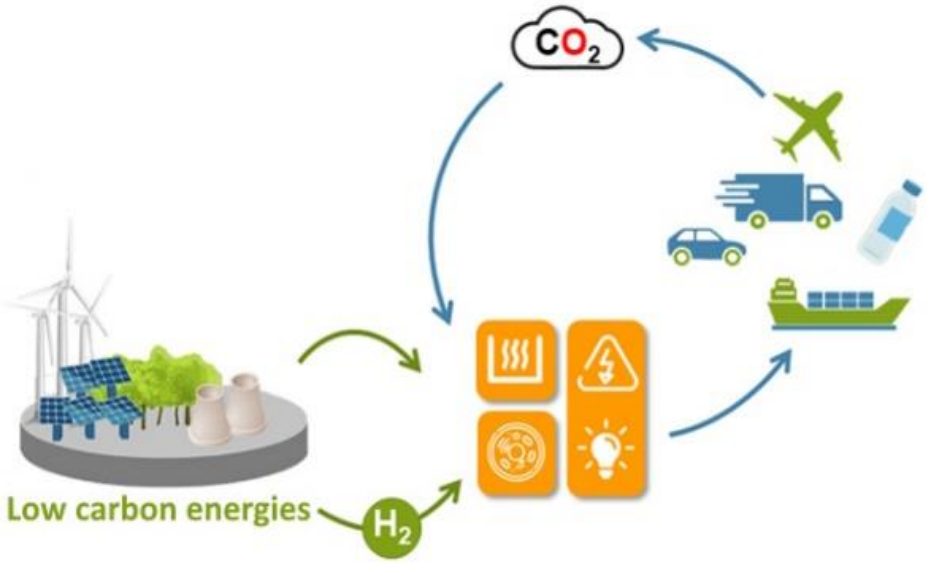
CO_2 conversion using catalysis: Why? How?

Prof. Thibault Cantat

CEA – Université Paris Saclay



2024

Services to society

Electrical power on the grid

Power available on demand

Heat

Fuels for mobility

Industrial products (chemicals, materials, fertilizers)

Ressources

Sun

Wind

Geothermy

Surfaces

Water

Uranium

Inorganics

metals
N, Si, P

Carbon feedstocks

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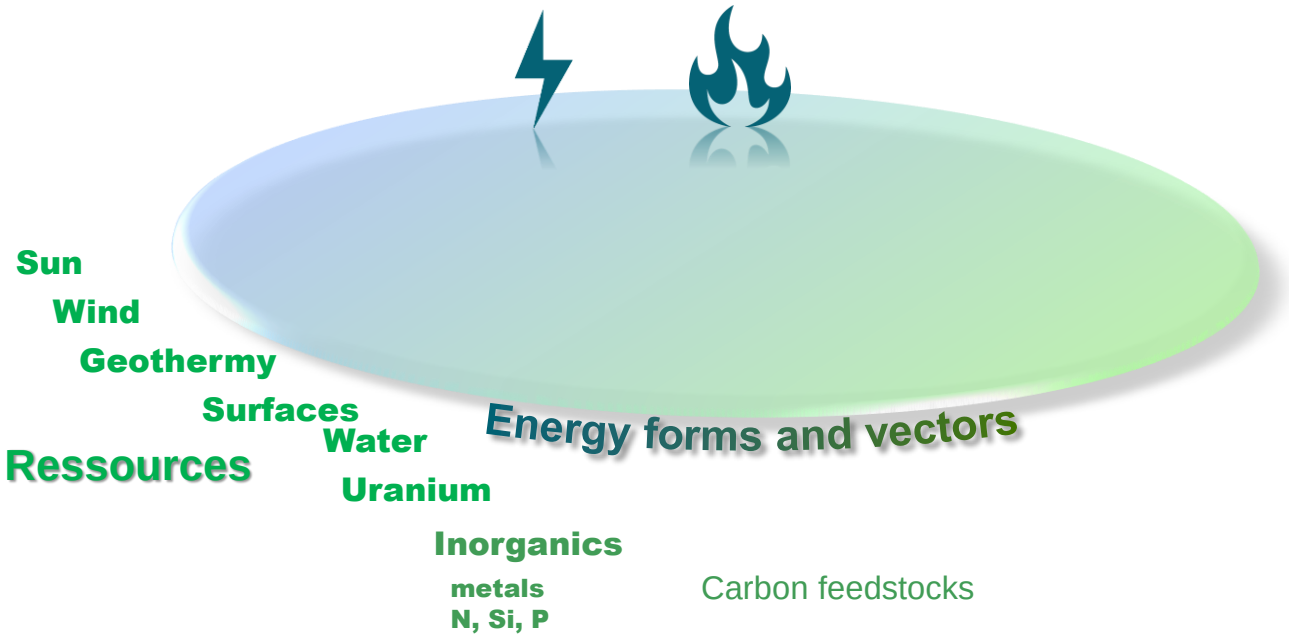

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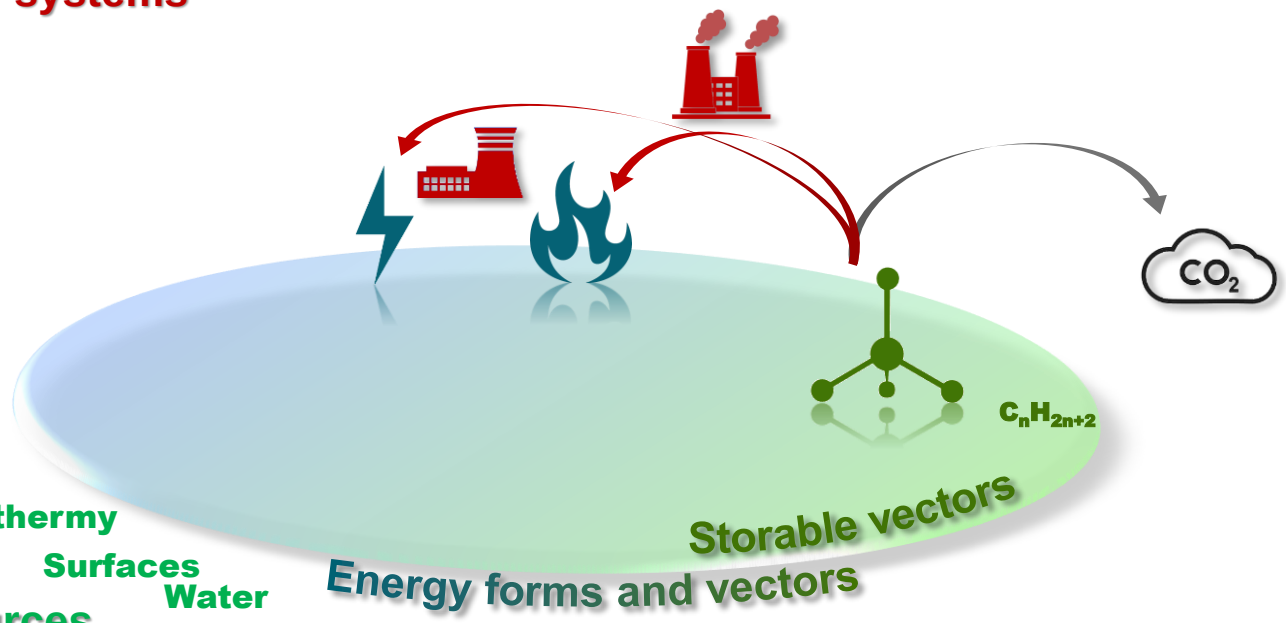
Interconversion systems



Sun
Wind
Geothermy
Surfaces
Water
Uranium
Ressources

Inorganics
metals
N, Si, P

Carbon feedstocks
fossils

An energy system dominated by fossil feedstocks…

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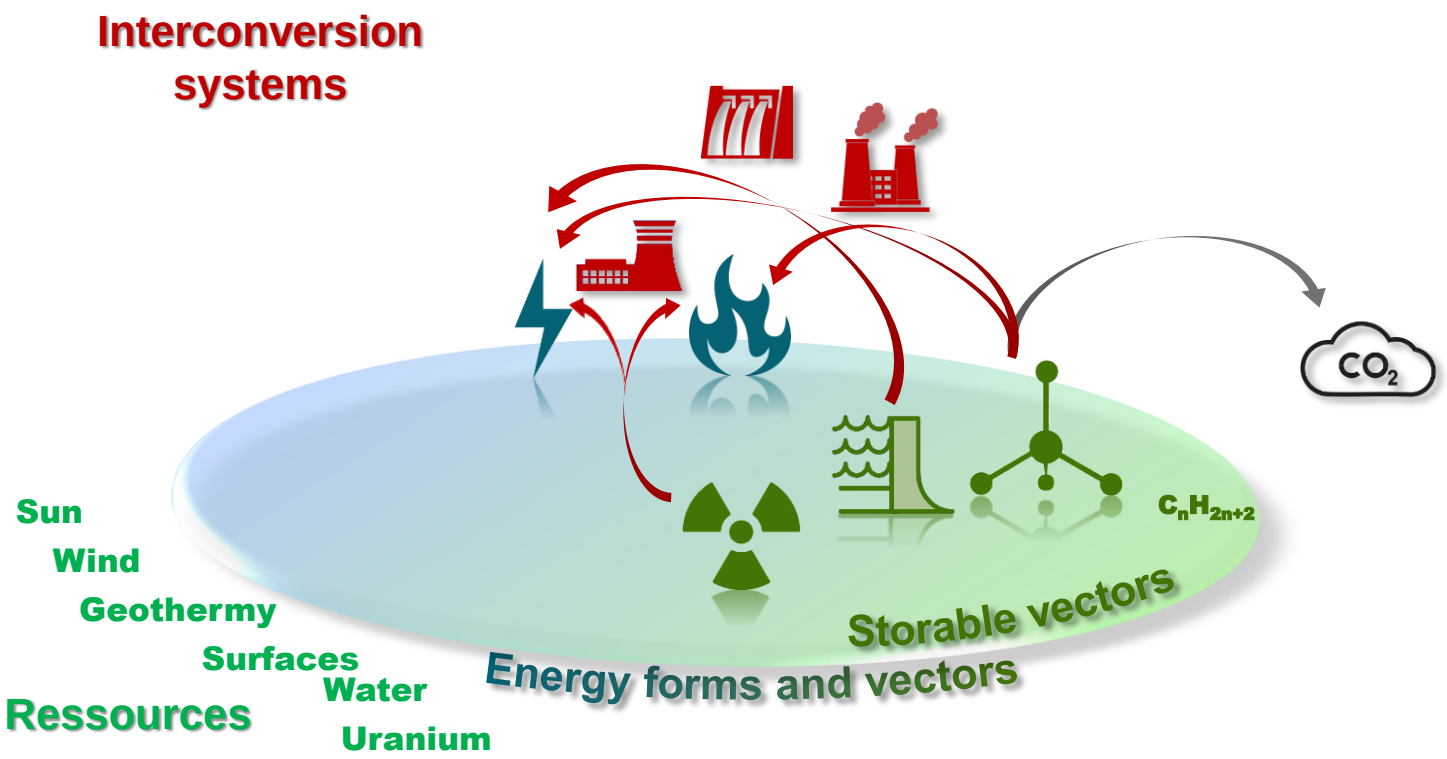


…which benefits from low carbon energy sources for the production of electricity.

Services to society

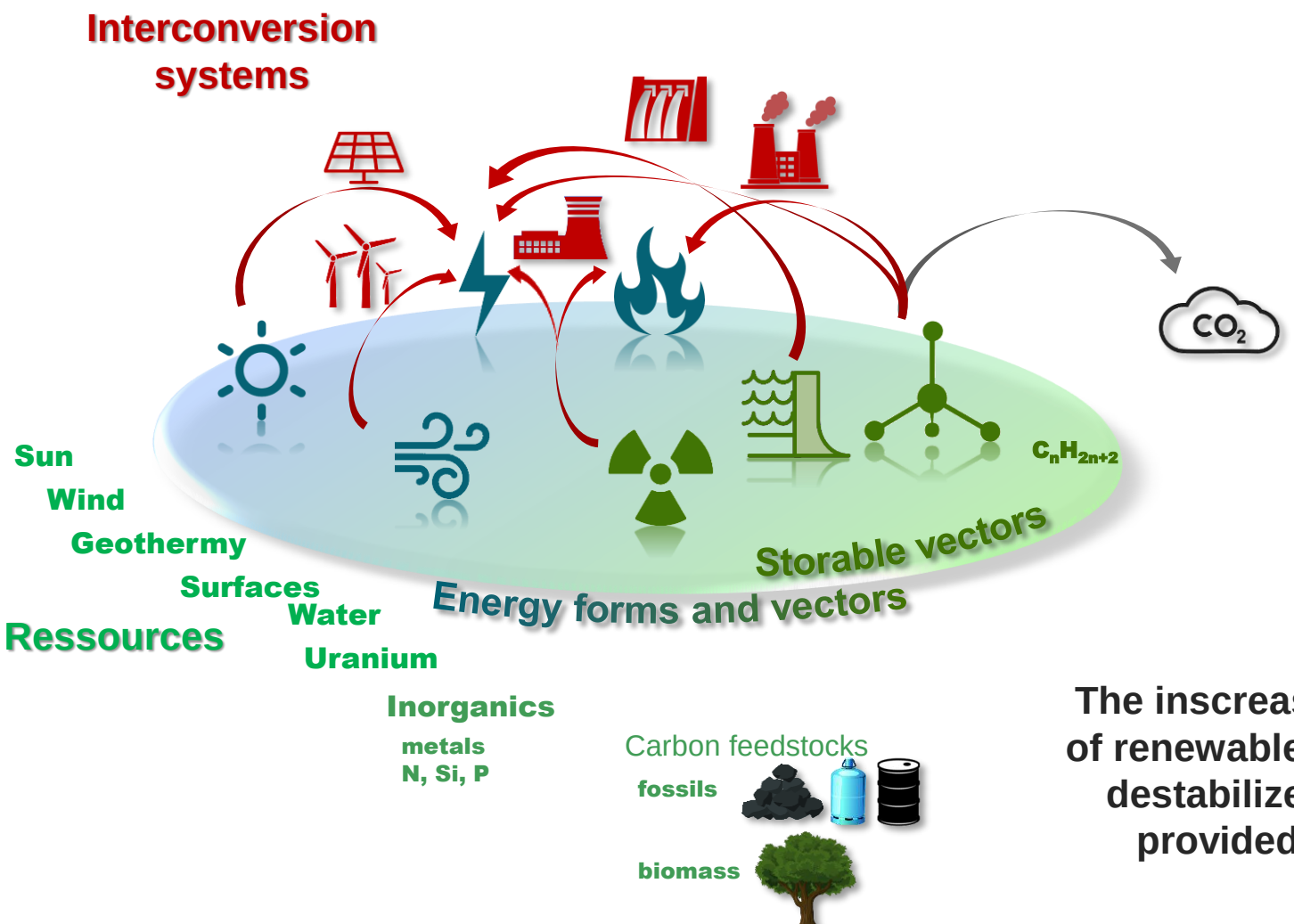
Electrical power on the grid

Power available on demand

Heat

Fuels for mobility

Industrial products (chemicals, materials, fertilizers)



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

Services to society

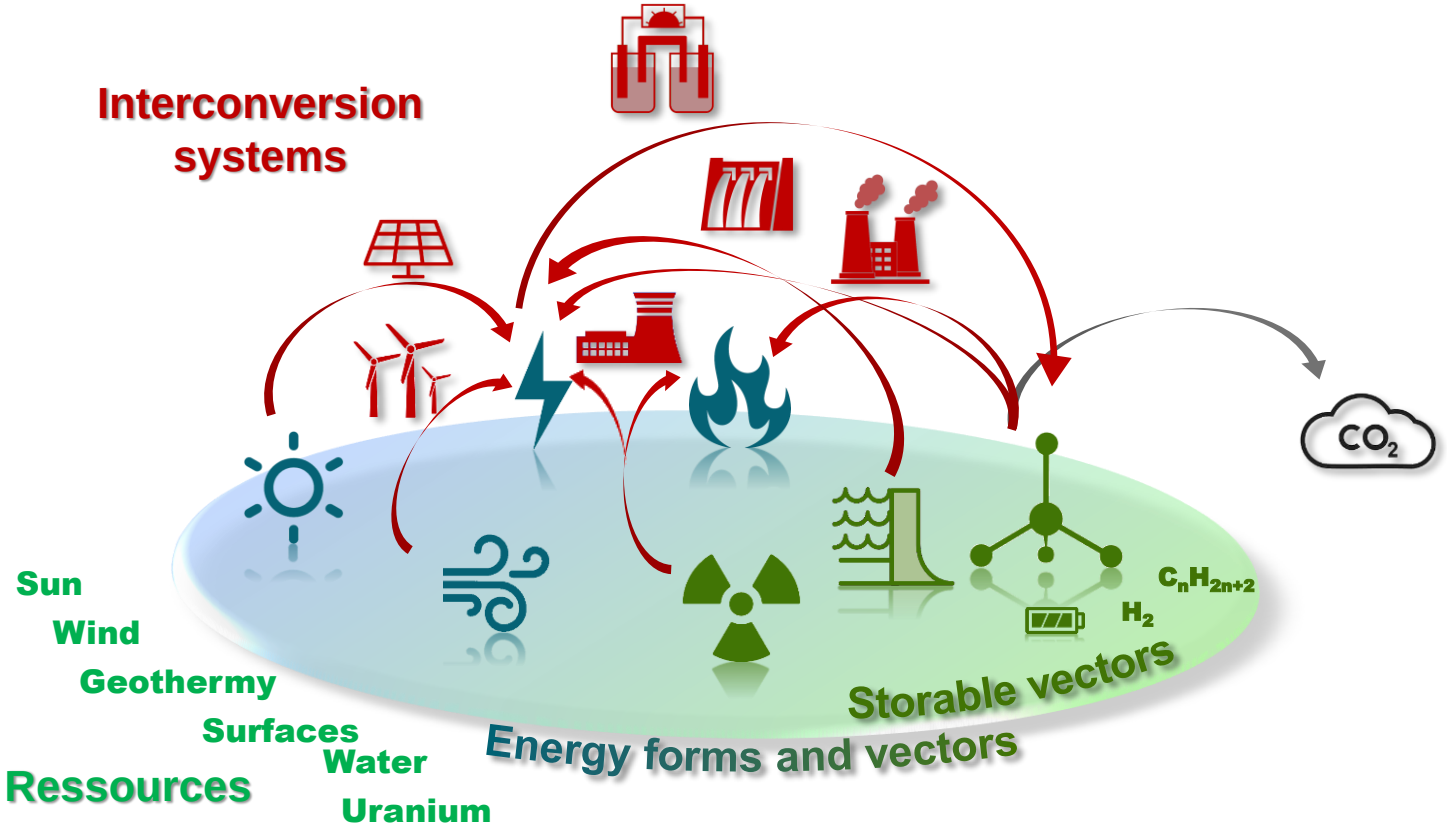
Electrical power on the grid

Power available on demand

Heat

Fuels for mobility

Industrial products (chemicals, materials, fertilizers)



