Electroréduction du CO_2 en hydrocarbures/alcools : défis et opportunités

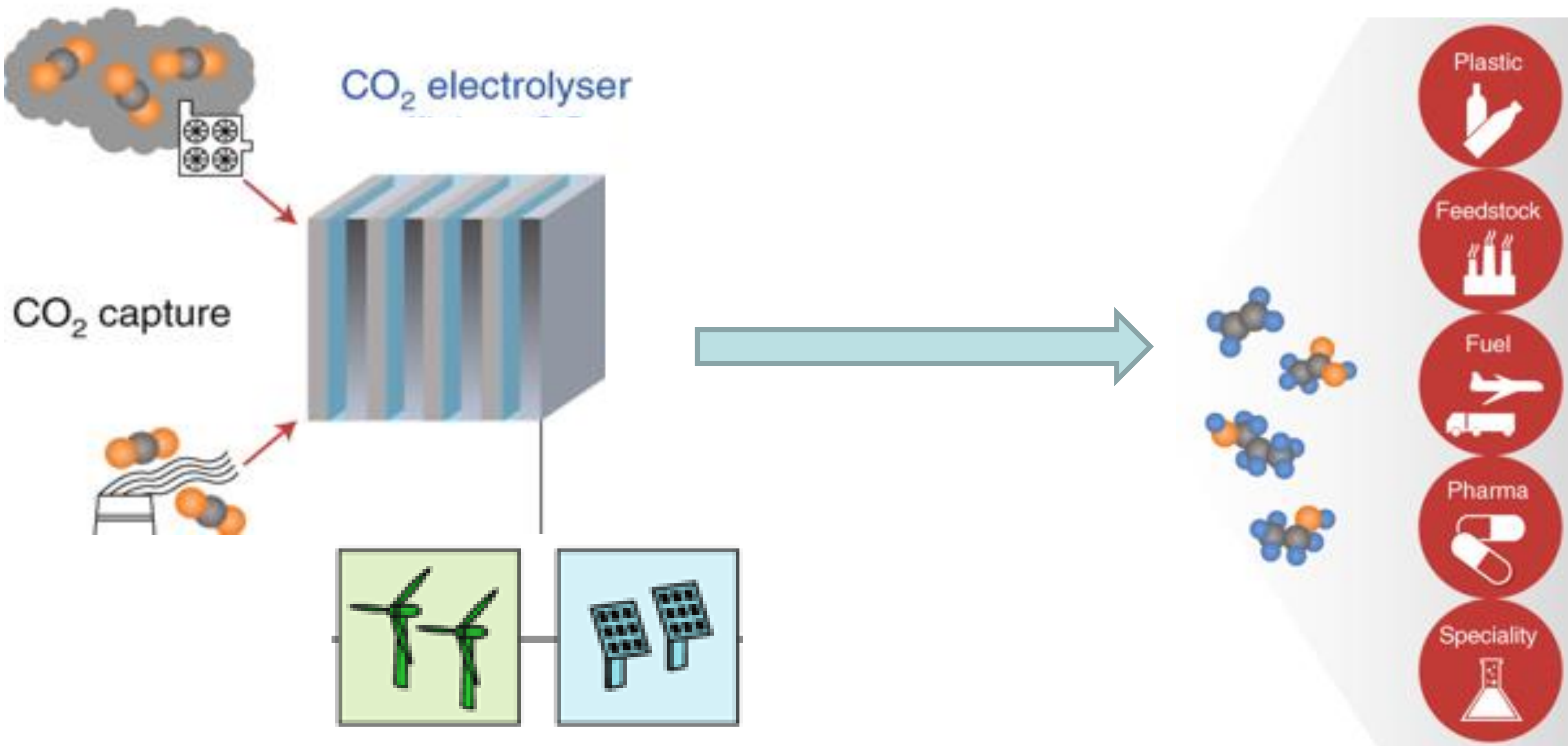
CO_2 electroreduction towards hydrocarbons and alcohols:challenges

Marc Fontecave

Laboratoire de Chimie des Processus Biologiques, UMR 8229 CDF/CNRS/UPMC
Collège de France, 11 Place Marcelin Berthelot, 75231 Paris Cedex 05
marc.fontecave@college-de-france.fr; Phone: (0033)144271360

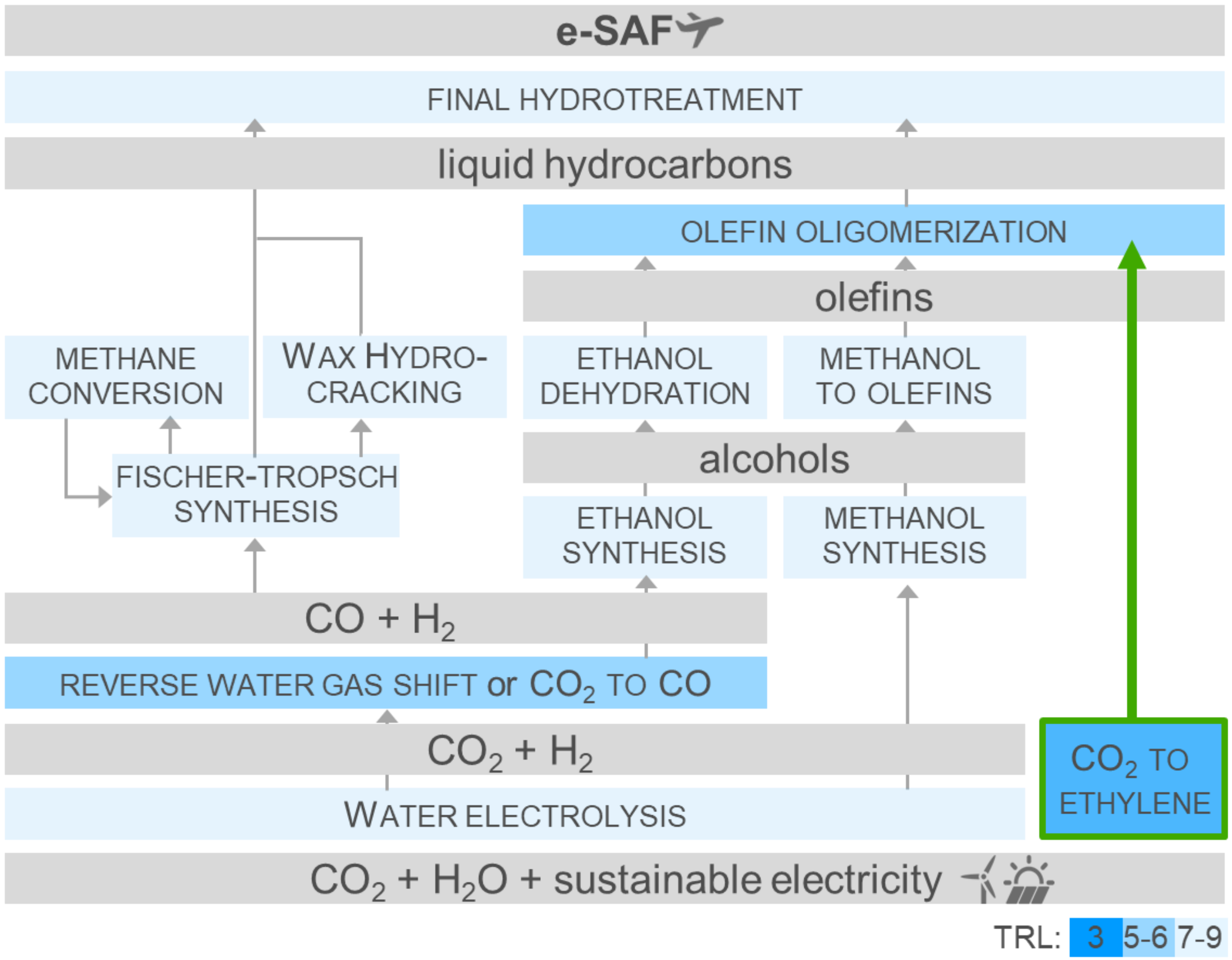
Electrolysis of CO_2: from CO_2 to hydrocarbons/alcohols

- ✓ **Less CO_2** in the atmosphere
- ✓ Storage of intermittent energies (**chemical storage**)
- ✓ A **carbon source** for production of useful carbon compounds



$$\boxed{xCO_2 + yH_2O + ne^- \rightarrow C_xH_{(2y-n)}O_{(2x+y-n)} + nOH^-}$$

Electrolysis of CO_2: from CO_2 to hydrocarbons/alcohols



TRL (Technology Readiness Levels): parameter measuring the maturity of a given technology

ETHYLENE

47.2 MJ/kg; 0.055 MJ/L

Ethylene → Polyethylene
(polyvinyl chloride, polystyrene)

Ethylene: 180 millions tons in 2024
(the largest of any organic chemical)
≈ 1000 $/ton

Currently

Steam cracking of naphta or saturated hydrocarbons
(750-950°C)

- Enormous energy inputs
(8% de the total primary energy consumption in chemical industry)
- Production of 2 tons CO_2 / ton ethylene

⇩

CO_2 + (low C) electrons + protons → C_2H_4 ??

