

DE LA RECHERCHE À L'INDUSTRIE

cea

CATALYTIC STRATEGIES FOR THE CONVERSION OF CO₂ AND BIOMASS WASTE

CEA / CNRS | Thibault Cantat



www.cea.fr

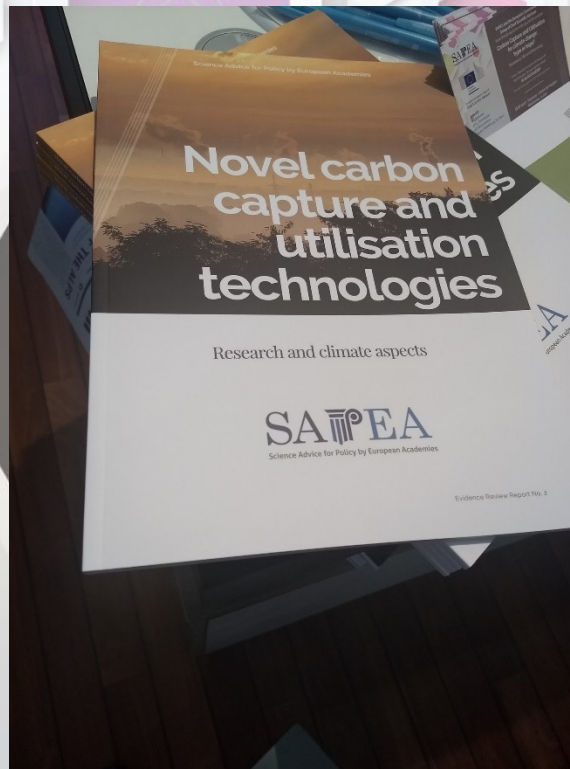
JOURNÉE X – ENS – ESPCI
ENS PARIS – MAY 09-2019

SCIENTIFIC ADVICE ON CCU FOR THE EC



Prof. Elvira Fortunato

Nova University Lisbon and member of the EC's Group of Chief Scientific Advisors



European Commission's Group of Chief Scientific Advisors

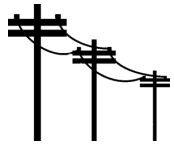


#SAPEA


#CCU

#SAMGroup_EU

Services to society



Electrical power on the grid

Power available on demand 

Heat 

Fuels for mobility 

Industrial products (chemicals, materials, fertilizers)



Sun

Wind

Geothermy

Surfaces

Water

Uranium

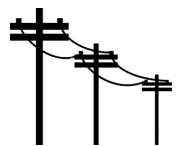
Inorganics

metals
N, Si, P

Carbon feedstocks

Ressources

Services to society



Electrical power on the grid

Power available on demand 

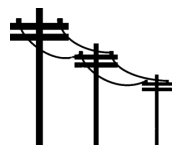
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Fuels for mobility 

Industrial products (chemicals, materials, fertilizers)



Services to society



Electrical power on the grid

Power available on demand

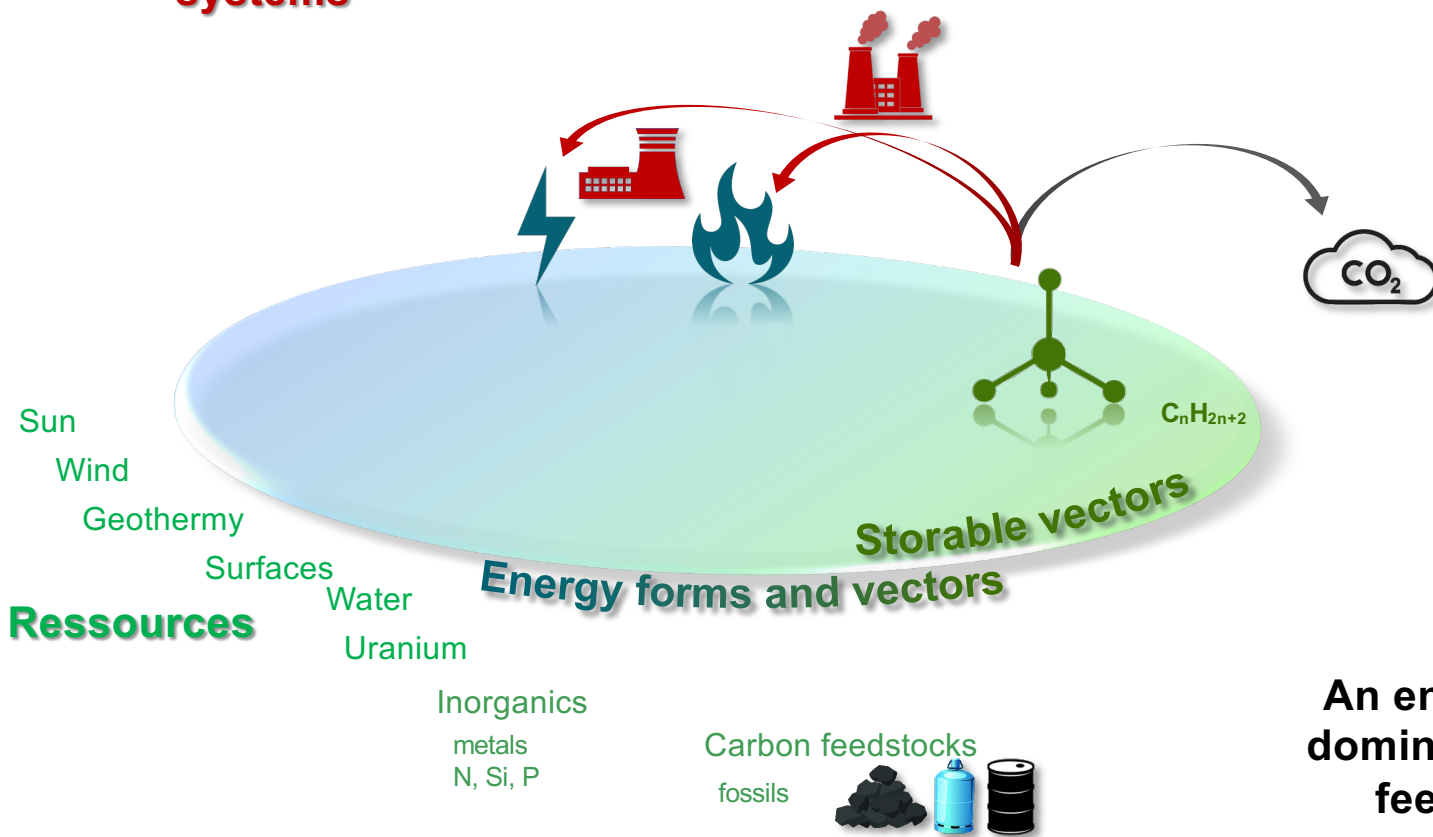
Heat

Fuels for mobility

Industrial products (chemicals, materials, fertilizers)

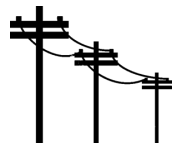


Interconversion systems



An energy system dominated by fossil feedstocks...

Services to society



Electrical power on the grid

Power available on demand

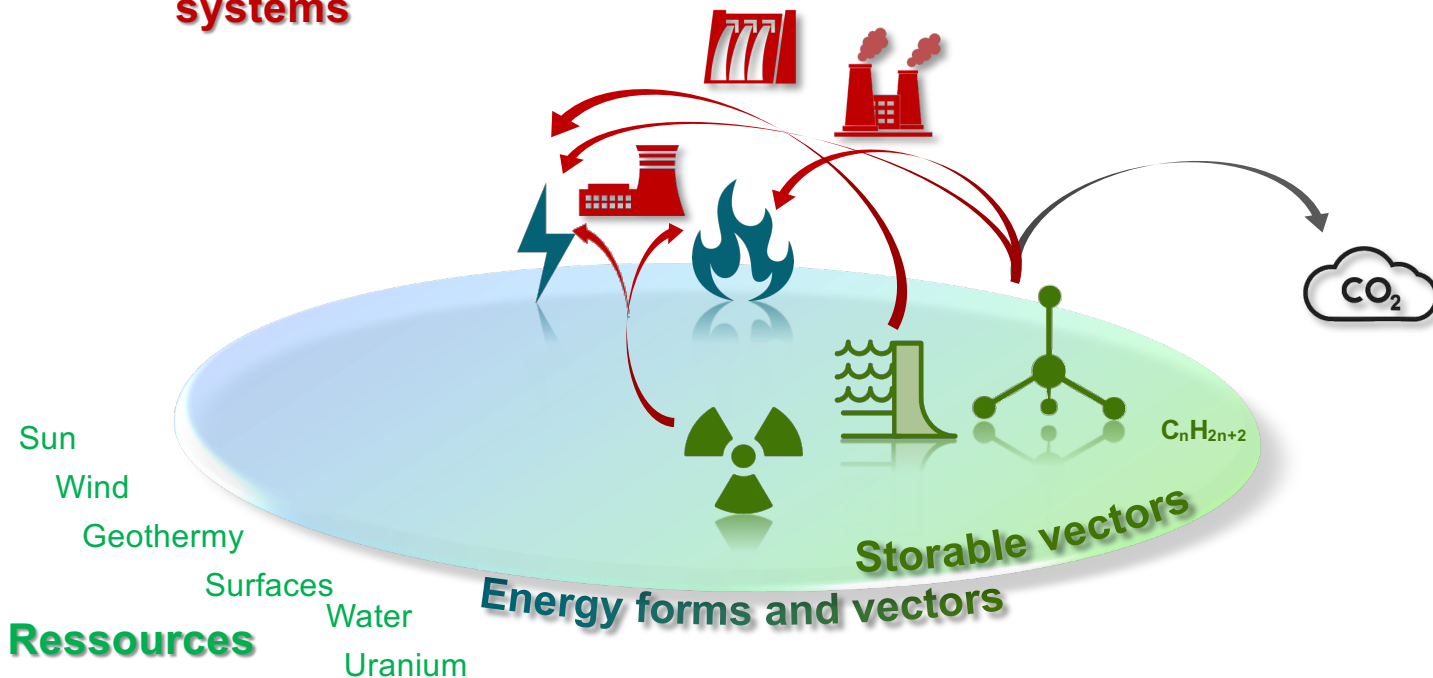
Heat

Fuels for mobility

Industrial products (chemicals, materials, fertilizers)



Interconversion systems



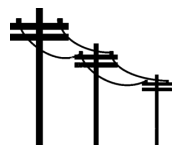
- Ressources**
- Sun
 - Wind
 - Geothermy
 - Surfaces
 - Water
 - Uranium

- Inorganics
- metals
- N, Si, P

- Carbon feedstocks**
- fossils
 - biomass

...which benefits from low carbon energy sources for the production of electricity.

Services to society



Electrical power on the grid

Power available on demand



Heat



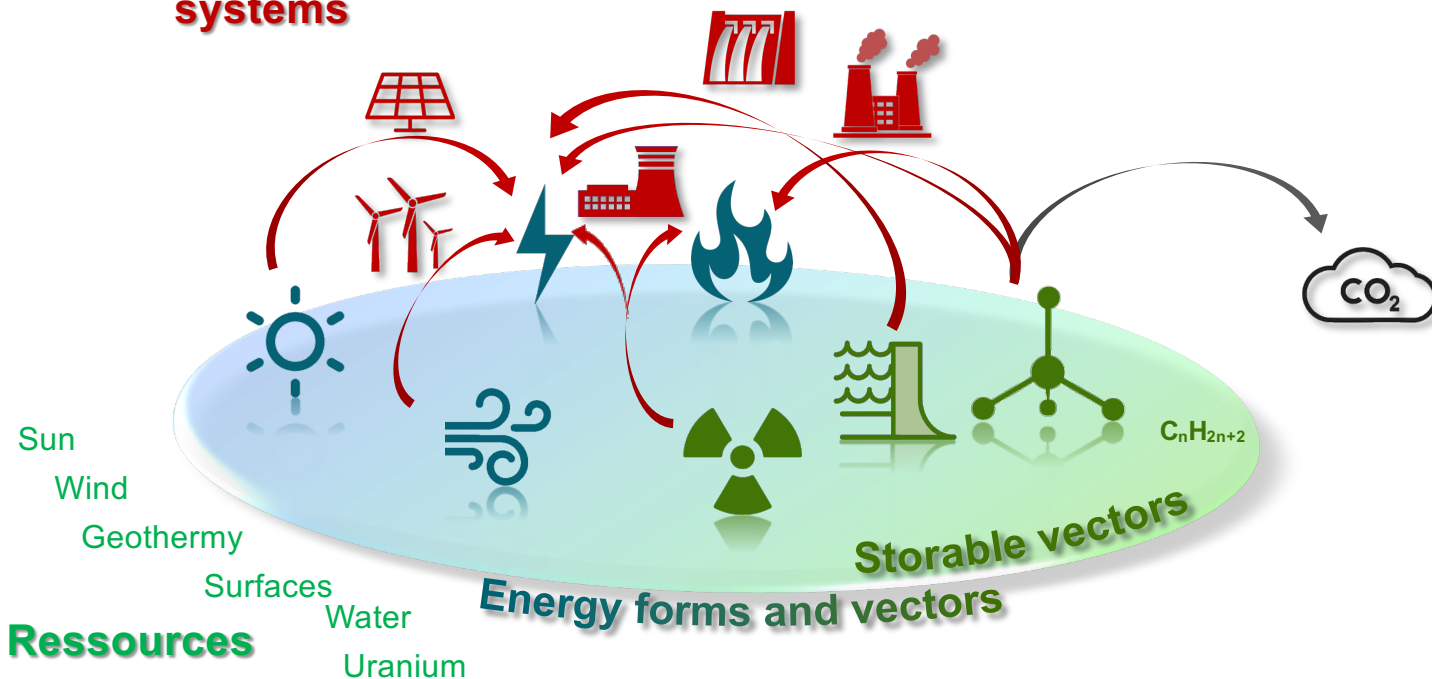
Fuels for mobility



Industrial products (chemicals, materials, fertilizers)



Interconversion systems



Ressources

- Sun
- Wind
- Geothermy
- Surfaces
- Water
- Uranium

Energy forms and vectors

Storable vectors

Inorganics
metals
N, Si, P

Carbon feedstocks

fossils

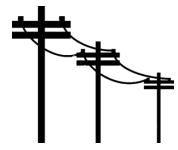


biomass



The inscreasing penetration of renewable energy sources destabilizes the services provided to society...

Services to society



Electrical power on the grid

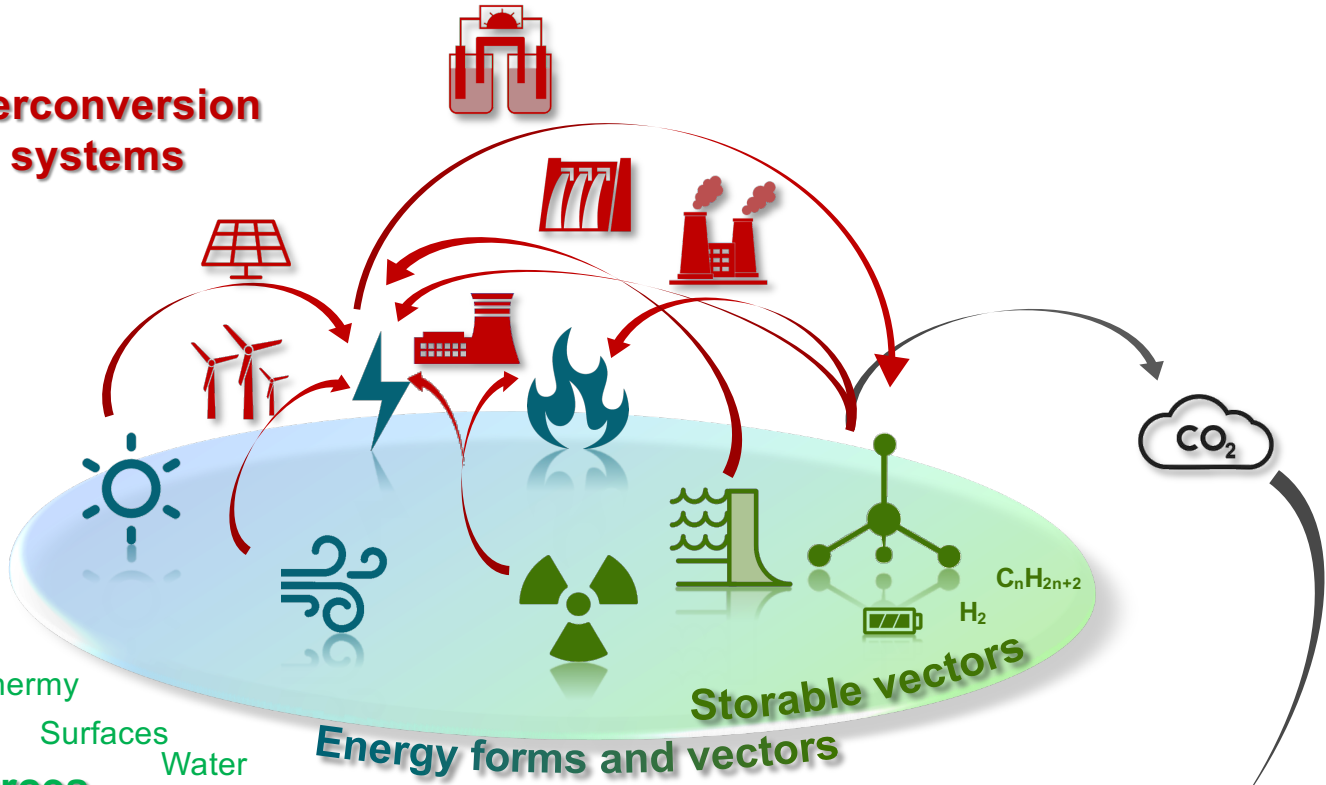
Power available on demand

Heat

Fuels for mobility

Industrial products (chemicals, materials, fertilizers)

Interconversion systems



Ressources

- Sun
- Wind
- Geothermy
- Surfaces
- Water
- Uranium

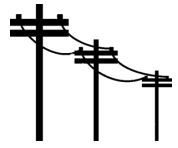
Inorganics
metals
N, Si, P

Carbon feedstocks
fossils

biomass

...and imposes the development of conversion and storage solutions...

Services to society



Electrical power on the grid

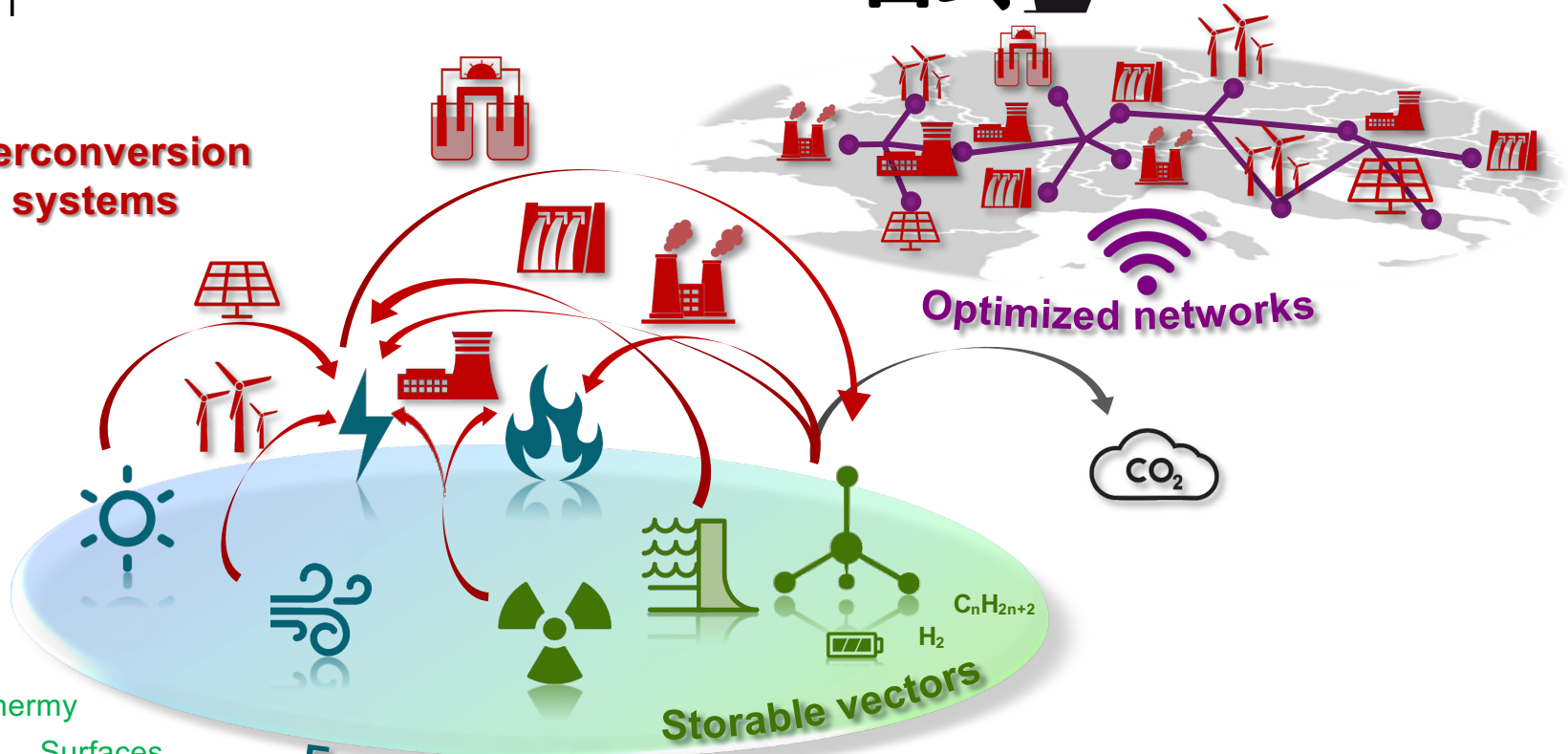
Power available on demand

Heat

Fuels for mobility

Industrial products (chemicals, materials, fertilizers)

Interconversion systems



- Sun
- Wind
- Geothermy
- Surfaces
- Water
- Uranium

Energy forms and vectors

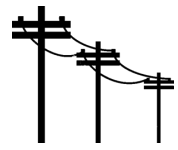
Inorganics
metals
N, Si, P

Carbon feedstocks
fossils

biomass

... to form a multi-vectors and multi-networks energy system to be optimized...