Inorganics

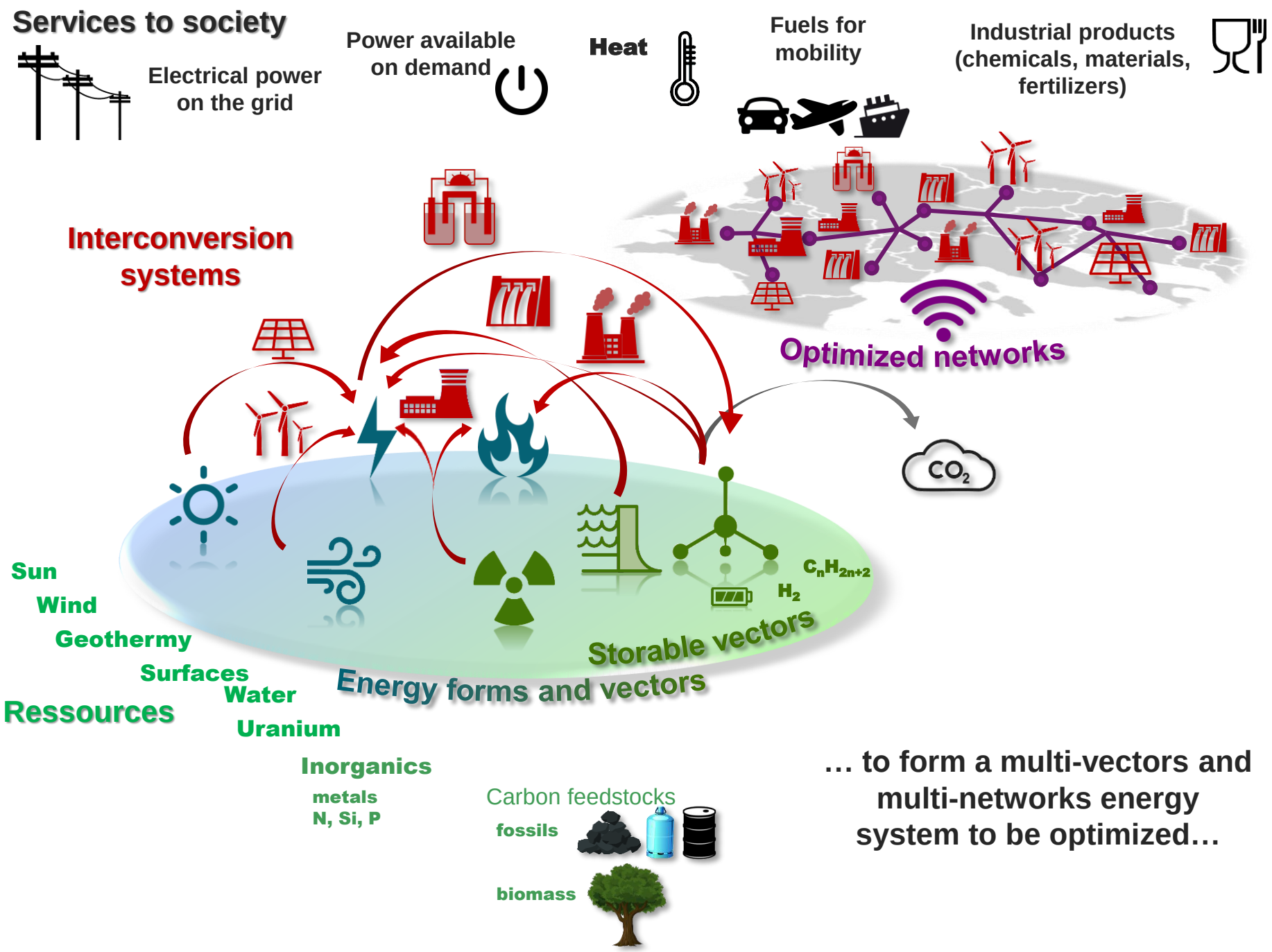
metals
N, Si, P

Carbon feedstocks

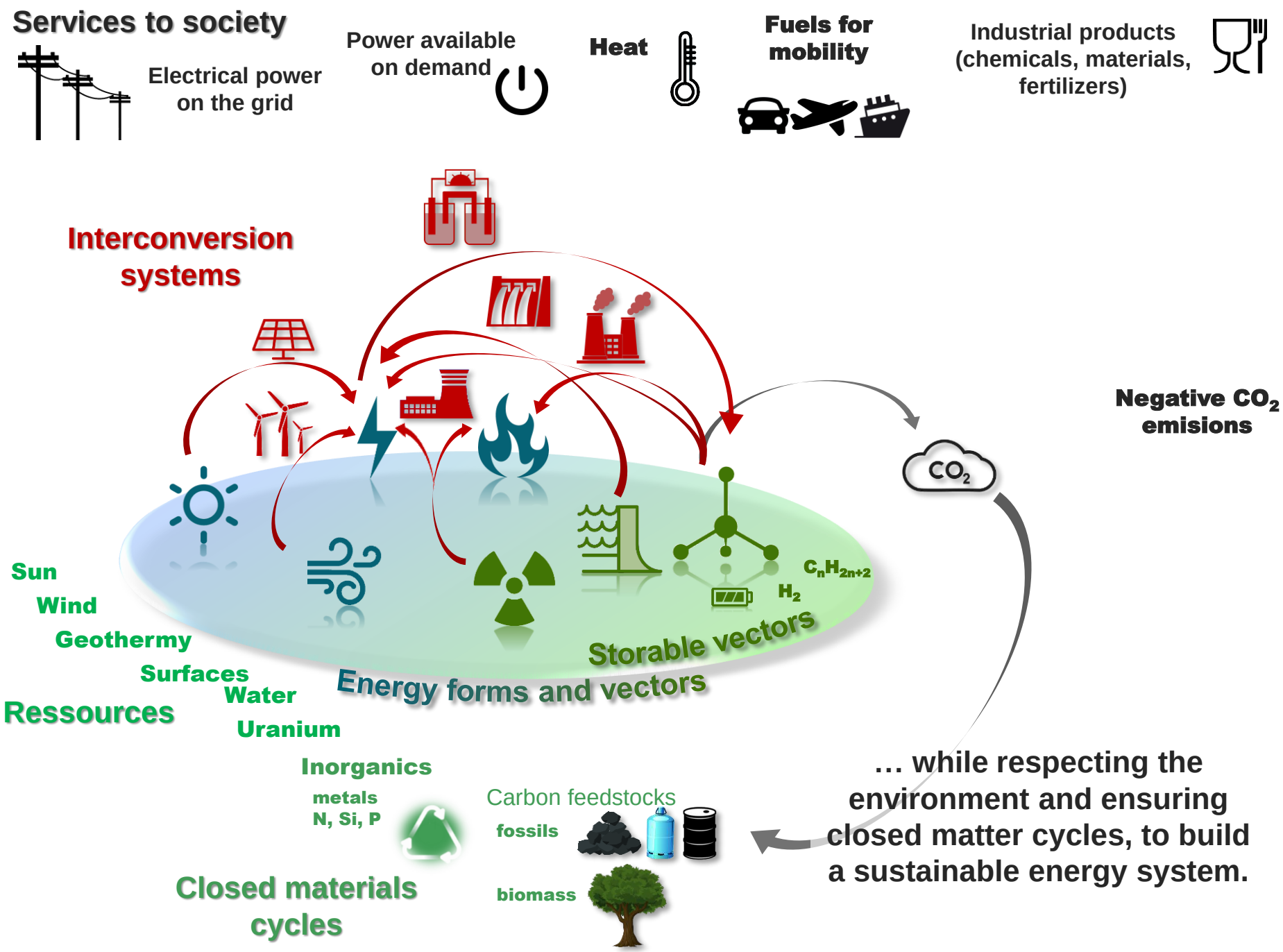
fossils

biomass

…and imposes the development of conversion and storage solutions…

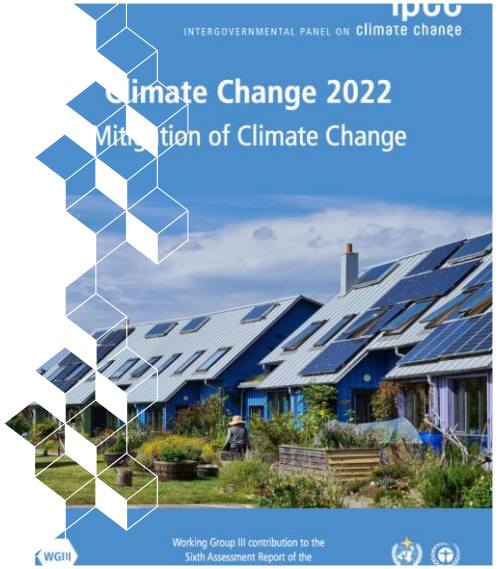


… to form a multi-vectors and multi-networks energy system to be optimized…

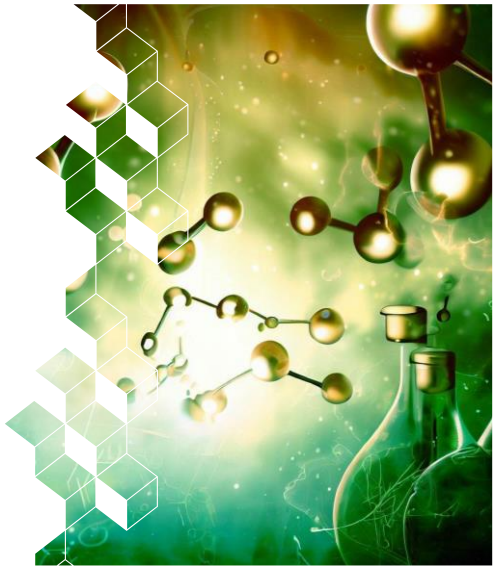

Services to society
Electrical power on the grid
Power available on demand
Heat
Fuels for mobility
Industrial products (chemicals, materials, fertilizers)
Interconversion systems
Negative CO_2 emisions
CO_2
C_nH_{2n+2}
H_2
Storable vectors
Energy forms and vectors
Sun
Wind
Geothermy
Surfaces
Water
Uranium
Ressources
Inorganics
metals
N, Si, P
Carbon feedstocks
fossils
biomass
Closed materials cycles
… while respecting the environment and ensuring closed matter cycles, to build a sustainable energy system.

The menu

CO_2 conversion: What for?



CO_2 activation, the basics



CO_2 conversion using catalysis: reduction and functionalization

Conversion of CO_2 Coupling electrocatalysis and thermocatalysis

Carbon based products are at the core of energy systems

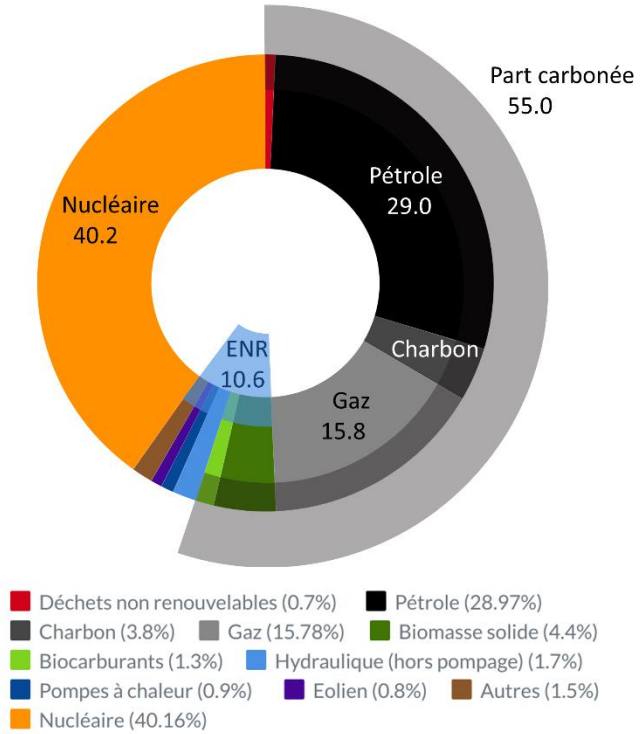
What is the place of carbon products in the French energy system?

The consumption of primary energy in France (2900 TWh) relies for 40% on nuclear energy (for the production of electricity) and for 55% on carbon fuels

A third (1/3) of the uses of carbon products cannot be substituted with carbon-free alternatives such as electrification, H_2 or batteries technologies

46 Mtoe of carbon-based products will need to be produced from renewable energy and carbon sources to ensure services dealing with:

- Liquid fuels for long range transportation
- Production of materials (steel, cast iron, cements)
- Production of chemicals (plastics, agrochemicals, solvents, etc,)



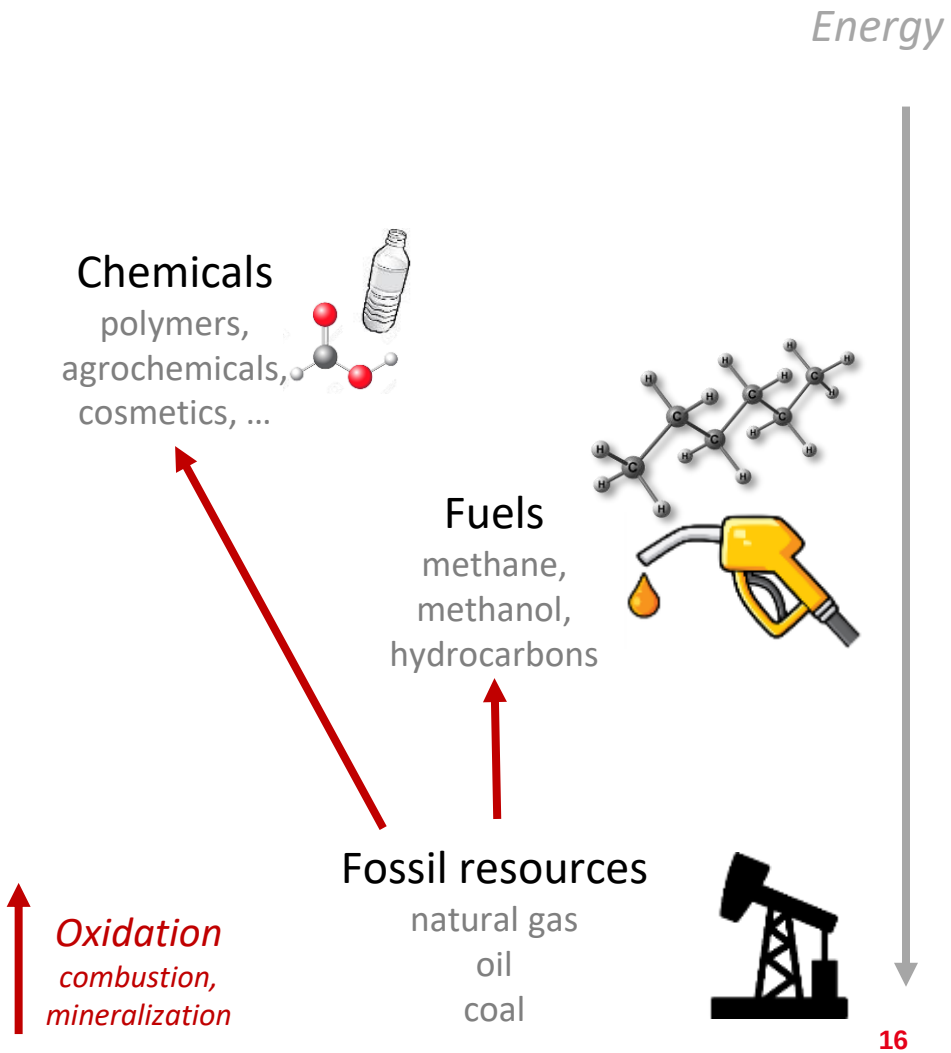
Répartition de la consommation d'énergie primaire en France, pour un total de 2900 TWh, en 2018. Données exprimées en % (données non corrigées de variations climatiques) ; ENR = énergies renouvelables ; d'après « Chiffres clés de l'énergie - Edition 2018 », données SDES; Commissariat général au développement durable.

The circular carbon economy appears in the IPCC reports

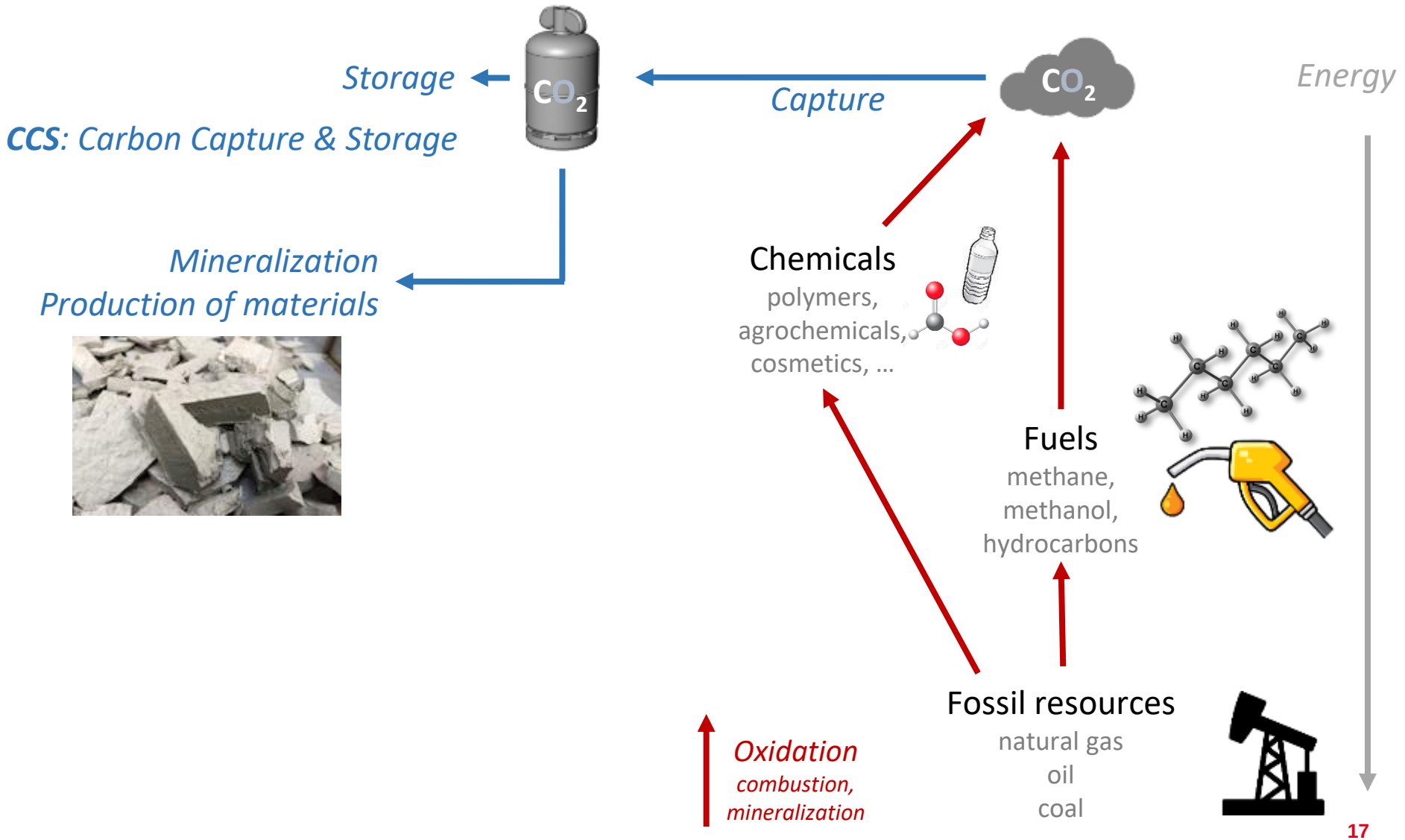
“Carbon is a key building block in organic chemicals, fuels and materials and will remain important (high confidence).”

*“There is growing interest in “circular bioeconomy” concepts applied to bio-based and even a “**circular carbon economy**”, wherein carbon captured via CCU or CDR is converted into reusable materials, which is especially relevant for the transitions of economies dependent on fossil fuel revenue.”*

A linear carbon economy …



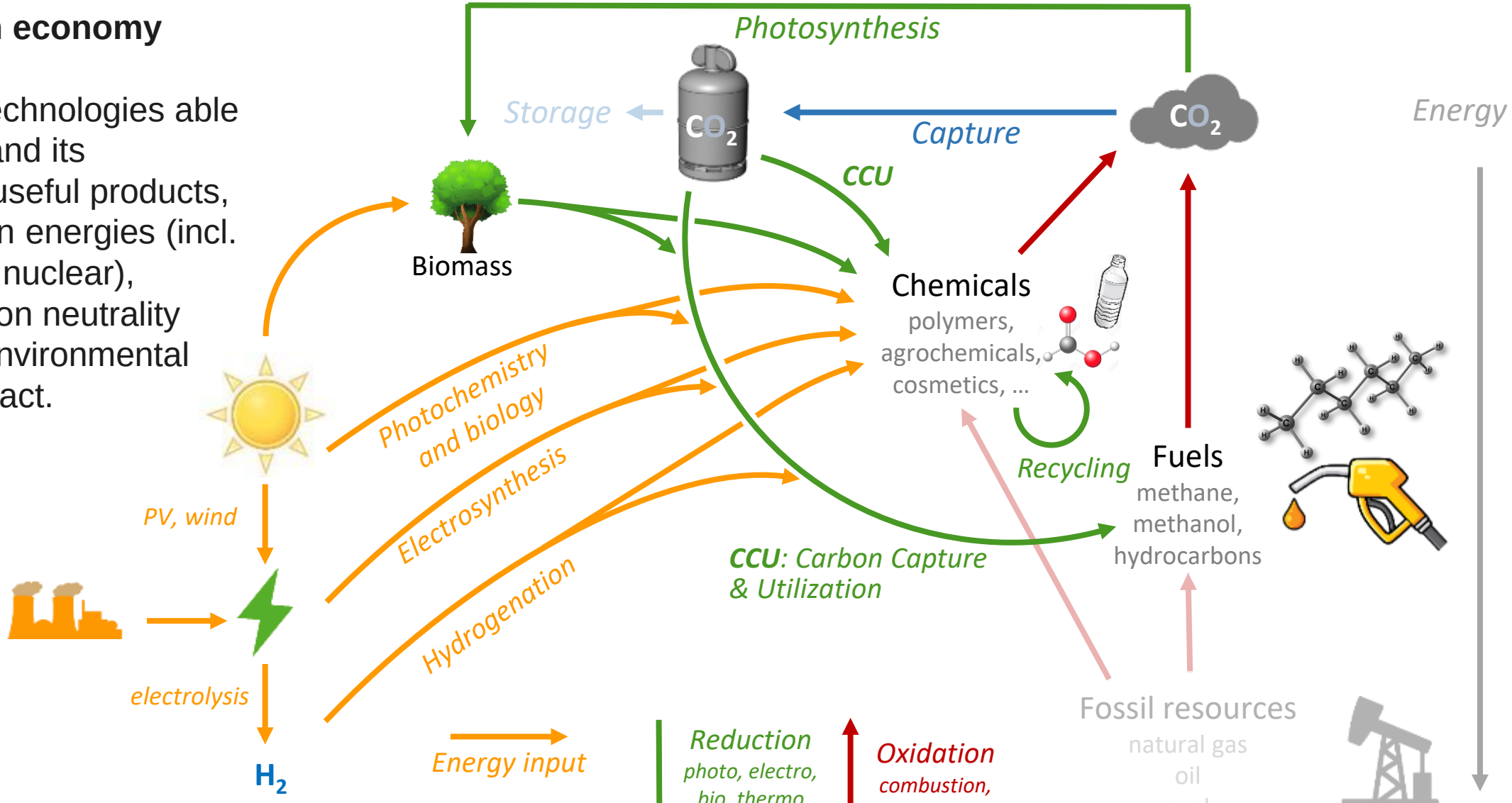
A linear carbon economy assisted with carbon capture and storage?



