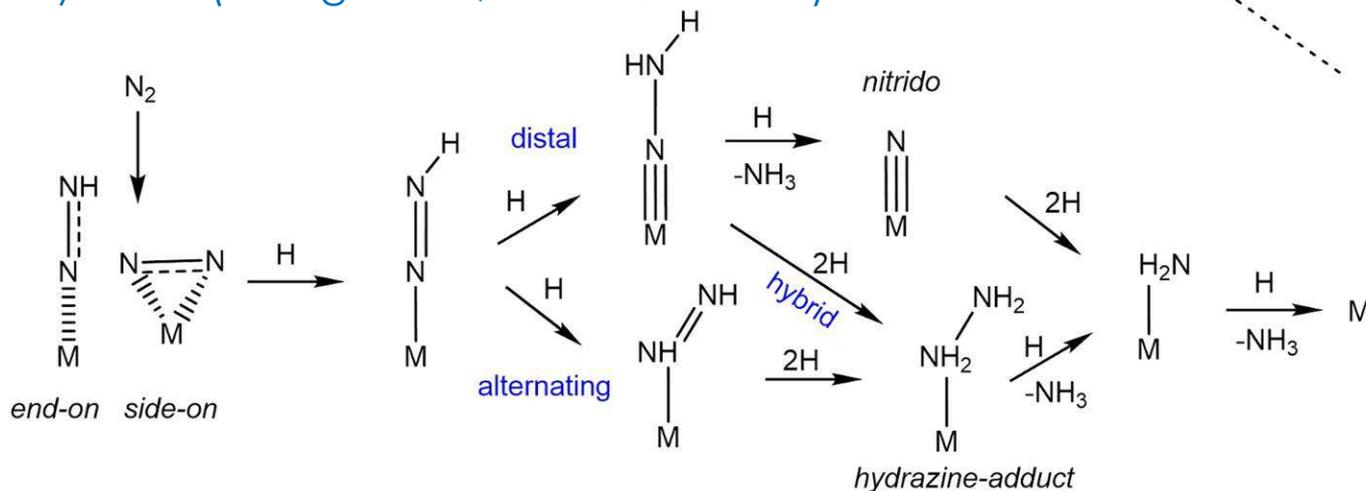
Difference enzymatic & (thermal) catalytic mechanisms