Towards alcohols ?

ETHANOL

90 Mt/year
Fuel blend component
Precursor of chemical compounds (medical and food industries).
Produced from starch-based biomass (sugar cane, corn) through fermentation.

PROPANOL

0.3 Mt/year (growth 6.6 % until 2030).
Solvent
Feedstock for the coating and polymer industry (automobile..)
Precursor in the chemical and pharmaceutical industry
Produced by catalytic hydrogenation of propionaldehyde, itself derived from hydroformylation of fossil-derived ethylene with hydrogen and carbon monoxide.

https://ethanolrfa.org/resources/annual-industry-outlook.
https://www.grandviewresearch.com/industry-analysis/propanol-market.
Industrial & Engineering Chemistry Research, 2018, **57**, 2165-2177.

Electrolysis of CO_2:
from CO_2 to hydrocarbons/alcohols

Complexity of CO2R

- Low CO_2 solubility
- High cell voltages
- Carbonate formation/precipitation
- Low selectivity (multiple products + H_2)

⇨

Catalyst optimization

E-cell optimization

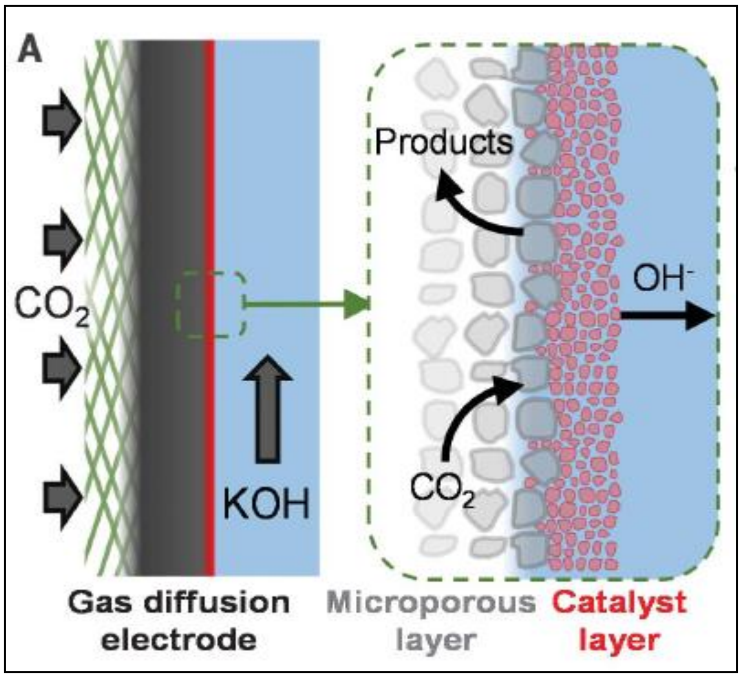
⇩

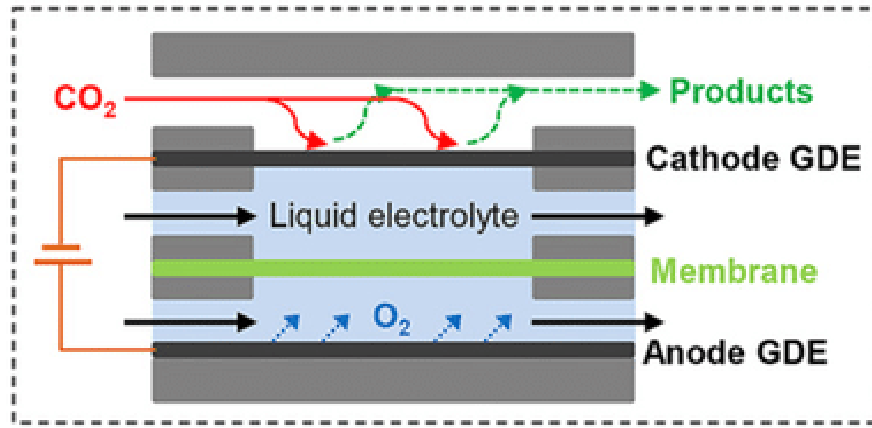
I > 150-200 $mA.cm^{-2}$
FE > 80 %
E_{cell} < 2.5 V

Electrolysis of CO_2:
from CO_2 to hydrocarbons/alcohols

Complexity of CO2R

➢ Low CO_2 solubility ⇨ ➢ Gas diffusion electrodes/ Flow cells



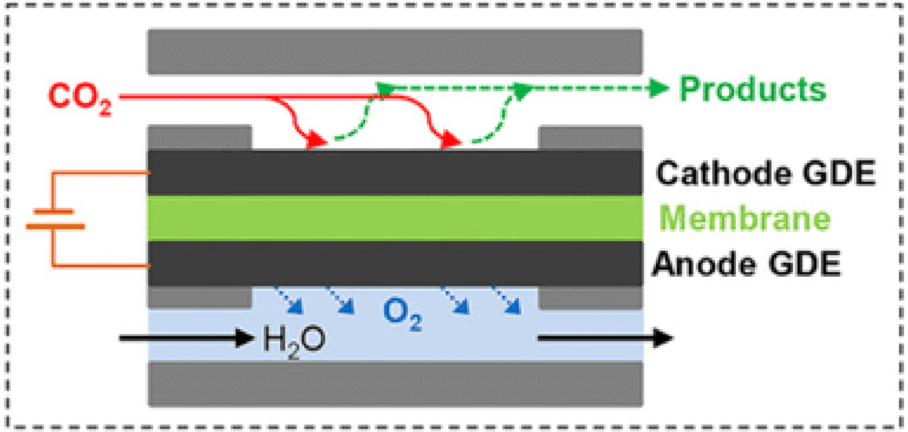


D. Wakerley, S. Lamaison, J. Wicks, A. Clemens, J. Feaster, D. Corral, M. Fontecave, E. Duoss, S. Baker, E. Sargent, T. F. Jaramillo, C. Hahn
Nature Energy 2022, 7, 130-143

Electrolysis of CO_2: from CO_2 to hydrocarbons/alcohols

Complexity of CO2R

- Low CO_2 solubility ⇨ Gas diffusion electrodes/ Flow cells
- High cell voltages ⇨ Membrane Electrode Assembly



D. Wakerley, S. Lamaison, J. Wicks, A. Clemens, J. Feaster, D. Corral, M. Fontecave, E. Duoss, S. Baker, E. Sargent, T. F. Jaramillo, C. Hahn
Nature Energy 2022, 7, 130-143

Electrolysis of CO_2: from CO_2 to hydrocarbons/alcohols

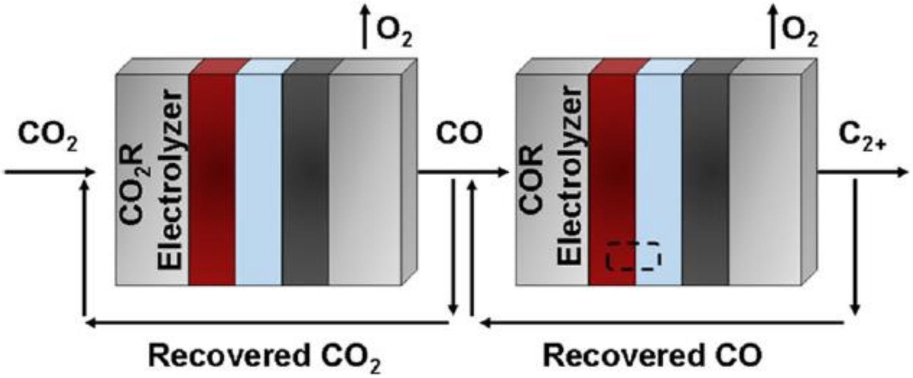
Complexity of CO2R

- Low CO_2 solubility ⇨ Gas diffusion electrodes/ Flow cells
- High cell voltages ⇨ Membrane Electrode Assembly
- Carbonate formation/precipitation ⇨
  - Acidic electrolysis
  - Tandem CO_2-to-CO-to-product

$$CO_2 + n\,e^- + m\,H_2O \longrightarrow \mathit{CO_2R\ products} + x\,OH^-$$

$$CO_2 + 2\,OH^- \longrightarrow CO_3^{2-} + H_2O$$

Low CO_2 utilization efficiency



D. Wakerley, S. Lamaison, J. Wicks, A. Clemens, J. Feaster, D. Corral, M. Fontecave, E. Duoss, S. Baker, E. Sargent, T. F. Jaramillo, C. Hahn
Nature Energy 2022, 7, 130-143

Electrolysis of CO_2: from CO_2 to hydrocarbons/alcohols

Complexity of CO2R

➢ Low CO_2 solubility	⇨	➢ Gas diffusion electrodes/ Flow cells
➢ High cell voltages	⇨	➢ Membrane Electrode Assembly
➢ Carbonate formation/precipitation	⇨	➢ Acidic electrolysis tandem CO_2-to-CO-to-product
➢ Low selectivity (multiple products + H_2)	⇨	➢ Tuning catalysts (composition, morphology, molecular surface modification…)