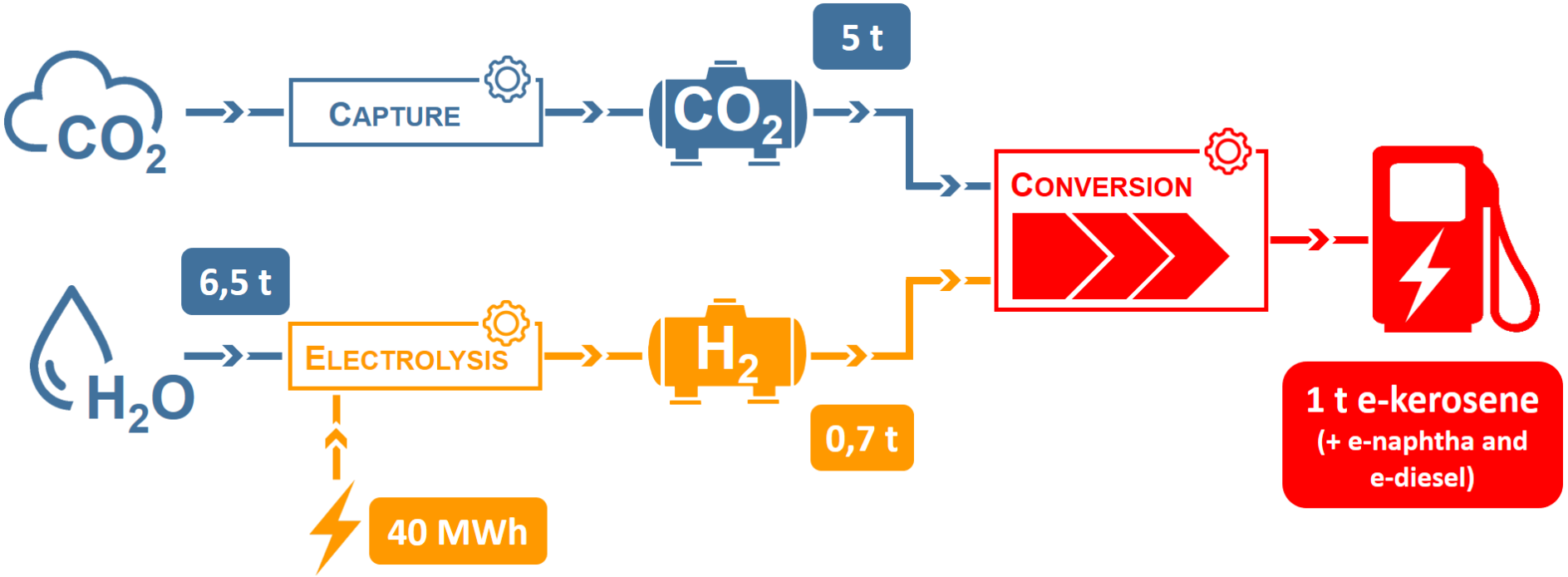
Our vision: a circular carbon economy

A circular carbon economy involves:

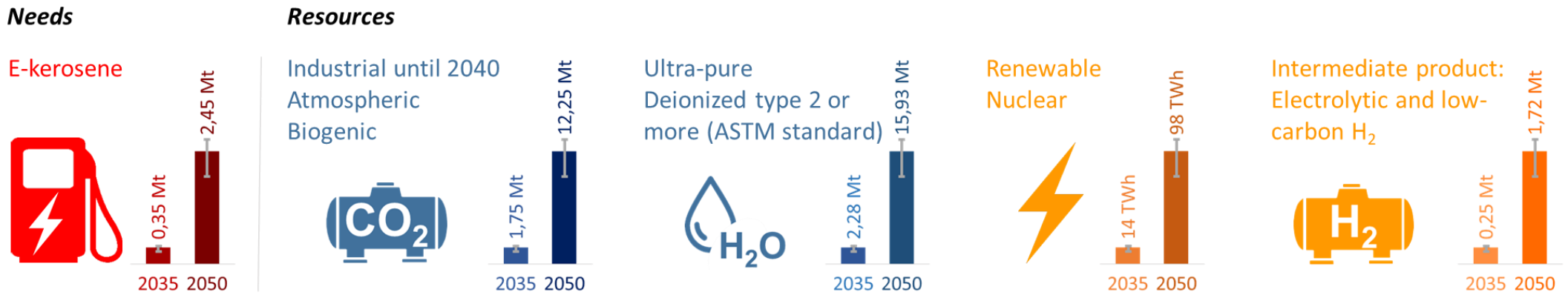
- A collection of technologies able to convert CO_2 and its derivatives into useful products,
- Using low-carbon energies (incl. renewables and nuclear),
- To achieve carbon neutrality with a positive environmental and societal impact.



Ressources are key in the implementation of e-fuels

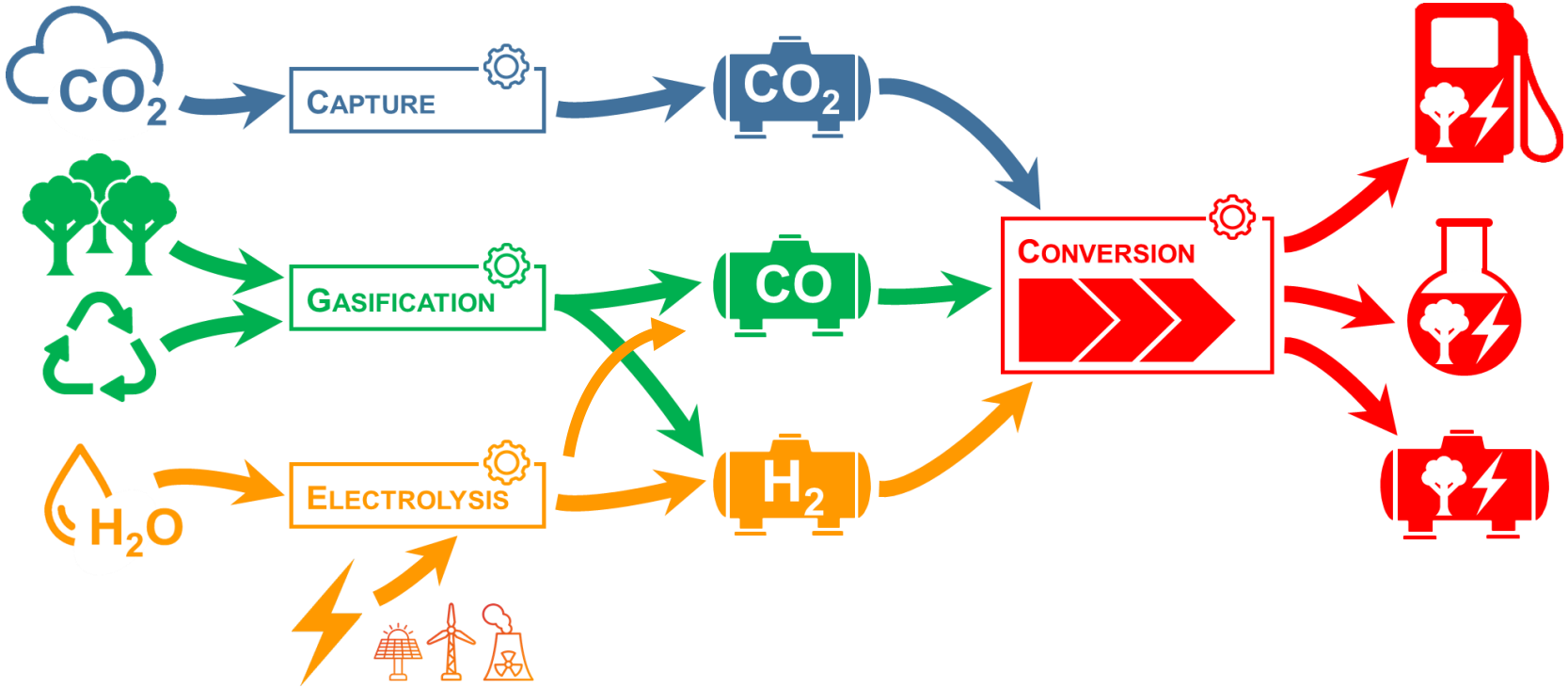


Needs to comply with the ReFuelEU legislation in France, in 2035 and 2050:

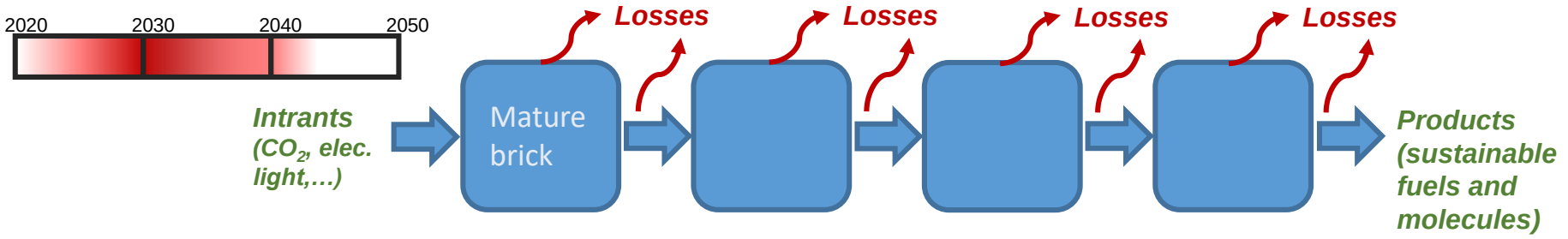


Key challenges …

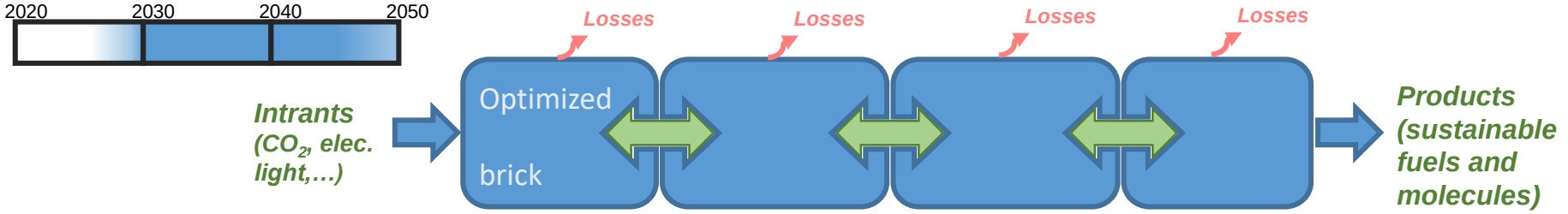
- Accelerate the implementation of CCU products and in particular e-(bio)fuels by:
  - **Lowering production costs**
  - **Minimising losses** in carbon and energy, and use biomass resources optimally
  - **Minimising the overall environmental impacts** of SAF/SMF beyond the sole criterion of CO_2 emissions



Our strategy: accelerate the emergence of e-(bio)molecules through R&D

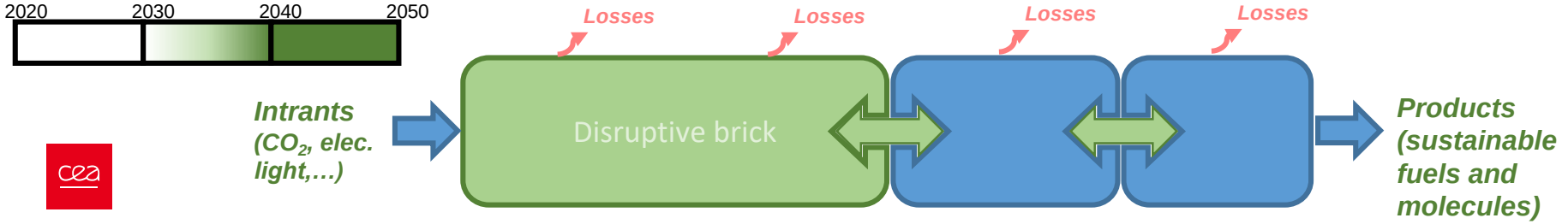


A generation of production of sustainable fuels, based on revisited, optimised and integrated conversion bricks, to optimize yields and energy efficiency



Support our industrial partners with the development of optimized and integrated technological bricks.

A future generation of production of sustainable fuels based on disruptive and innovative bricks, able to shorten value chains and maximize efficiencies



Intensify academic research to propose disruptive processes capable of streamlining and shortening value chains.

CO_2 activation, the basics

Outline

I. CO_2 chemistry: back to basics

II. CO_2 Transformation : Reduction

- III.1. Electro- and photoelectro-reduction
- III.2. Hydrogenation
- III.3. Hydrosilylation and hydroboration

III. CO_2 Transformation: functionalization

IV. CO_2 transformation: reductive Functionalization

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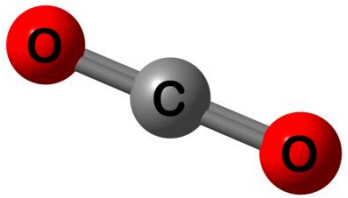
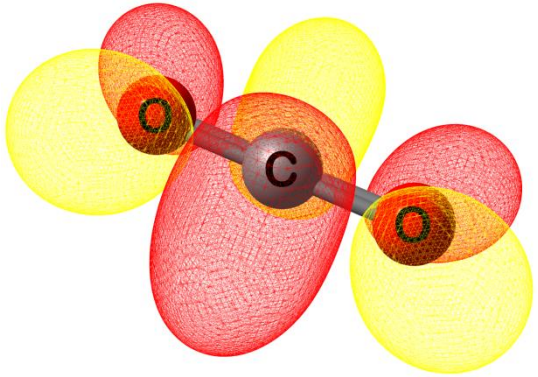
CO_2 stability

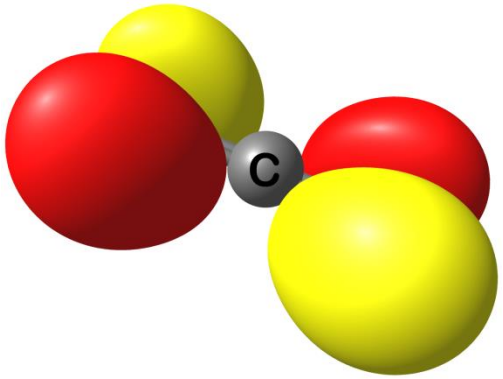
Frontier molecular orbitals



C-O: 1.16 Å



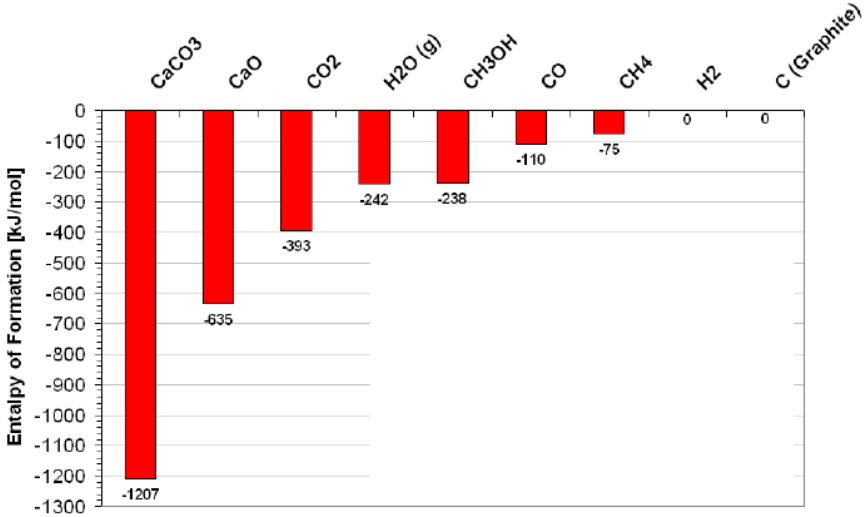
LUMO
$2\pi_u$



HOMO
$1\pi_g$

$$\overset{\delta^-}{O}=\overset{2\delta^+}{C}=\overset{\delta^-}{O}$$

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

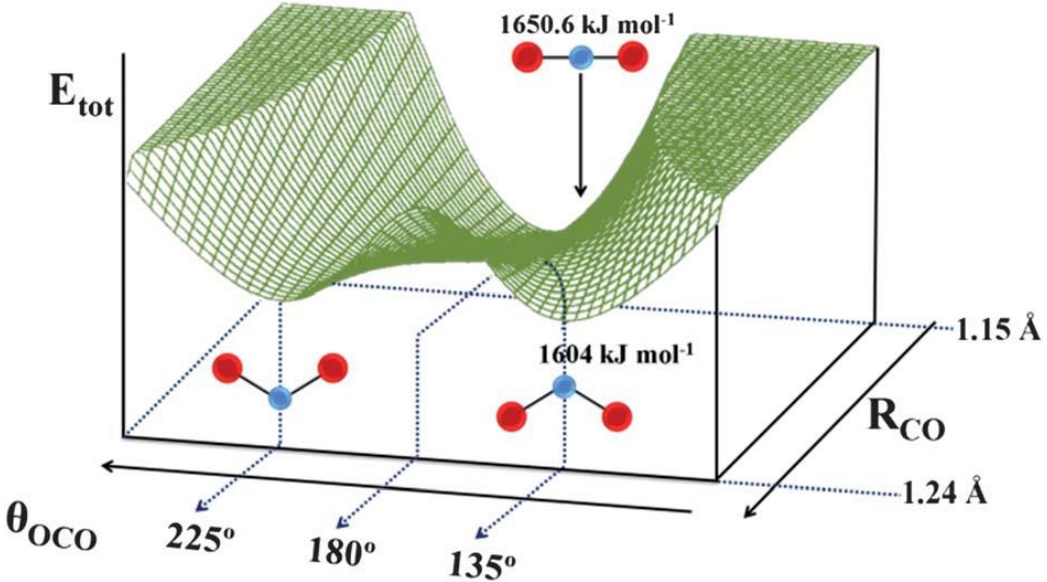


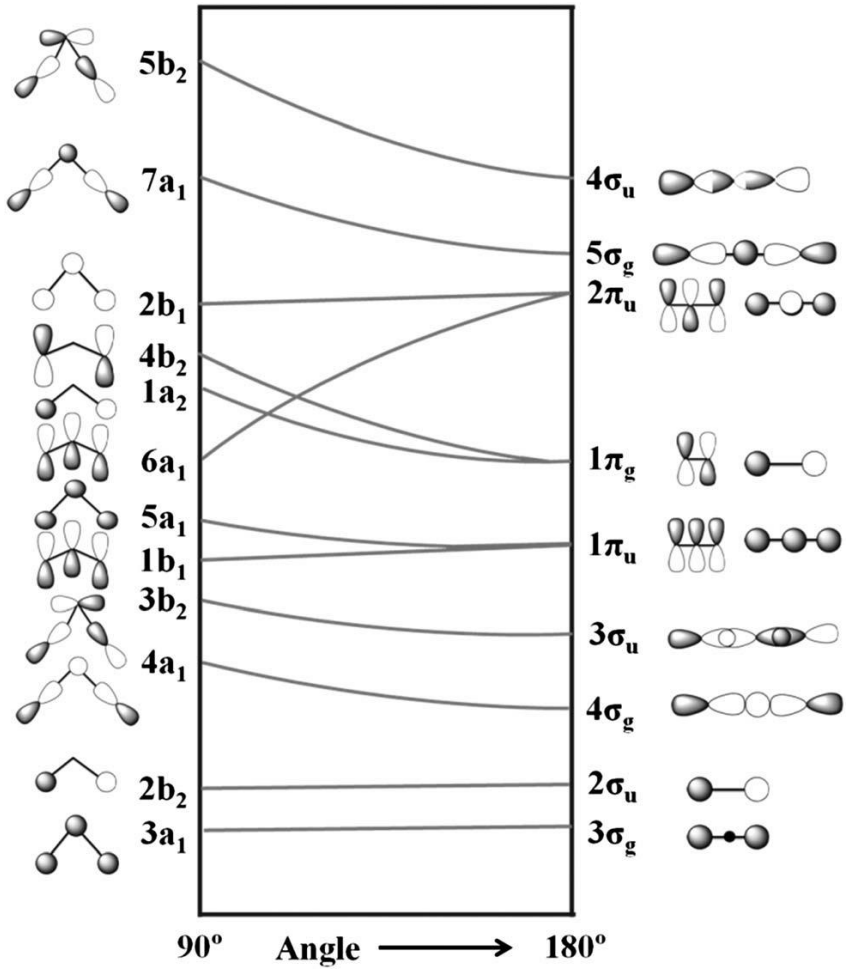
CO_2 stability: kinetics and thermodynamics