Services to society



Electrical power on the grid

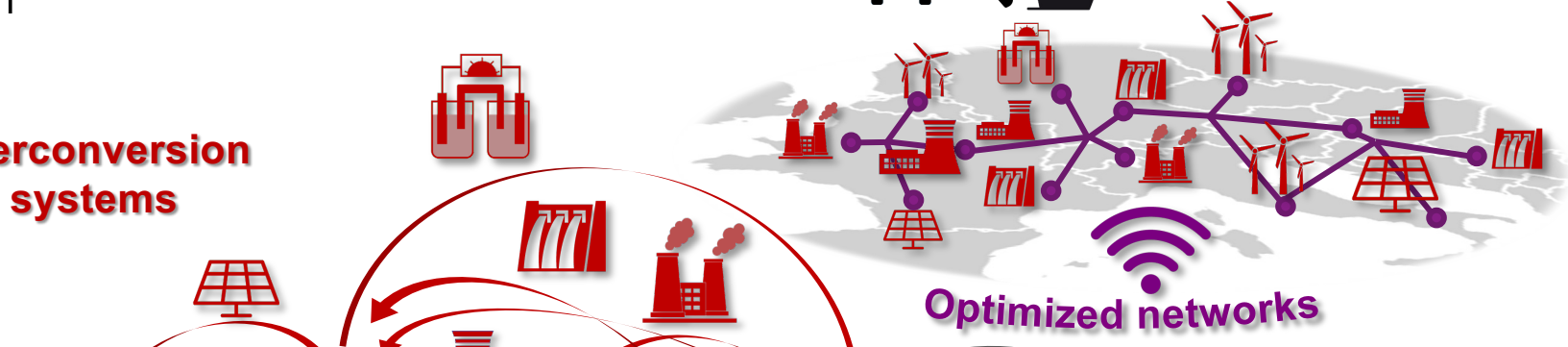
Power available on demand

Heat

Fuels for mobility

Industrial products (chemicals, materials, fertilizers)

Interconversion systems



Optimized networks

Negative CO₂ emissions

Ressources
Sun
Wind
Geothermy
Surfaces
Water
Uranium

Energy forms and vectors

Storable vectors
C_nH_{2n+2}
H₂

Closed materials cycles
Inorganics
metals
N, Si, P

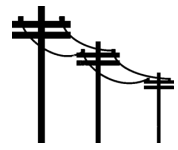


Carbon feedstocks
fossils
biomass

... while respecting the environment and ensuring closed matter cycles, to build a sustainable energy system.



Services to society



Electrical power on the grid

Power available on demand

Heat

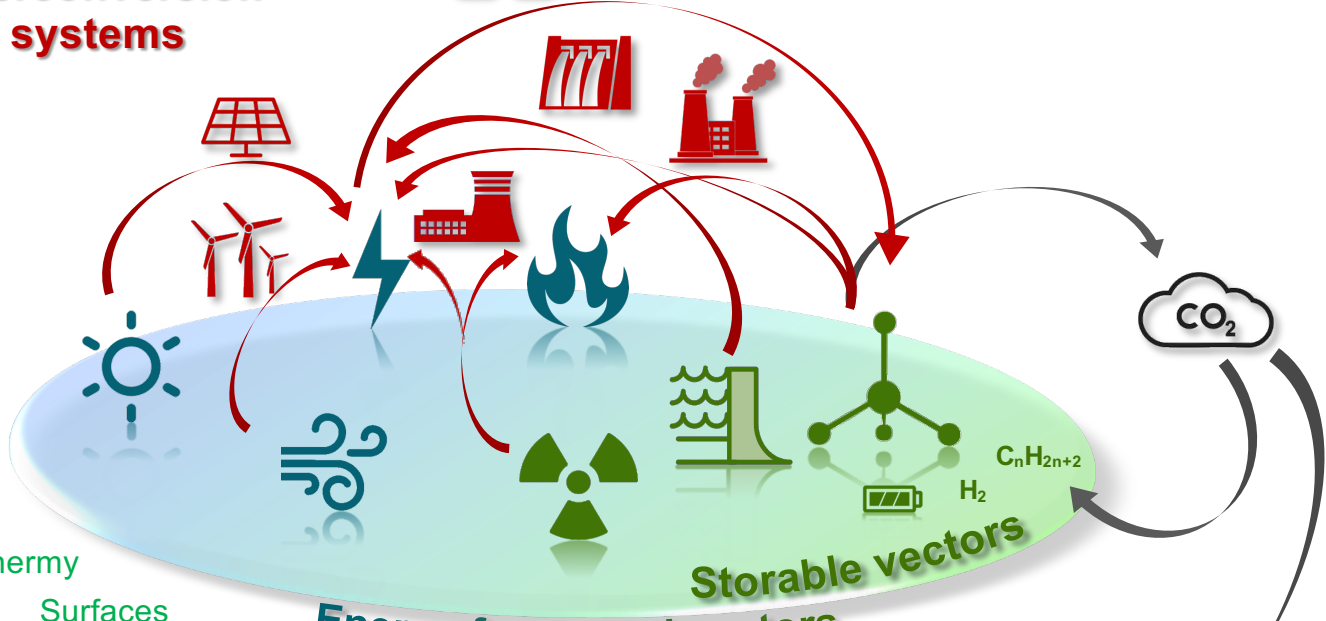
Fuels for mobility

Industrial products (chemicals, materials, fertilizers)

CCU vs biomass?

CCU vs batteries, H₂ fuel cells?

Interconversion systems



- Sun
- Wind
- Geothermy
- Surfaces
- Water
- Uranium

Energy forms and vectors

Storable vectors
C_nH_{2n+2}
H₂

Ressources

Inorganics
metals
N, Si, P



Closed materials cycles

Carbon feedstocks

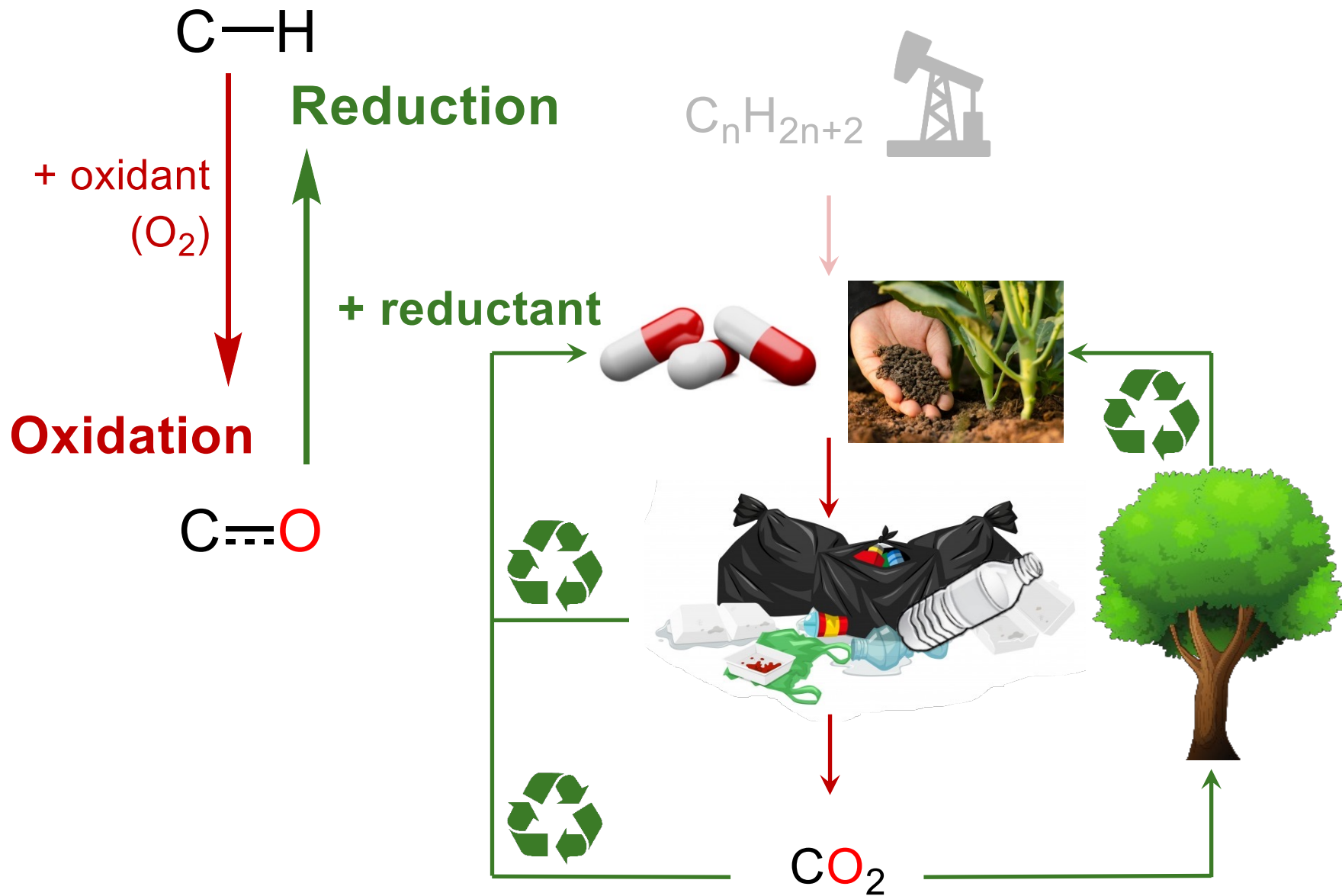


biomass

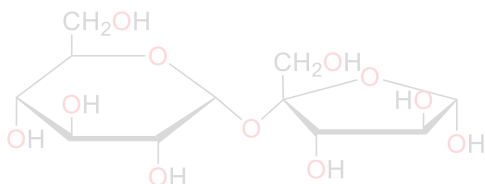


Carbon Capture and Utilization is an option to achieve sustainability in an energy system

A CHANGE OF PARADIGM



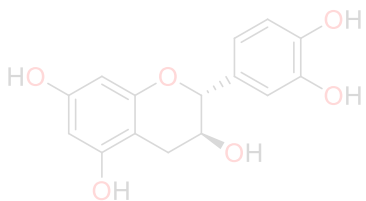
RENEWABLE CARBON FEEDSTOCKS



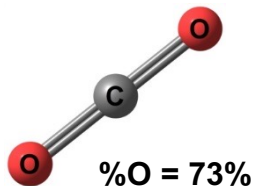
Saccharose
(beetroot)

%O = 27%

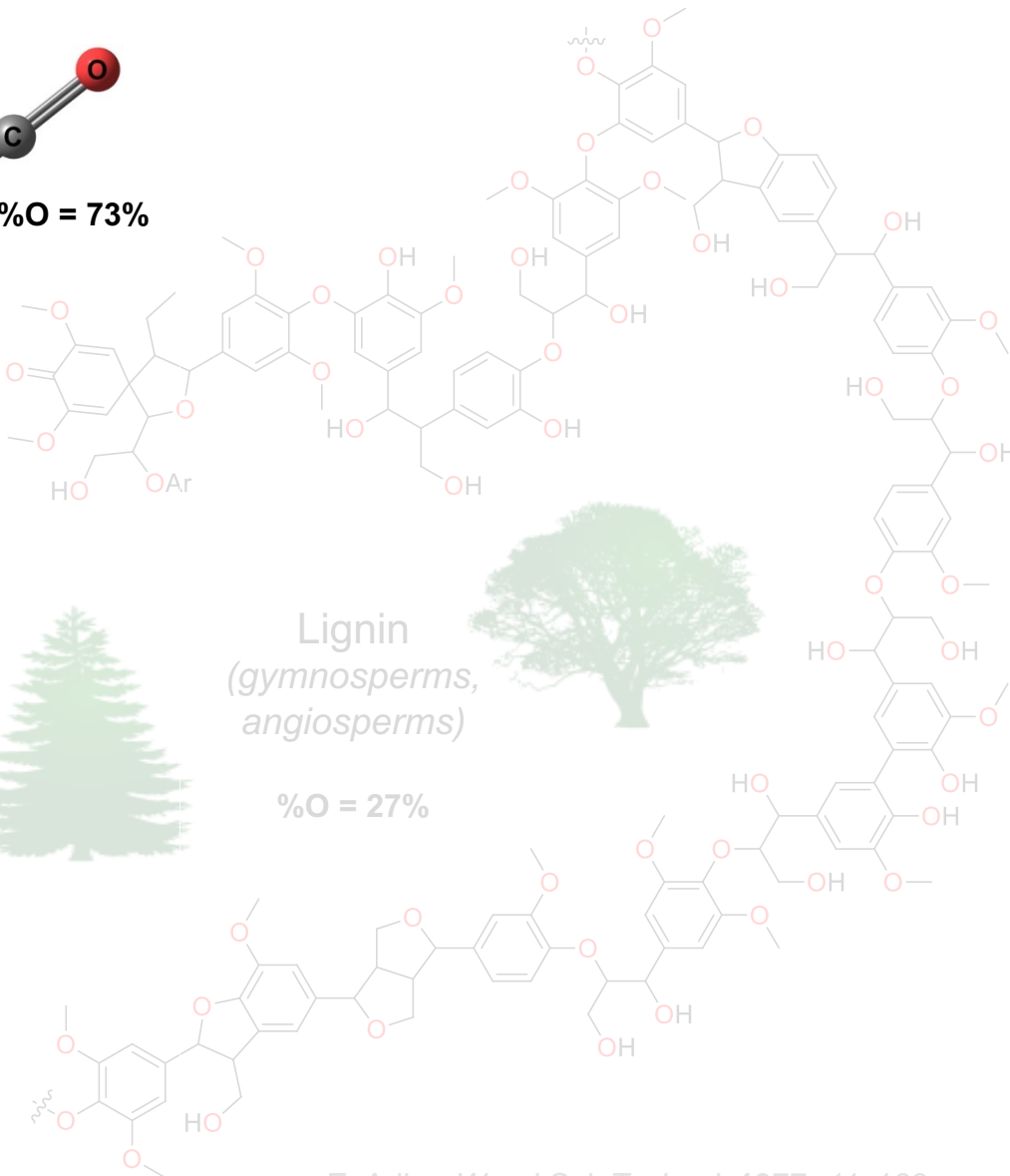
D-catechin
(*Senegalia catechu*)



%O = 33%



%O = 73%

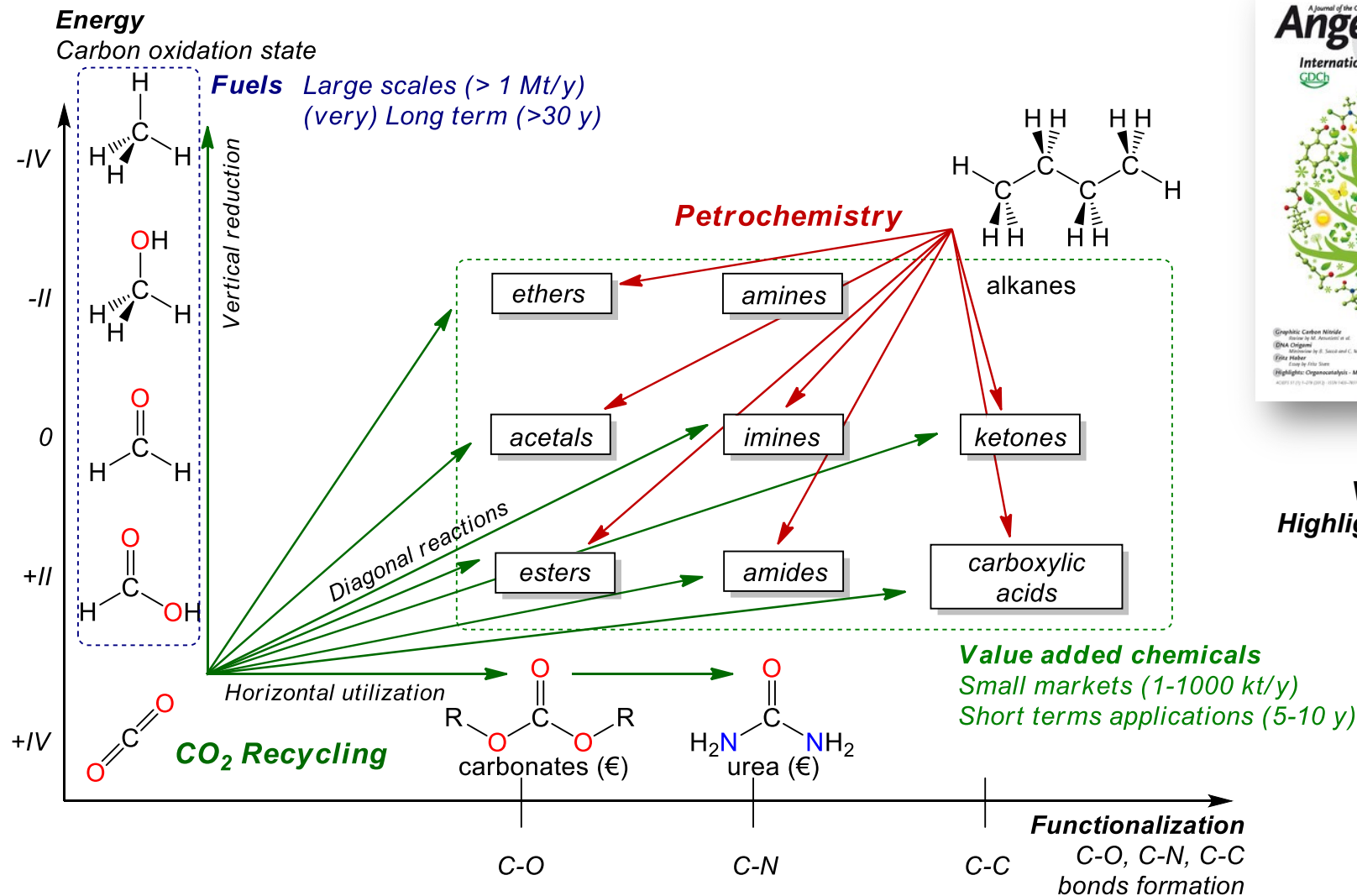


Lignin
(gymnosperms,
angiosperms)

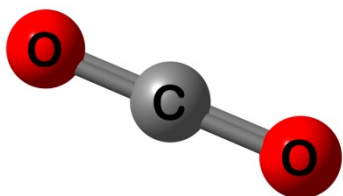
%O = 27%



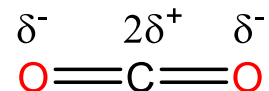
VARIOUS OPPORTUNITIES TO CO₂ RECYCLING...