D. Wakerley, S. Lamaison, J. Wicks, A. Clemens, J. Feaster, D. Corral, M. Fontecave, E. Duoss, S. Baker, E. Sargent, T. F. Jaramillo, C. Hahn
Nature Energy 2022, 7, 130-143

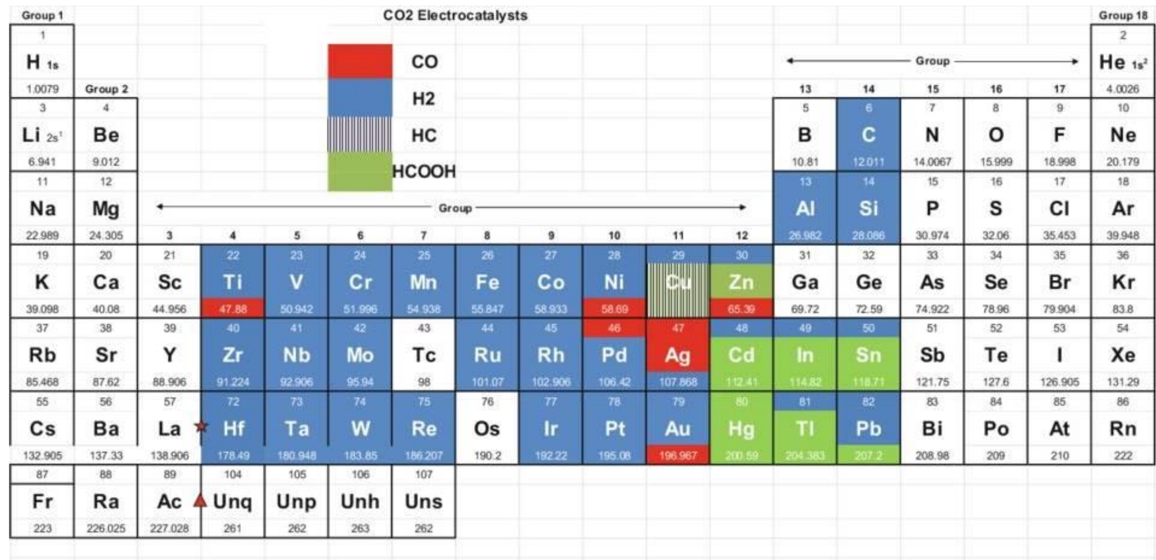
The selectivity issue

Pt, Fe, Co, Ni — H_2

Ag, Au, Pd, Zn — **CO**

Pb, Sn, In — HCO_2H

Cu — **Hydrocarbons**, **Alcohols**



$CO_2 + 2\,H^+ + 2\,e^- \rightarrow \mathbf{CO} + H_2O$

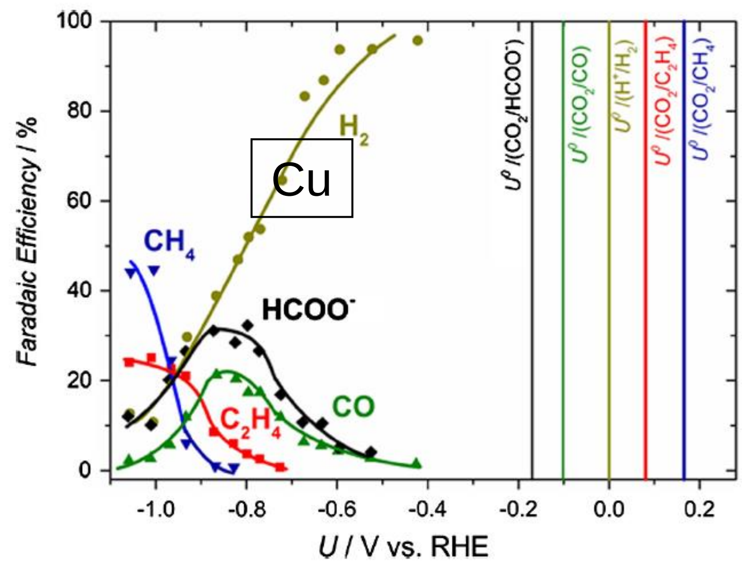
$CO_2 + 2\,H^+ + 2\,e^- \rightarrow \mathbf{HCOOH}$

$CO_2 + 8\,H^+ + 8\,e^- \rightarrow \mathbf{CH_4} + 2\,H_2O$

$2\,CO_2 + 12\,H^+ + 12\,e^- \rightarrow \mathbf{C_2H_4} + 4\,H_2O$

$2\,CO_2 + 12\,H^+ + 12\,e^- \rightarrow \mathbf{C_2H_6O} + 3\,H_2O$

$2\,H^+ + 2\,e^- \rightarrow \mathbf{H_2}$

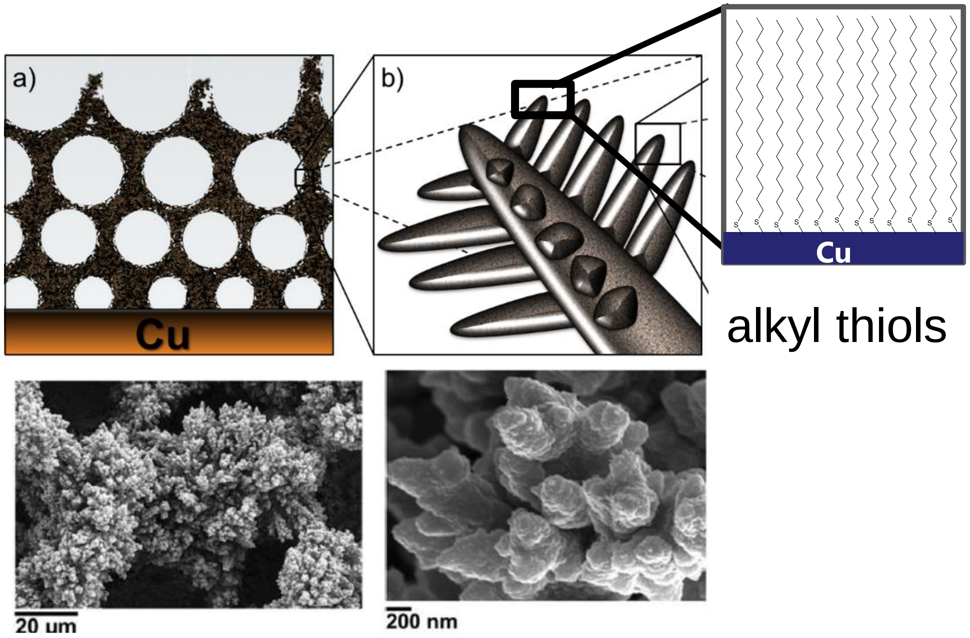


Hori et al., J. Chem. Soc. Faraday Trans. **1989**

Bocarsly et al. *Chem Rev*, **2015**, *115*, *12888*.

Towards more selective CO_2 reduction: (hydrophobic) surface modification

Porous dendritic Cu
(functionalized with alkyl thiols)



Tran N.H., Fontecave M and coll

Angew. Chem. 2017 <u>56</u> 4792

Proc. Natl. Acad. Sci. 2019, 116, 9735

ACS Catalysis 2022, <u>12</u>, 10285-10293

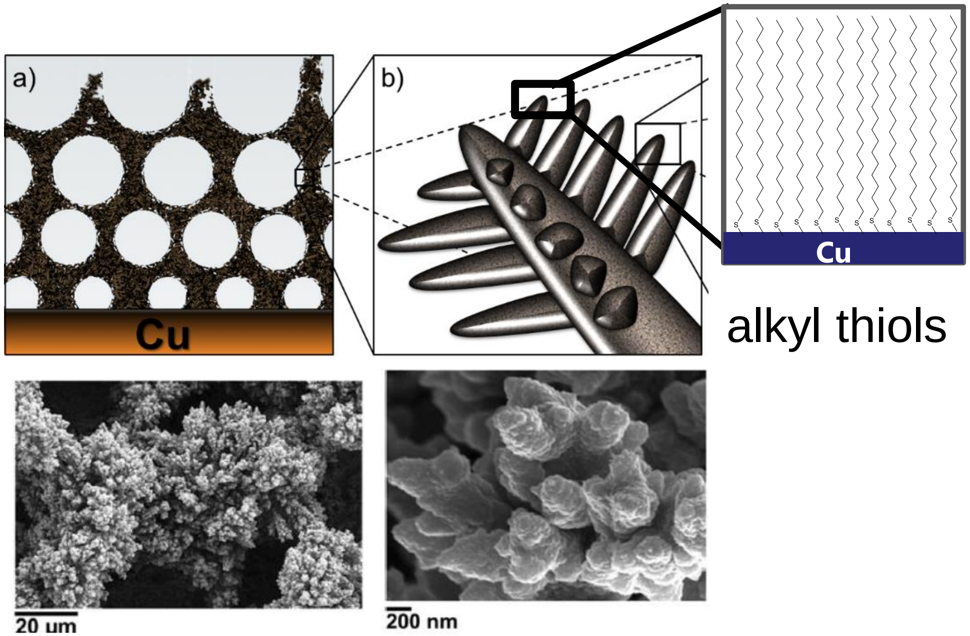
Towards more selective CO_2 reduction: (hydrophobic) surface modification