Redox potentials

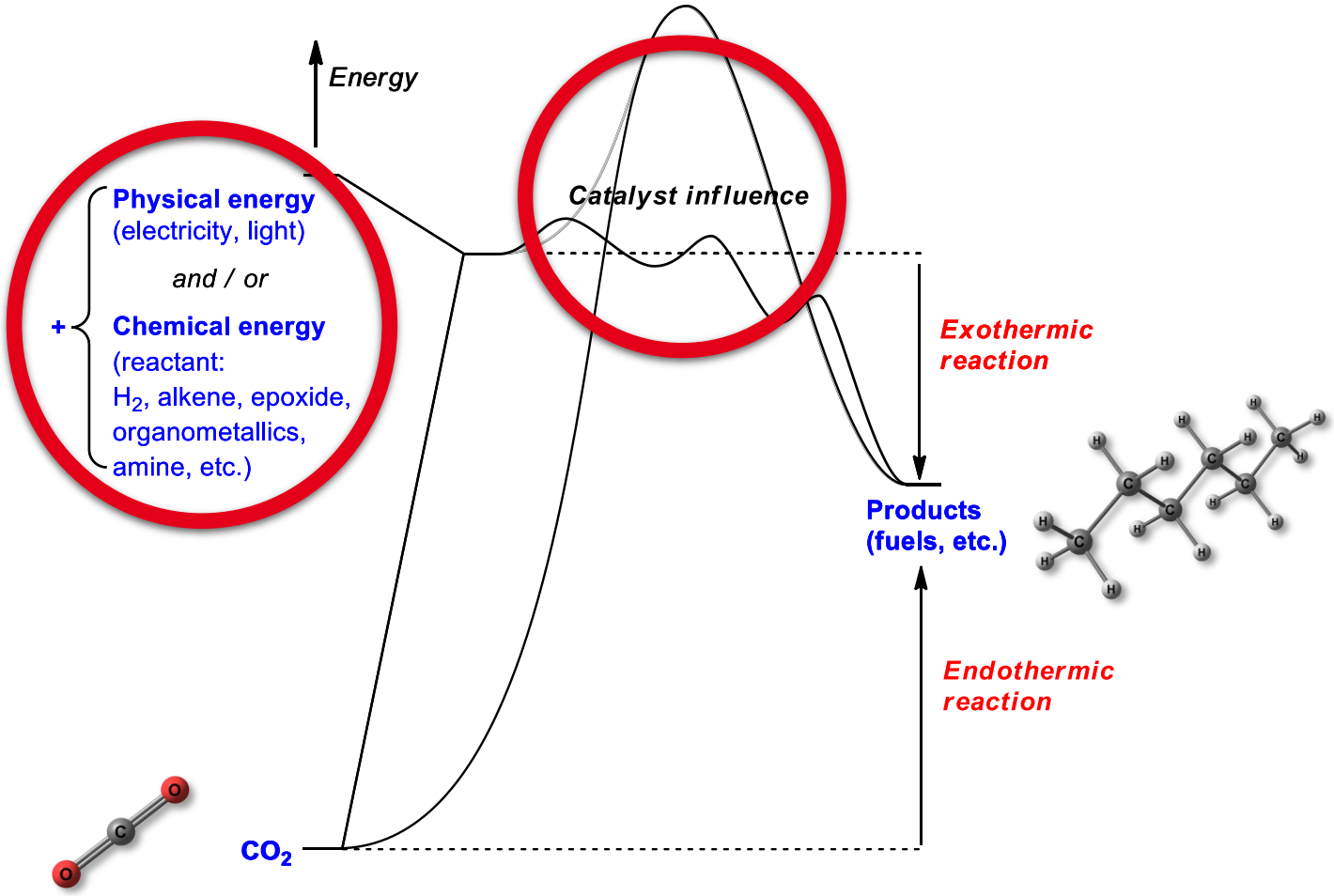
Multi-electron reduction of CO_2 in water (pH=7) vs. SCE

$CO_2 + e^-$	$\longrightarrow$	$CO_2^{\bullet -}$	E° = -1.90 V
$CO_2 + 2\,H^+ + 2\,e^-$	$\longrightarrow$	$CO + H_2O$	E° = -0.76 V
$CO_2 + 2\,H^+ + 2\,e^-$	$\longrightarrow$	$HCOOH$	E° = -0.85 V
$CO_2 + 4\,H^+ + 4\,e^-$	$\longrightarrow$	$HCOH + H_2O$	E° = -0.72 V
$CO_2 + 6\,H^+ + 6\,e^-$	$\longrightarrow$	$CH_3OH + H_2O$	E° = -0.62V
$CO_2 + 8\,H^+ + 8\,e^-$	$\longrightarrow$	$CH_4 + 2\,H_2O$	E° = -0.48 V



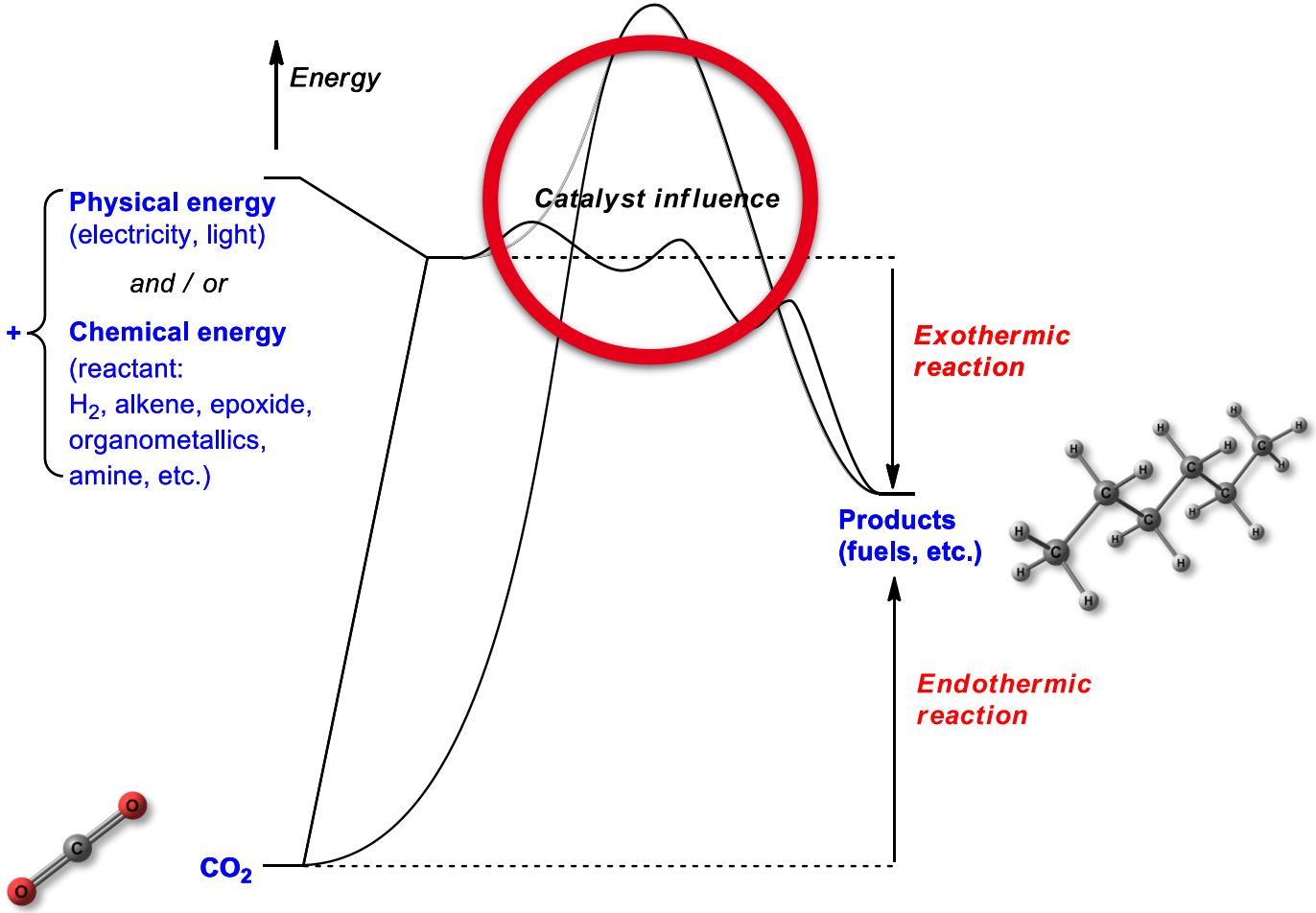


Chemical transformation of CO_2



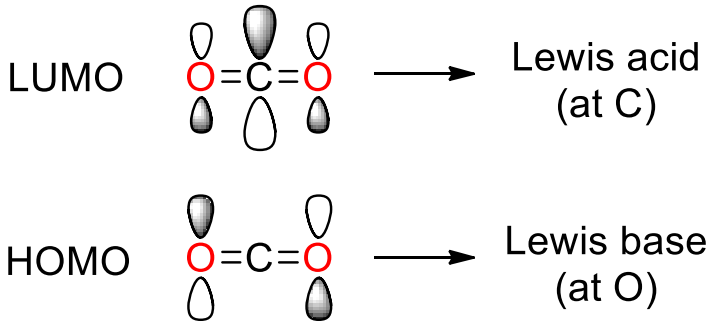
Two energetic challenges: thermodynamic and kinetic

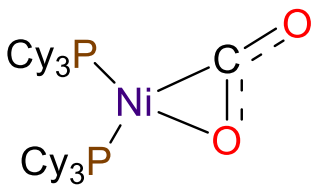
Chemical transformation of CO_2



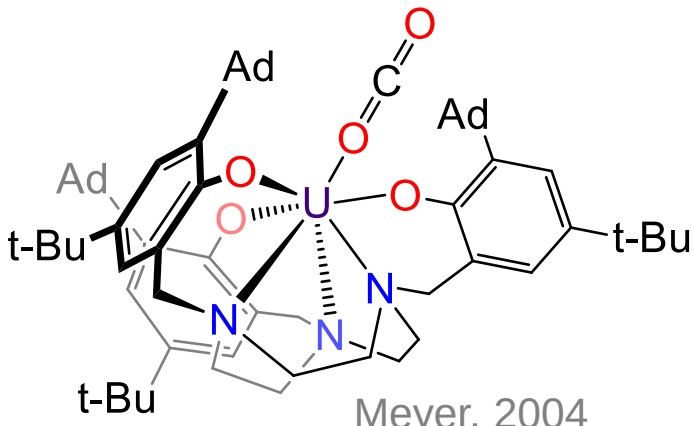
Is CO_2 activation required?

CO_2 Activation by transition metals



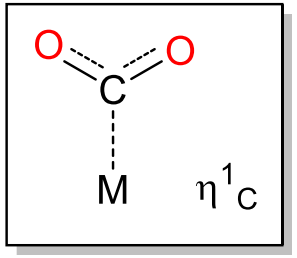


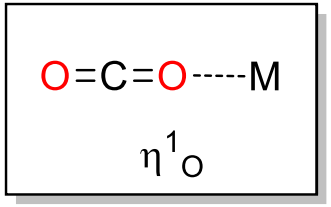
Aresta, 1975

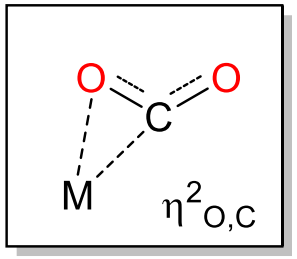


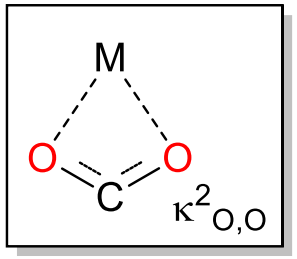
Meyer, 2004

CO_2 + M →

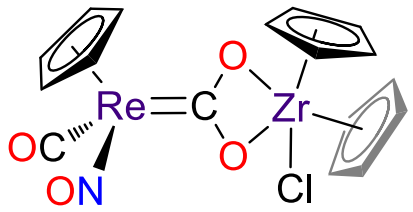








Bimetallic activation



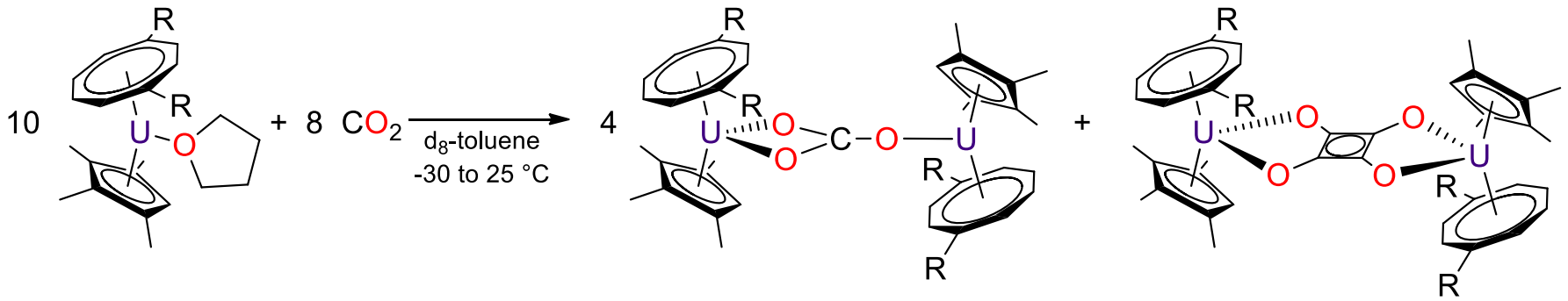
μ^2-η^3

Cutler, 1986

CO_2 Activation by transition metals

Reaction chemistry of metal complexes with CO_2

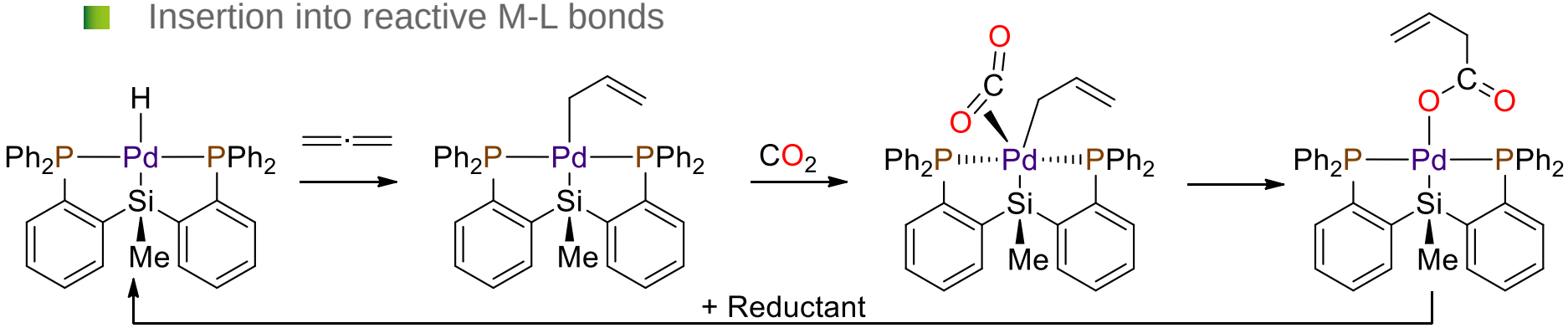
- Reduction and reductive coupling



$10\ e^- + 8\ CO_2 \longrightarrow 4\ CO_3^{2-} + C_4O_4^{2-}$

Cloke, 2009

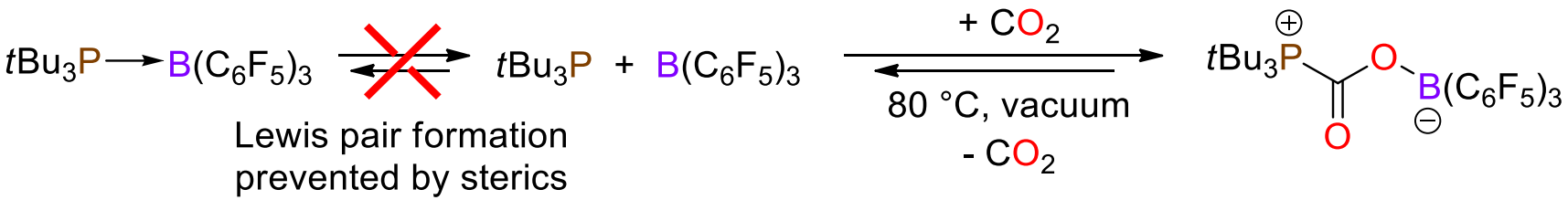
- Insertion into reactive M-L bonds



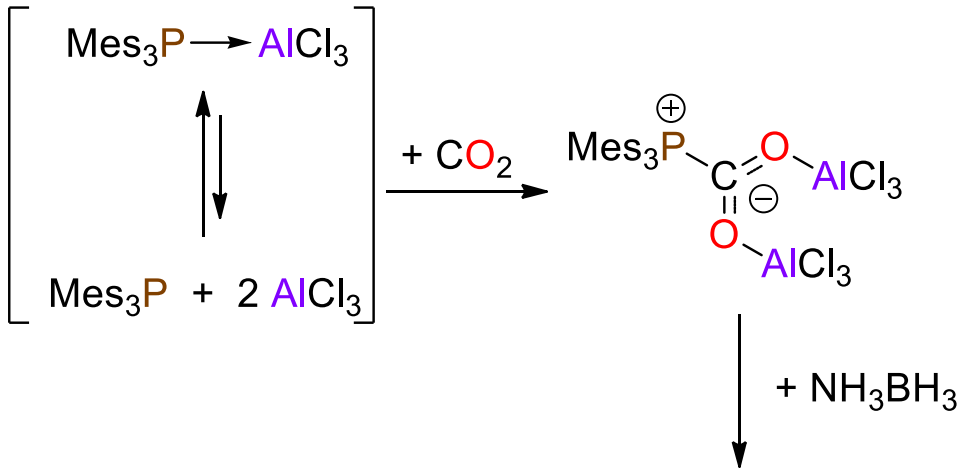
Iwasawa, 2008

CO_2 Activation by organic compounds

- Activation by Frustrated Lewis Pairs (FLPs)

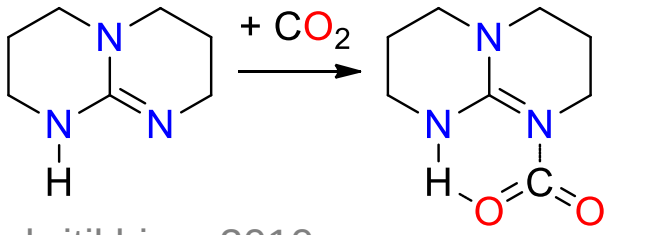


Stephan, 2009

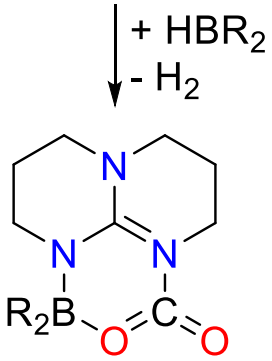


Stephan, 2010

- Activation by nitrogen bases



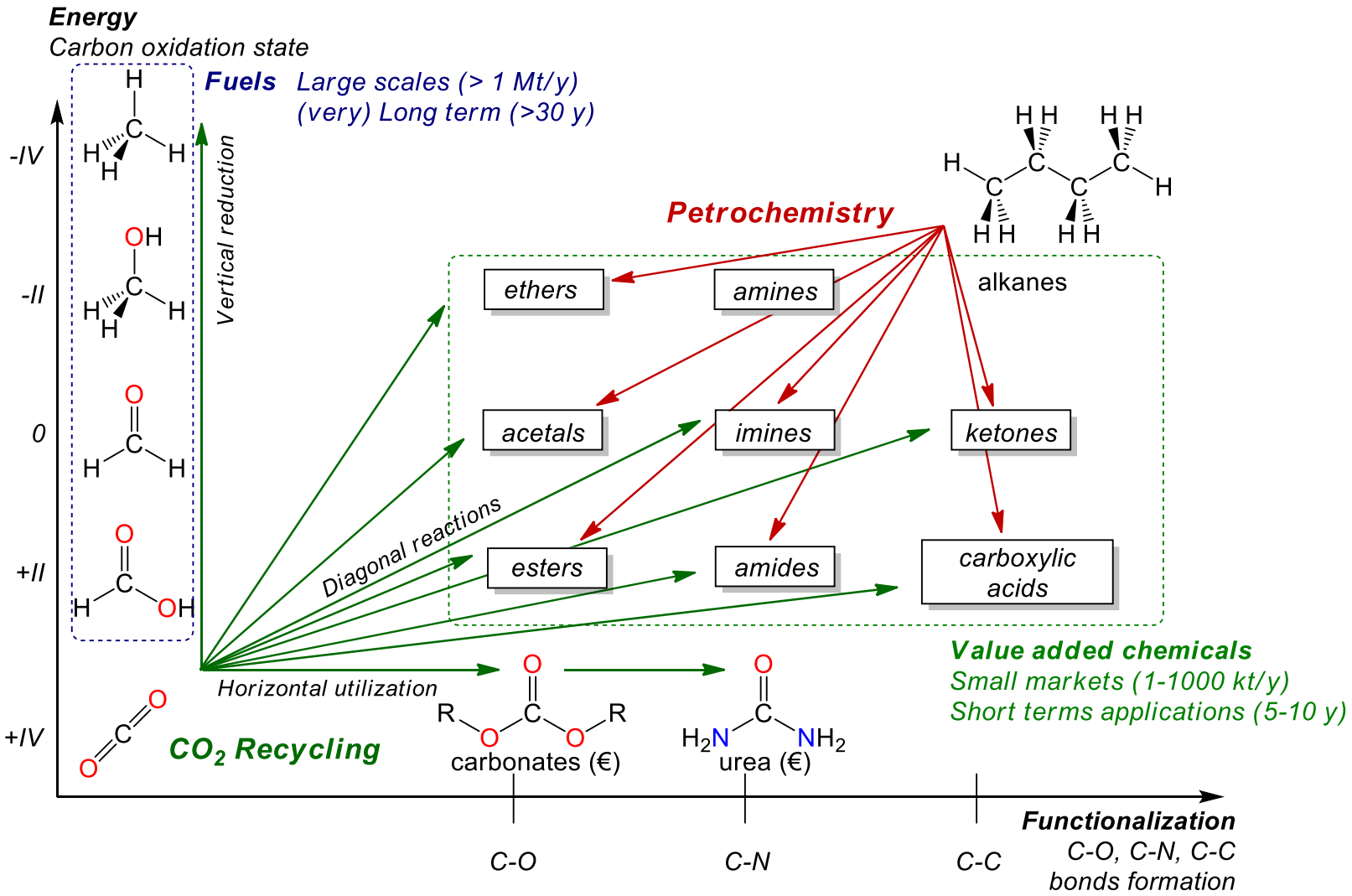
Ephritikhine, 2010



Cantat, 2013

Active in the catalytic hydroboration of CO_2

Various opportunities to CO_2 recycling…



Cantat et al., *Angew. Chem. Int. Ed.* **2012**, *51*, 187

CO_2 conversion using catalysis: reduction and functionalization

Outline

I. CO_2 chemistry: back to basics

II. CO_2 Transformation : Reduction

III.1. Electro- and photoelectro-reduction
III.2. Hydrogenation
III.3. Hydrosilylation and hydroboration