Difference enzymatic & electrocatal. mechanisms



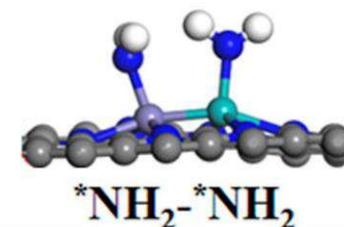
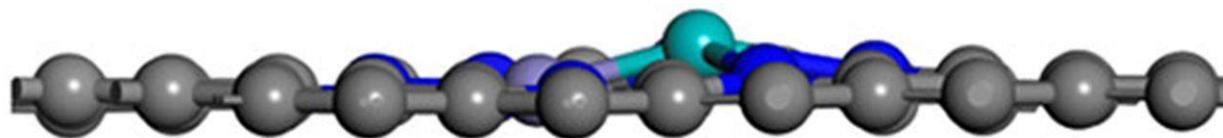
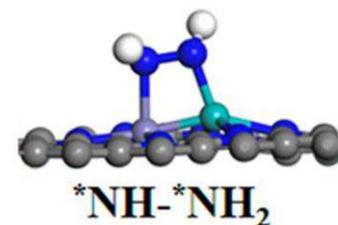
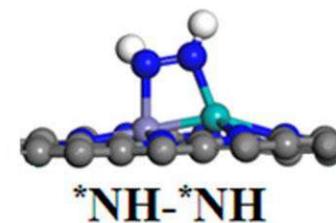
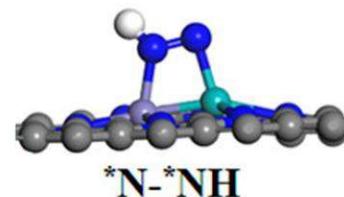
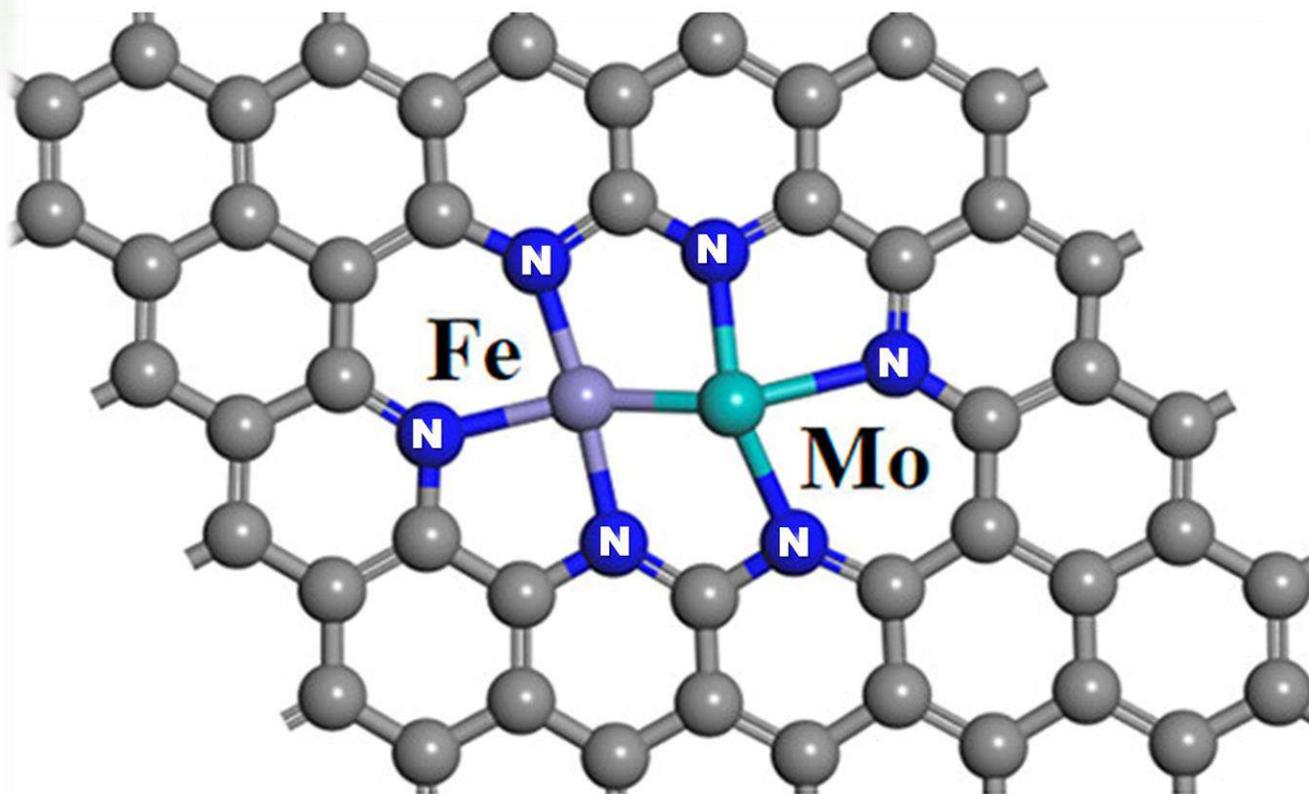
Enzymatic (Nitrogenase, FeMo cofactor) mechanism