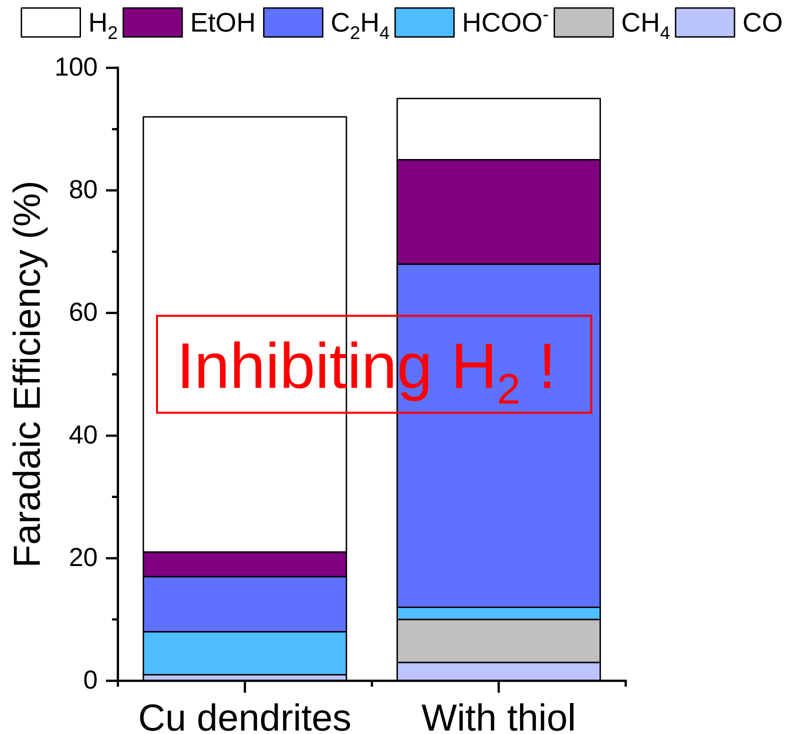
Controlled current electrolysis (30 mA.cm^{-2})

in 0.1 M $CsHCO_3$ with CO_2 at flow rate of 5 ml min^{-1}

Wettable dendrite : –1.1 V *vs.* RHE
Hydrophobic dendrite: –1.5 V *vs.* RHE

Porous dendritic Cu
(functionalized with alkyl thiols)



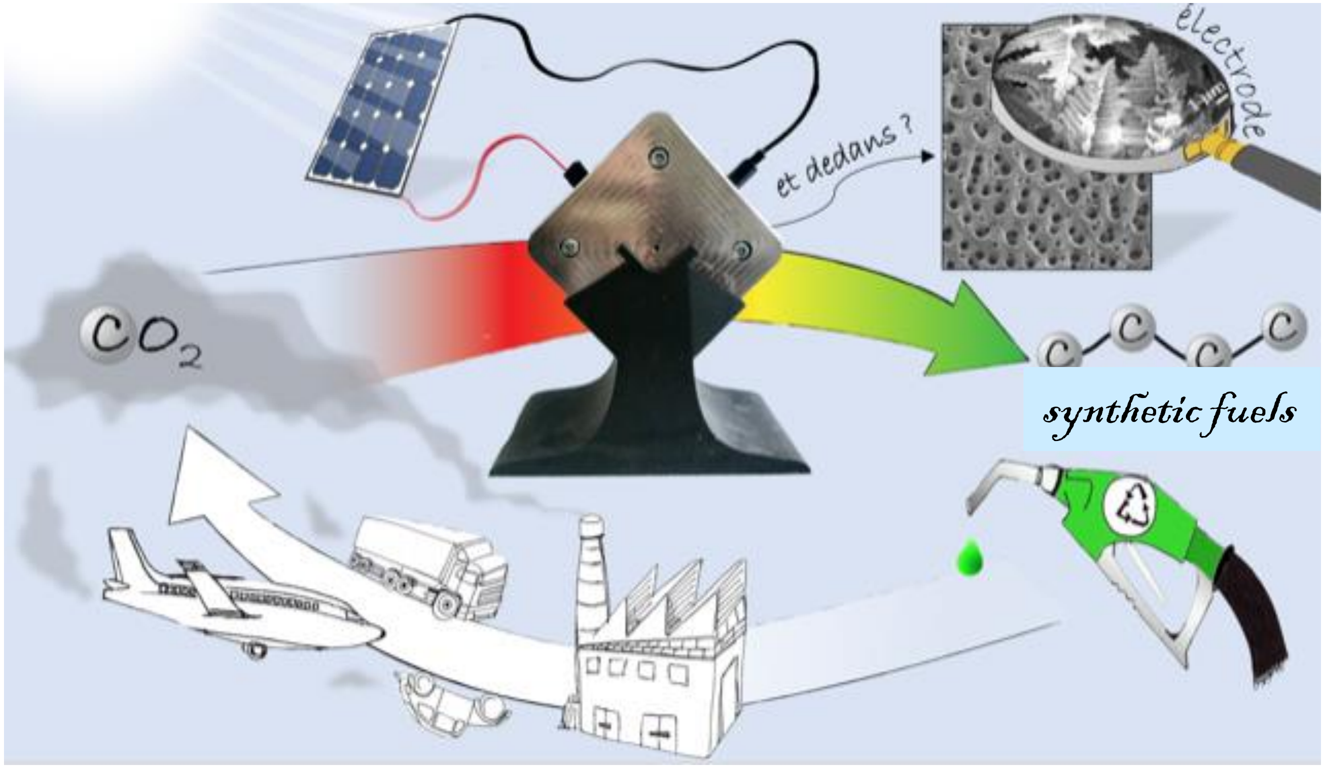


Tran N.H., Fontecave M and coll
Angew. Chem. 2017 56 4792
Proc. Natl. Acad. Sci. 2019, 116, 9735
ACS Catalysis 2022, 12, 10285-10293

Nature Materials 2019, 18, 1222-1227

Artificial photosynthesis of ethylene

CO_2 + electrons + protons + $h\nu \rightarrow C_2H_4$??

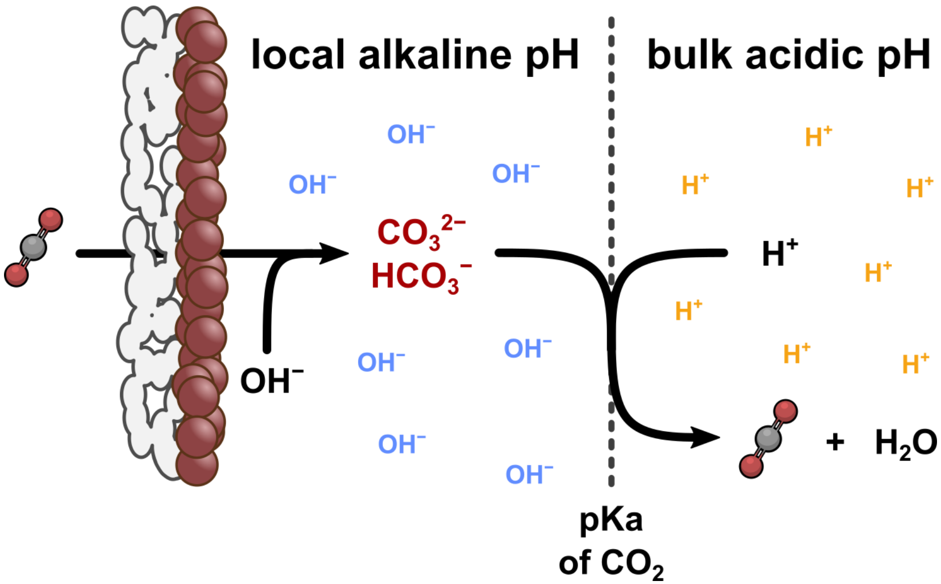


Ethylene C_2H_4 (34%); **Ethane C_2H_6** (7%)

Solar-to-hydrocarbon efficiency : 2.3 %

Low-cost high efficiency system for solar-driven conversion of CO_2 to hydrocarbons. M. Fontecave and collaborators *Proc. Natl. Acad. Sci.* 2019, 116, 9735-9740