III. CO_2 Transformation:
functionalization

IV. CO_2 transformation:
reductive Functionalization

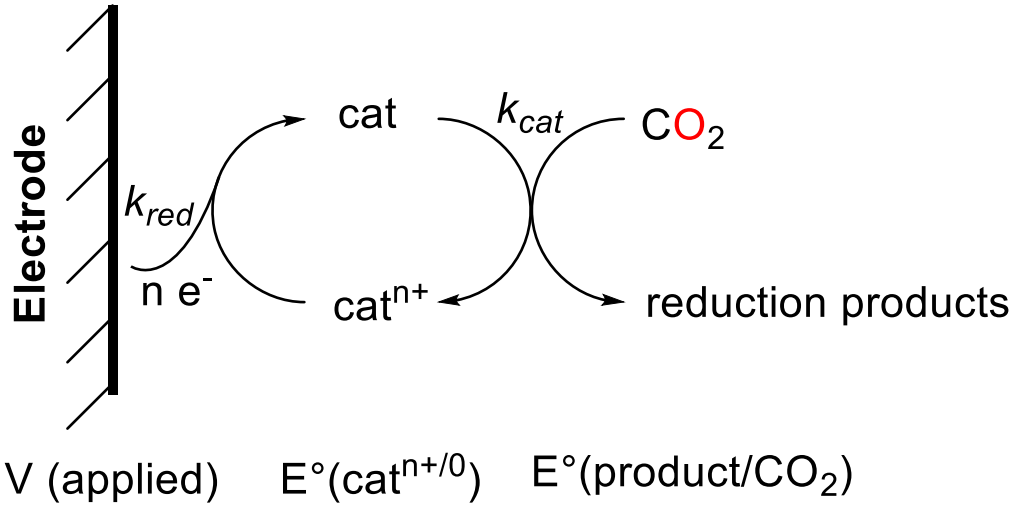
Available reductants for CO_2 conversion

$E°(CO_2/CH_3OH)$ = **-0.38 V**

$H^+ + e^-$	H_2	R_3SiH	R_2BH
Electrolysis	***Hydrogen***	***Hydrosilanes***	***Hydroboranes***
E°is fully tunable	$E°(H^+/H_2)$ = 0.0 V = **-0.41 V** at pH=7	$E°(SiO_2/SiH_4)$ = **-0.38 V**	$E°(B(OH)_3/BH_3)$ = **- 0.48 V**
Electron transfer is critical	BDE(H-H) = 104 kcal/mol	BDE(Si-H) = 92 kcal/mol	BDE(B-H) = 78 kcal/mol
Fully renewable	Renewable through water (photo)electrolysis	PMHS and TMDS are disposable hydrosilanes	non-renewable
available on large scale	available on 10-100 Mtons/year scale	available on 10-100 ktons/year scale	

CO_2 electroreduction

Principle of CO_2 electroreduction



Multi-electron reduction of CO_2 in water (pH=7) vs. SCE

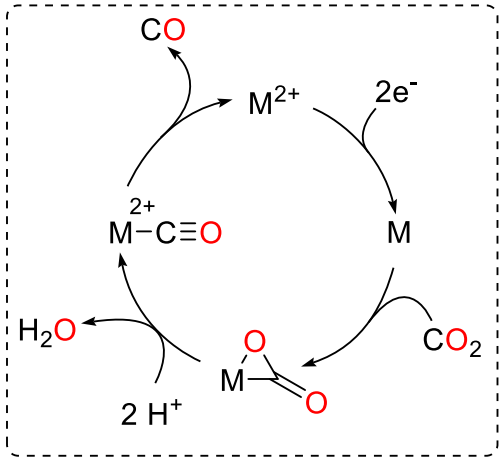
$CO_2 + e^-$	$\longrightarrow$	$CO_2^{\bullet -}$	E° = -1.90 V
$CO_2 + 2\,H^+ + 2\,e^-$	$\longrightarrow$	$CO + H_2O$	E° = -0.76 V
$CO_2 + 2\,H^+ + 2\,e^-$	$\longrightarrow$	$HCOOH$	E° = -0.85 V
$CO_2 + 4\,H^+ + 4\,e^-$	$\longrightarrow$	$HCOH + H_2O$	E° = -0.72 V
$CO_2 + 6\,H^+ + 6\,e^-$	$\longrightarrow$	$CH_3OH + H_2O$	E° = -0.62V
$CO_2 + 8\,H^+ + 8\,e^-$	$\longrightarrow$	$CH_4 + 2\,H_2O$	E° = -0.48 V
$2\,H^+ + 2\,e^-$	$\longrightarrow$	H_2	E° = -0.41 V

Review: Kubiak et al., *Chem. Soc. Rev.* **2009**, *38*, 89

CO_2 electroreduction to CO

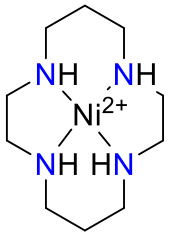
$$CO_2 + 2\,H^+ + 2\,e^- \longrightarrow CO + H_2O \qquad E° = -0.76\ V$$

Mechanistic scheme

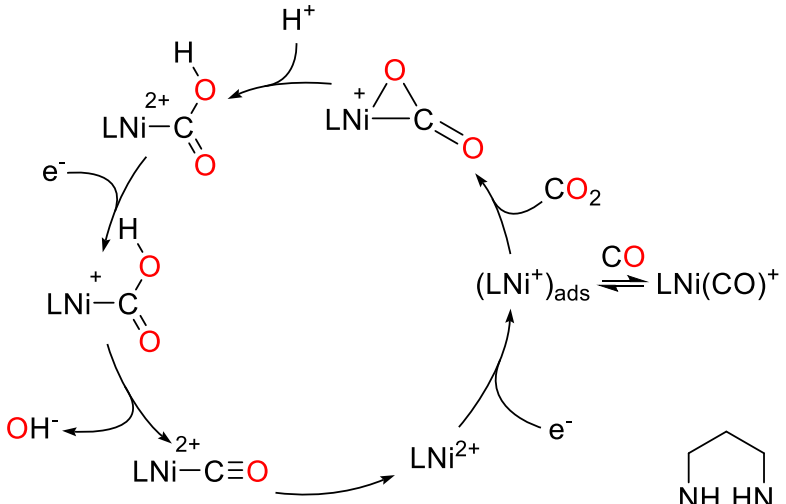


Example:

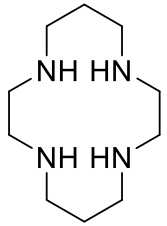
M^{2+} =

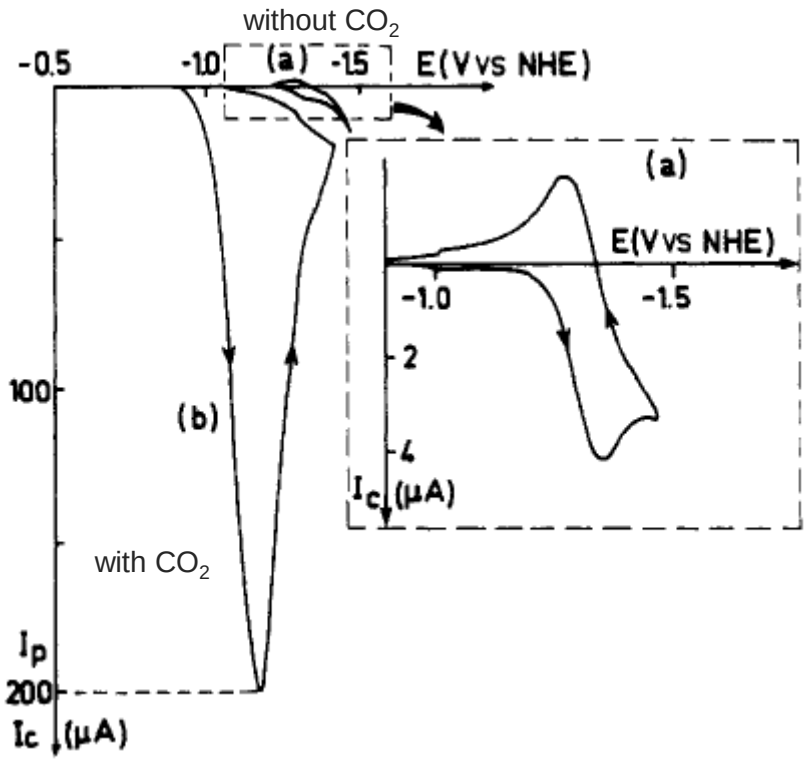


Sauvage, 1984



L = cyclam:





Voltammogram for the electroreduction of CO_2 catalyzed by $Ni(cyclam)^{2+}$

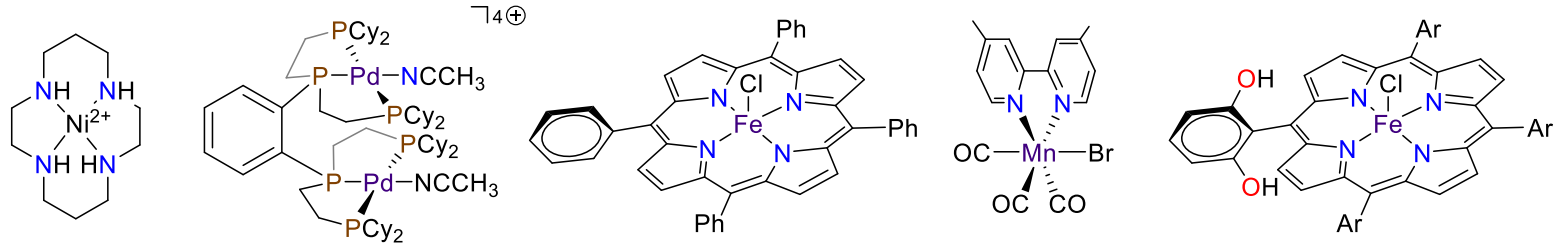
Overpotential: $\eta = 0.55\ V$ ($V = -1.31\ V$)
TurnOver Frequency: $TOF = 1250\ s^{-1}$

Sauvage et al. *JACS*, **1986**, *108*, 7460

CO_2 electroreduction to CO

State of the art catalysts and performances

$$CO_2 + 2\,H^+ + 2\,e^- \longrightarrow CO + H_2O \qquad E° = -0.76\ V$$



	Sauvage, 1984	Dubois, 1990	Savéant, 1994	Deronzier, 2011	Savéant, 2012
η (V)	0.6	0.8	0.9	0.5	0.5
log*TOF* (s^{-1})	2.2	0.7	2	-0.1	3
logTOF_0 (s^{-1}) at η = 0 V	-7.1	-7.5	-14	-8.4	-4.6

- Concomittant H_2 evolution is observed for all the catalysts
- Fine management of the local concentration of H^+ is crucial

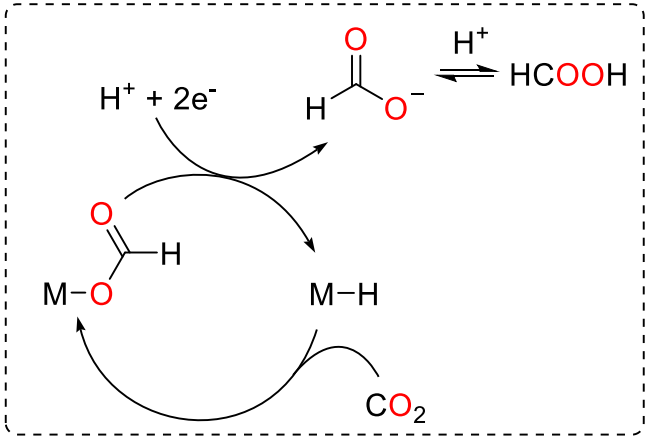
Savéant et al., *Science* **2012**, *338*, 90

CO_2 electroreduction to formic acid

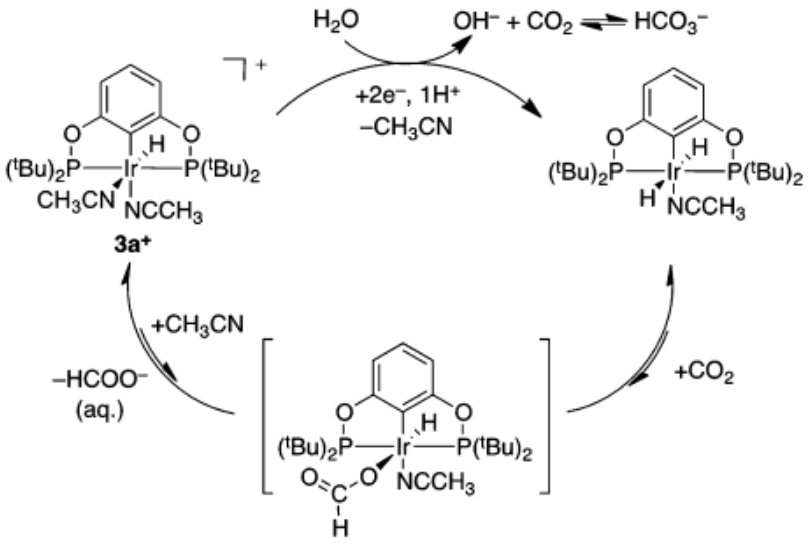
$$CO_2 + 2\,H^+ + 2\,e^- \longrightarrow HCOOH \qquad E° = -0.85\ V$$

- Molecular catalysts: Copper, rhodium and iridium complexes are good catalysts

Mechanistic scheme



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 H_2 and CO

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

- Formate dehydrogenase (FDH) selectively reduces CO_2 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)

CO_2 electroreduction to methanol

A completely different story !

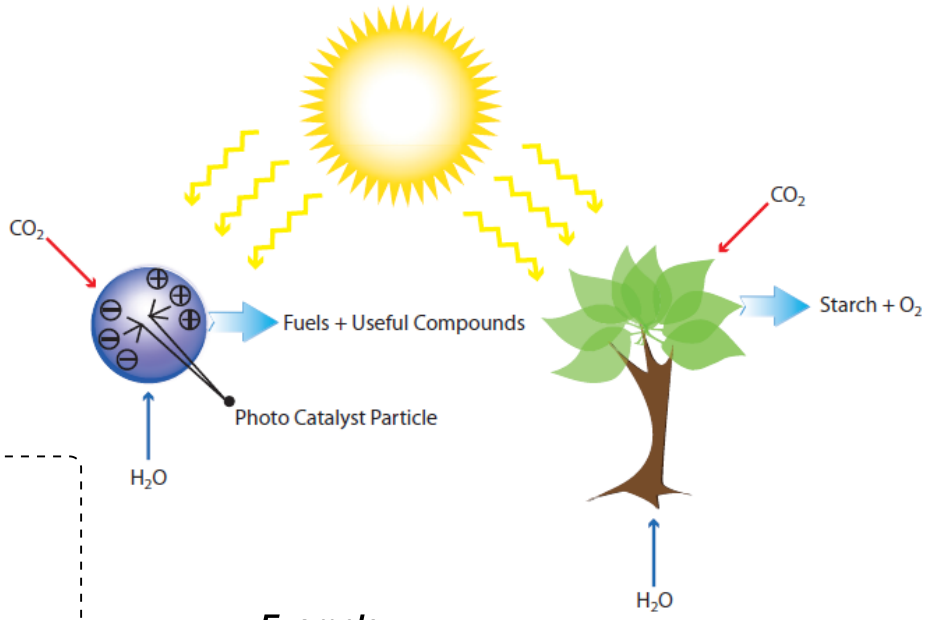
$$CO_2 + 6\,H^+ + 6\,e^- \longrightarrow CH_3OH + H_2O \quad E° = -0.62V$$

- Much more difficult because of multiple H^+ and e^- transfers to synchronize
- Mostly observed as a side product in CO_2 electroreduction to formates

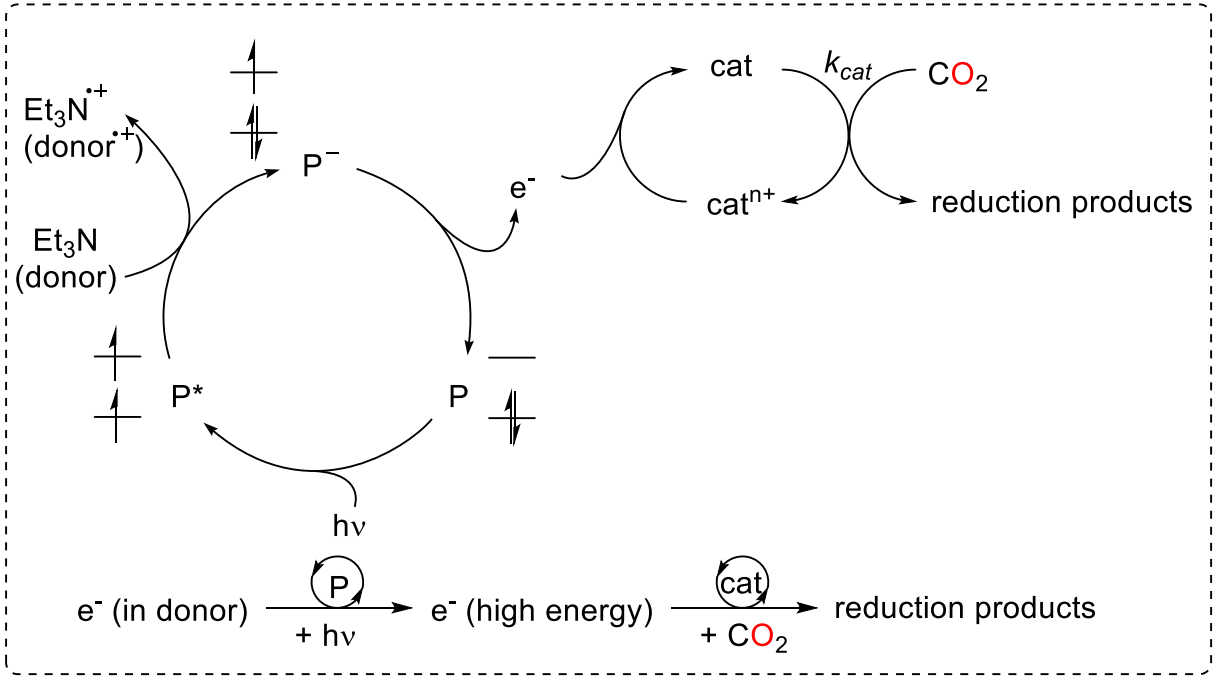
CO_2 photoelectroreduction

The *dream* reaction

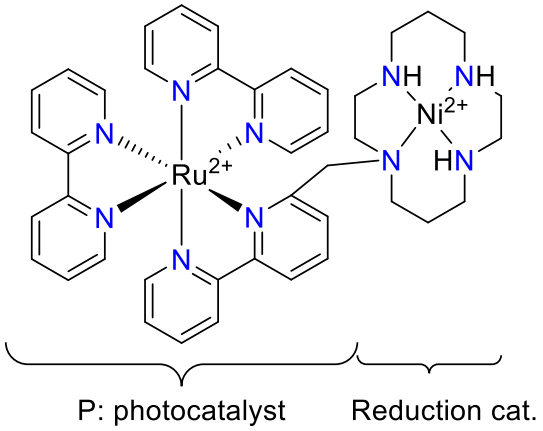
- $CO_2 + H_2 + light = reduction$
- Artificial photosynthesis:



Mechanistic scheme



Example:



Review: Meyer, Fujita et al., *Acc. Chem. Res.* **2009**, *42, 1983*

CO_2 conversion using catalysis: reduction and functionalization

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- III.3. Hydrosilylation and hydroboration

III. CO_2 Transformation: functionalization

IV. CO_2 transformation: reductive Functionalization

CO_2 hydrogenation: thermodynamics

	+IV	+II	0	-II	-IV	ΔH_{298K} kJ/mol	ΔG_{298K} kJ/mol
$CO_2 + H_2 \longrightarrow$		$CO + H_2O$				+41.2	+28.6
$CO_2 + H_2 \longrightarrow$		$HCOOH$				-31.2	+32.9
$CO_2 + H_2 + NH_3 \longrightarrow$		$HCOO^- + NH_4^+$				-84.3	-9.5
		$CO + 2\,H_2 \longrightarrow$		CH_3OH		-91.1	-25.3
$CO_2 + 3\,H_2 \longrightarrow$				$CH_3OH + H_2O$		-49.4	-3.3
$CO_2 + 4\,H_2 \longrightarrow$					$CH_4 + 2\,H_2O$	-165.0	-113.3

- Catalysts are required to facilitate H_2 and CO_2 activation (non polar gases)
- Selectivity is less problematic than with electroreduction

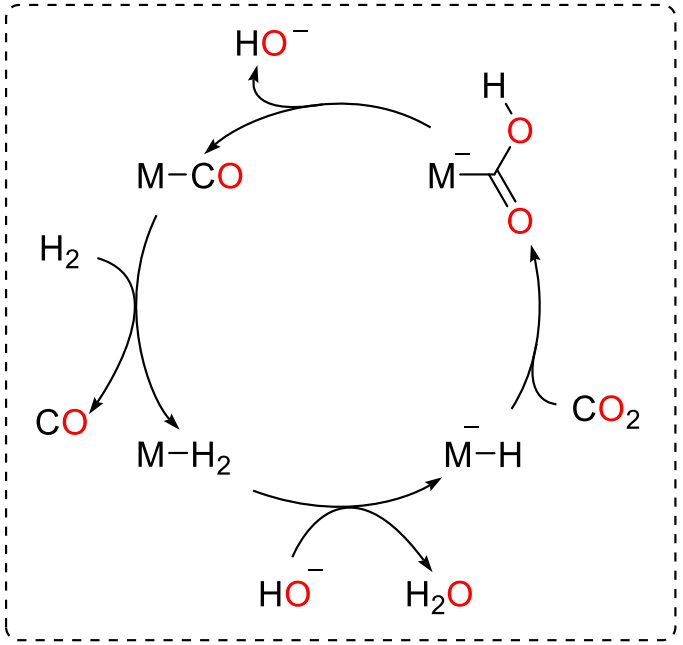
CO_2 hydrogenation to CO: RWGS reaction

CO_2 conversion to CO: Reverse Water Gas Shift

- Enables the formation of syngas (CO/H_2 mixture)
- Cu-Zn catalysts for low temperature shift
- Fe-Cr catalysts for high temperature shift
- Water removal is necessary to shift the equilibrium towards CO
- Rare molecular catalysts exist: e.g. $Fe(CO)_5$

	ΔH_{298K} kJ/mol	ΔG_{298K} kJ/mol
$CO_2 + H_2 \longrightarrow CO + H_2O$	+41.2	+28.6

Mechanistic scheme



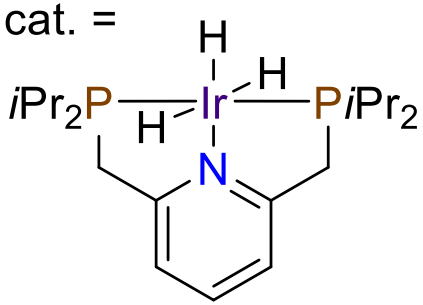
CO_2 hydrogenation to formates with iridium

	ΔH_{298K} kJ/mol	ΔG_{298K} kJ/mol
$CO_2 + H_2 \longrightarrow HCOOH$	-31.2	+32.9
$CO_2 + H_2 + NH_3 \longrightarrow HCOO^- + NH_4^+$	-84.3	-9.5

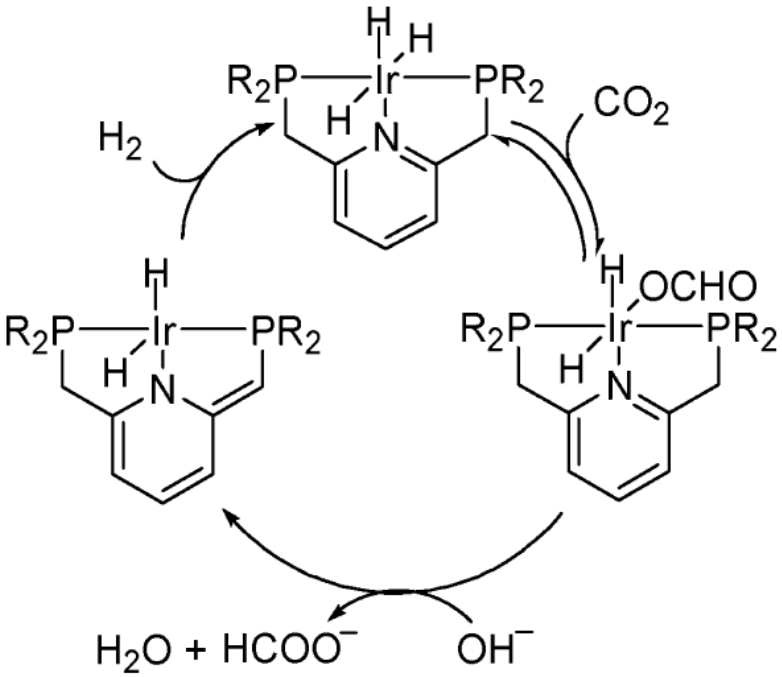
$CO_2 + H_2 \xrightarrow[\text{KOH aq. / THF (50:1)}]{\text{cat.}} HCO_2K$

60 bar (1:1)

cat. =



TON: 3,500,000 !



Nozaki et al., *JACS* **2009**, *131*, 14168

CO_2 hydrogenation to formates with cobalt

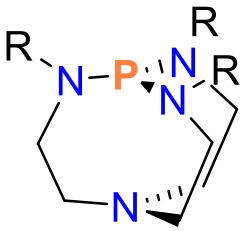
$CO_2 + H_2$ —cat., Base, **20 °C**→ $HCO_2^- + BaseH^+$

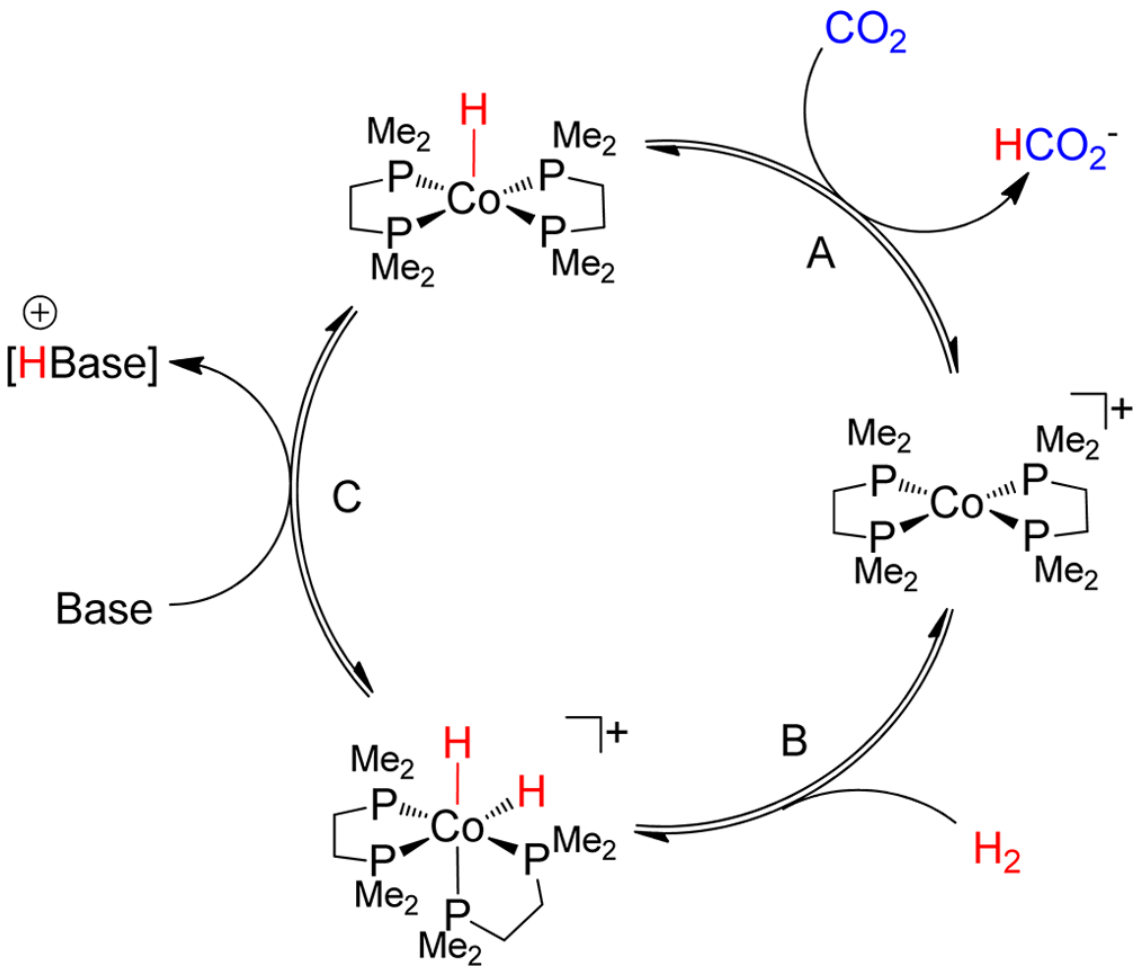
1-20 bar

TON: 74000

cat. = $Co(dmpe)_2H$

Base =





Linehan et al., *JACS* **2013**, *135*, 11533

CO_2 hydrogenation to methanol

Hydrogenation of CO_2 to methanol

- Direct hydrogenation to methanol

$$CO_2 + 6\ H_2 \xrightarrow{\text{cat.}} CH_3OH + H_2O$$

cat. = $CuO/ZnO/ZrO_2/Ga_2O_3/Al_2O_3$

600 g_{CH3OH}/kg_{cat}.hr at 250 °C and 50 bar

(NIRE/RITE Process)

Commercial developments from CRI (Island) and Mitsui Chemicals (Japan)

- Dehydration of methanol to DME

$$2\ CH_3OH \xrightarrow{\text{zeolites}} CH_3OCH_3 + H_2O$$

DME

High energy density – diesel substitute

Quadrelli et al., *ChemSusChem* **2011**, *4*, 1194

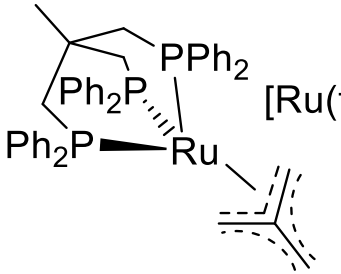
CO_2 hydrogenation to methanol

	ΔH_{298K} kJ/mol	ΔG_{298K} kJ/mol
$CO_2 + 3\ H_2 \longrightarrow CH_3OH + H_2O$	-49.4	-3.3

$$\underset{10\ \text{bar}}{CO_2} + \underset{30\ \text{bar}}{H_2} \xrightarrow[\text{THF, 140 °C + EtOH}]{\text{cat.}} CH_3OH + H_2O$$

TONs = up to 221

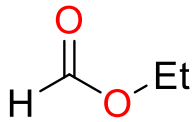
cat. =



[Ru(triphos)(tmm)]
2.5 mol%

CH_3SO_3H or $HNTf_2$ 5 mol%

EtOH enables the formation of the formate intermediate:



Klankermayer, Leitner et al., *Angew. Chem. Int. Ed.* **2012**, *51*, 7499

Available reductants for CO_2 conversion

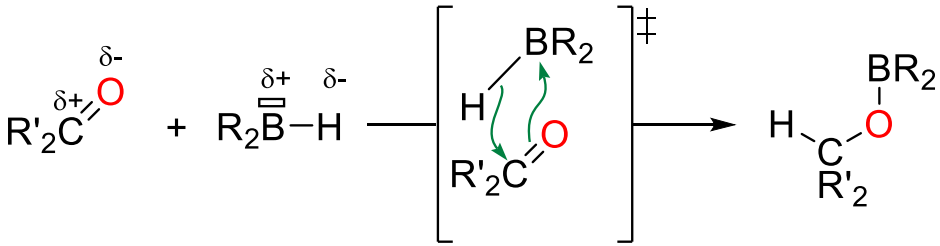
$E°(CO_2/CH_3OH)$ = **-0.38 V**

$H^+ + e^-$	H_2	R_3SiH	R_2BH
Electrolysis	***Hydrogen***	***Hydrosilanes***	***Hydroboranes***
E°is fully tunable	$E°(H^+/H_2)$ = 0.0 V = **-0.41 V** at pH=7	$E°(SiO_2/SiH_4)$ = **-0.38 V**	$E°(B(OH)_3/BH_3)$ = **- 0.48 V**
Electron transfer is critical	BDE(H-H) = 104 kcal/mol	BDE(Si-H) = 92 kcal/mol	BDE(B-H) = 78 kcal/mol
Fully renewable	Renewable through water (photo)electrolysis	PMHS and TMDS are disposable hydrosilanes	non-renewable
available on large scale	available on 10-100 Mtons/year scale	available on 10-100 ktons/year scale	

Renewable but "inert" reductants | ***Disposable hydrides***

Reduction with hydroboranes and hydrosilanes

Reduction of C-O bonds with R_2BH and R_3SiH



High energy transition state must be catalyzed

$R_2B{-}H \rangle R_3Si{-}H$

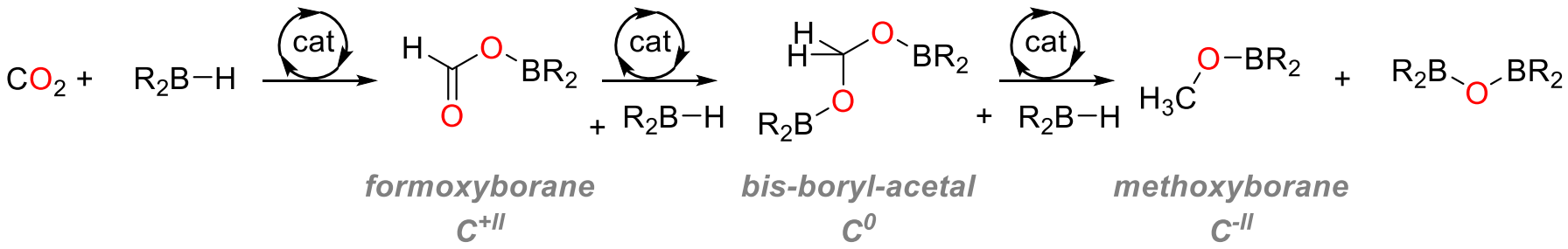
Hydroboranes are more Lewis acidic and display an enhanced reactivity compared to hydrosilanes

R_3SiH	R_2BH
Hydrosilanes	***Hydroboranes***
$E°(SiO_2/SiH_4)$ = **-0.38 V**	$E°(B(OH)_3/BH_3)$ = **- 0.48 V**
BDE(Si-H) = 92 kcal/mol	BDE(B-H) = 78 kcal/mol
PMHS and TMDS are disposable hydrosilanes	non-renewable
available on 10-100 ktons/year scale	

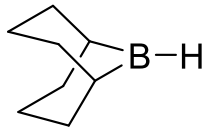
Disposable hydrides

Hydroboration of CO_2

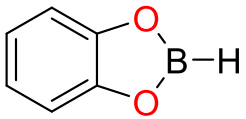
Reduction of CO_2 with R_2BH



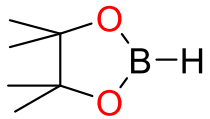
Typical hydroboranes:



9-Borabicyclo[3.3.1]nonane
(9-BBN)



catecholborane
(catBH)



pinacolborane
(pinBH)

$BH_3 \cdot THF$

Review: Bontemps, *Coord. Chem. Rev.* **2016**, *308*, 117

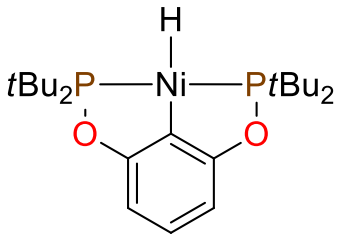
Hydroboration of CO_2

Catalysts for the hydroboration of CO_2

- A catalytic reaction discovered in 2010
- Most catalytic systems yield preferentially CH_3OBR_2
- Mild conditions: <100°C, <5 bars CO_2

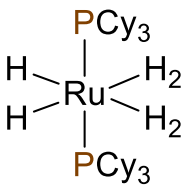
$$CO_2 + 3\ R_2B{-}H \xrightarrow[-\ catB_2O]{cat.} R_2B{-}OCH_3$$

cat.



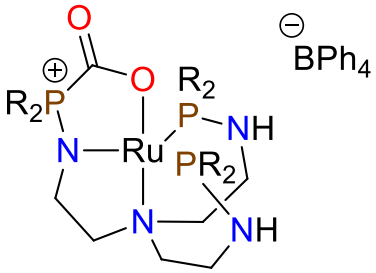
TOF = 495 h^{-1}

Guan et *al*, JACS, 2010, p. 8872



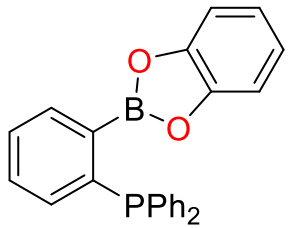
TOF = 10 h^{-1}

Sabo-Etienne, Bontemps, et *al*, ACIE, 2012, p. 1671



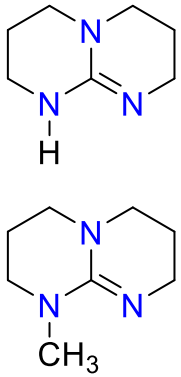
TOF = 0,1 h^{-1}

Stephan et *al*, ACIE, 2012, p. 11343



TOF: 166 h^{-1}

Fontaine et *al*, JACS 2013, p. 9326



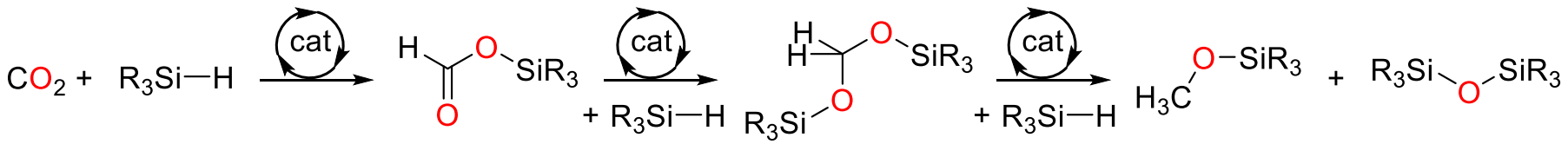
TOF = 32 h^{-1}

Cantat et *al*, Chem. Eur. J. 2014, p. 7098

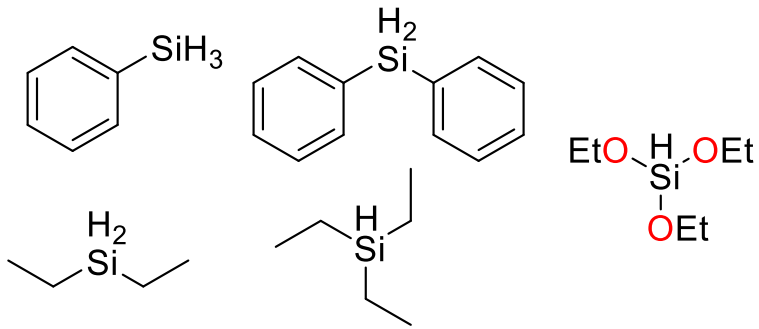
- All the reduction products are observed: $HCOOBR_2$, $H_2C(OBR_2)_2$ and CH_3OBR_2

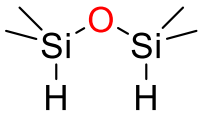
Hydrosilylation of CO_2

Reduction of CO_2 with R_3SiH

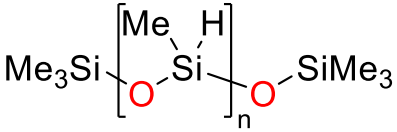


Typical hydrosilanes:





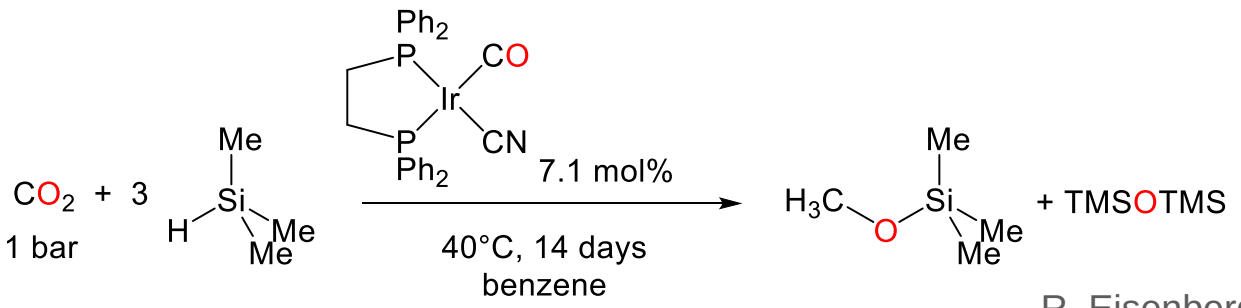
tetramethyldisiloxane (TMDS)



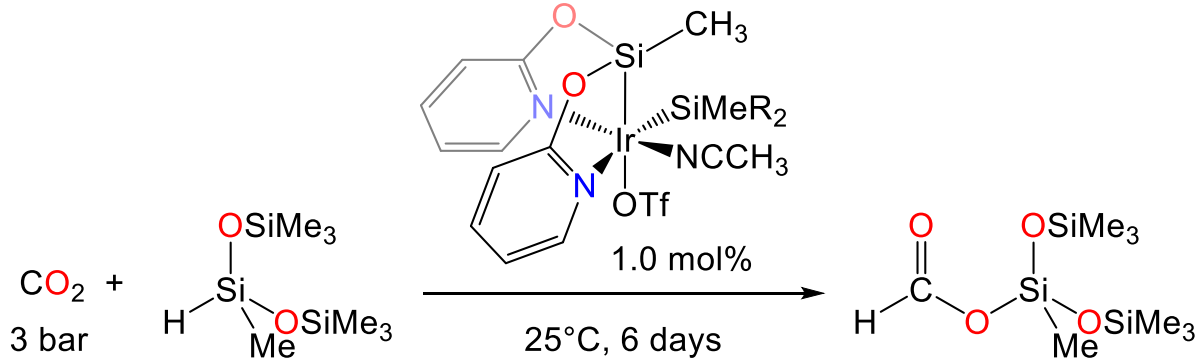
polymethylhydrosiloxane (PMHS)

Hydrosilylation of CO_2

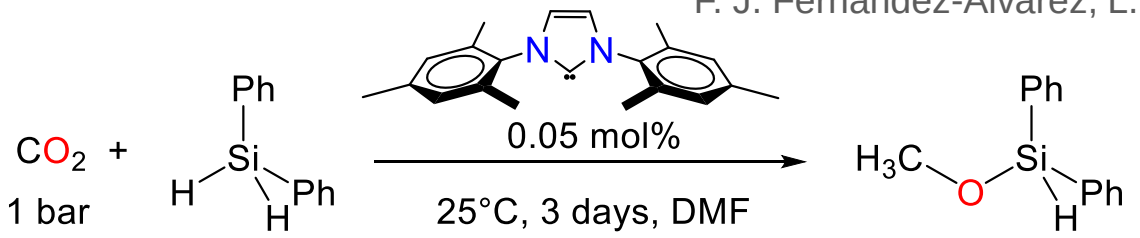
Catalysts for the hydrosilylation of CO_2



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



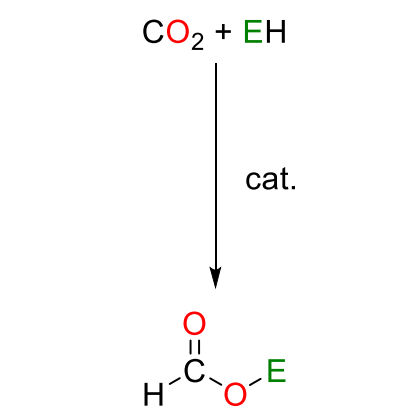
F. J. Fernández-Alvarez, L. Oro et al., *Angew. Chem. Int. Ed.* **2012**, *51*, 12824



Y. Zhang, J. Y. Ying et al., *Angew. Chem. Int. Ed.* **2009**, *48*, 3322

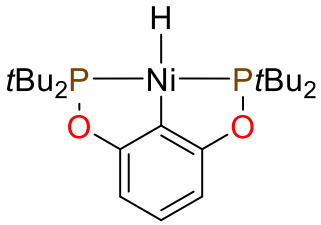
Hydrosilylation and hydroboration: mechanisms

Different mechanistic schemes

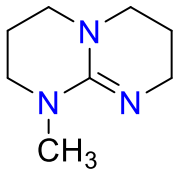


EH = $R_3Si—H$ or $R_2B—H$

M-H (metal hydride)



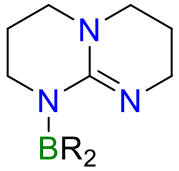
Lewis base (LB)



Lewis acid (LA)

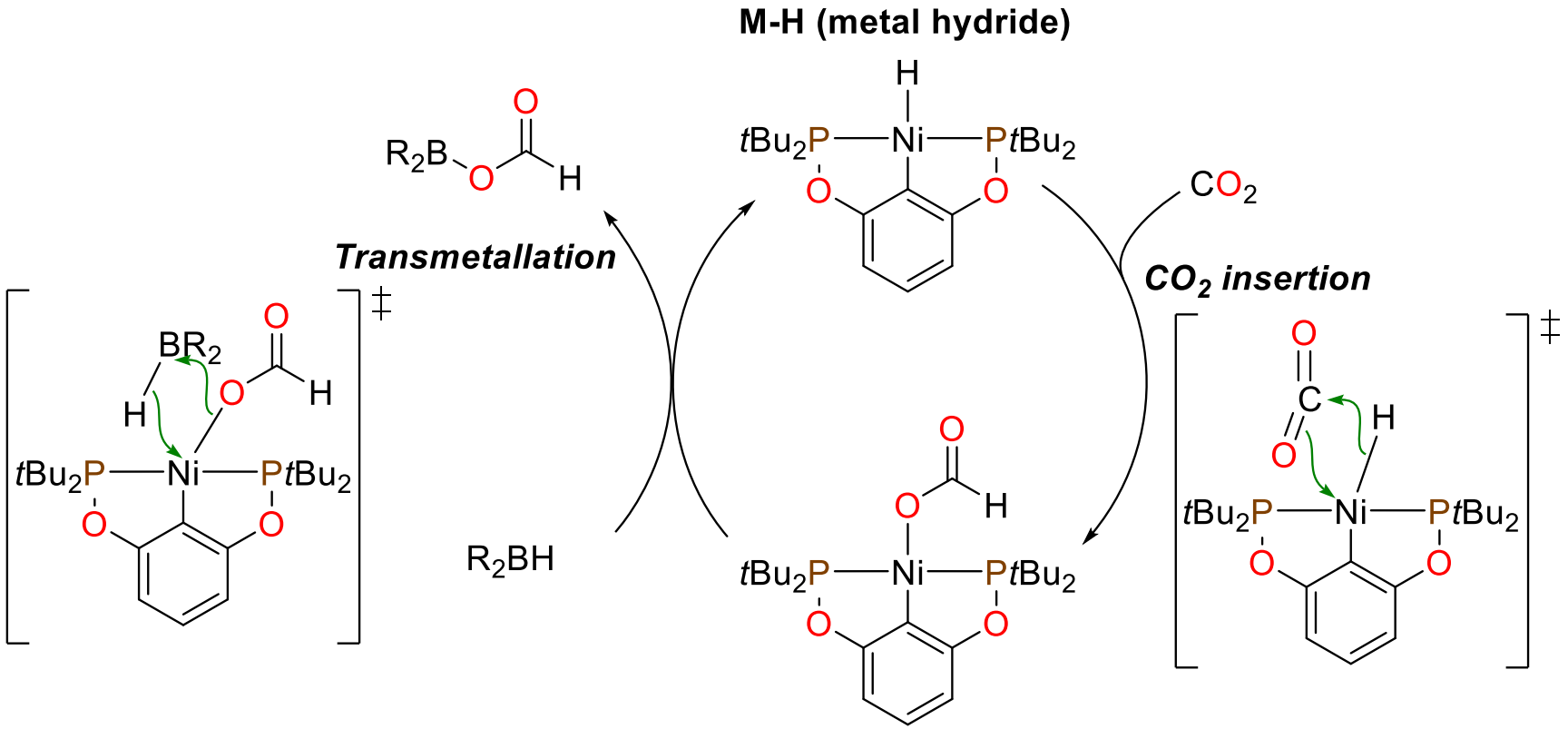
$B(C_6F_5)_3$

Bifunctional catalyst



Hydrosilylation and hydroboration: mechanisms

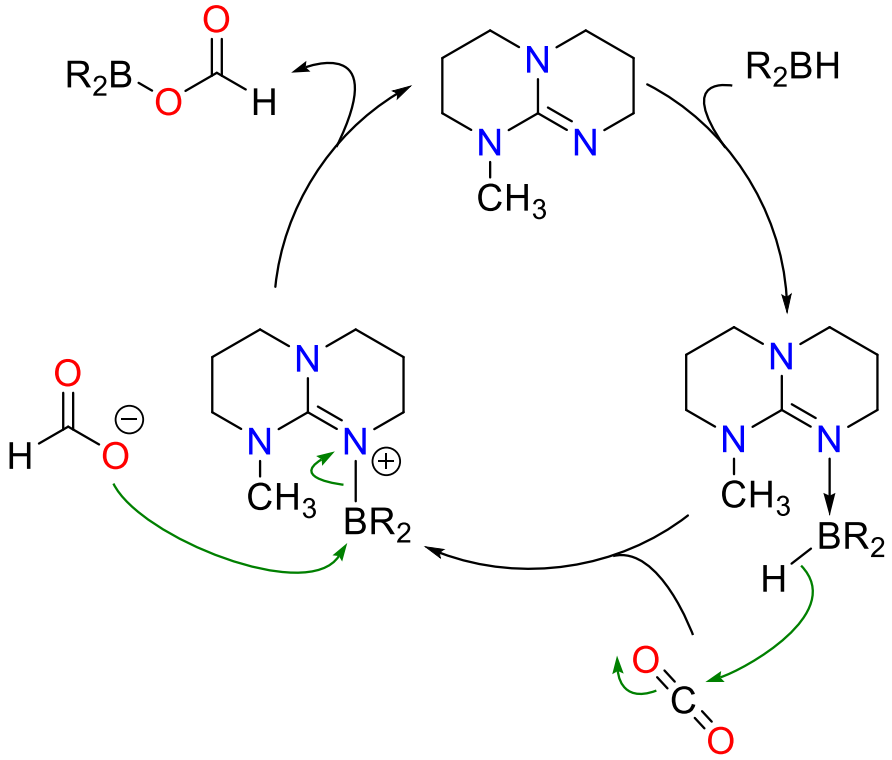
Hydroboration via metal hydrides



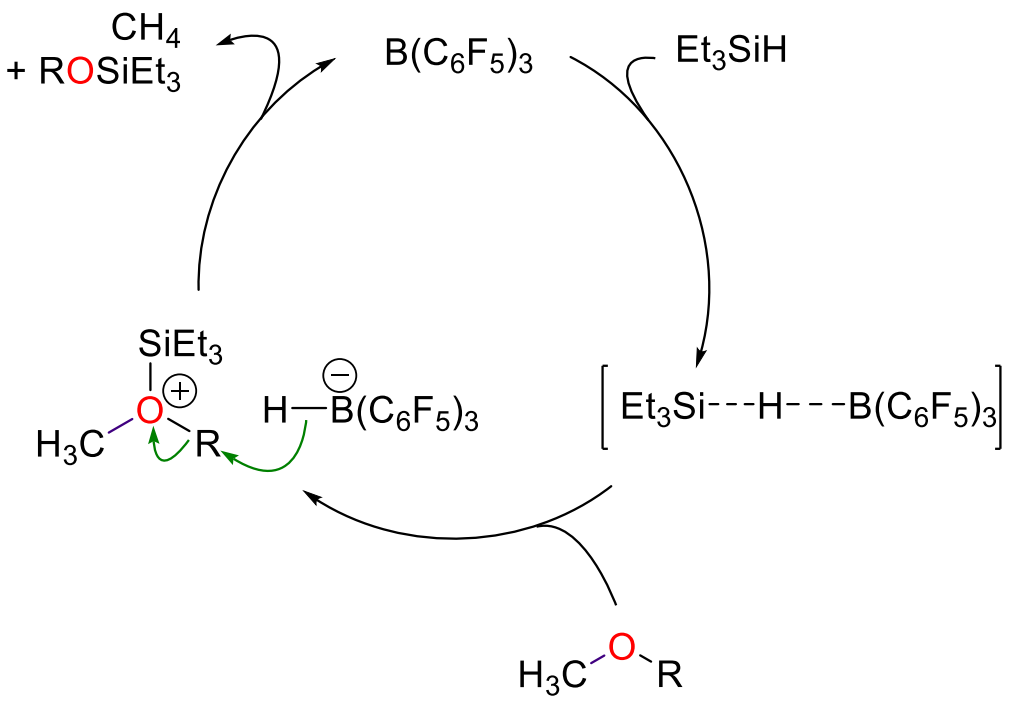
Hydrosilylation and hydroboration: mechanisms

Hydroboration with Lewis bases and Lewis acids

Lewis base (LB)

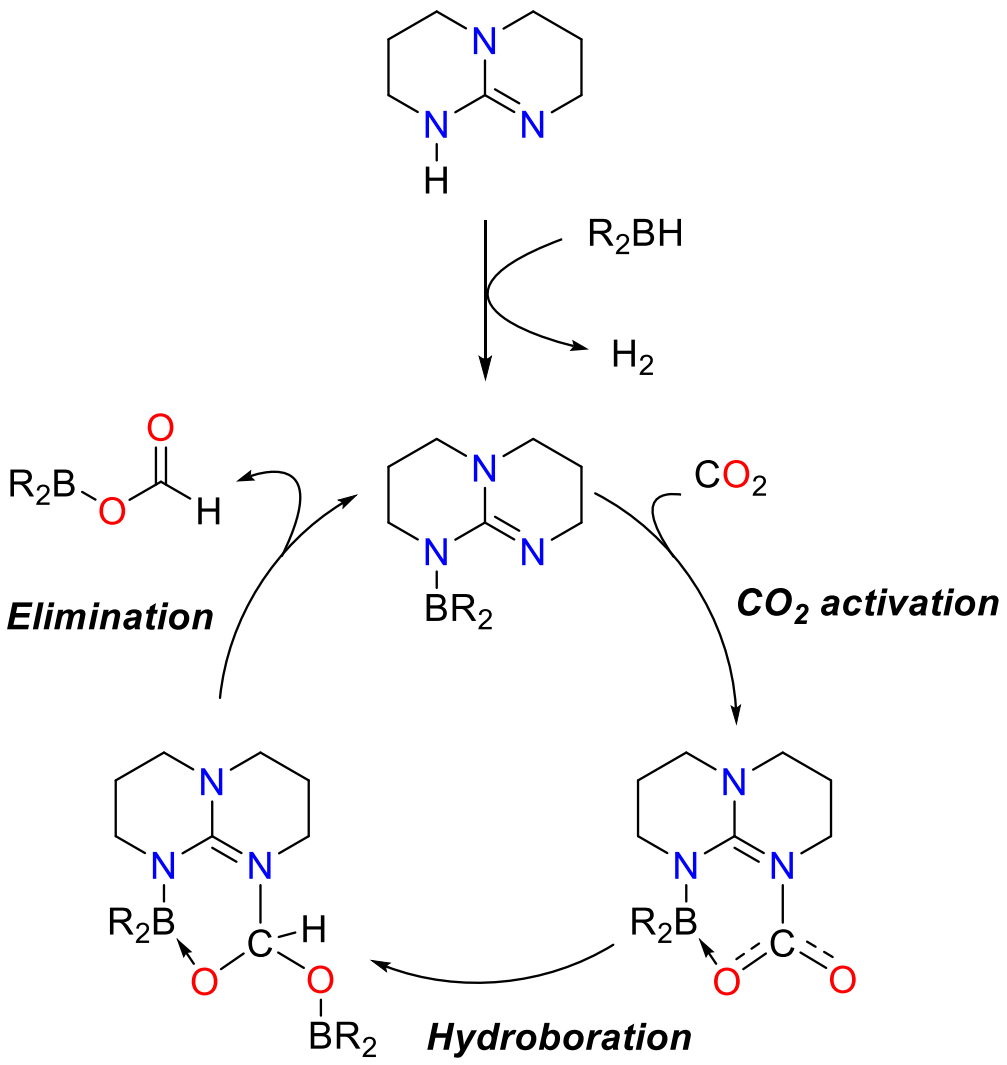


Lewis acid (LA)



Hydrosilylation and hydroboration: mechanisms

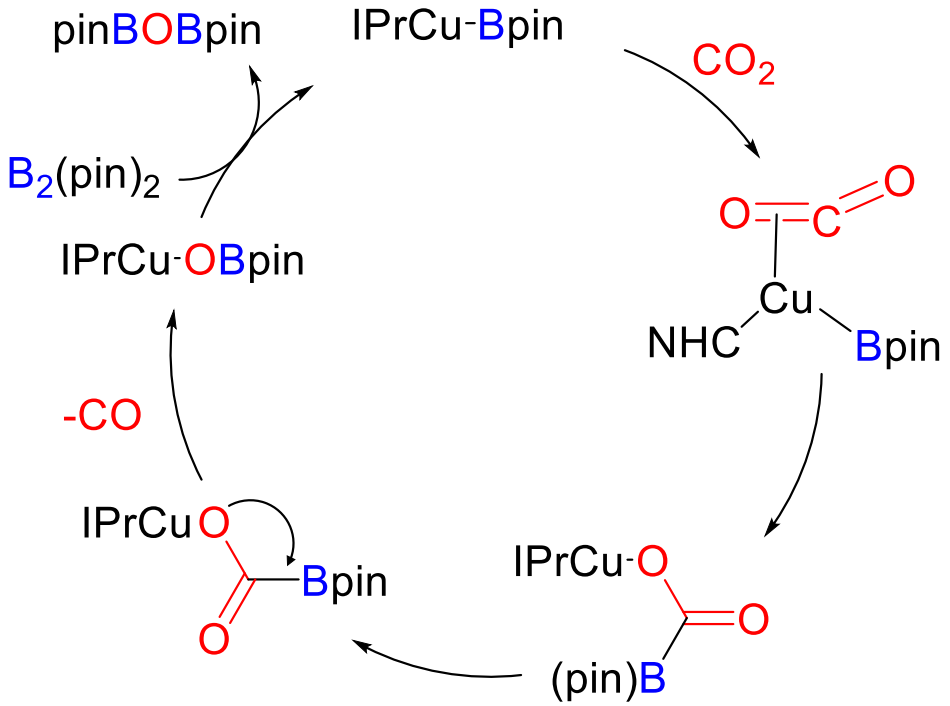
Hydroboration/silylation with bifunctional catalysts