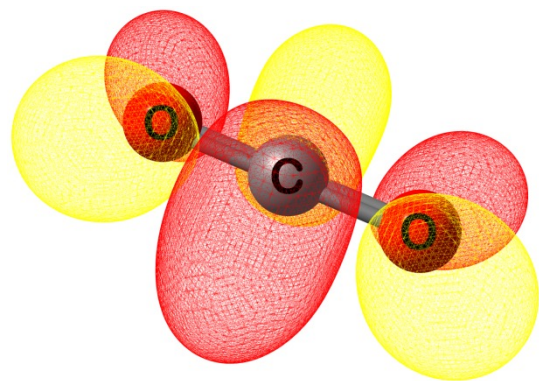
CO₂ functionalization and reduction steps
coupled in a single process



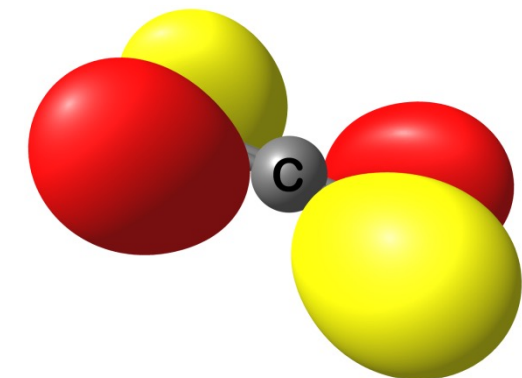
C-O: 1.16 Å



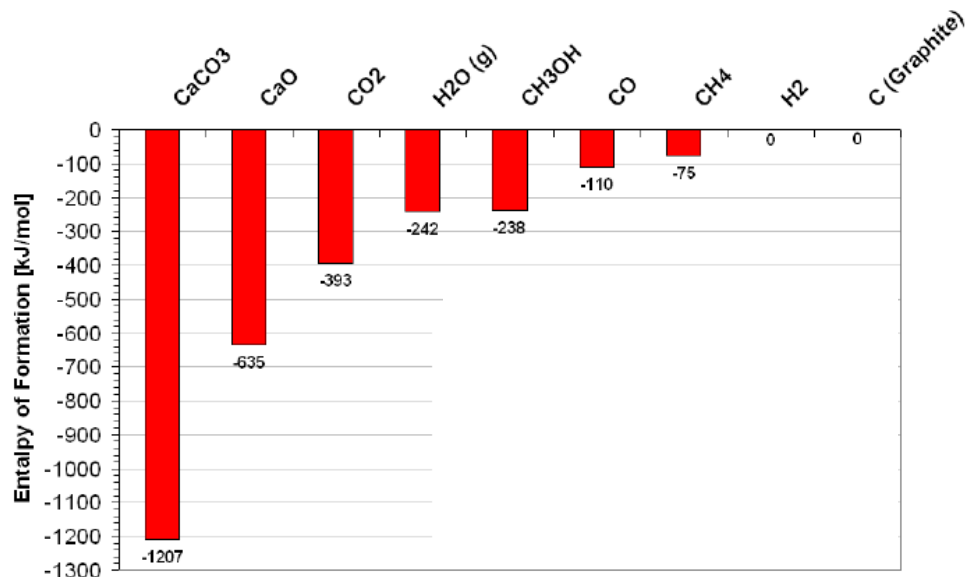
- Non-polar
- Electrophilic at C (Lewis acid)
- Nucleophilic at O (Lewis base)



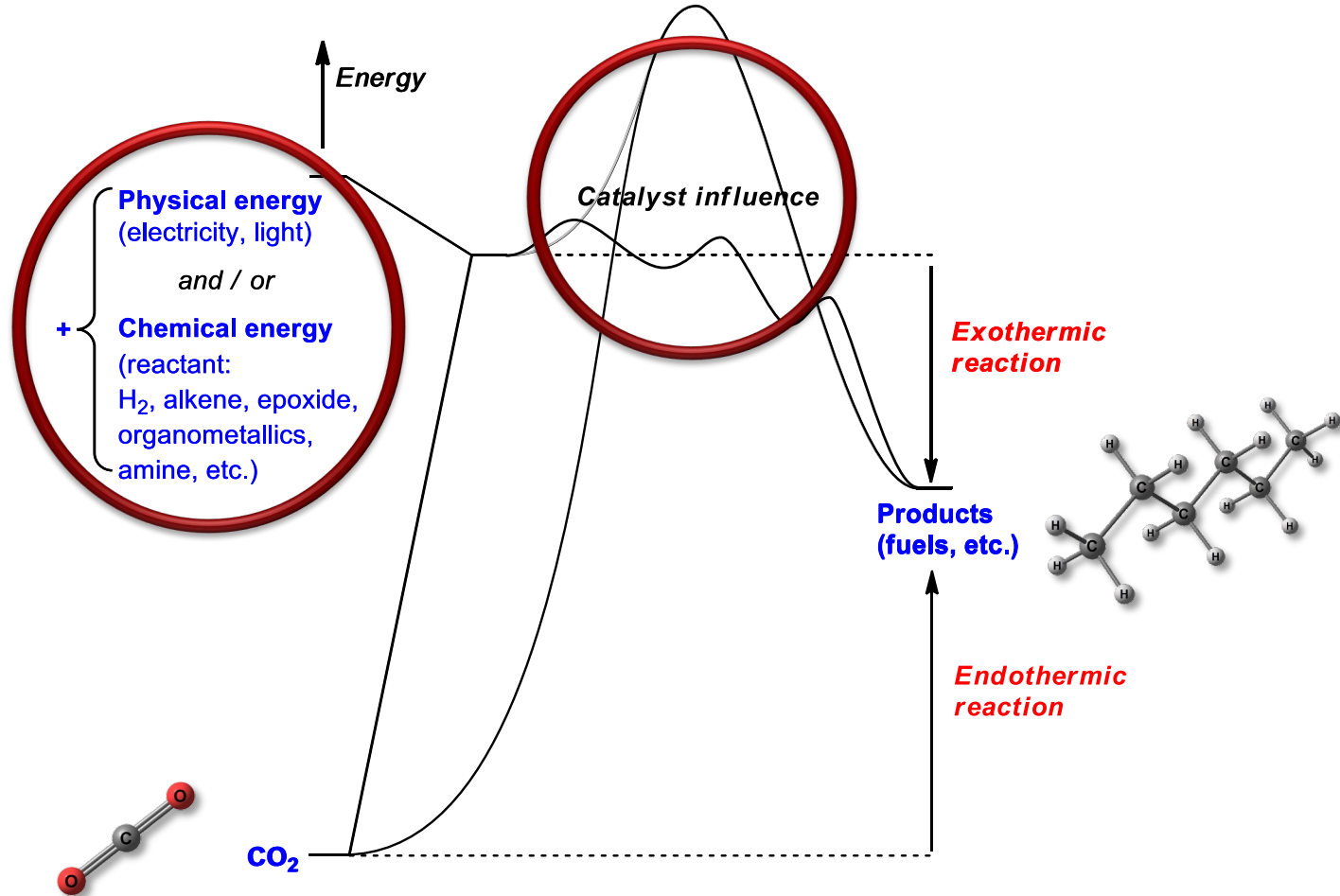
— LUMO
2π_u



↕ HOMO
1π_g

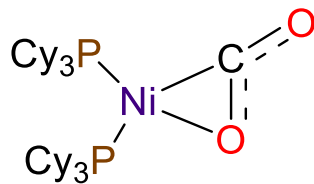
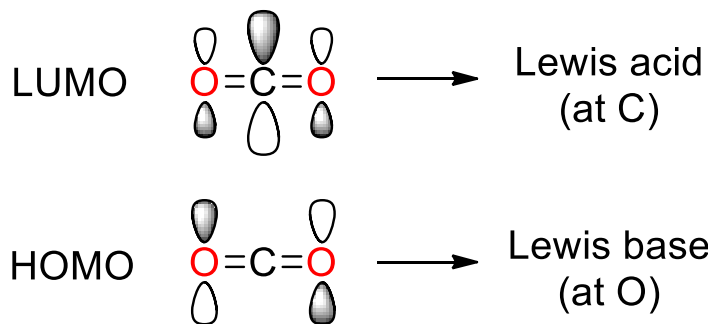


CHEMICAL TRANSFORMATION OF CO₂

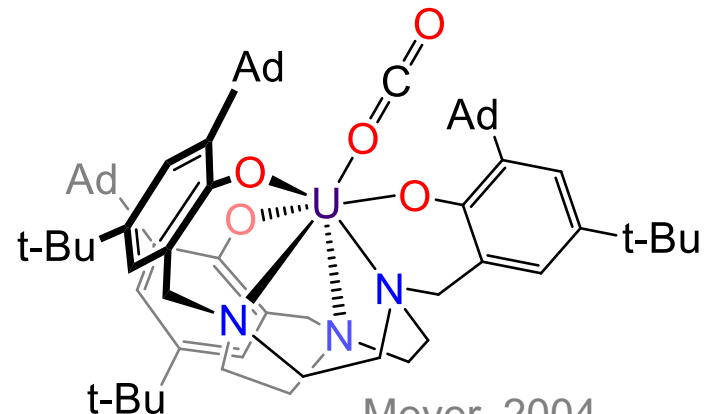


Two energetic challenges: thermodynamic and kinetic

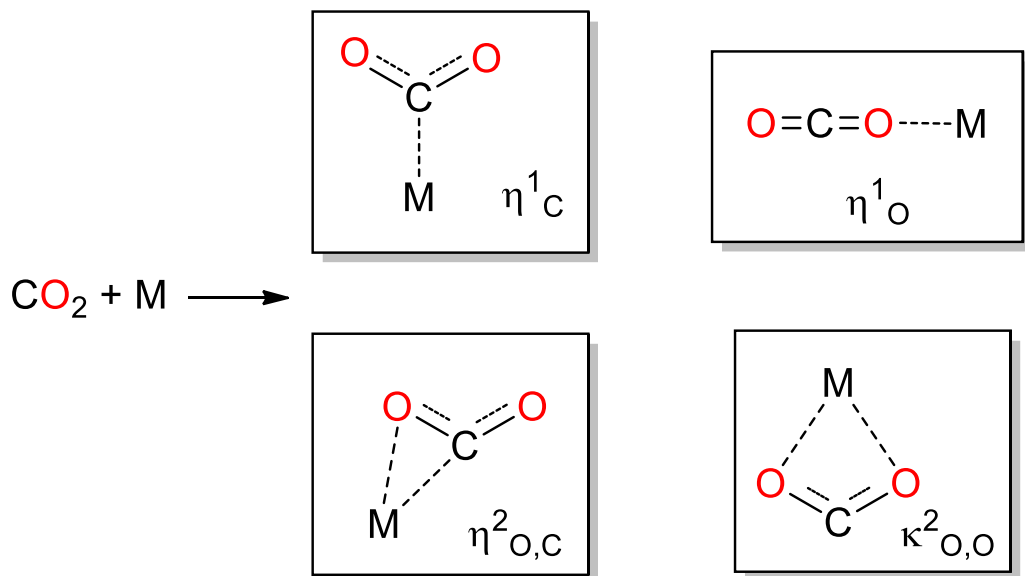
CO₂ ACTIVATION BY TRANSITION METALS



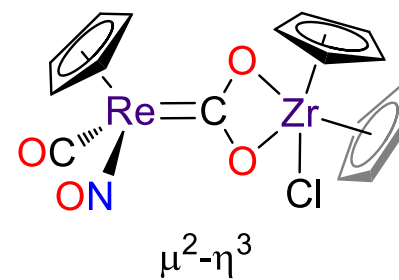
Aresta, 1975



Meyer, 2004



Bimetallic activation



Cutler, 1986

CO₂ ACTIVATION BY ORGANIC COMPOUNDS

■ Activation by Frustrated Lewis Pairs (FLPs)



Lewis pair formation
prevented by sterics

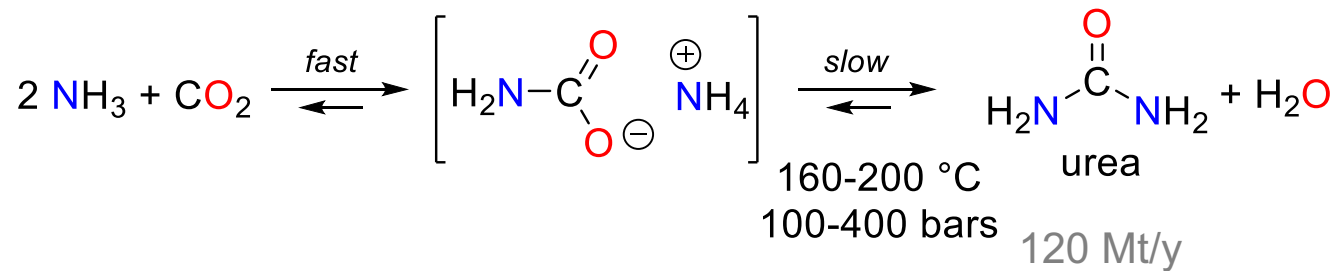


CO₂ CONVERSION IN THE INDUSTRY

INDUSTRIAL PROCESSES UTILIZING CO₂

Industrial routes from CO₂

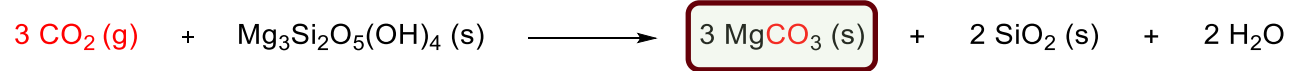
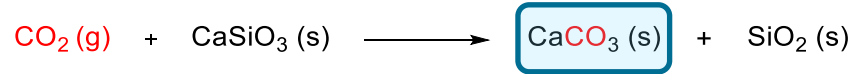
- Bosch-Meiser process for urea production



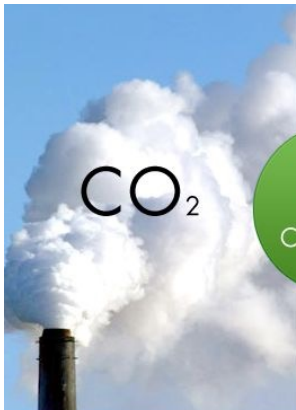
CO₂ CAPTURE AND MINERALIZATION



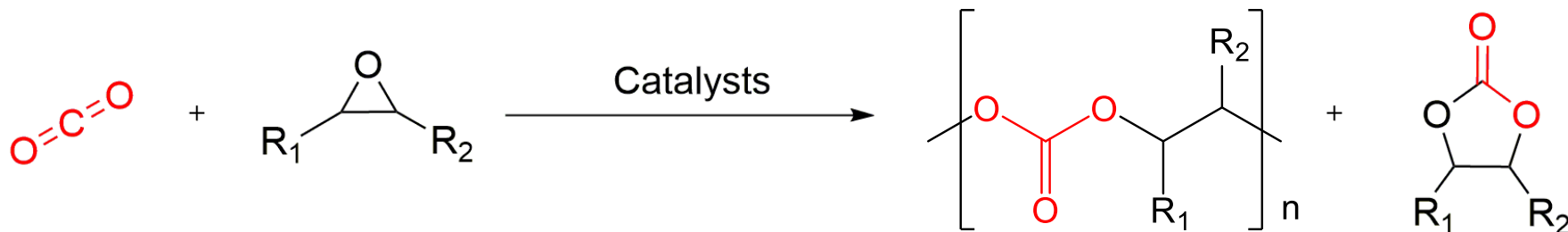
Strategy



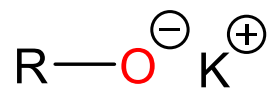
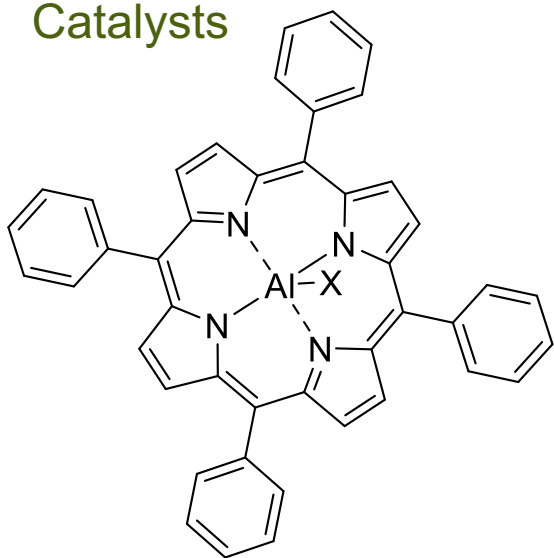
Brick and ciment made from CO₂



Strategy



Catalysts



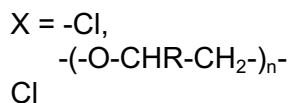
+



Metal free catalyst

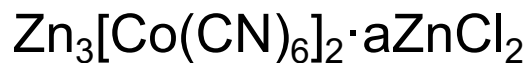


1st generation: Inoue
et al (1983)



J. Am. Chem. Soc., Vol. 105, No. 5, 1983

J. Am. Chem. Soc., 2016, 138, 11117

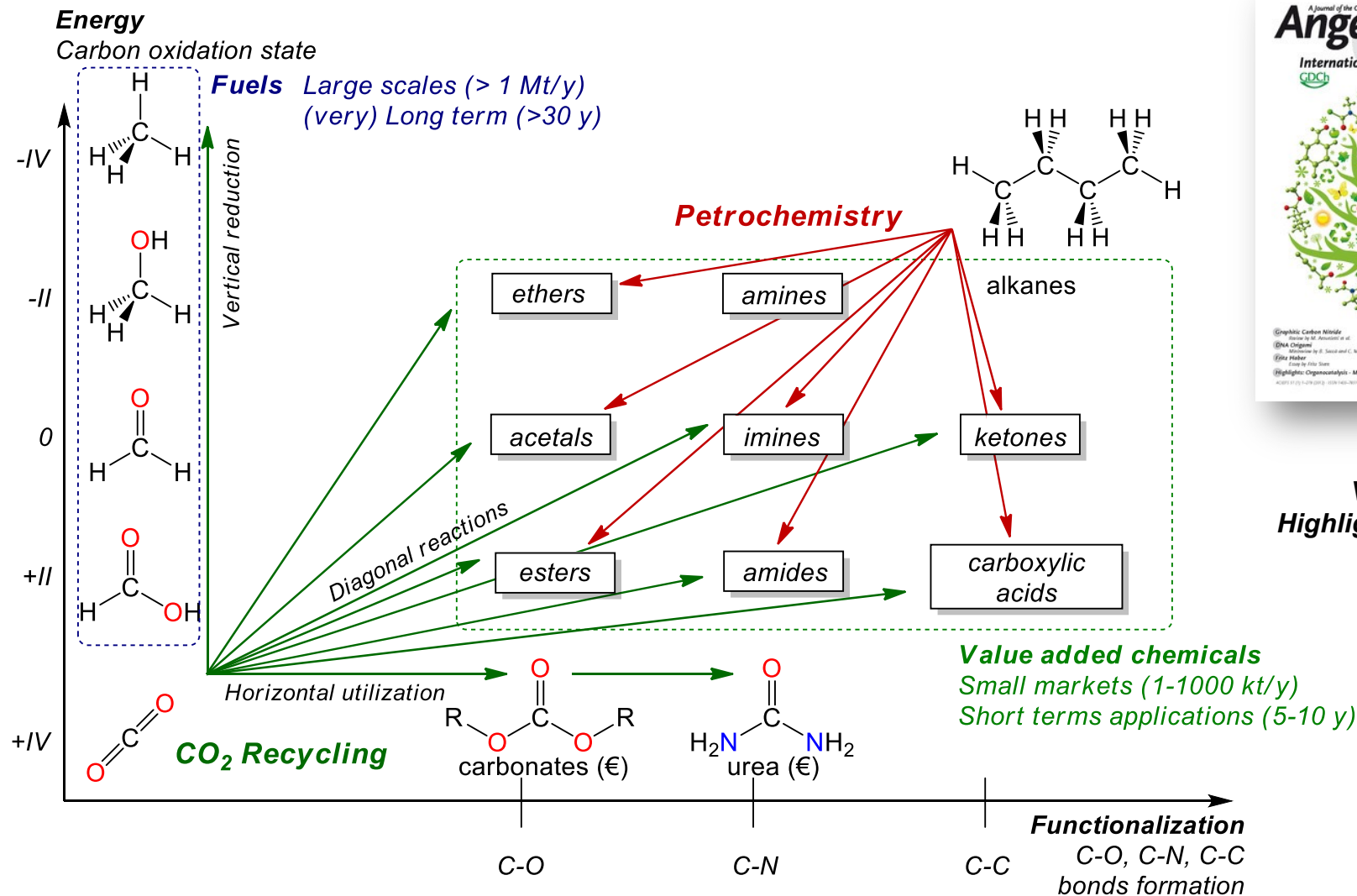


Industrial catalyst

Double metal cyanide



VARIOUS OPPORTUNITIES TO CO₂ RECYCLING...