Combining acidic CO2R and surface modification



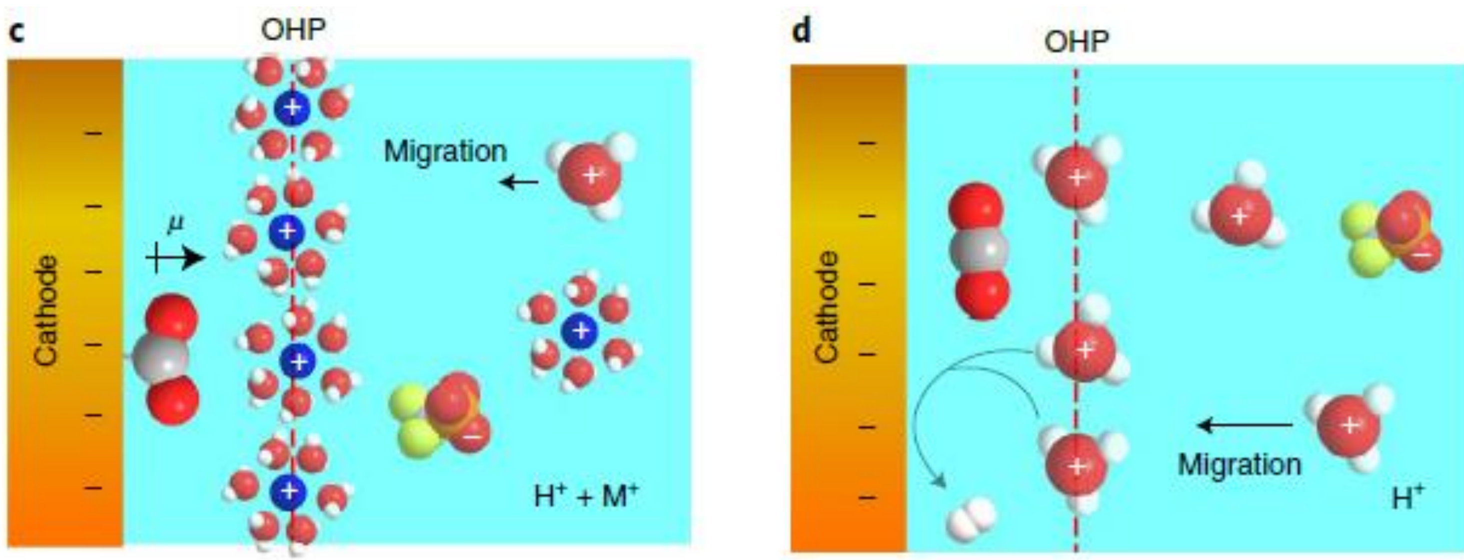
Acidic electrolytes

$$CO_2 + n\,e^- + m\,H^+ \rightarrow CO_2R\ products + x\,H_2O$$

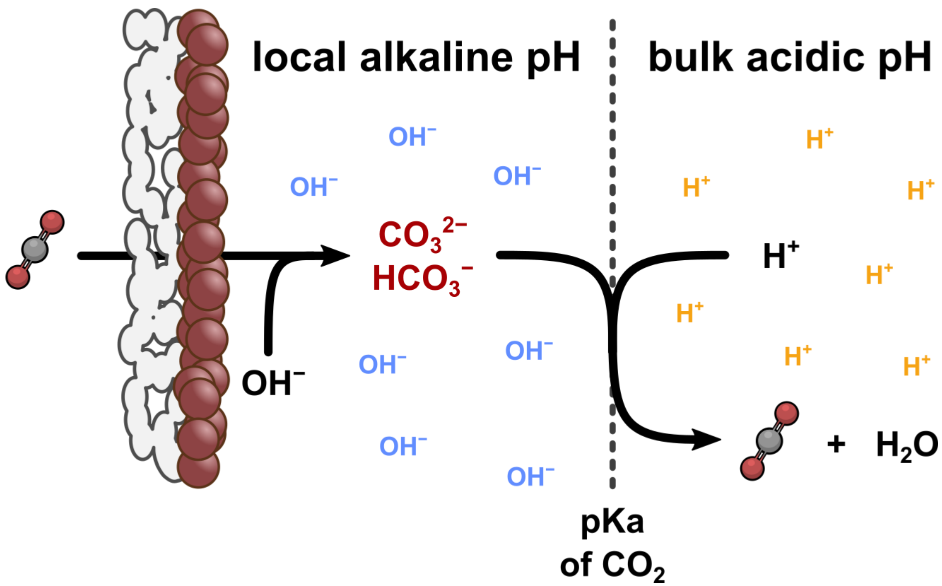
$$2\,H^+ + 2\,e^- \rightarrow H_2$$

HER outcompetes CO_2R

High K^+ conc limits
H_2 production



Combining acidic CO2R and surface modification



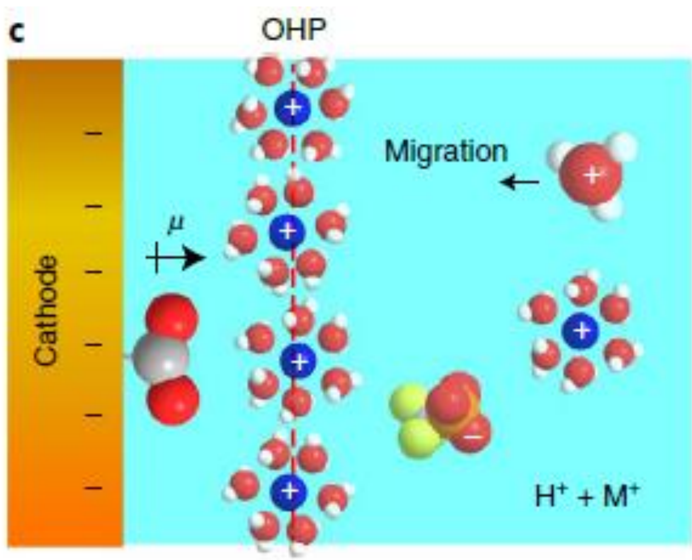
Acidic electrolytes

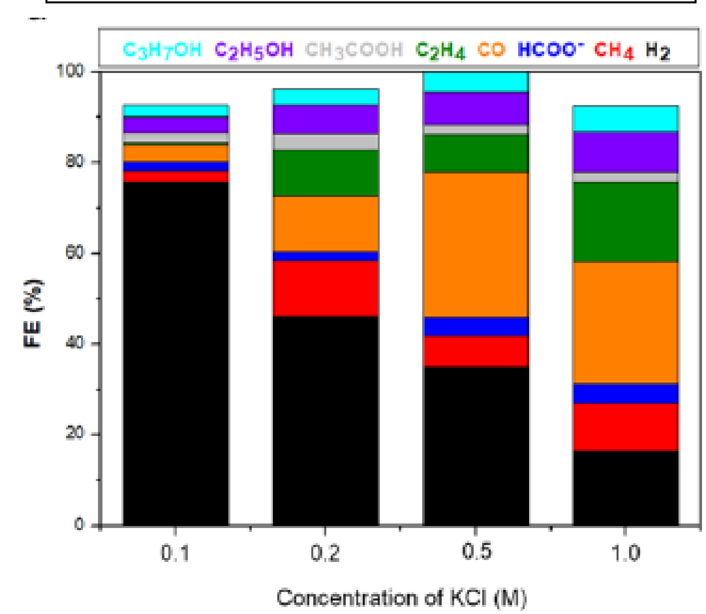
$$CO_2 + n\,e^- + m\,H^+ \longrightarrow CO_2R\ products + x\,H_2O$$