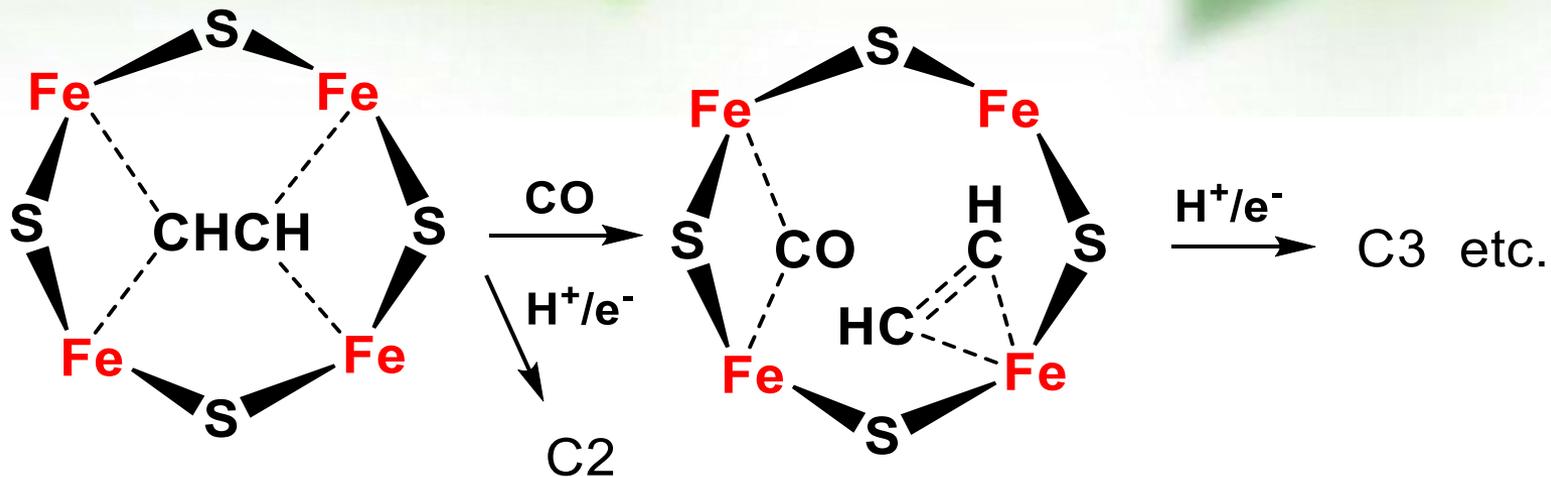
NRR mechanism on biomimetic metal-complexes and electrocatalysts

The key features of the enzymatic mechanism **rarely** are accounted in the proposed mechanisms for electrocatalysts and metal-complexes.