COVER
VIP Paper
Highlighted in Nature

CO₂ functionalization and reduction steps
coupled in a single process

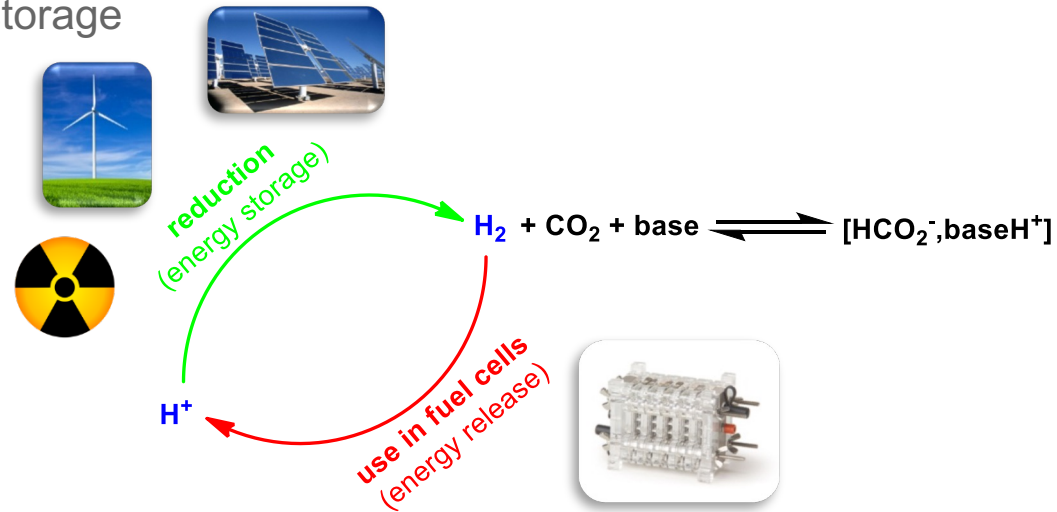


CO₂ REDUCTION TO FUELS

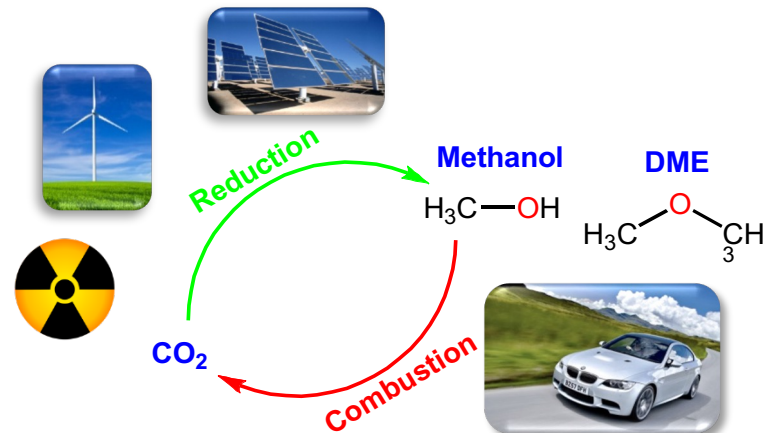
CO₂ FOR ENERGY STORAGE

CO₂ reduction: recycling to fuels

- CO₂ hydrogenation for hydrogen storage
 - CO₂ to formic acid
 - CO₂ to methanol

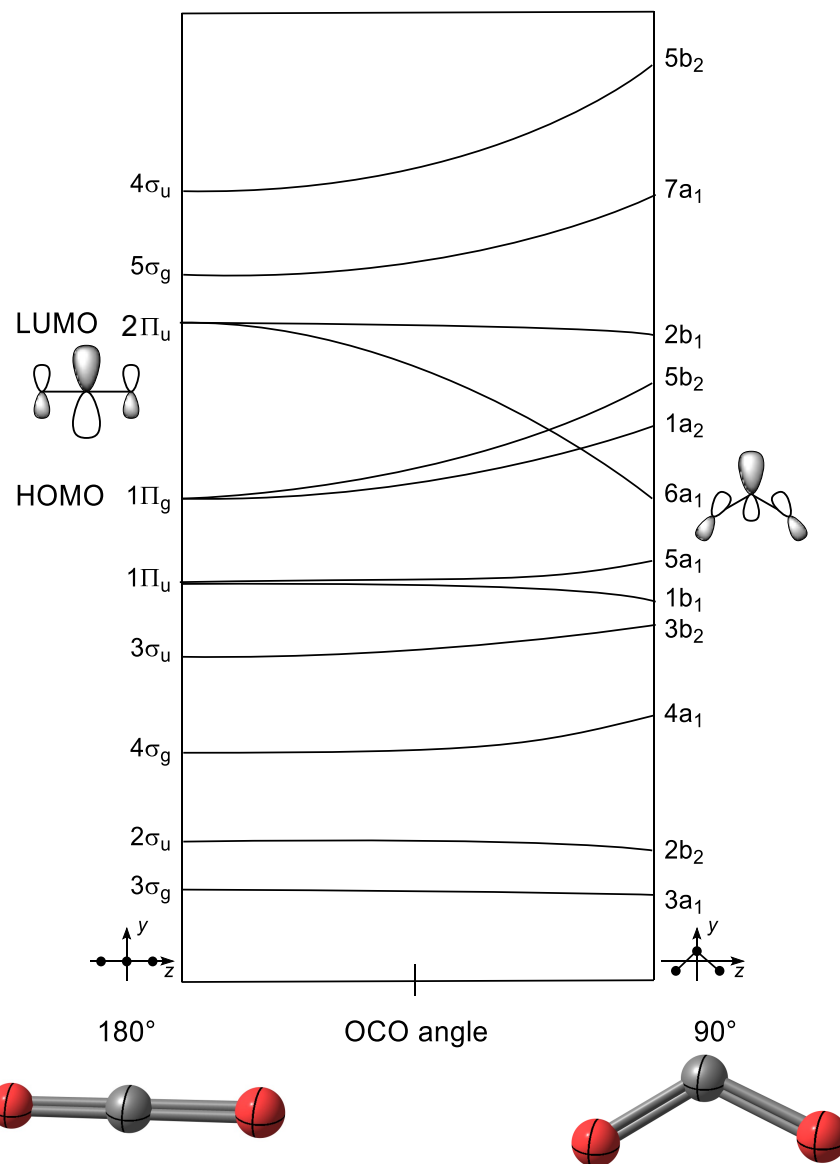
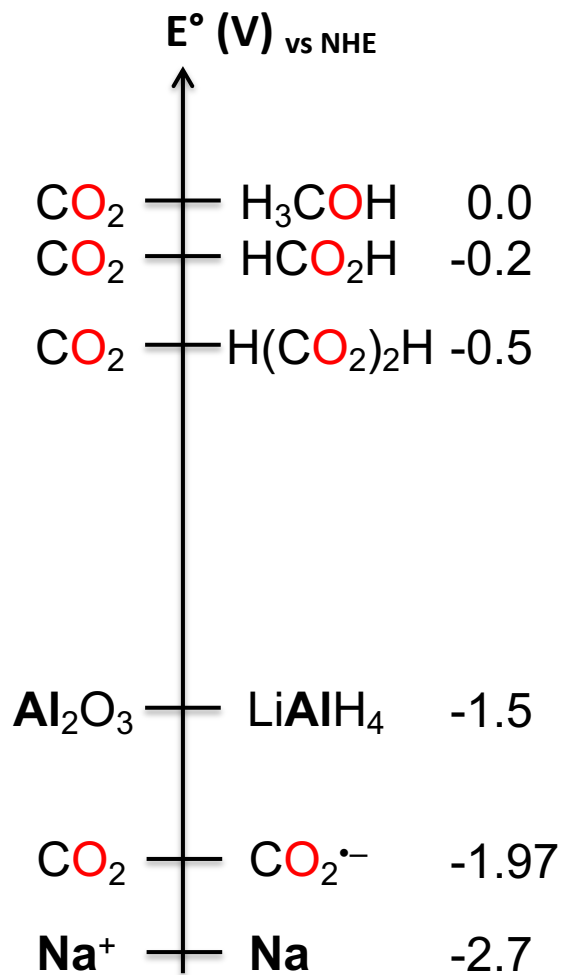


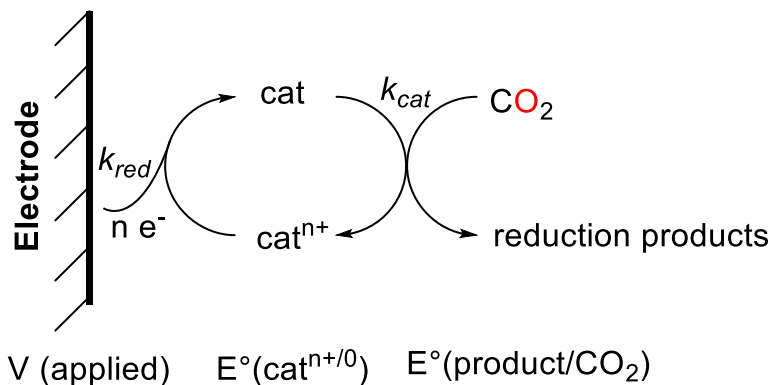
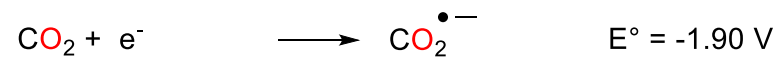
- CO₂ electro- and photoelectrocatalytic reduction to CO, formic acid, methanol, etc.



CO₂ REDUCTION: THERMODYNAMICS

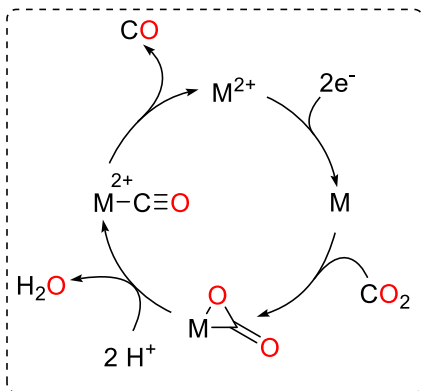
Thermodynamics



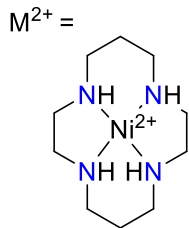
Principle of CO₂ electroreductionMulti-electron reduction of CO₂ in water (pH=7) vs. SCE

CO₂ ELECTROREDUCTION TO CO

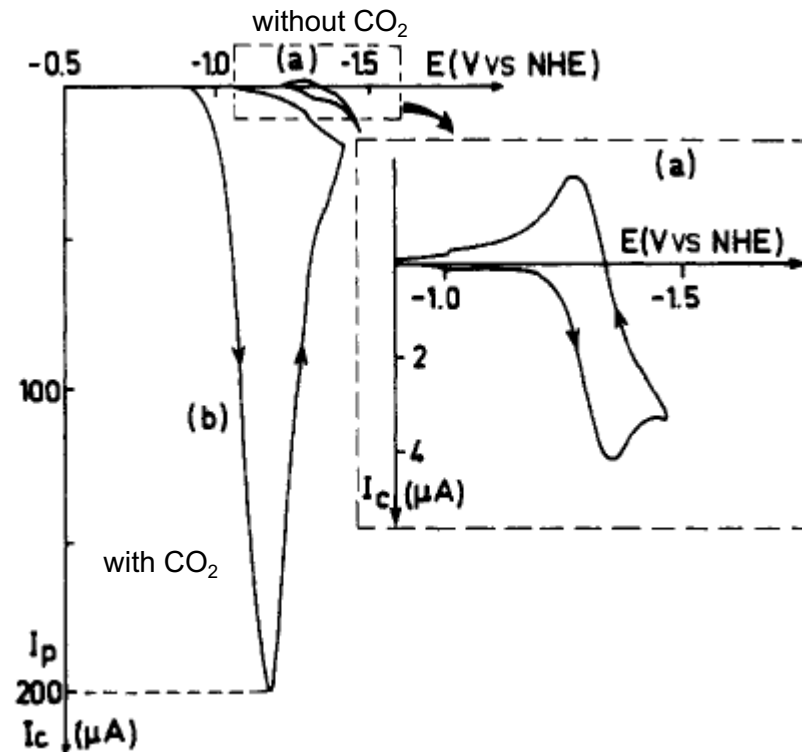
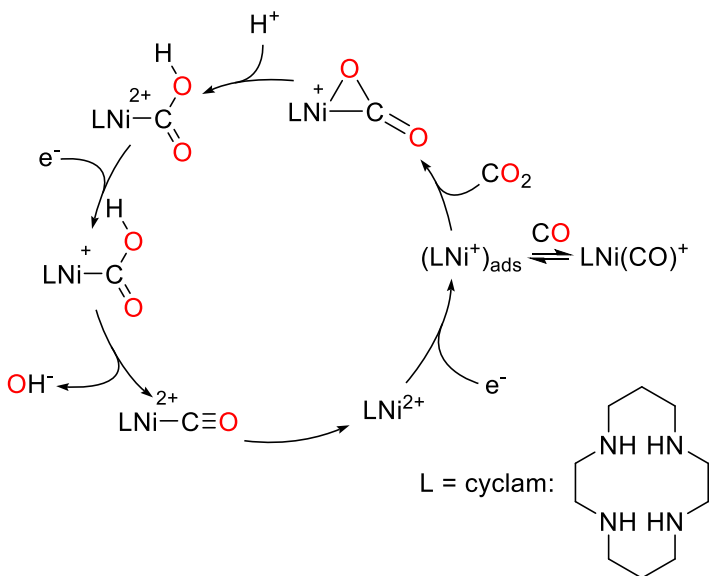
Mechanistic scheme



Example:



Savage, 1984

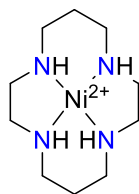


Voltammogram for the electroreduction of CO₂ catalyzed by Ni(cyclam)²⁺

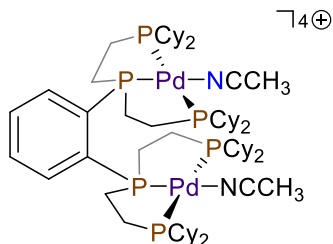
Overpotential: $\eta = 0.55 \text{ V}$ ($V = -1.31 \text{ V}$)
 TurnOver Frequency: TOF = 1250 s⁻¹

CO₂ ELECTROREDUCTION TO CO

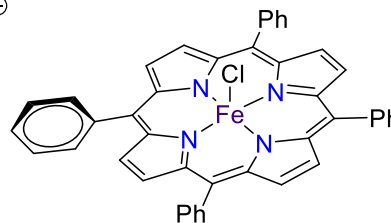
Improved catalysts and performances



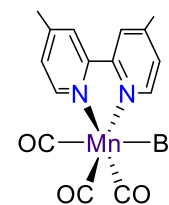
Savage, 1984



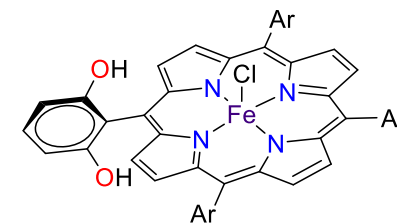
Dubois, 1990



Savéant, 1994



Deronzier, 2011



Savéant, 2012

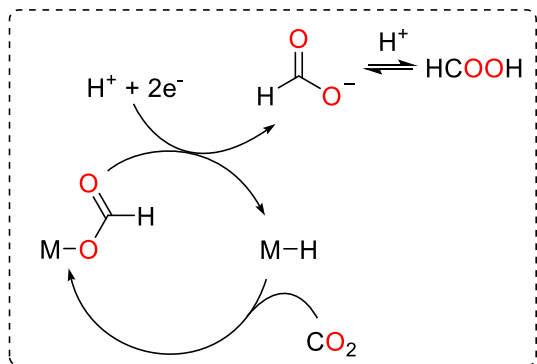
η (V)	0.6	0.8	0.9	0.5	0.5
$\log \text{TOF}$ (s ⁻¹)	2.2	0.7	2	-0.1	3
$\log \text{TOF}_0$ (s ⁻¹) at $\eta = 0 \text{ V}$	-7.1	-7.5	-14	-8.4	-4.6

- Concomitant H₂ evolution is observed for all the catalysts
- Fine management of the local concentration of H⁺ is crucial



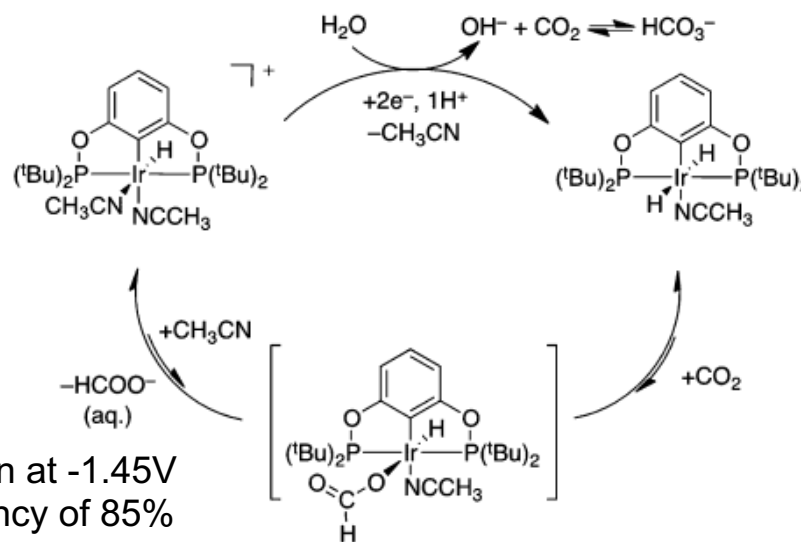
Molecular catalysts:

Mechanistic scheme



Copper, rhodium and iridium complexes are good catalysts

Example with iridium:



Formic acid production at -1.45V
with a Faraday efficiency of 85%
and a TOF of 20 s⁻¹

High selectivity: Low contamination of the products with H₂ and CO

Brookhart, JACS **2012**, 134, 5500

- Formate dehydrogenase (FDH) selectively reduces CO₂ to formate at the thermodynamic potential with a TOF of ca. 280 s⁻¹
- Industrial developments are underway, using modified copper(0) metal electrodes (Farady efficiencies >90%, overpotential ~1V)

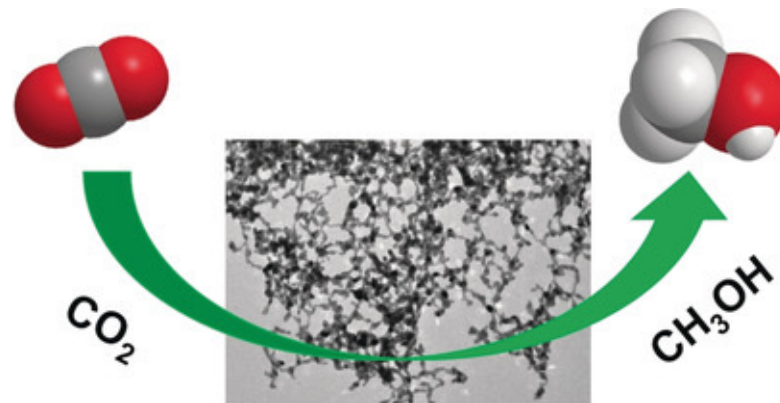
CO₂ ELECTROREDUCTION TO METHANOL

A completely different story !