$$2\,H^+ + 2\,e^- \longrightarrow H_2$$

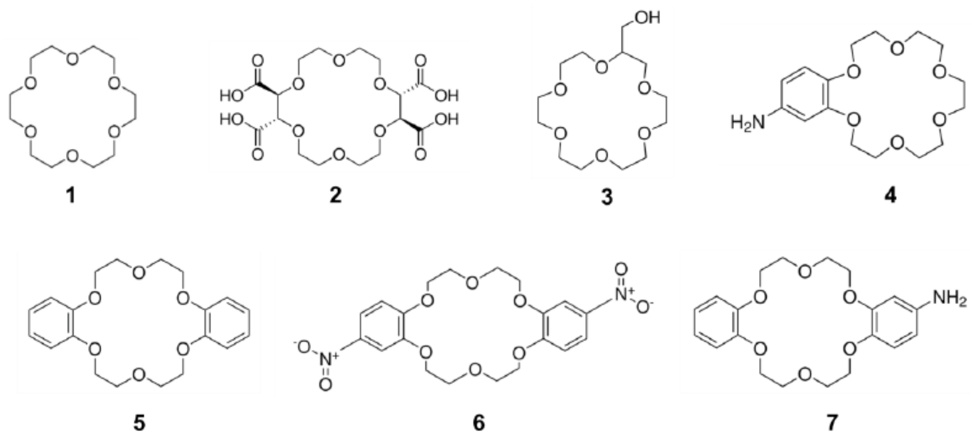
HER outcompetes CO_2R

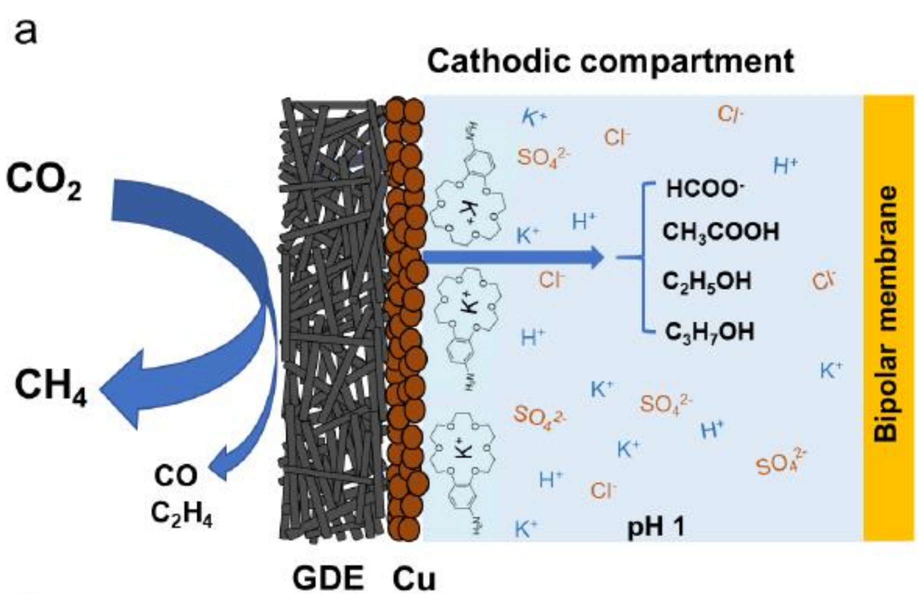
High K^+ conc limits **H_2 production**

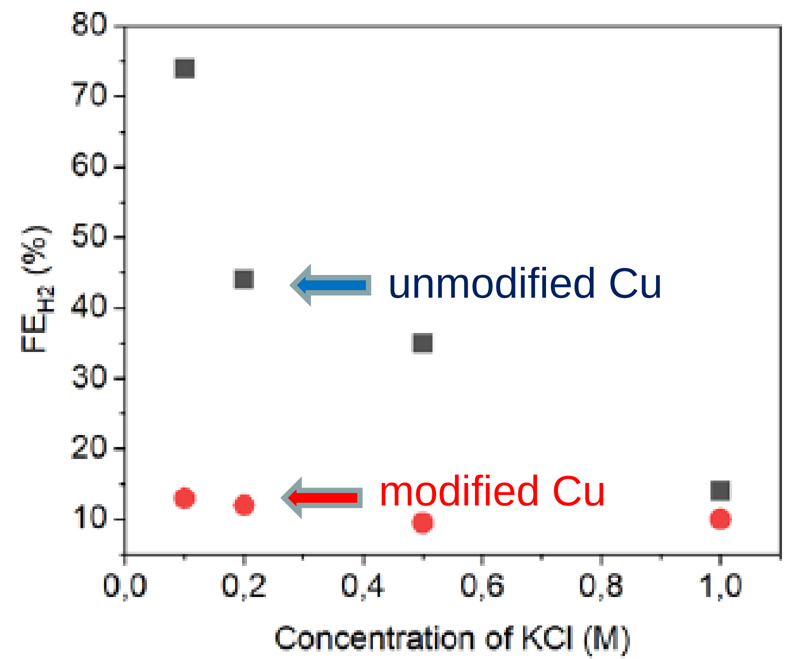




Combining acidic CO2R and surface modification

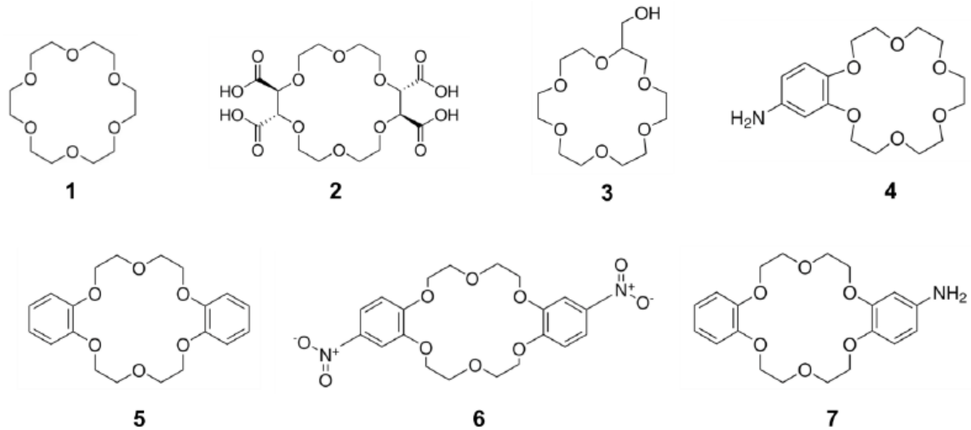




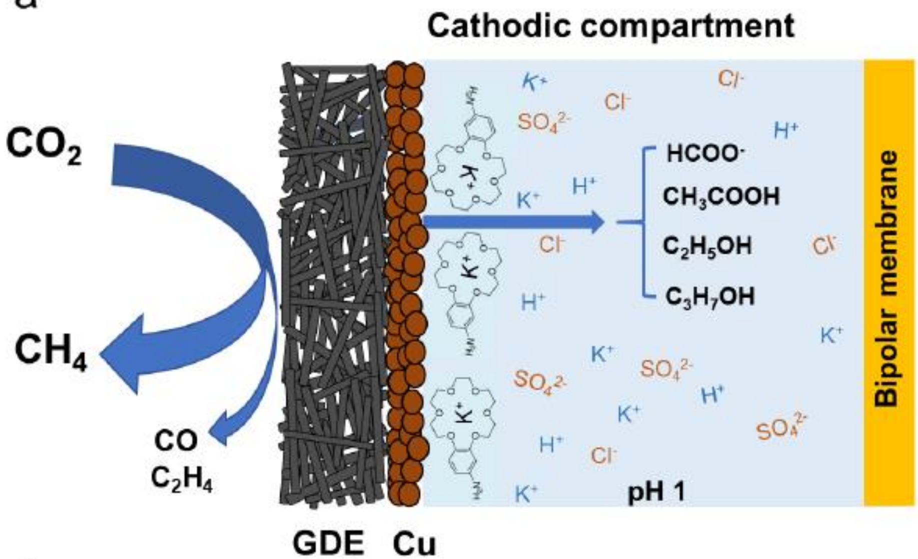


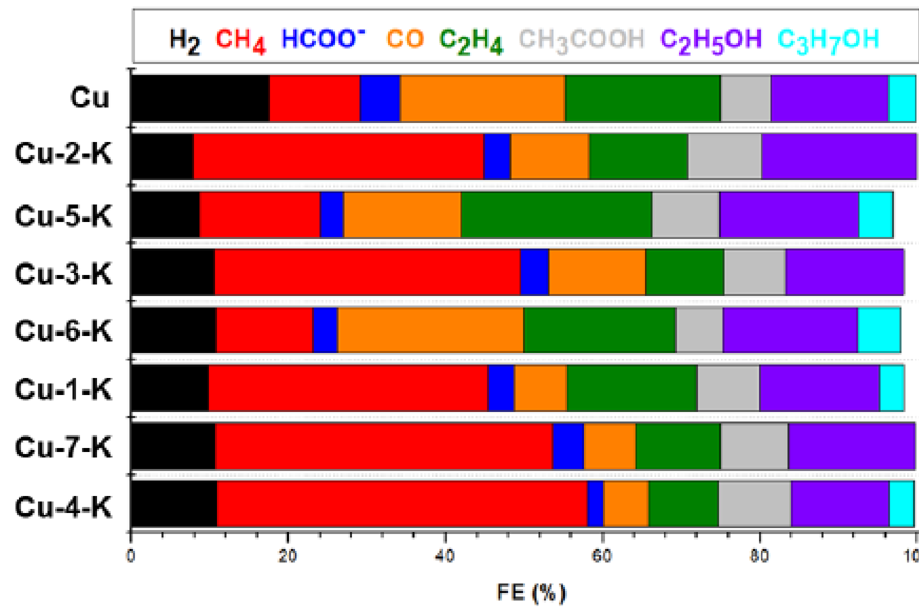
Hai Nam Ha et al submitted 2025

Combining acidic CO2R and surface modification



a





FE_{CH4} = 50 %

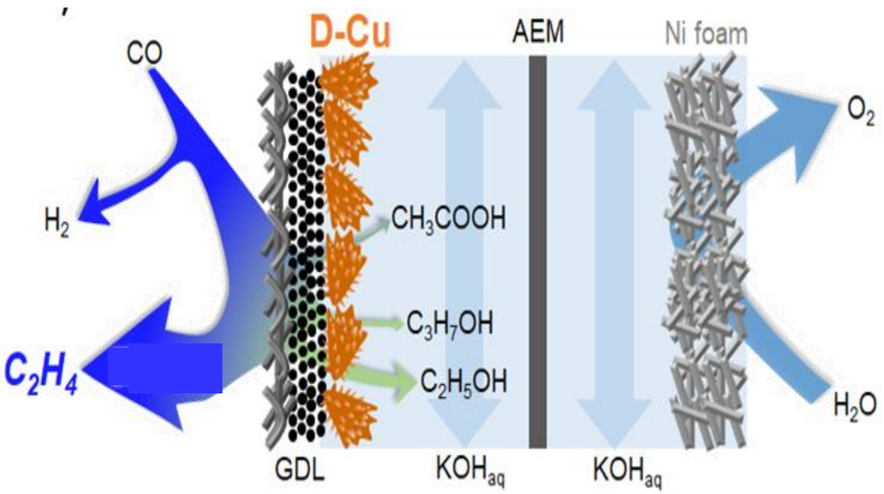
Hai Nam Ha et al submitted 2025

Porous dendritic Cu: CO reduction to ethylene

Alkaline electrolysis:

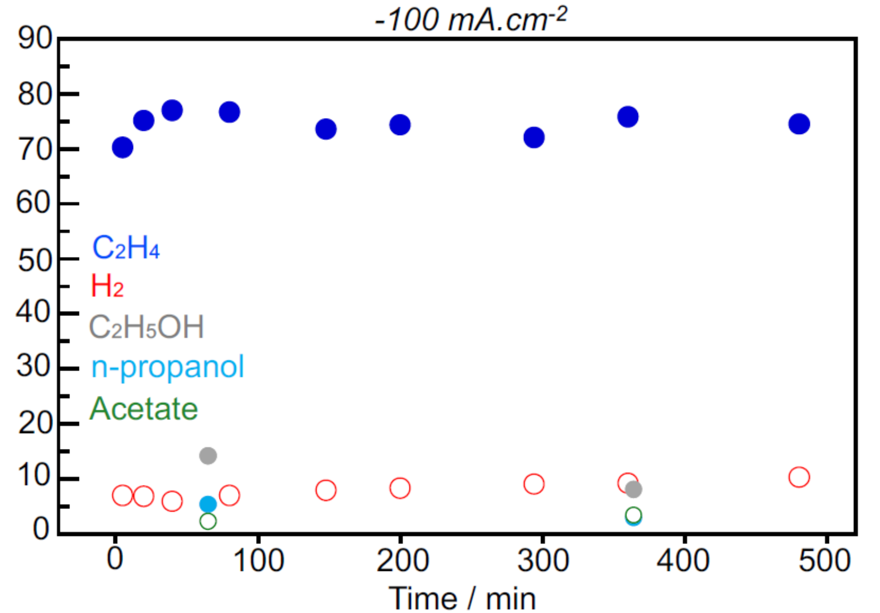
> CO + HO$^-$ $\not\longrightarrow$ carbonate

> anode: Ni foam



Long-term CO reduction using Cu-dend

CO reduction using Cu-dend synthesized with H_2SO_4 2 M



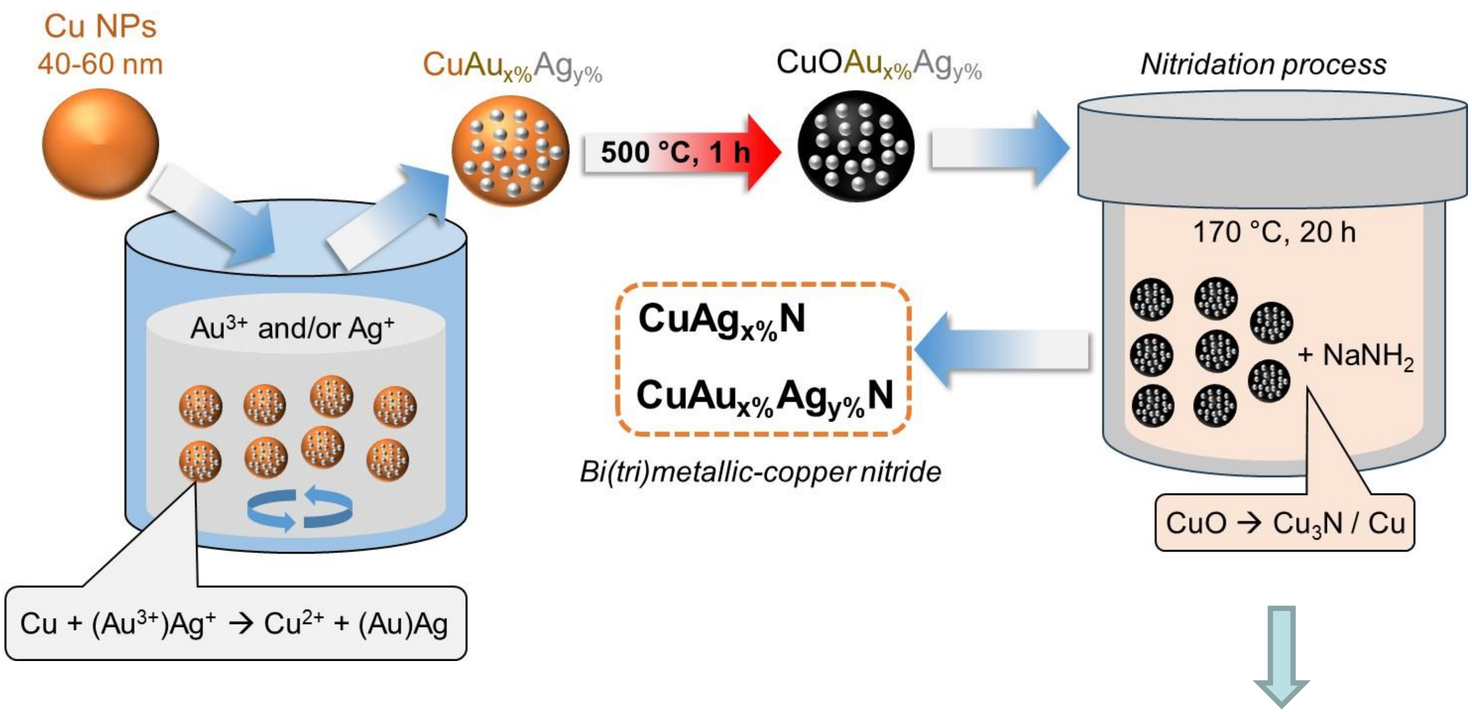
FE for C_2H_4 was stable after 8 h.

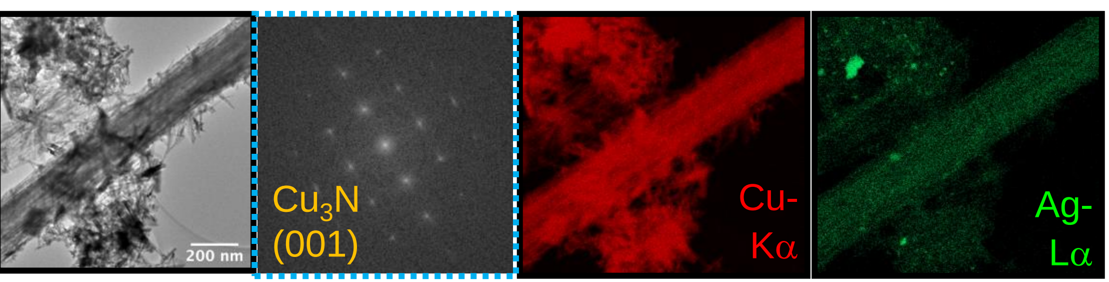
A **selective/stable** catalyst
- Ethylene ~ **80 %**
- C2 (C_2H_4+C_2H_5OH) ~ 93 %

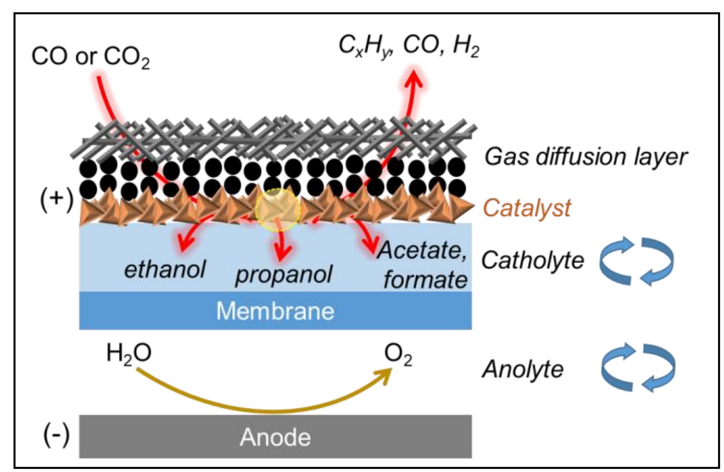
ACS Appl. Mat. Int. 2022, 14, 31933-31941

ACS Catalysis 2022, 12, 10285-10293

Metal-doped Copper Nitride: CO to alcohols !