An example of proposed NRR mechanisms



Nitrogenase in CO₂ reduction

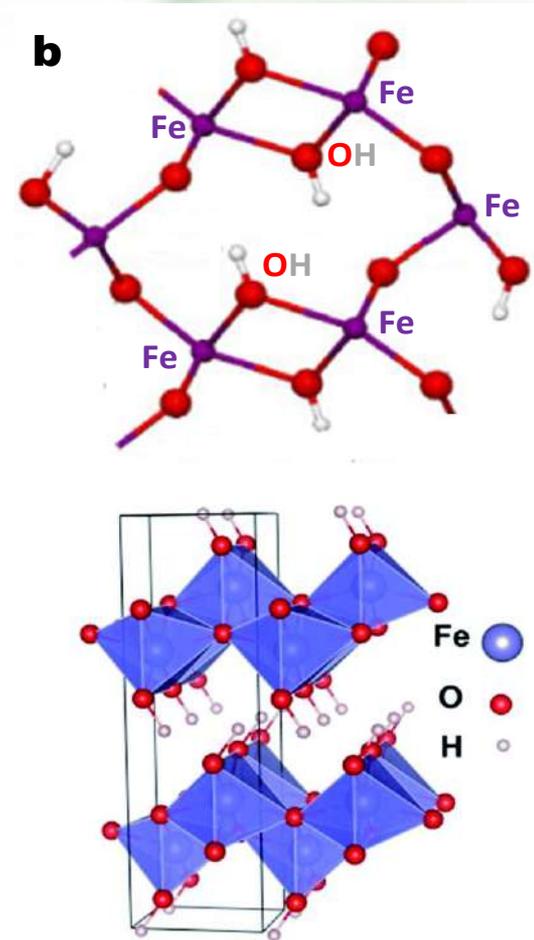
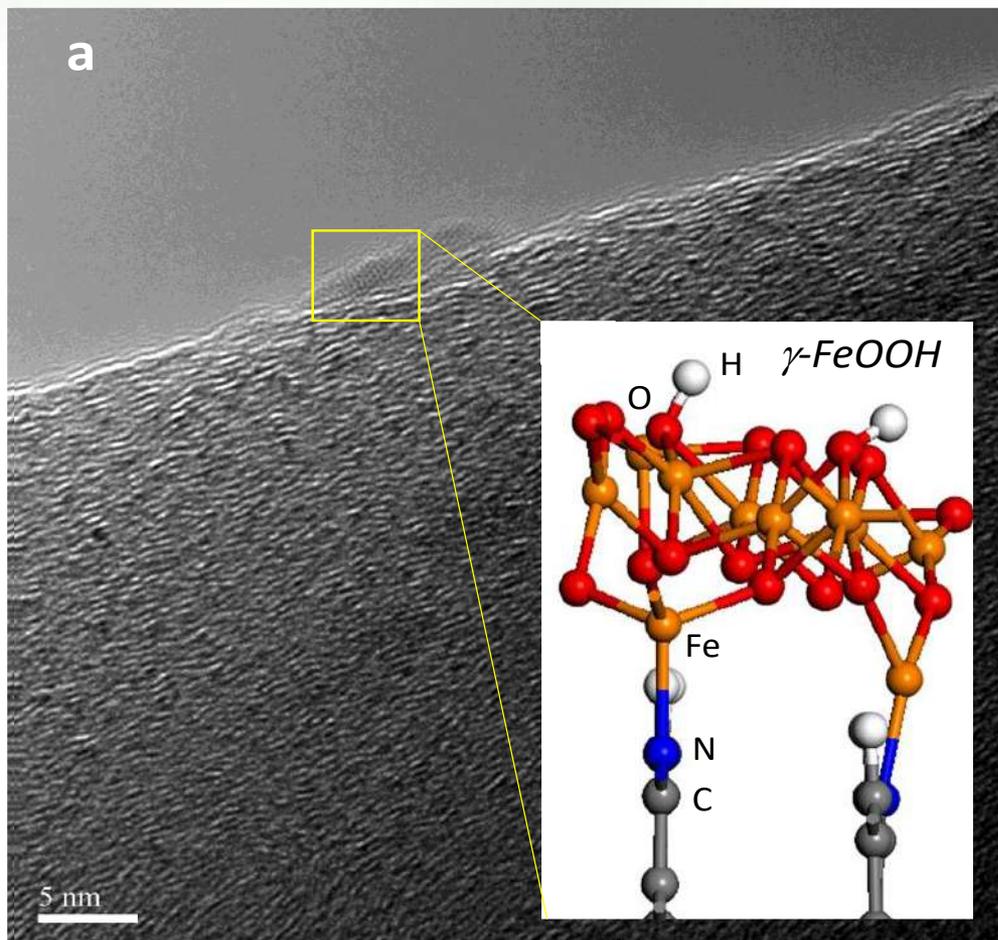


- Nitrogenase can also catalyse the reductive carbon–carbon coupling of CO_x into hydrocarbon products
 - *Janus intermediate* reacts with two CO molecules (produced on the Fe protein) to form an ethyne like intermediate → hydrogenated to ethylene or could react further to form a ferracycle leaving other Fe free to form other Fe-hydride species and further coordinate CO → C₂ → C₃ product

an effective biomimetic electrocatalyst should reproduce all features (multi H⁺/e⁻, hydride, multi-atom binding intermediate, forming C₂+ from CO₂)