- Much more difficult because of multiple H⁺ and e⁻ transfers to synchronize
- Few successes:

Faradaic efficiency of CH₃OH production can reach 80.0% with a current density of 31.8 mA.cm⁻²

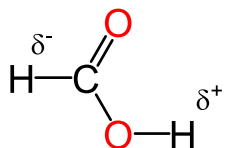


CO₂ ELECTROREDUCTION TO CH₃OH VIA HCOOH

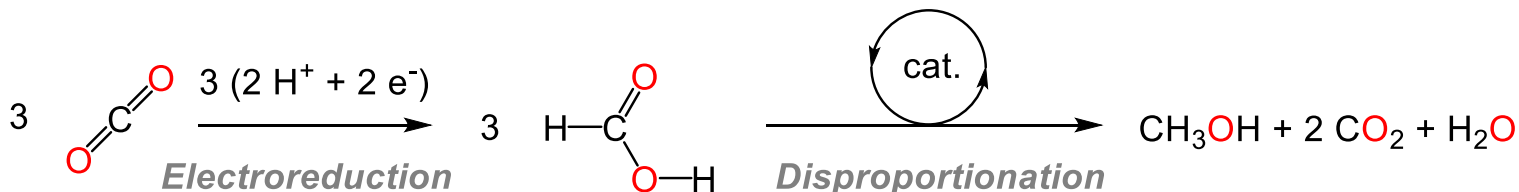
$$E^\circ(\text{CO}_2/\text{HCOOH}) = -0.61 \text{ V}$$

$$\text{BDE}(\text{C-H}) = 91 \text{ kcal/mol}$$

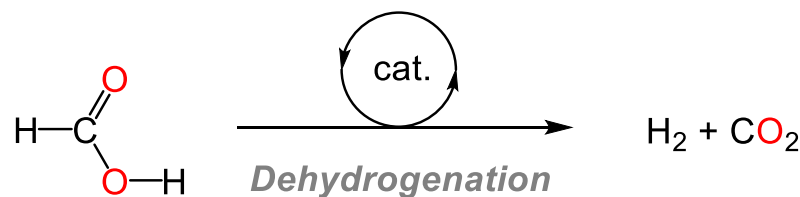
Renewable through CO₂ electrolysis



**Thermodynamic
and kinetic advantage**

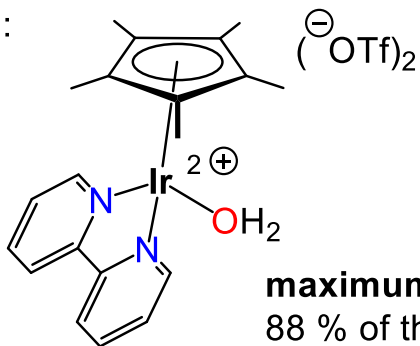


$$rG^\circ(298 \text{ K}) = -25.8 \text{ kcal/mol}$$



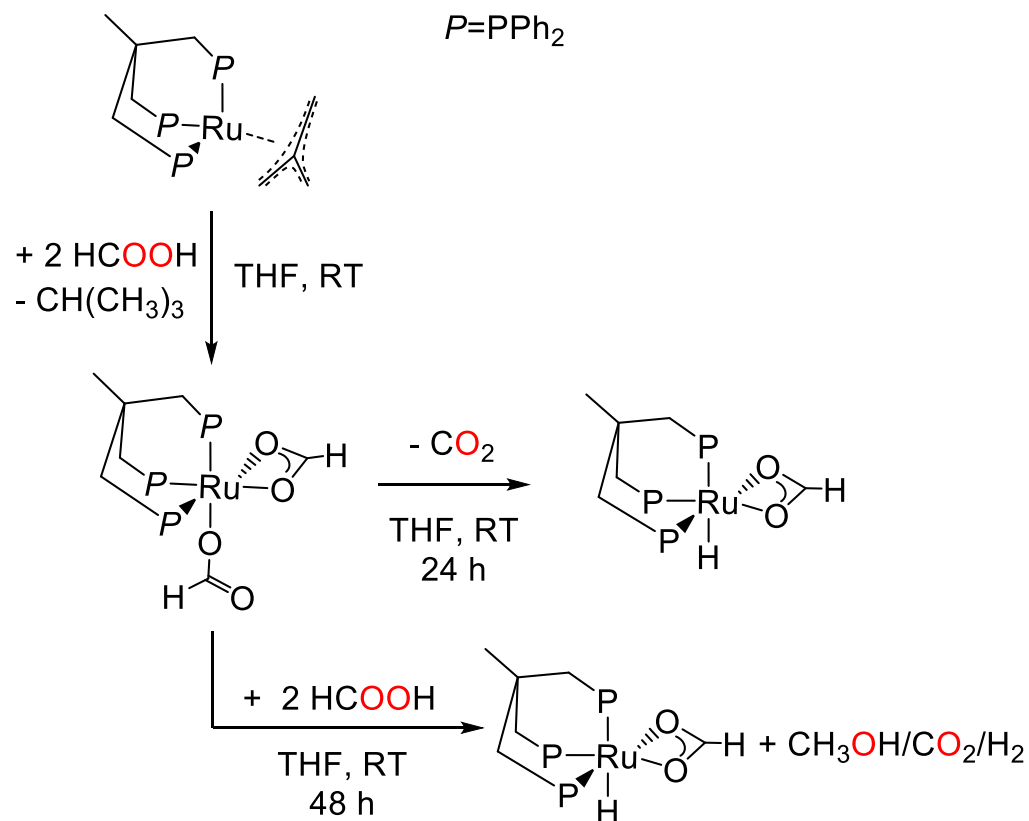
$$rG^\circ(298 \text{ K}) = -3.2 \text{ kcal/mol}$$

cat.:

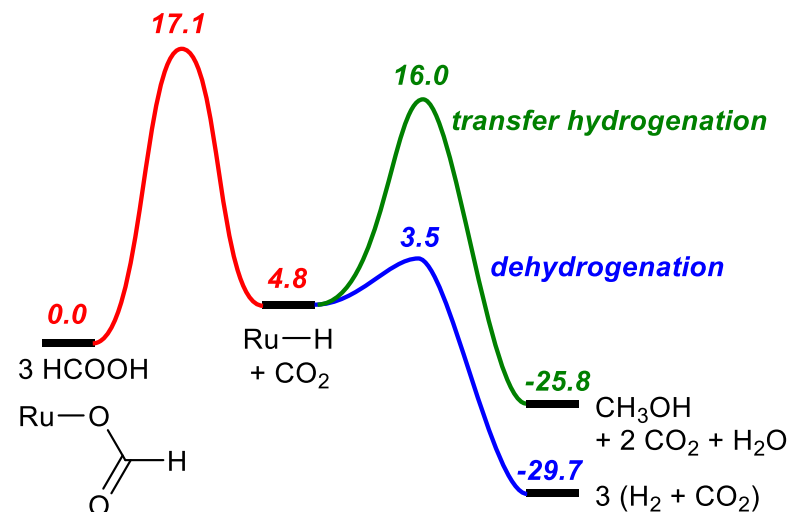


maximum CH₃OH yield = 1.9 %
88 % of the C-H bonds yield H₂

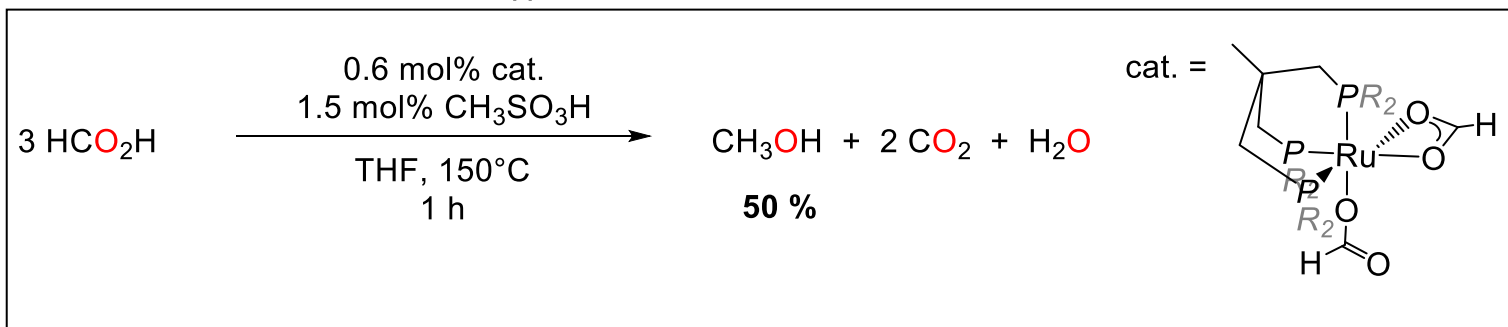
CO₂ ELECTROREDUCTION TO CH₃OH VIA HCOOH



M06-2X/6-31+G*(H,C,O,P)+SDD(Ru) PCM(THF)



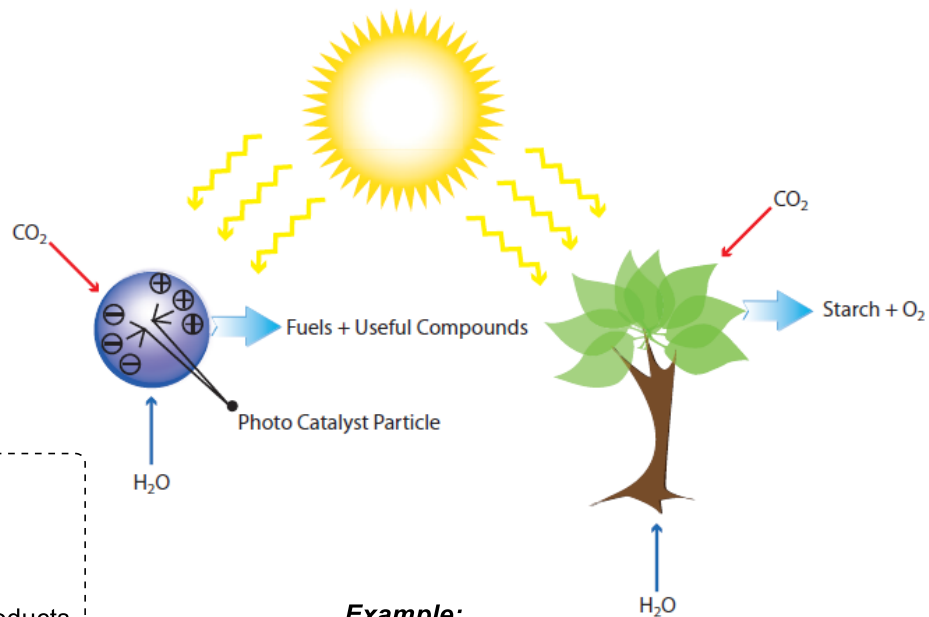
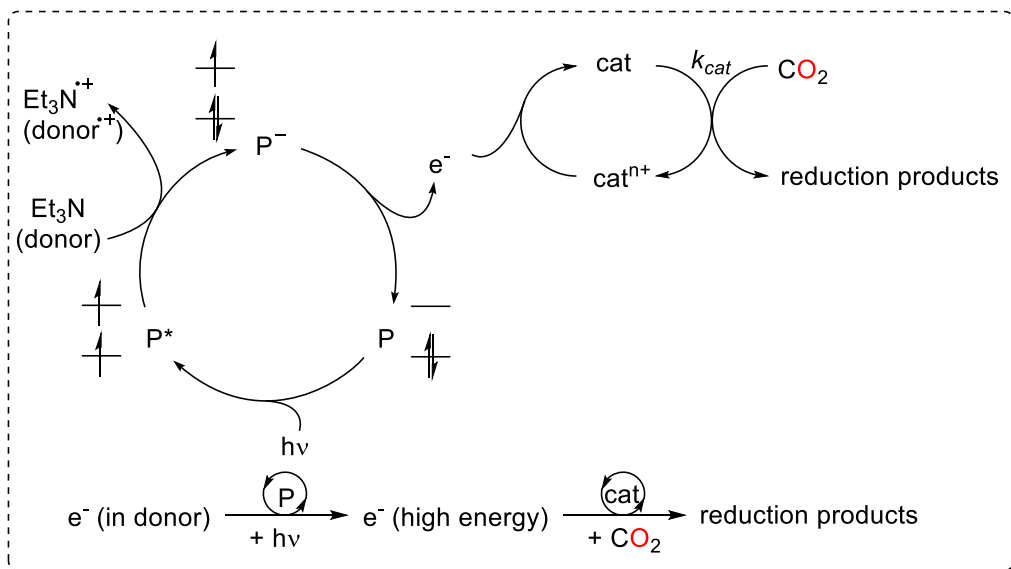
**Selectivity is under
thermodynamic control**



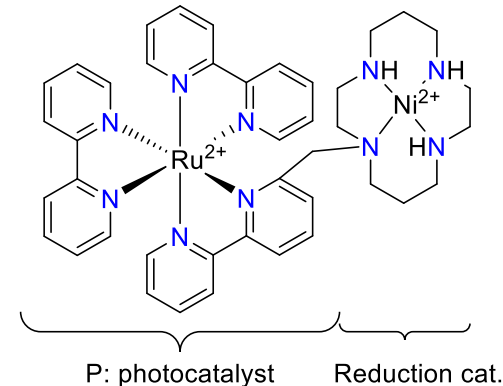
The *dream* reaction

- CO₂ + H₂O + light = reduction
- Artificial photosynthesis:

Mechanistic scheme

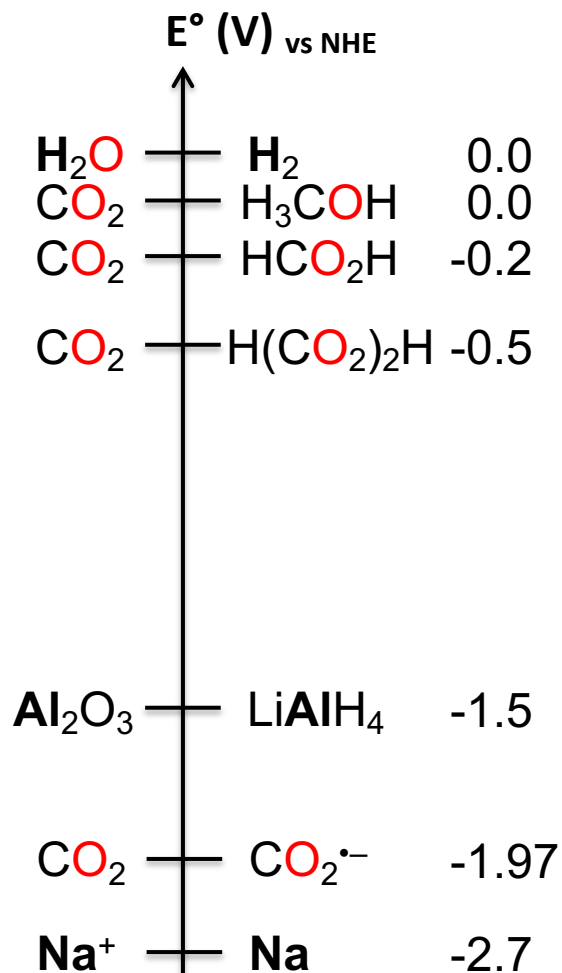


Example:



REDUCTION OF C-O BONDS BY HYDROGENATION

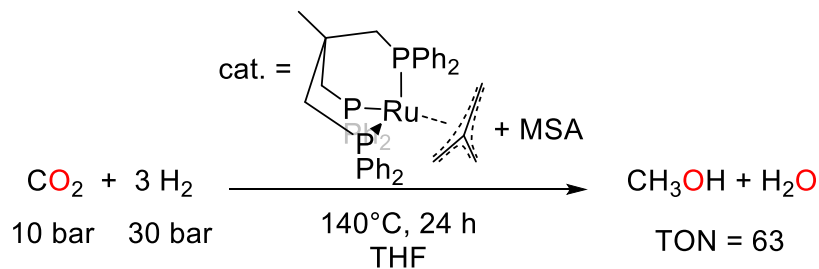
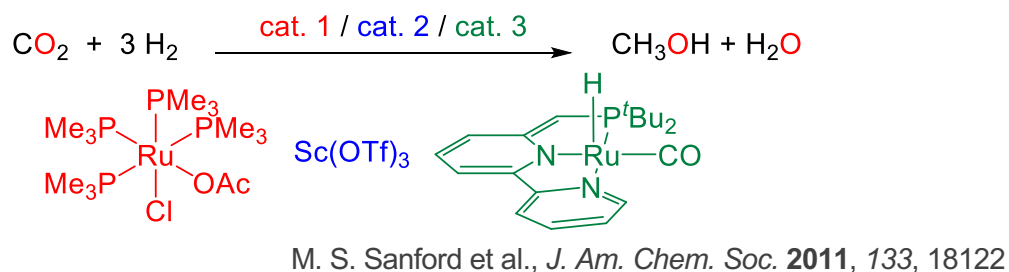
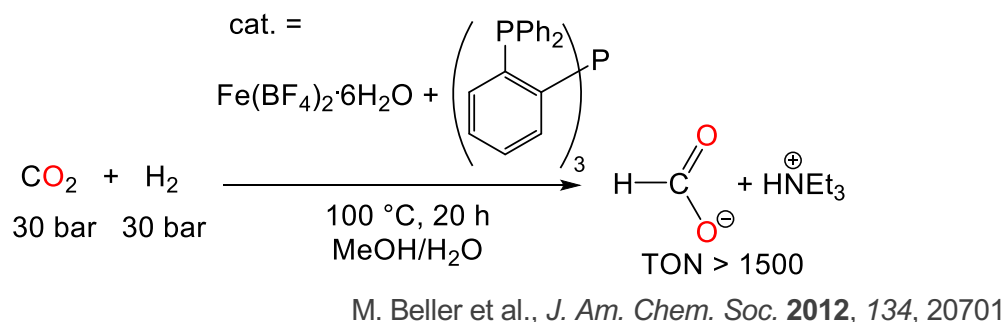
Thermodynamics



Cantat *et al.*, *ACS Catal.* **2017**, *7*, 2107
 Savéant *et al.*, *Chem. Soc. Rev.* **2013**, *42*, 2423

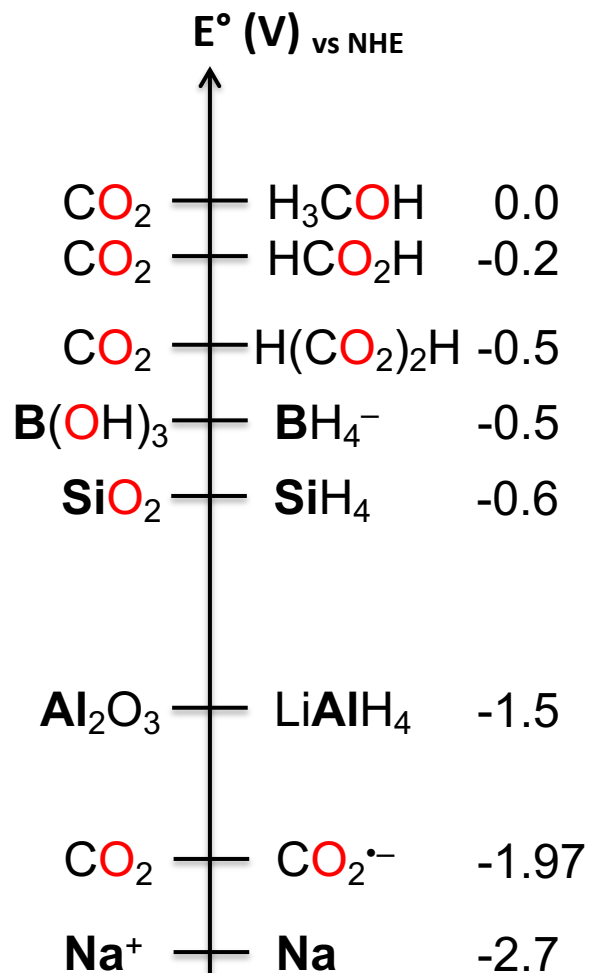
Kinetics

H-H Bond Dissociation Energy (BDE): **104 kcal/mol**



REDUCTION OF C-O BONDS BY HYDROSILYLATION

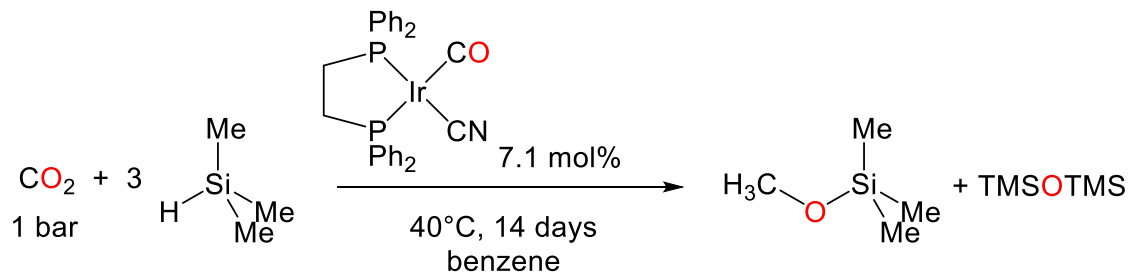
Thermodynamics



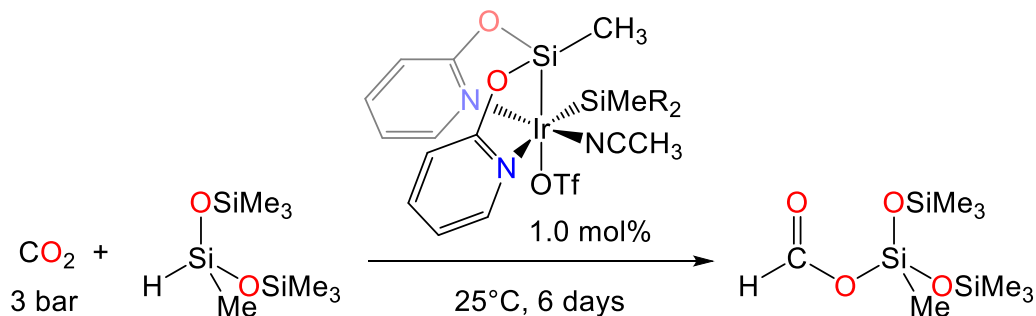
Cantat et al., *ACS Catal.* **2017**, *7*, 2107
 Savéant et al., *Chem. Soc. Rev.* **2013**, *42*, 2423

Kinetics

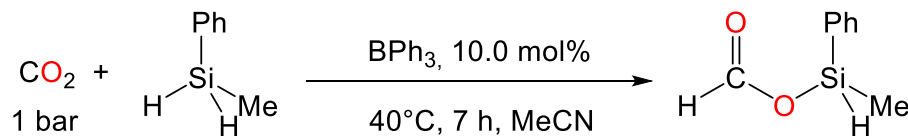
Si-H Bond Dissociation Energy (BDE): 92 kcal/mol