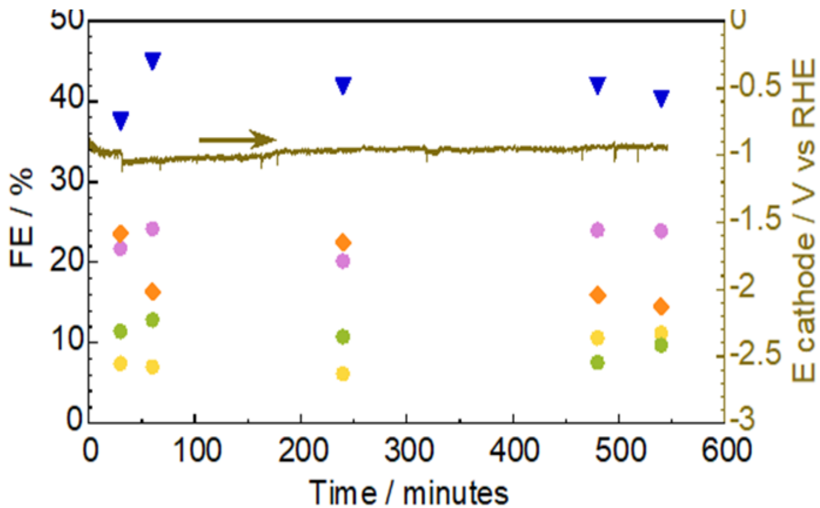




- Cu_3N: nanorods and nanoparticles
- Cu^0 nanoparticles
- Homogeneous Ag doping (3 %)

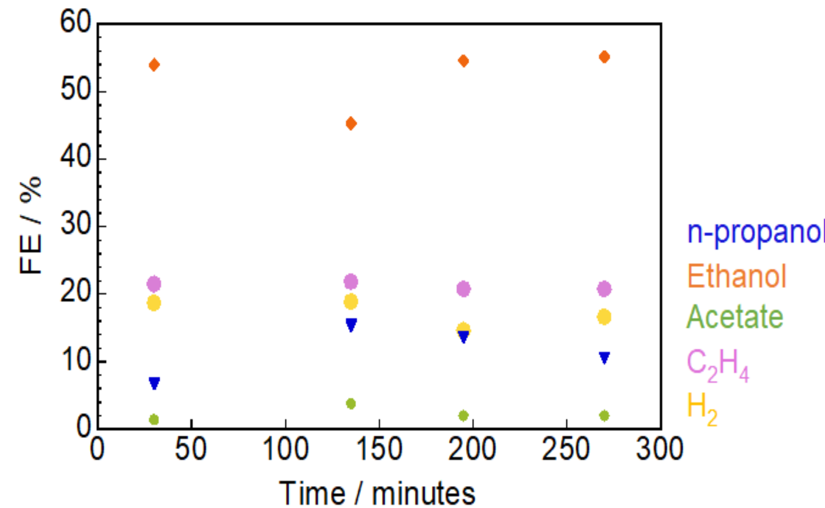
Angew. Chem., 2023, 49, 1521; patent filed.

Ag-doped copper nitride: CO to alcohols !



150 mA.cm^{-2}, **KOH 1M**, flow cell

- **FE propanol: 45 % !**
- FE C_{2+}: 93 % !
- FE liquid products: 75 %!



150 mA.cm^{-2}, **KOH 0.1M**, flow cell

- **FE ethanol: 58 % !**
- FE C_{2+}: 84 % !
- FE liquid products: 67 %!

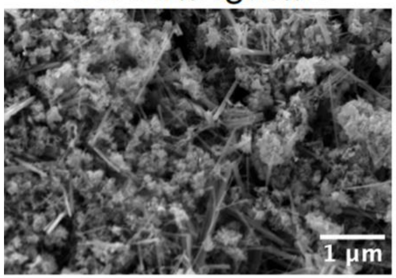
150 mA.cm^{-2}, **KOH 5M** : no H2, liquid: 90% !

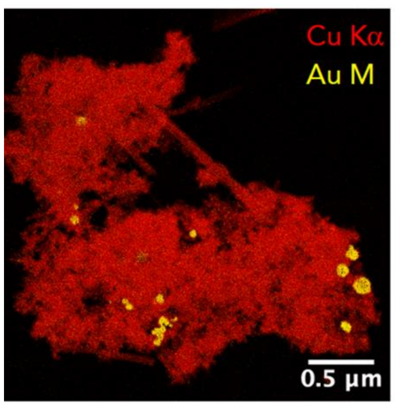
Angew. Chem., 2023, 49, 1521; patent filed.

Ag/Au-doped copper nitride: CO to alcohols !

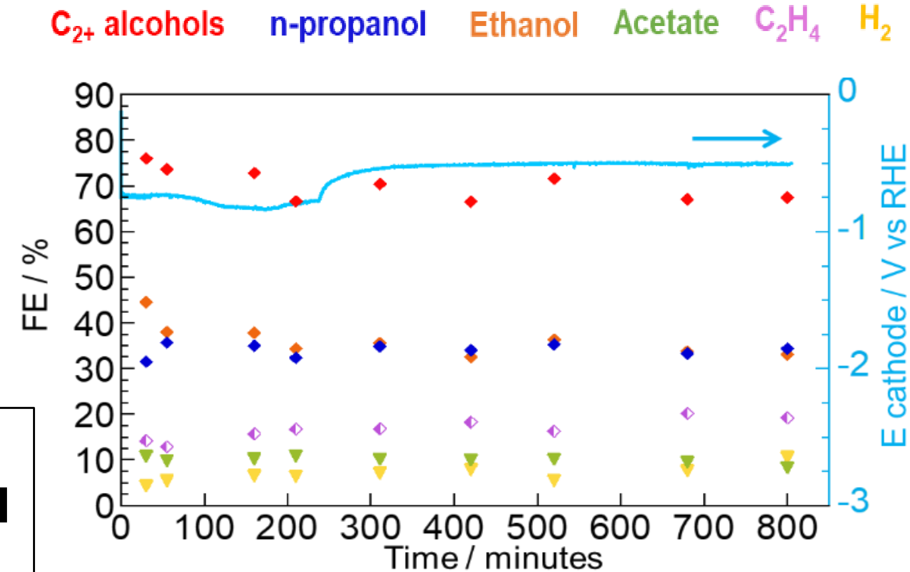
- Cu_3N: nanorods and nanoparticles
- Homogeneous Ag doping
- Small particles of Au

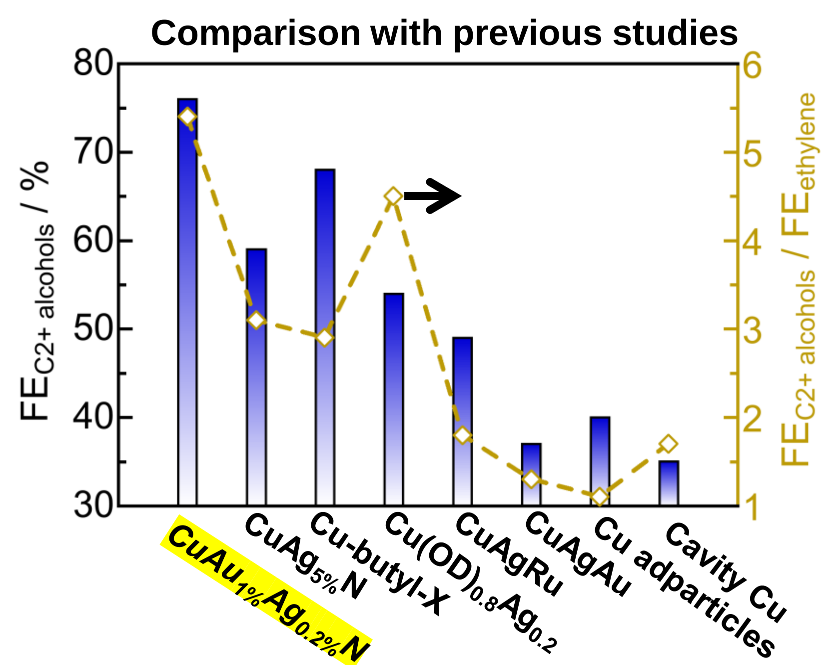
$CuAu_{1\%}Ag_{0.3\%}N$





Faradic efficiency:
76% ethanol/propanol
96 % C2+ products
86 % for C2+ liquids
100 mA cm^{-2}.





- Ag + Au doping > surface carbophobicity ↗ (DFT calculations)

Nature Materials 2025, 24, 900-906

COLLÈGE DE FRANCE 1530

Huan Ngoc Tran

Sarah Lamaison

David Wakerley

Charles Creissen

Jose G Rivera de la Cruz

Alessandro Perazio

Hong-Phong Duong

Hai Nam Ha

- C. Hahn, T. Jaramillo (Univ. Stanford)

- V. Mougel (ETH Zurich)

Sphere Energy

TotalEnergies

Electroréduction du CO_2 en hydrocarbures/alcools : défis et opportunités

CO_2 electroreduction towards hydrocarbons and alcohols:challenges

Marc Fontecave

Laboratoire de Chimie des Processus Biologiques, UMR 8229 CDF/CNRS/UPMC
Collège de France, 11 Place Marcelin Berthelot, 75231 Paris Cedex 05
marc.fontecave@college-de-france.fr; Phone: (0033)144271360