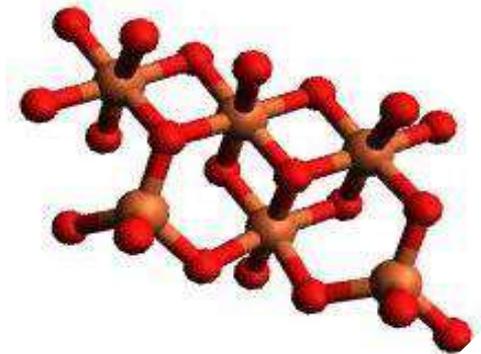
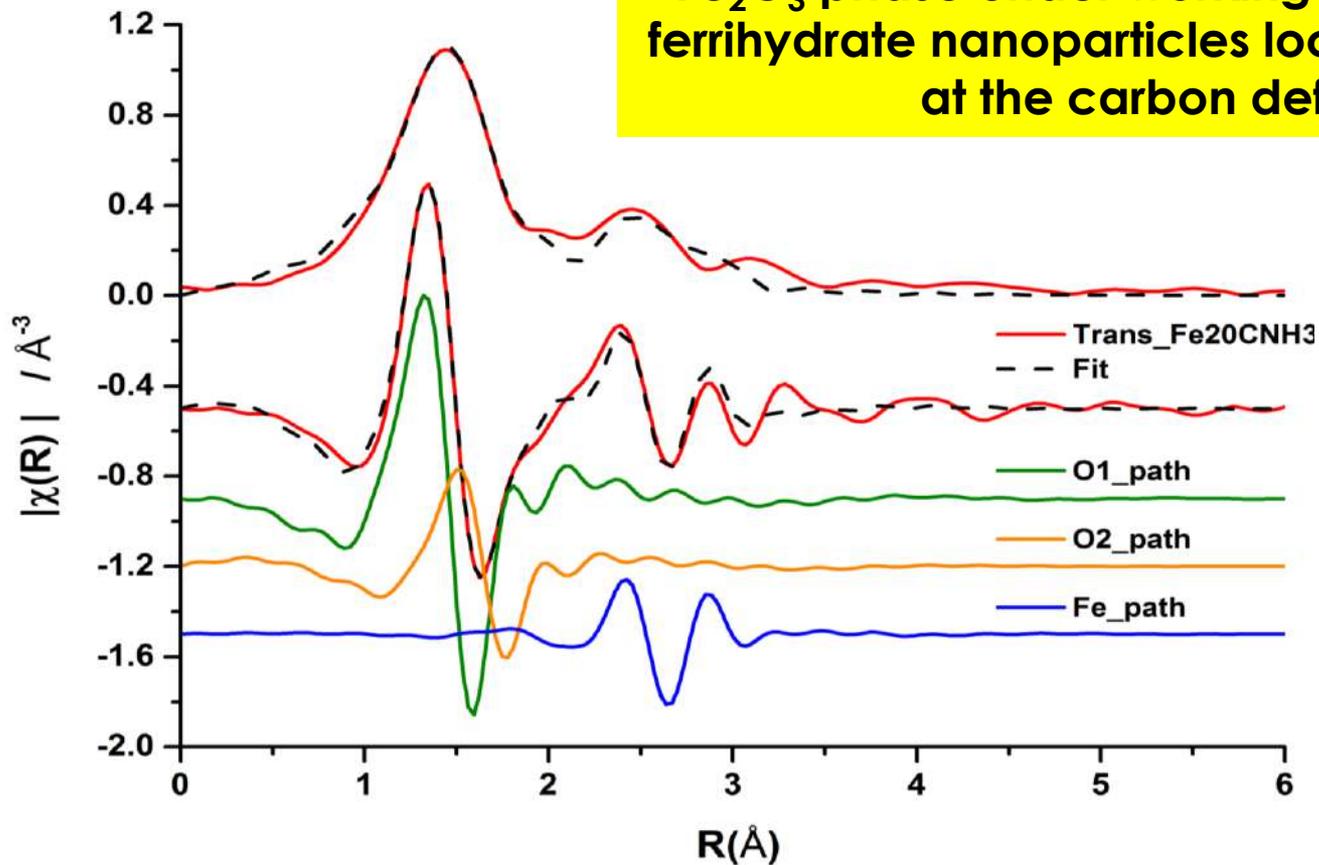