R. Eisenberg et al., *Organometallics* **1989**, *8*, 1822



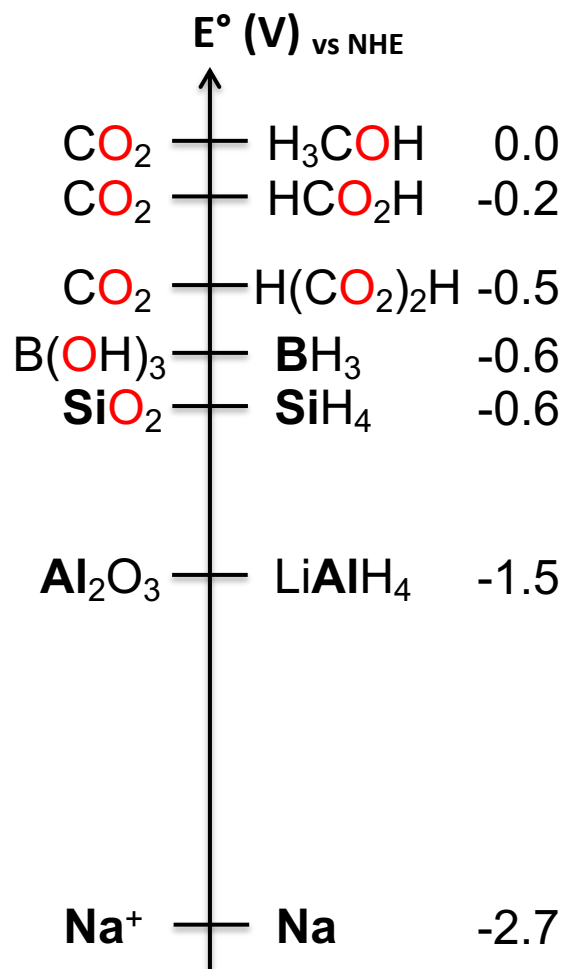
F. J. Fernández-Alvarez, L. Oro et al., *Angew. Chem. Int. Ed.* **2012**, *51*, 12824



J. Okuda et al., *Chem. Eur. J.* **2016**, *22*, 7730

REDUCTION OF C-O BONDS BY HYDROSILYLATION

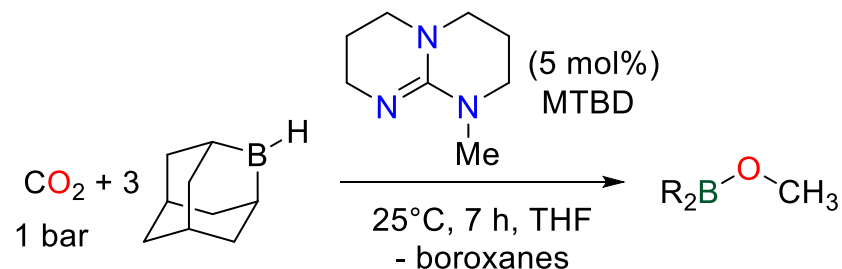
Thermodynamics



Kinetics

Si-H Bond Dissociation Energy (BDE): 92 kcal/mol

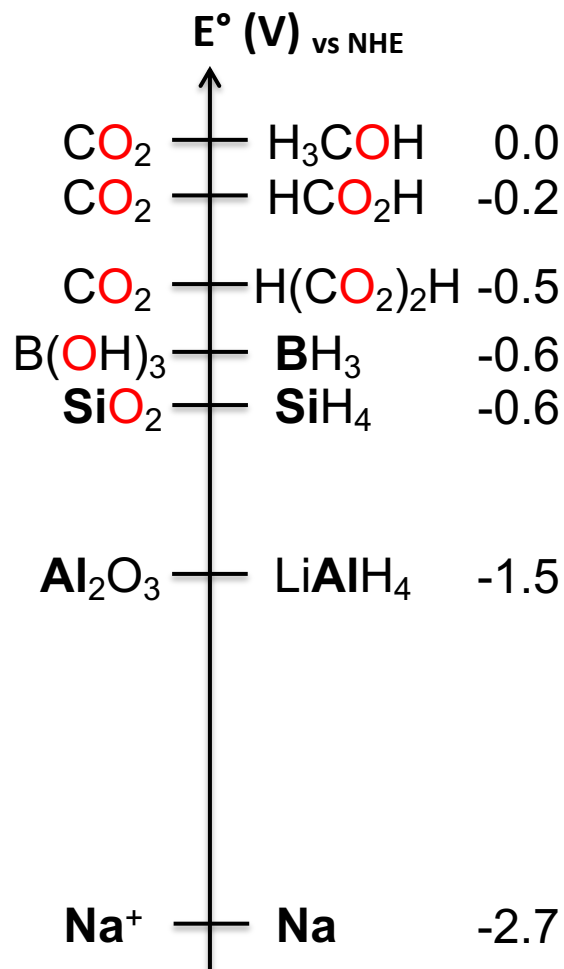
B-H Bond Dissociation Energy (BDE): 78 kcal/mol



Cantat et al., *Chem. Eur. J.* **2014**, *20*, 7098.
 Patent WO2014162266 (2013/04)

REDUCTION OF C-O BONDS BY HYDROSILYLATION

Thermodynamics

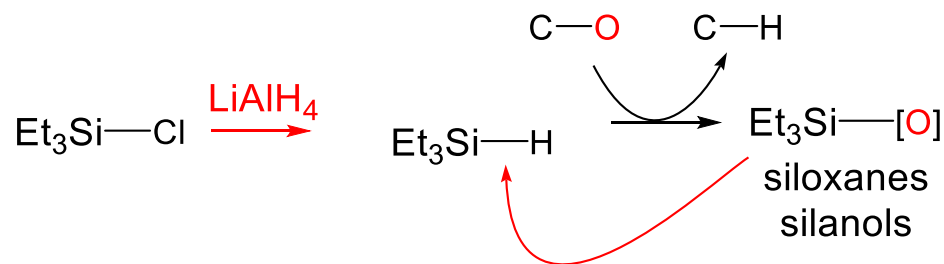


Kinetics

Si-H Bond Dissociation Energy (BDE): 92 kcal/mol

B-H Bond Dissociation Energy (BDE): 78 kcal/mol

Generation and recyclability

 H_2

- Energy efficiency
- Reactivity and selectivity
- Recyclability

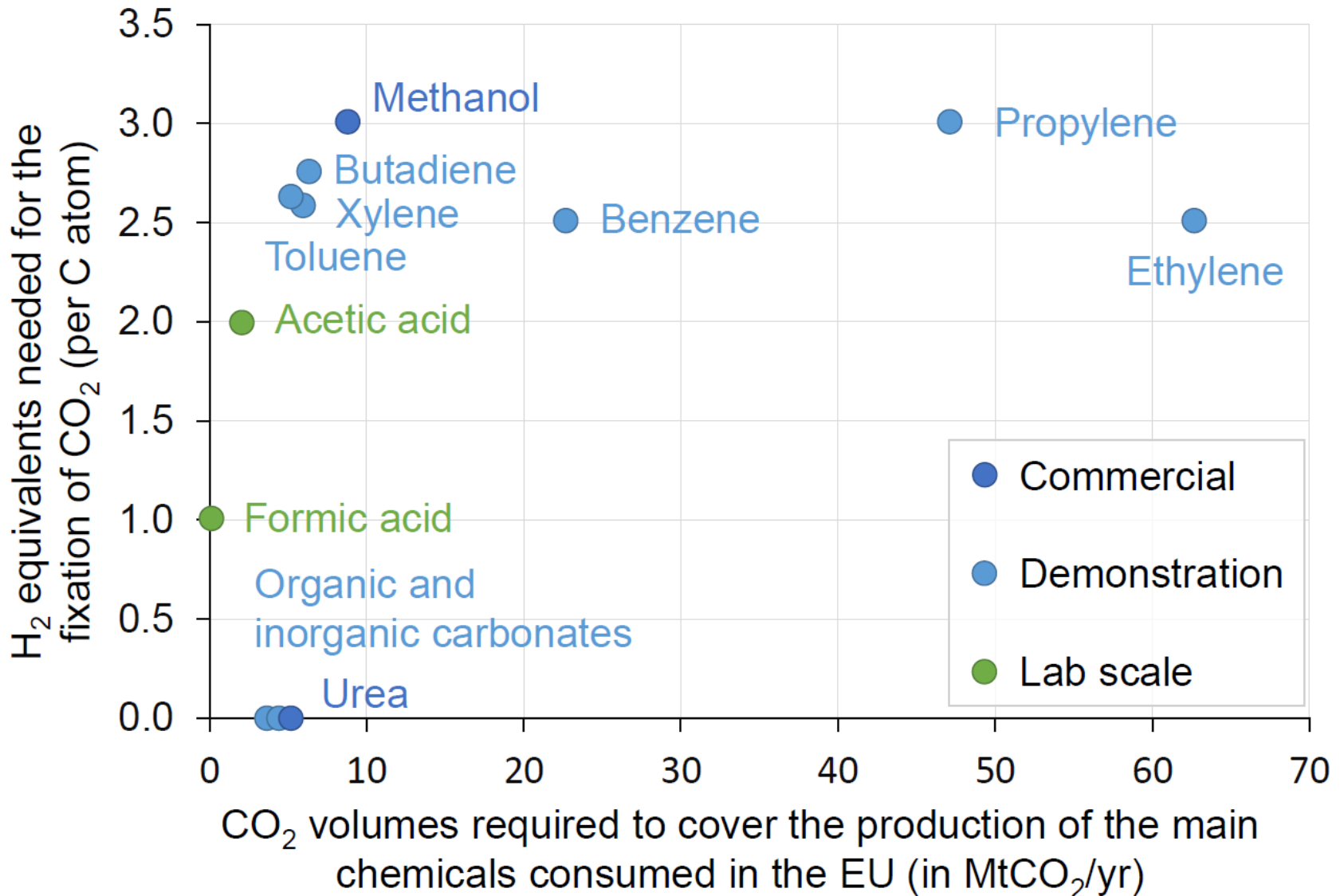
 $\text{R}_3\text{SiH}, \text{R}_2\text{BH}$

- Energy efficiency
- Reactivity and selectivity
- Recyclability

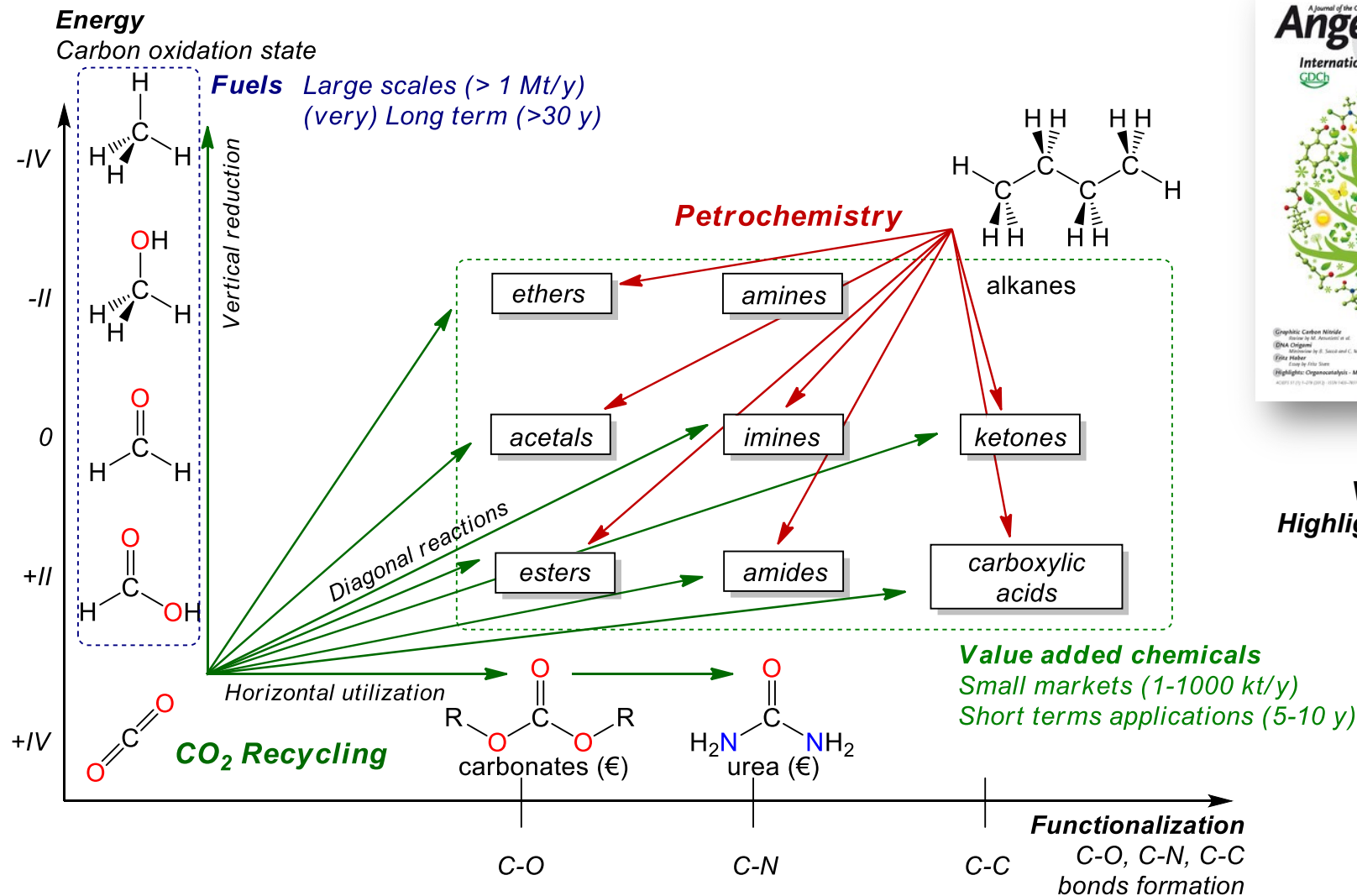


CO₂ CONVERSION TO VALUE-ADDED CHEMICALS

CARBON BASED PRODUCTS IN AN ENERGY SYSTEM



VARIOUS OPPORTUNITIES TO CO₂ RECYCLING...

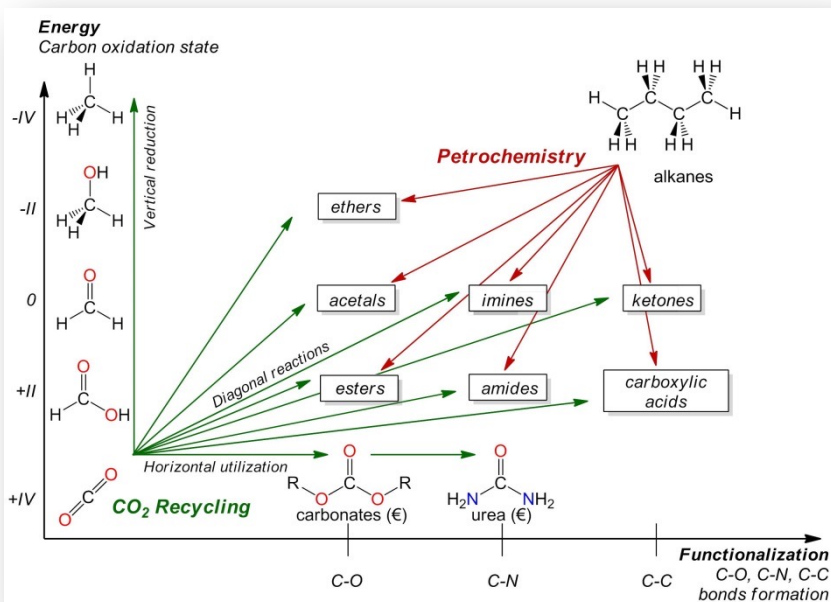


COVER
VIP Paper
Highlighted in Nature

CO₂ functionalization and reduction steps
coupled in a single process

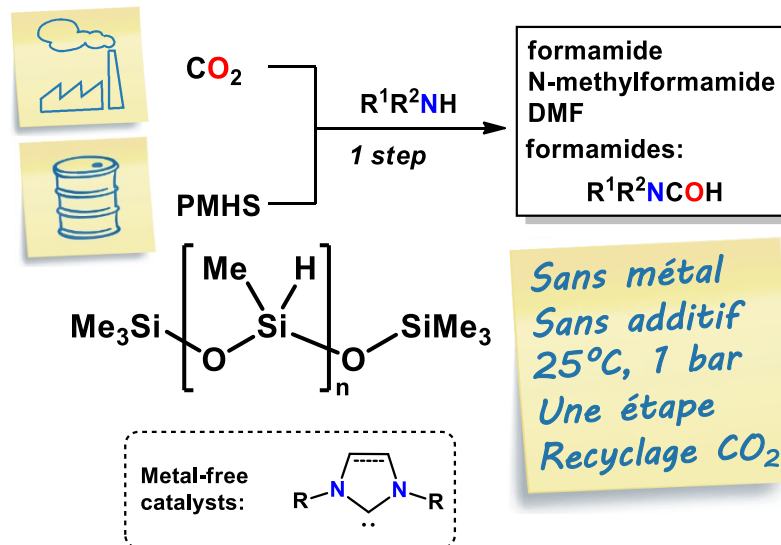
PROOF-OF-CONCEPT: NEW CATALYTIC PROCESS

Proof-of-concept for the diagonal approach



Co-recycling CO₂/PMHS (CEA/DSM technology)

Metal-free catalysts, room temperature, single step



World production: 500 kt/y from oil
Utilization as solvents and reactants

- CO₂ as an alternative to petrochemistry
Utilization of an energy vector (H, Si) coupled with a functionalizing reactant



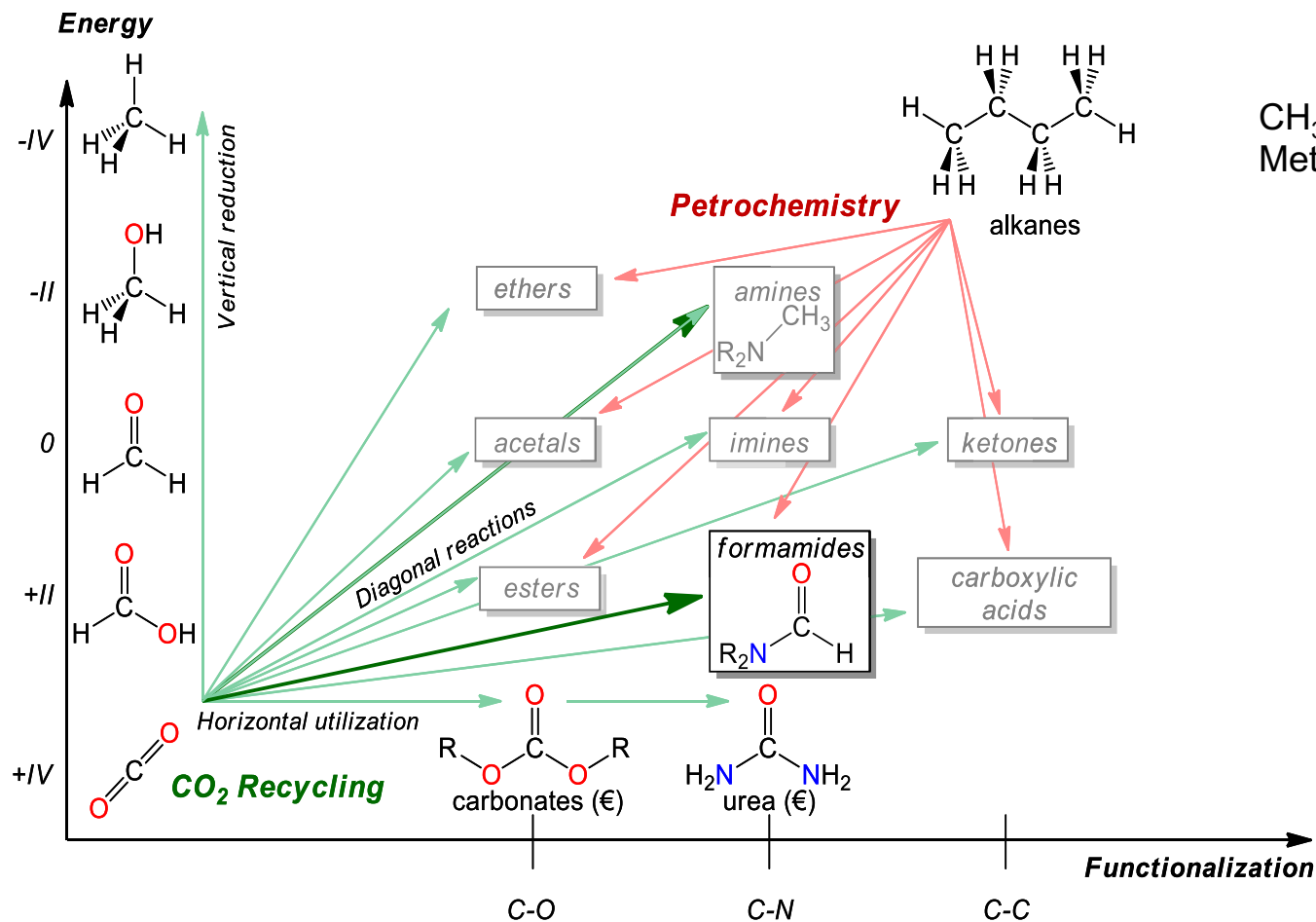
- Cover picture in **Angewandte Chemie**
- **Very Important Paper** (top 5%)
- Highlighted in **Nature**

Cantat et al., *Angewandte Chemie* 2012, *JACS* 2012, WO2012137152

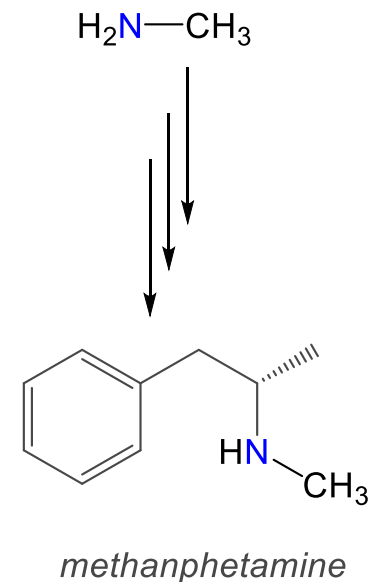
SECOND CHALLENGE: METHYLATION USING CO₂

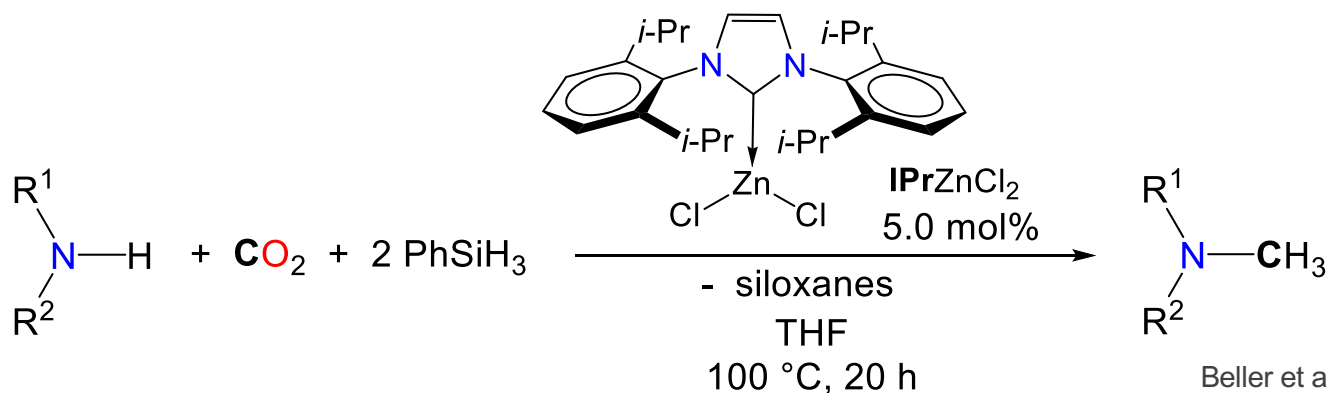
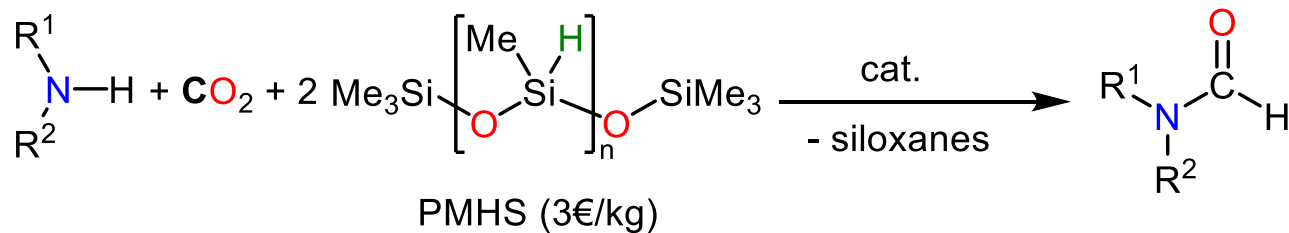
CO₂ as a methylating reagent

- Goal: diagonal reactions with large slope (access to highly reduced compounds)

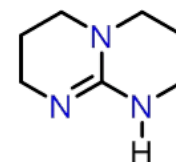


CH₃OH: 400 €/ton
Methylamines: > 4,000 €/ton

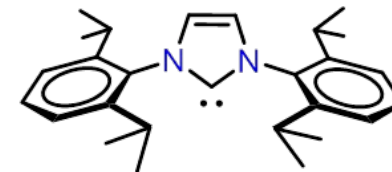


NEW REACTIONS INVOLVING CO₂

Catalysts:

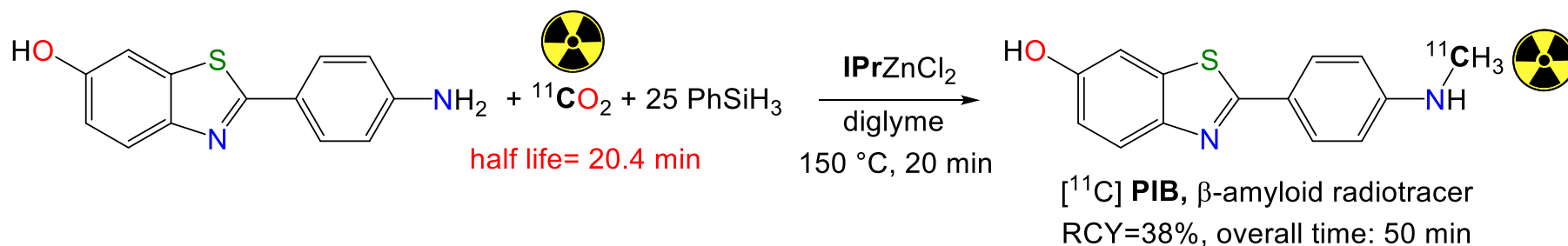


TBD



IPr

For a Ru cat., see:
 Beller et al. *Angew. Chem. Int. Ed.* **2013**, 52, 9568



Angew. Chem. Int. Ed. **2012**, 51, 187

J. Am. Chem. Soc. **2012**, 134, 2934

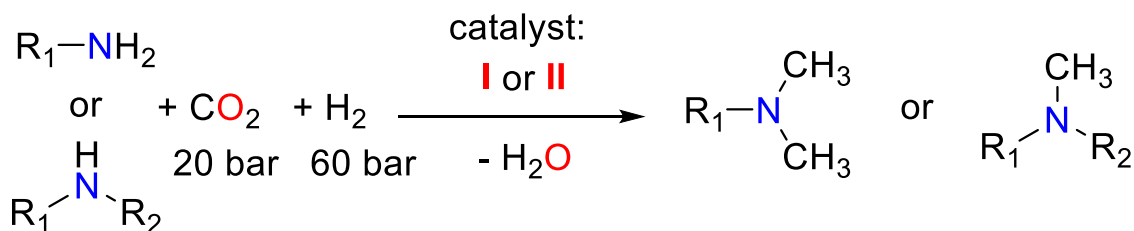
Chem. Sci. **2013**, 4, 2127

ChemCatChem **2013**, 5, 117

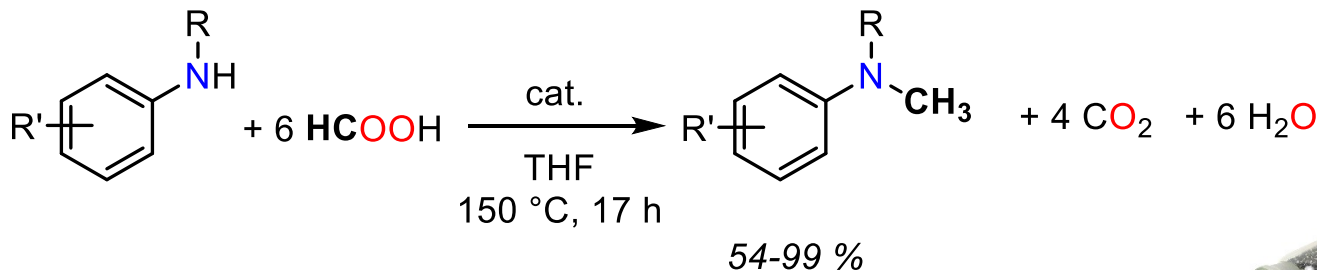
Liger et al., *EurJOC*, **2015**, 6434

Cantat et al., *Patent PCT/IB2013/054599*

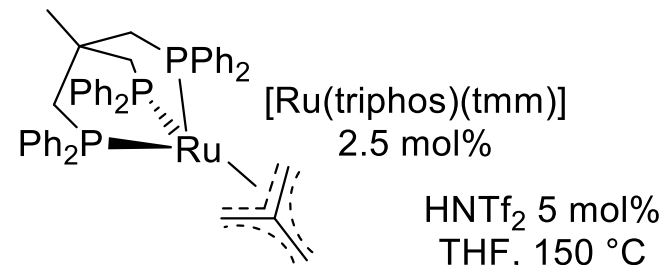
METHYLATION OF AMINES USING HCOOH

■ H₂ as a reductant

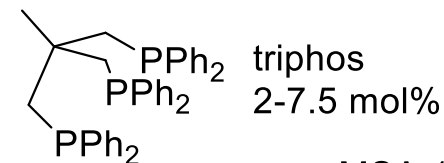
Klankermayer *et al.*, *Angew. Chem. Int. Ed.* **2013**, 52, 9554.
 Beller *et al.*, *Angew. Chem. Int. Ed.* **2013**, 52, 12156.
 Cantat *et al.*, *Angew. Chem. Int. Ed.* **2014**, 53, 2543 [Highlight]

■ HCO₂H as a carbon and hydrogen source

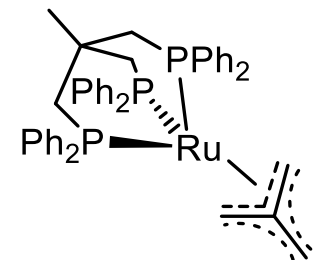
Cantat *et al.*, *Chem. Commun.* **2014**, 50, 14033

I, Klankermayer *et al.*II, Beller *et al.*

[Ru-(acac)₃] 1-5 mol%



MSA 1.5 mol%
THF, 140 °C



[Ru(triphos)(tmm)]
1.0 mol%
HNTf₂ 1.5 mol%

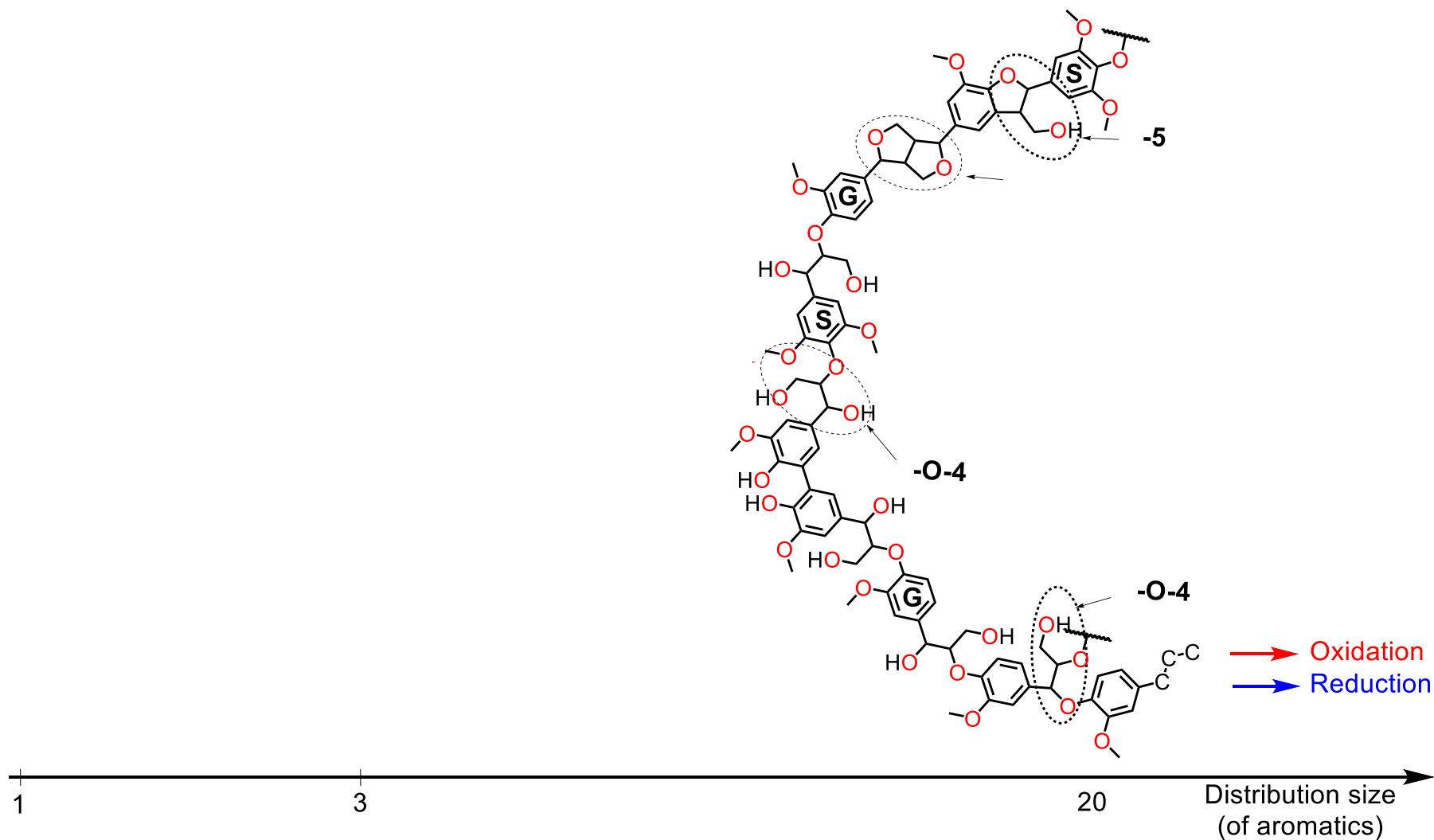


or Pd/In₂O₃



BEYOND CO₂ REDUCTION: DEPOLYMERIZATION OF WASTE PLASTICS AND LIGNIN

CONVERGENT REDUCTIVE DEPOLYMERIZATION



Cantat et al., *Energy Environ. Science*, **2015**, 8, 2734

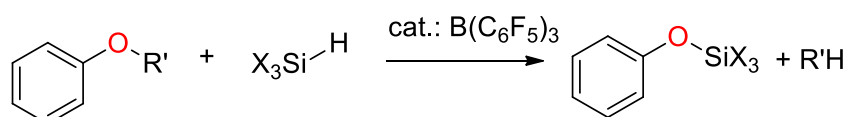
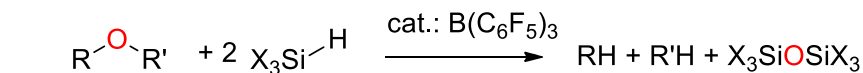
For lignin oxidation see: Weckhuysen et al. *Chem. Rev.*, **2010**, 110, 3552

Stahl et al. *Nature* **2014**, 515, *J. Am. Chem. Soc.* **2013**, 135, 6415

Zhang et al. *Chem. Rev.*, **2015**, 115, 11559

CATALYTIC HYDROSILYLATION OF ETHERS

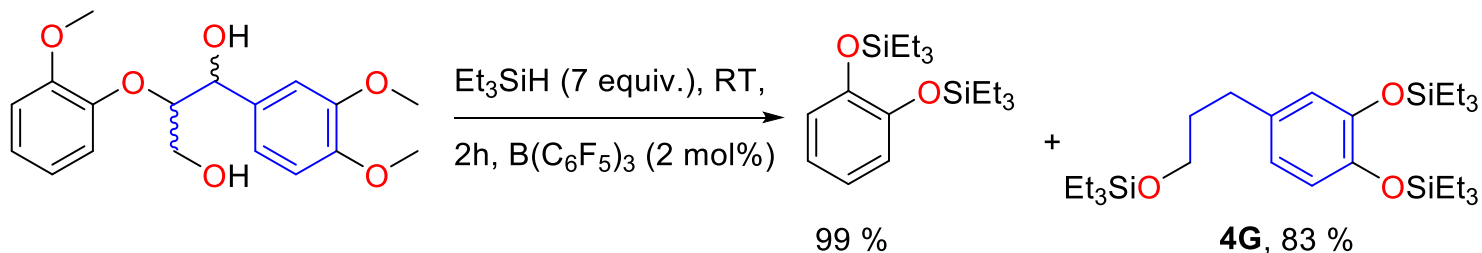
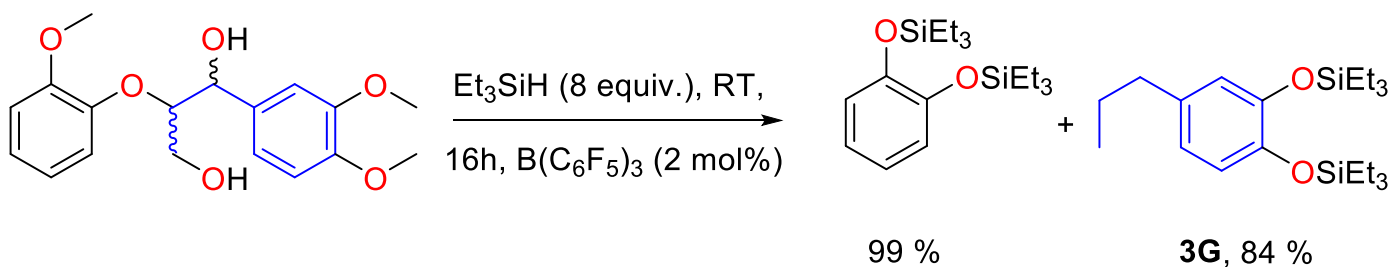
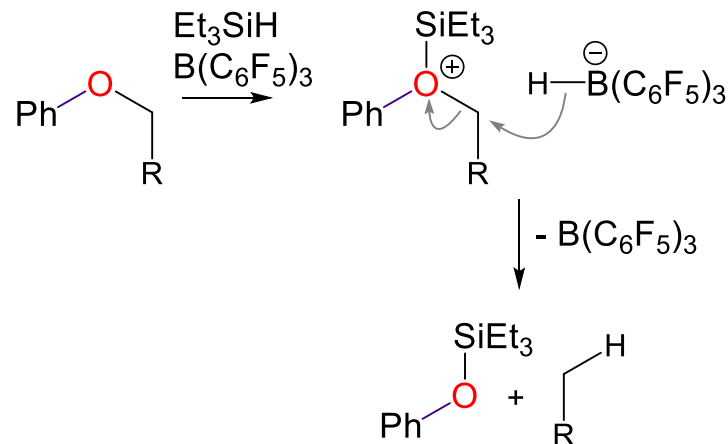
Catalytic hydrosilylation of ethers (Piers and Gevorgyan)



Utilized in organic chemistry only
Never applied to biomass molecules

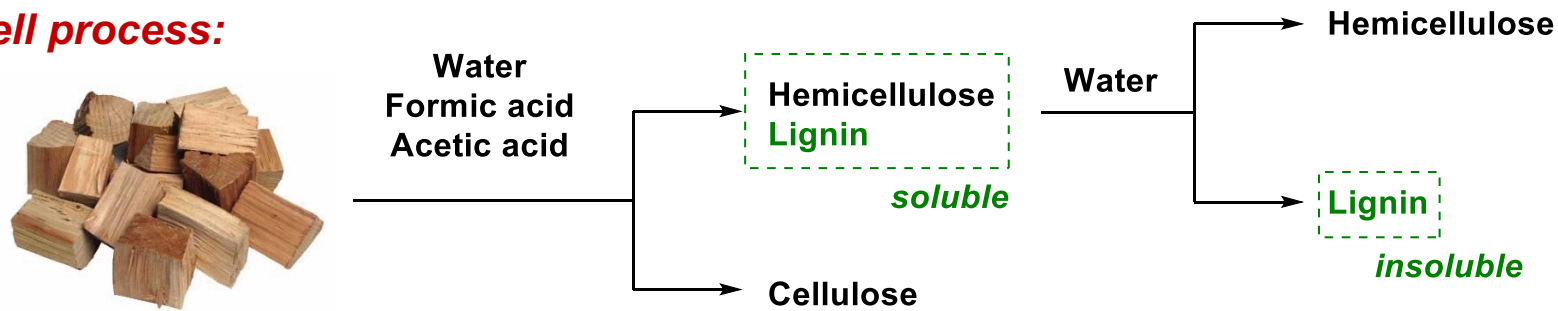
V. Gevorgyan, et al. *J. Org. Chem.* **2000**, 65, 6179

Piers et al, *J. Org. Chem.* **2000**, 65, 3090





Formacell process:



SEC chromatograms

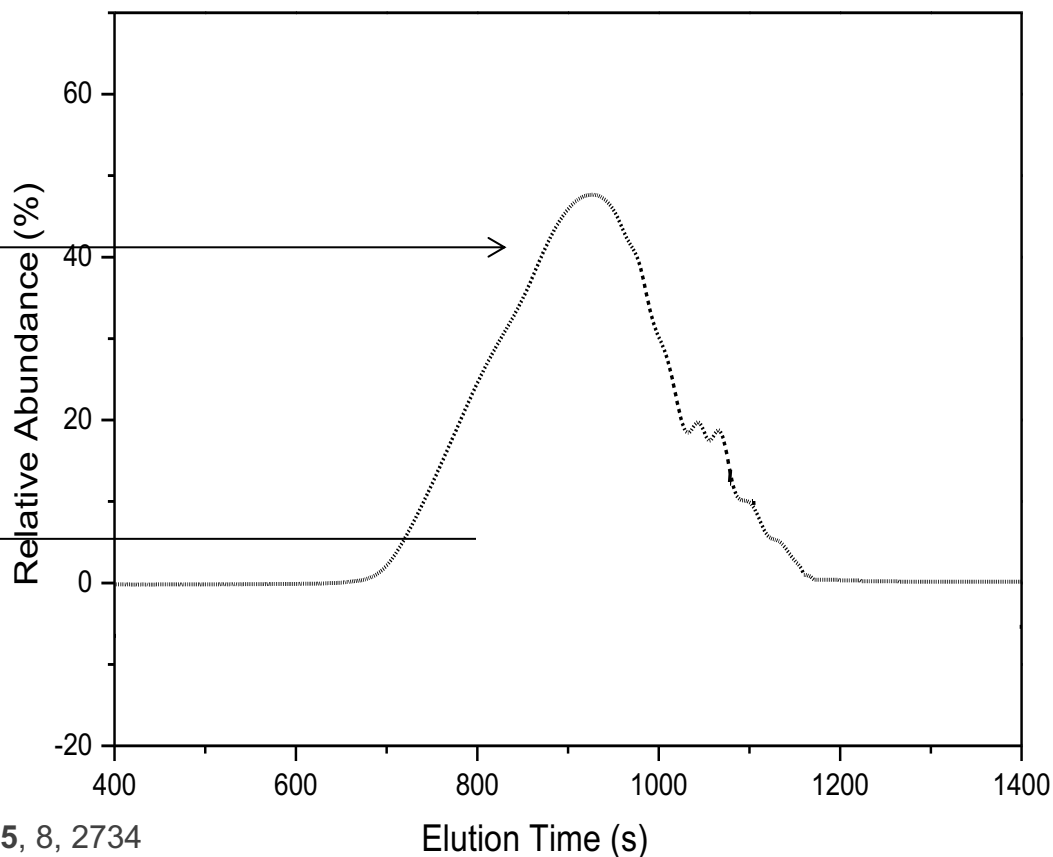
Black poplar lignin

Black poplar lignin

+ 276 wt% Et_3SiH

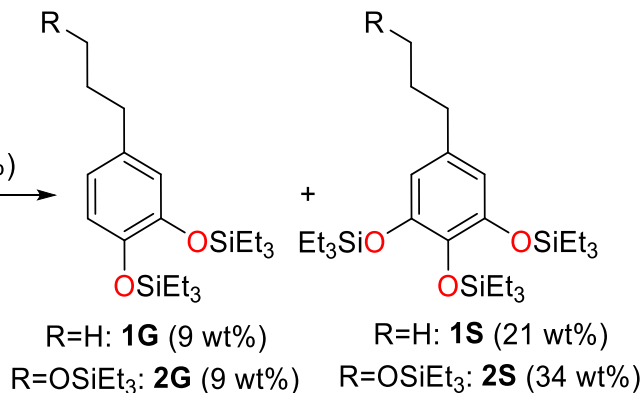
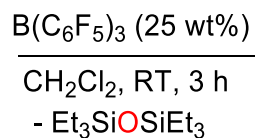
+ 25 wt% $\text{B}(\text{C}_6\text{F}_5)_3$

After 20 h at RT in CH_2Cl_2

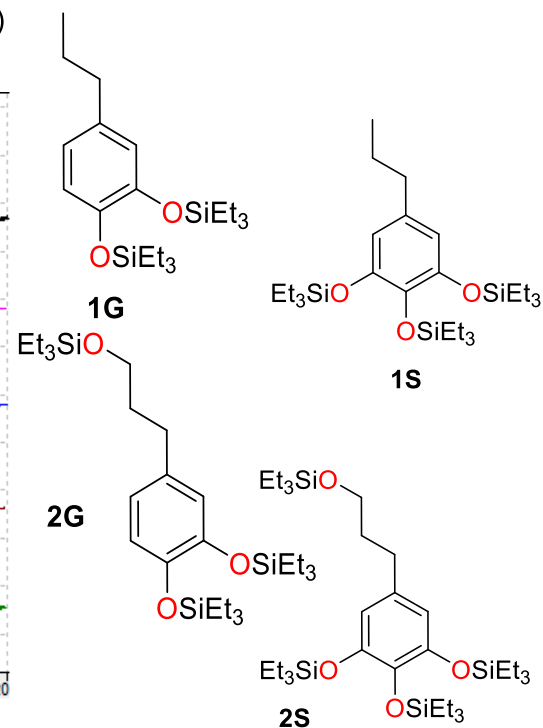
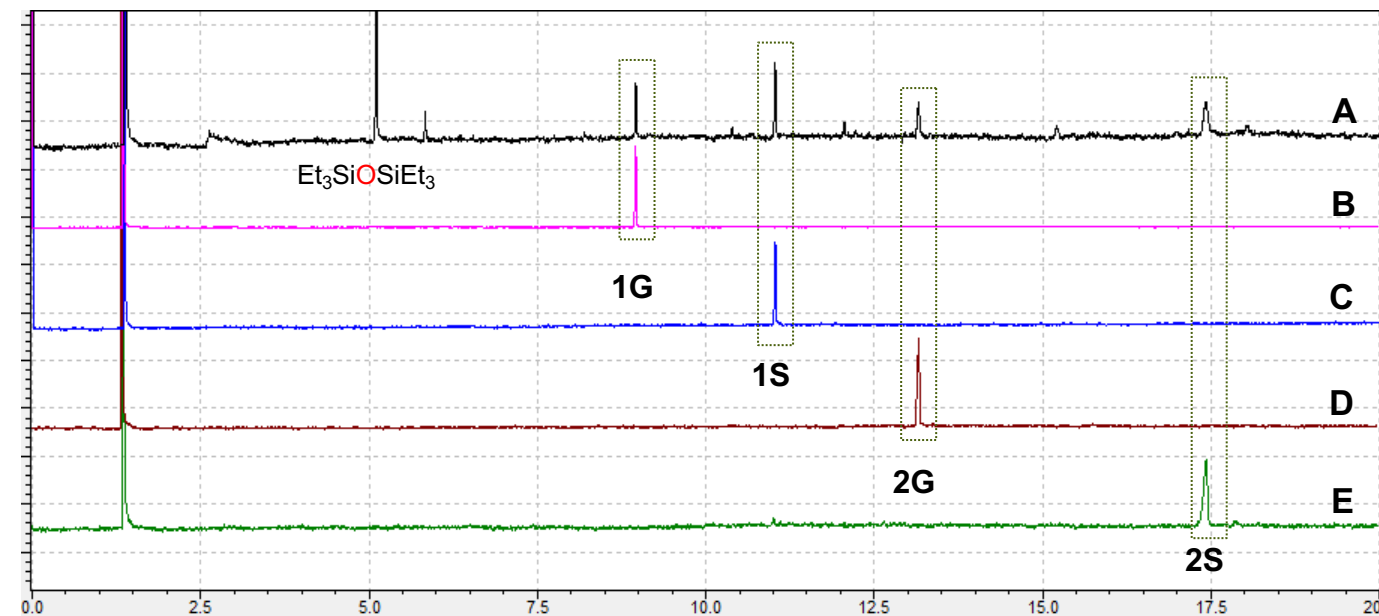


REDUCTIVE DEPOLYMERIZATION OF LIGNIN

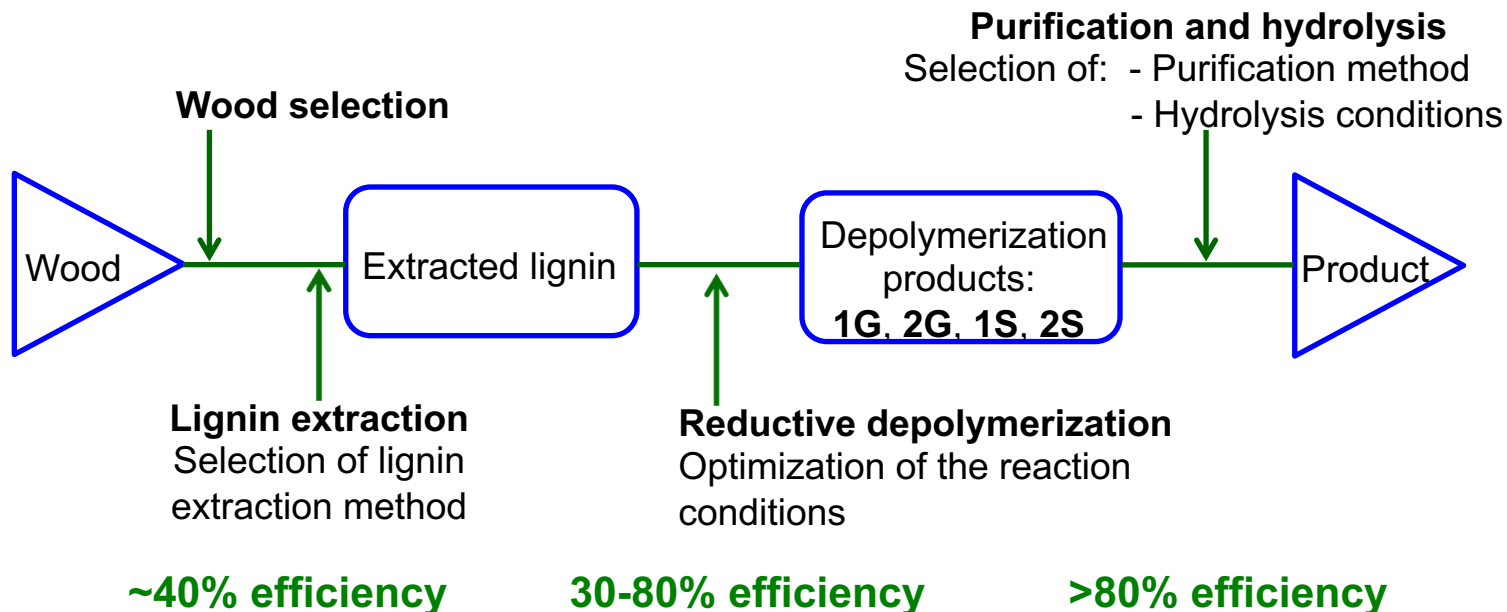
Black poplar
(Formacell) + 276 wt% Et₃SiH



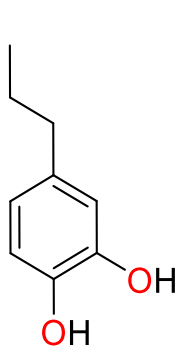
Conditions correspond to:
10 mol% catalysts
5 equiv. Si-H per aromatic unit



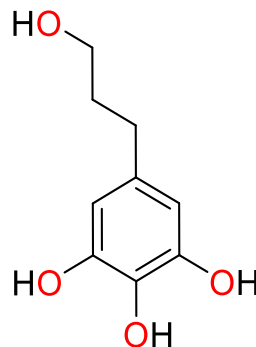
AN INTEGRATIVE APPROACH



Global efficiency = 5-25%

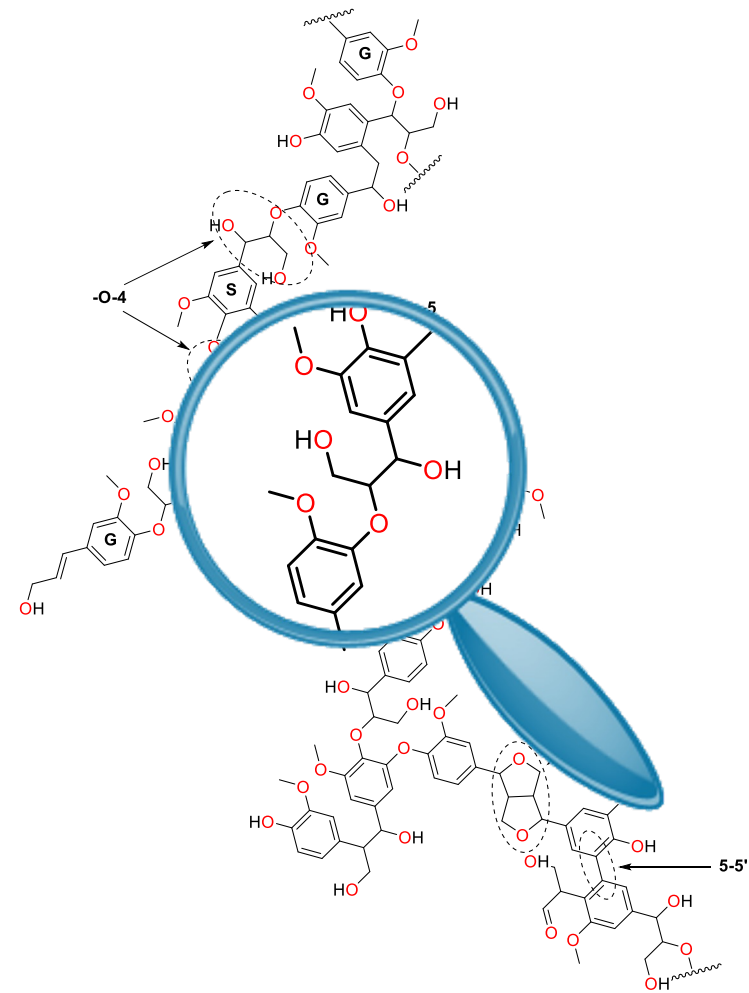


0.5 wt% from wood!
7.0 wt% from lignin

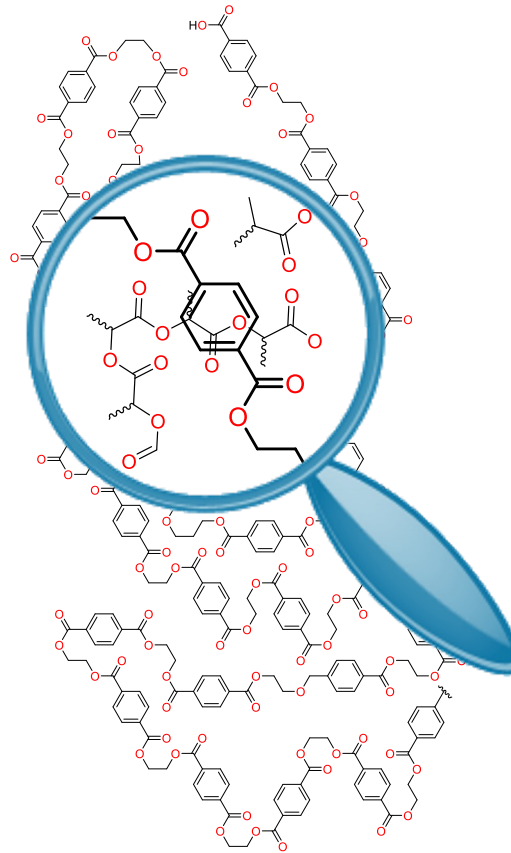


2.4 wt% from wood!
24.0 wt% from lignin

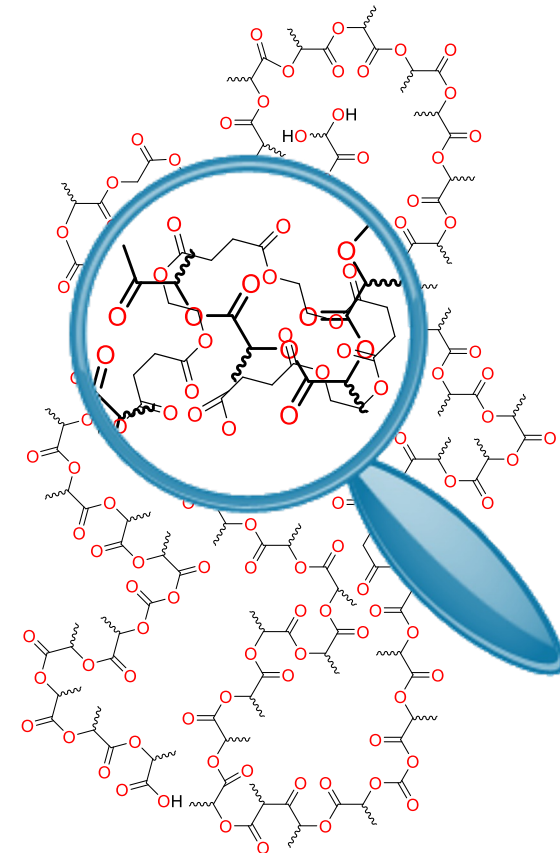
BIOMASS/PLASTIC DEPOLYMERIZATION, SAME CHALLENGE ?



Lignin

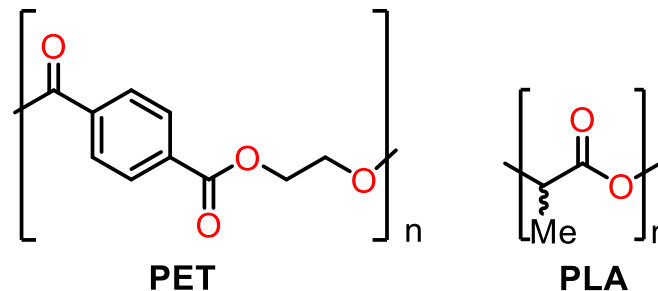


Poly(Ethylene Terephthalate)

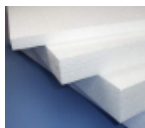
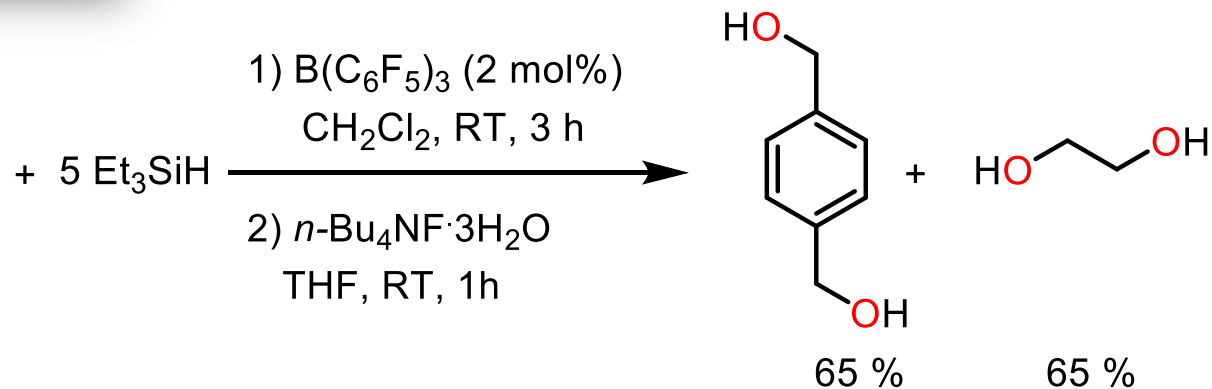


Poly(Lactic Acid)

DEPOLYMERIZATION OF WASTE PLASTICS



PET



PS



PVC

PLA



ChemSusChem, **2015**, 8, 980; *ACS Sust. Chem. Eng.* **2018**, 6, 10481

Patent app. PCT/IB2016/059684

For the hydrogenation of pure PET, see: Robertson *et al.*, *Chem. Commun.* **2014**, 50, 4884

RECYCLING STRATEGIES

REWEAR

CLOTHING THAT CAN BE WORN AGAIN IS MARKETED WORLDWIDE AS SECOND-HAND GOODS.

ENERGY

WHEN REWEAR, REUSE AND RECYCLE ARE NOT OPTIONS, TEXTILES ARE USED TO PRODUCE ENERGY.

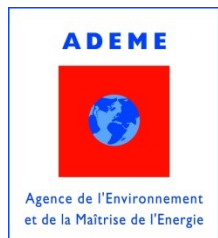


REUSE

TEXTILES THAT ARE NO LONGER SUITABLE TO WEAR ARE CONVERTED INTO OTHER PRODUCTS, SUCH AS CLEANING CLOTHS.

RECYCLE

TEXTILES THAT CAN'T BE REUSED GET A NEW CHANCE AS TEXTILE FIBRES, OR ARE USED TO MANUFACTURE PRODUCTS SUCH AS DAMPING AND INSULATING MATERIALS FOR THE AUTO INDUSTRY.



European Research Council
Established by the European Commission
StG 2013-2018
CoG 2019-2024



ACKNOWLEDGMENTS

PhD Students:

F. Dulong
C. Gomes
X. Frogneux
E. Feguali
E. Blondiaux
S. Savourey
N. von Wolf
C. Chauvier
J. Char
A. Aloisi
L. Monsigny
T. Nasr Allah
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L. Ponsard
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