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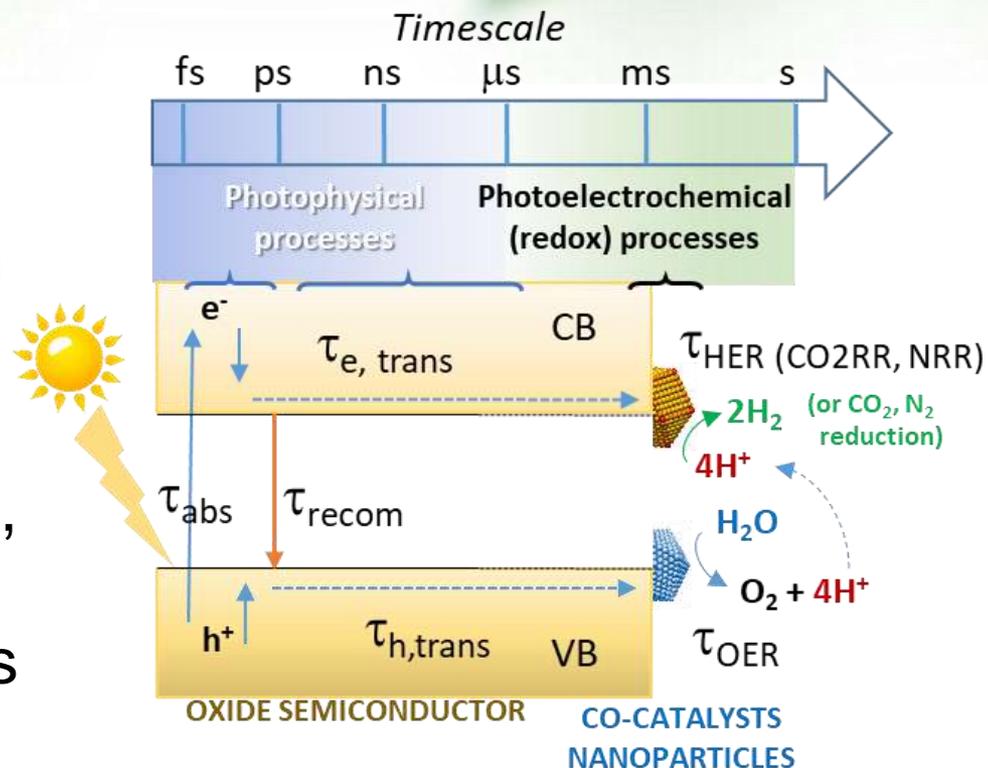
A ferrihydrate (FeOOH) is present rather than a Fe_2O_3 phase under working conditions, with the ferrihydrate nanoparticles located predominantly at the carbon defect sites.



Are we addressing the right problems?

photocatalysis

- photocatalysis → light harvesting and charge separation (fast processes) → slow step is the redox
- *co-catalysts*: phase boundaries/heterojunctions, etc. → trap charges, rather than accelerate the process



Focus should be on the **true catalytic effect**, rather than trapping (in cocatalyst nanoparticles)

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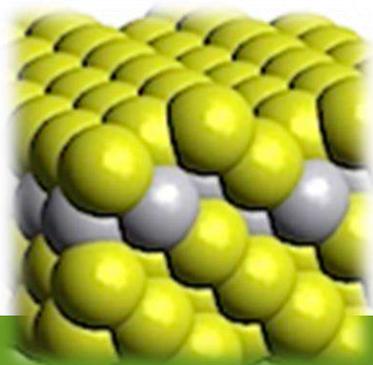


Conclusions



2/2

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