Reduction of CO_2 to CO with diboranes

R_2BBR_2 as a reductant for CO_2

$$CO_2 + B_2(pin)_2 \xrightarrow{(IPr)Cu(Bpin)} CO + pinBOBpin$$



CO_2 conversion using catalysis: reduction and functionalization

Outline

I. CO_2 chemistry: back to basics

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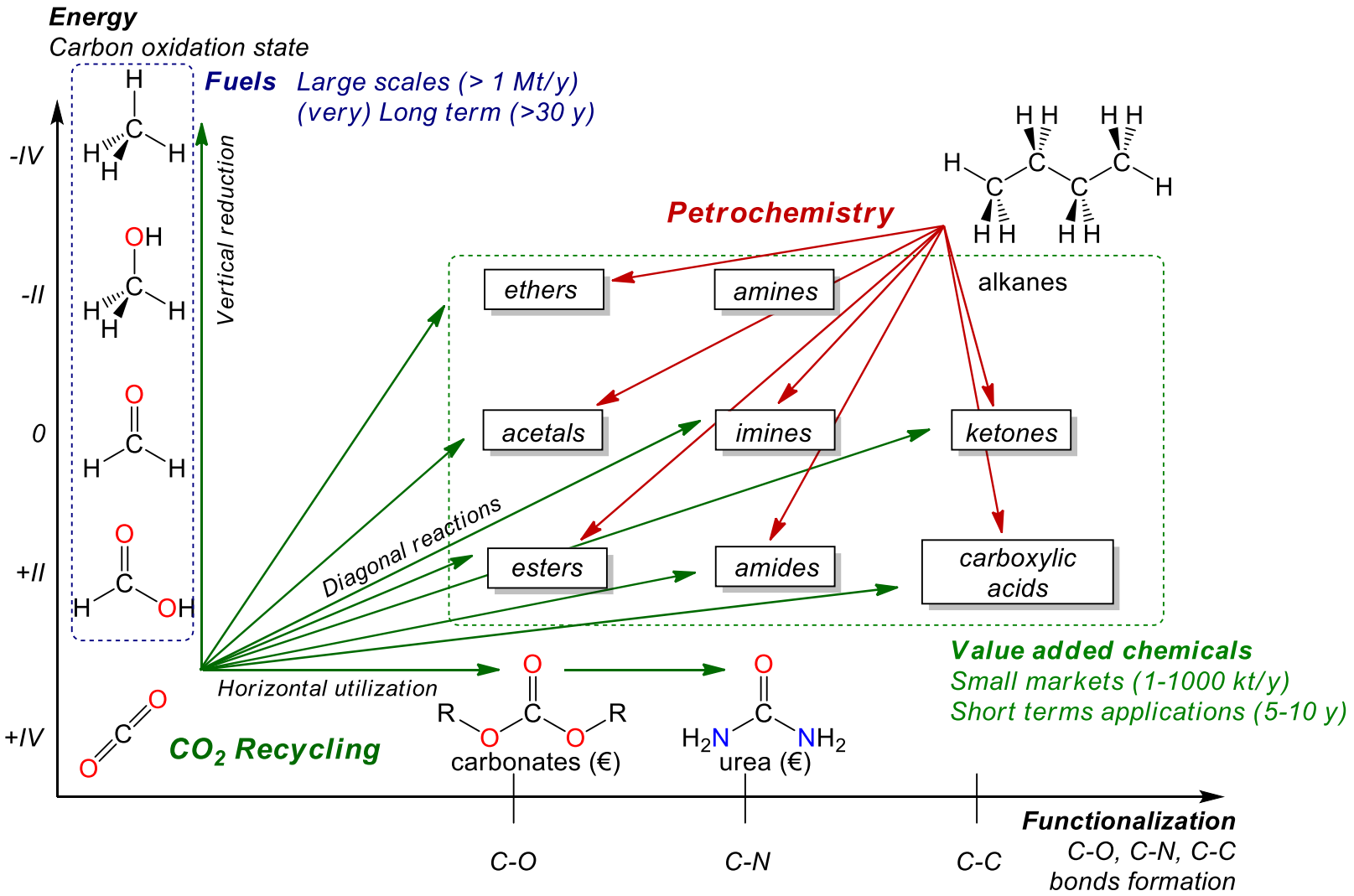
- III.1. Electro- and photoelectro-reduction
- III.2. Hydrogenation
- III.3. Hydrosilylation and hydroboration

III. CO_2 Transformation: functionalization

IV. CO_2 transformation: reductive Functionalization

Various opportunities to CO_2 recycling…

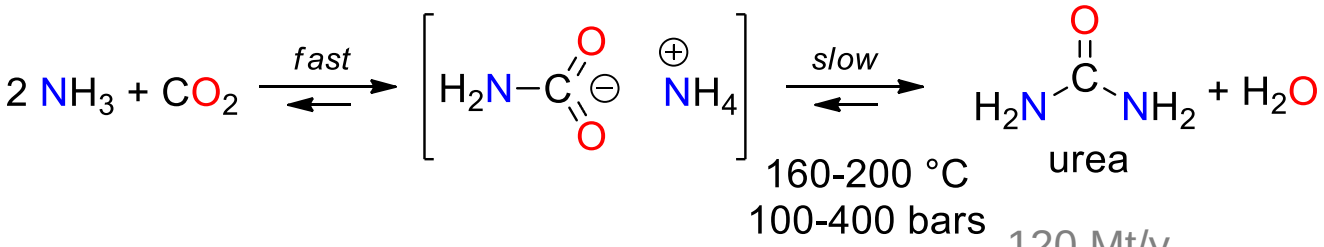


Cantat et al., *Angew. Chem. Int. Ed.* **2012**, *51*, 187

Industrial processes utilizing CO_2

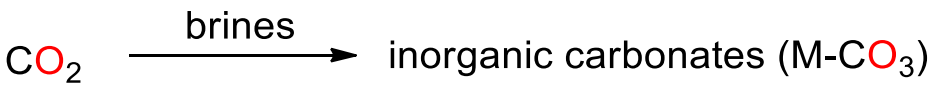
Industrial routes from CO_2

- Bosch-Meiser process for urea production



120 Mt/y

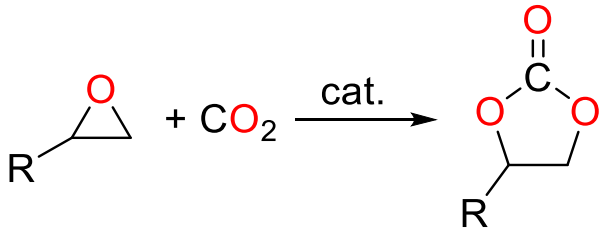
- Inorganic carbonates



for CCS applications

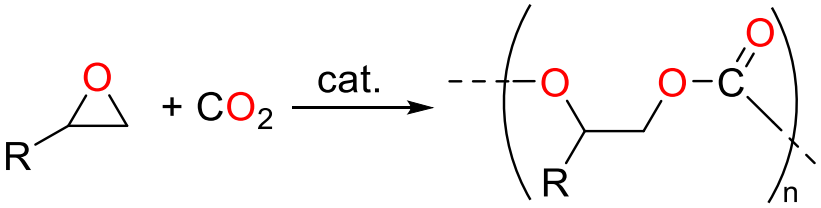
44 Mt/y

- Synthesis of cyclic and polymeric carbonates



solvents for
Li-ion batteries

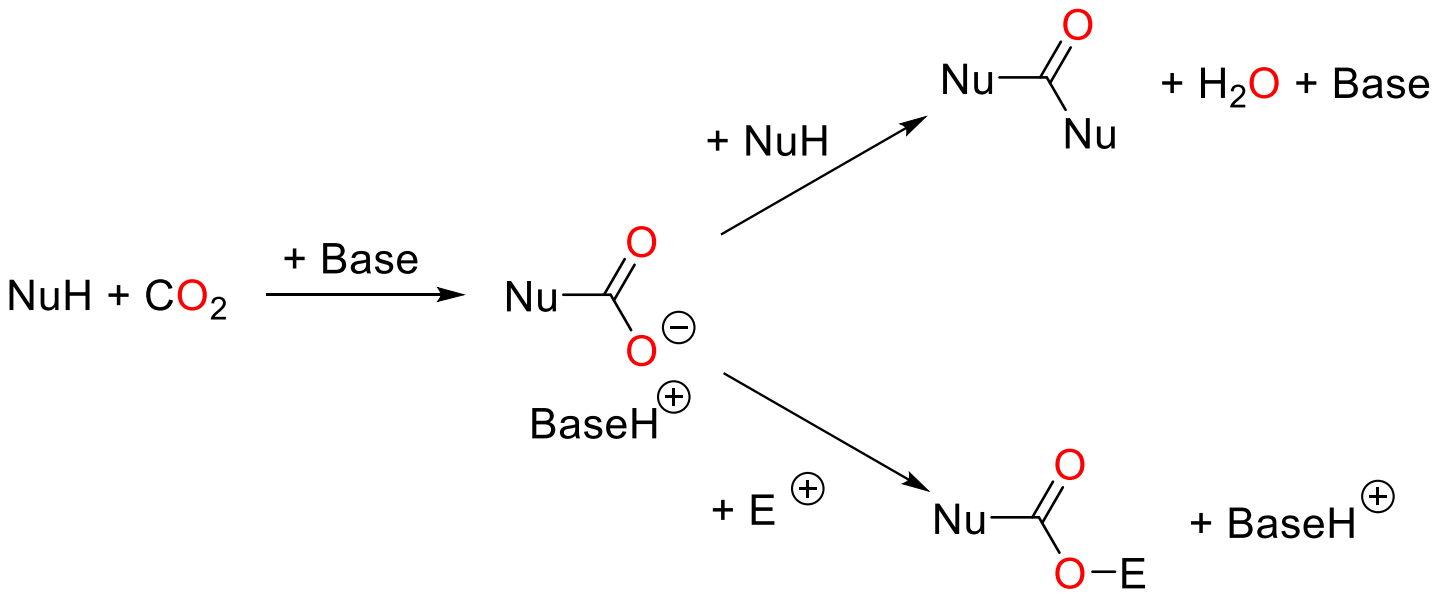
150 kt/y



polycarbonates

65 kt/y

CO_2 functionalization: general principles



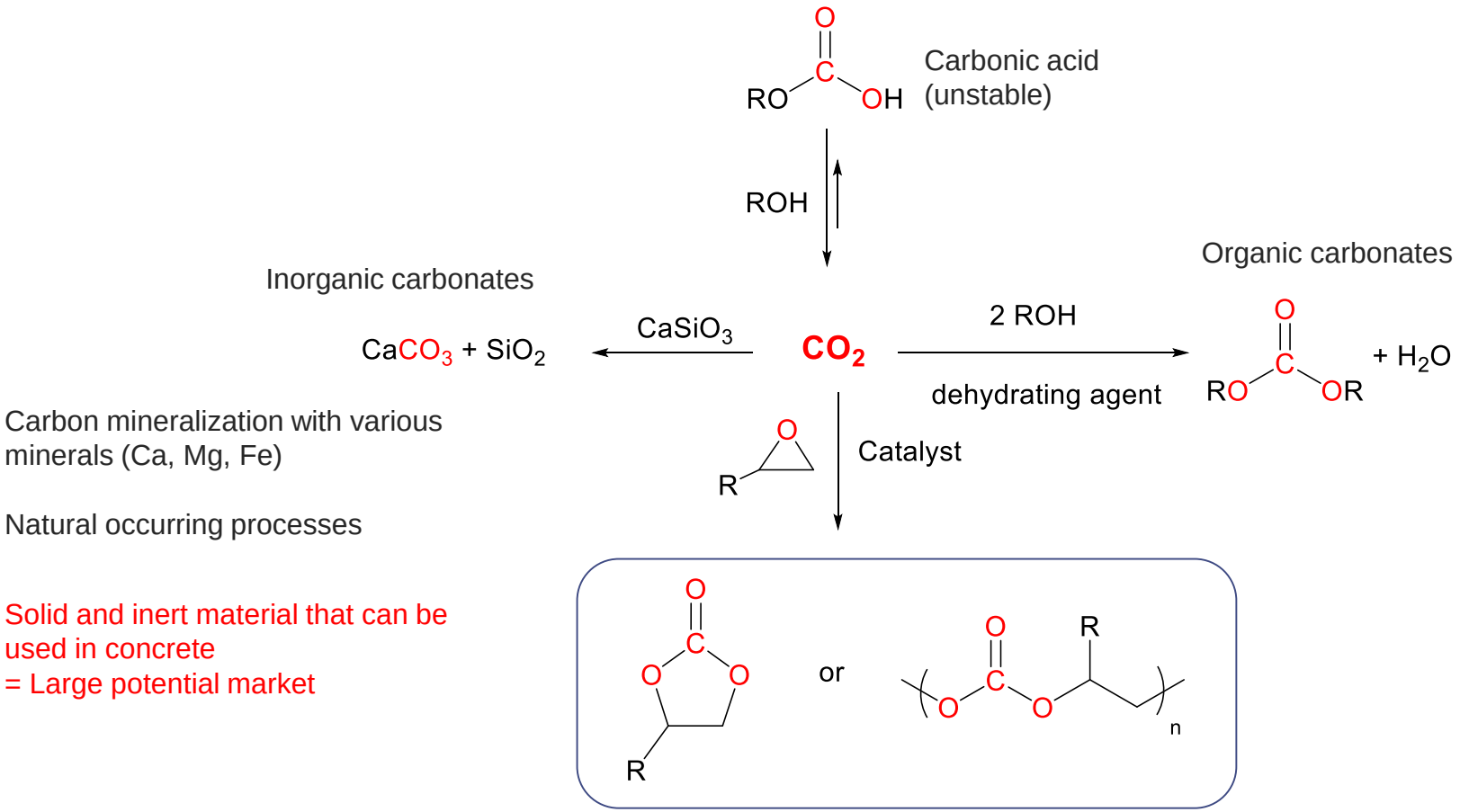
NuH = ROH, R_2NH, RH, etc.

Challenges and limitations:

- Choice of the base
- H_2O release
- Polarity mismatch

- Stoechiometric amount of base
- Direct quenching of the nucleophile with E^+

C-O bond formation from CO_2



Carbon mineralization with various minerals (Ca, Mg, Fe)

Natural occurring processes

Solid and inert material that can be used in concrete
= Large potential market

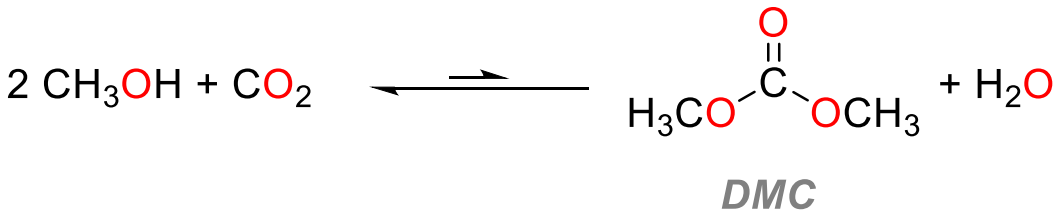
Cyclic *vs* polymeric carbonate

Chem. Rev. 2014, *114*, 1709

C-O bond formation from CO_2

Direct synthesis of DMC from CO_2 and MeOH

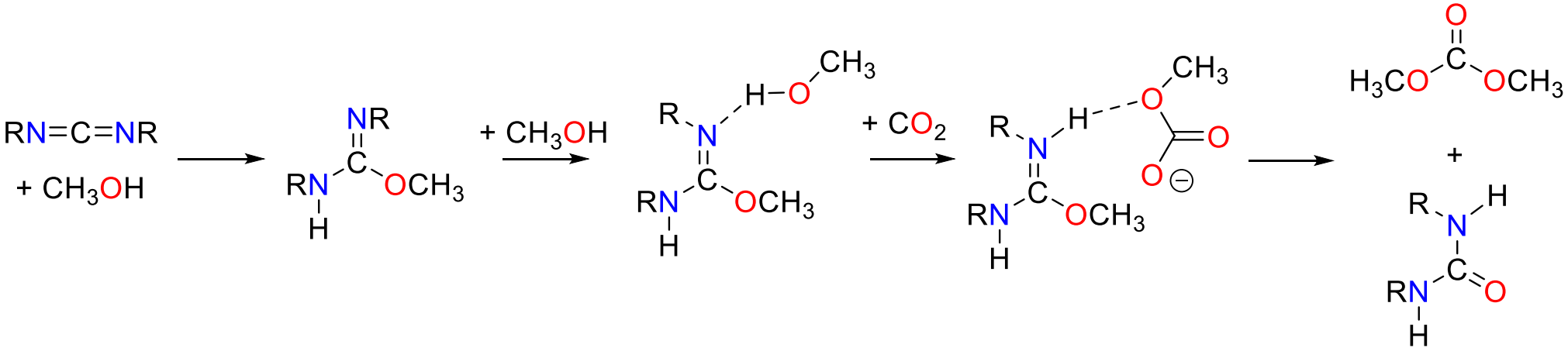
- A reaction strongly limited by thermodynamics



DMC

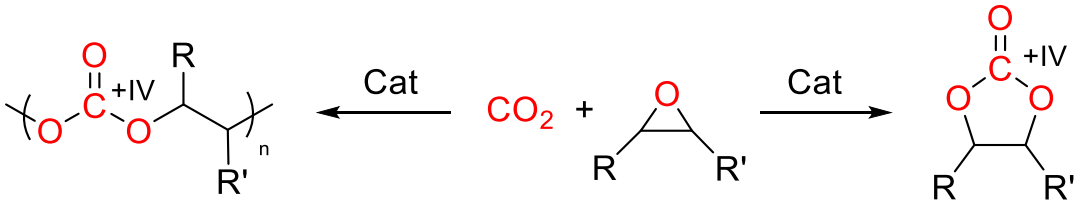
equilibrium concentration:
< 2% @433K

- Strategy: dehydration to shift the equilibrium
  Inorganic (e.g. zeolites) or organic traps (e.g. carbodiimides)



C-O bond formation from CO_2

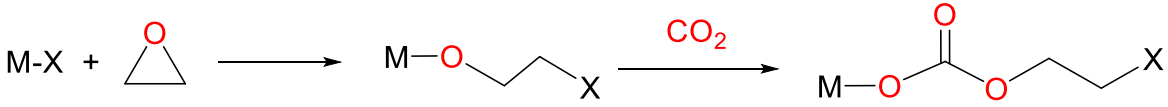
Carbonates from CO_2 and epoxides



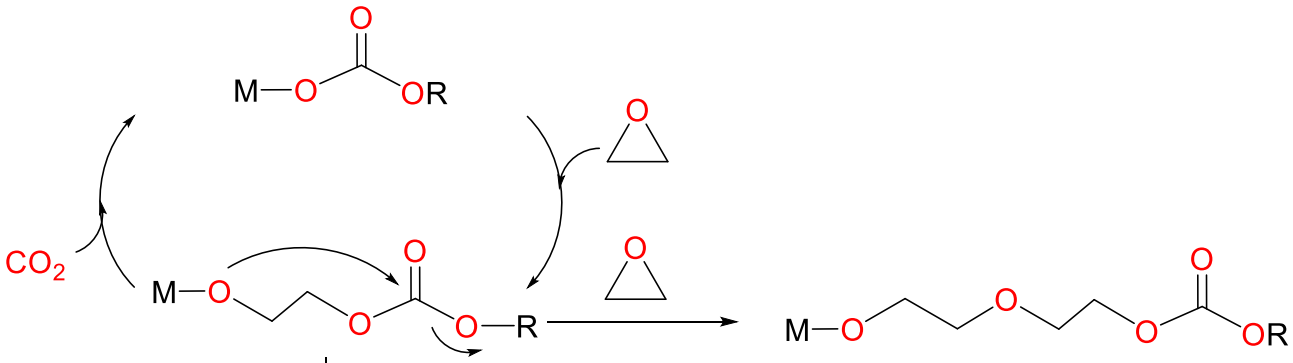
Uses: Binders, adhesives and coatings

Uses: High boiling Solvents, Electrolytes, Reagents

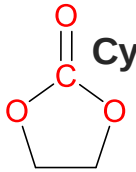
Initiation



Propagation



Ether linkage

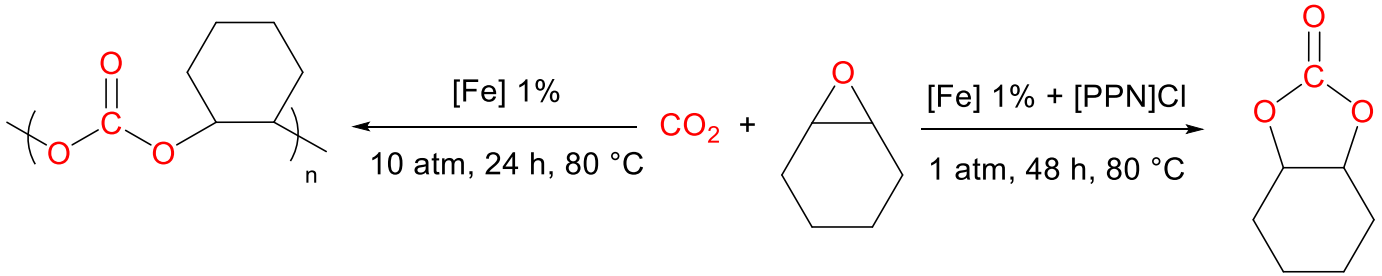


Cyclic carbonate by back-biting

Chem. Comm. **2011**, *47*, 141-163

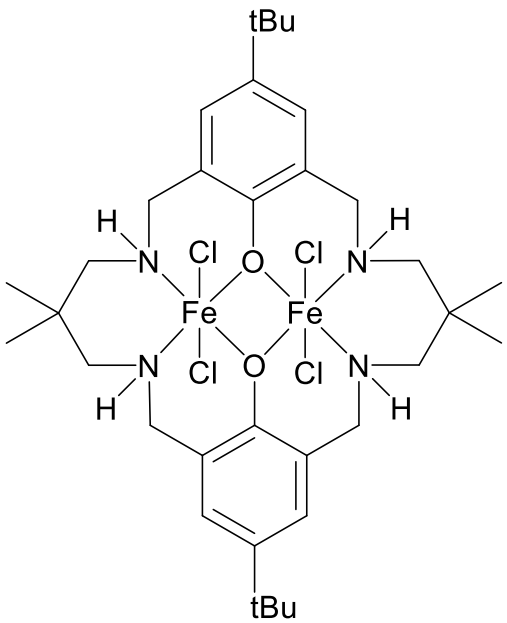
C-O bond formation from CO_2

Carbonates from CO_2 and epoxides: catalysts



[PPN]Cl = $[Ph_3P{=}N{=}PPh_3]^{\oplus}\ Cl^{\ominus}$

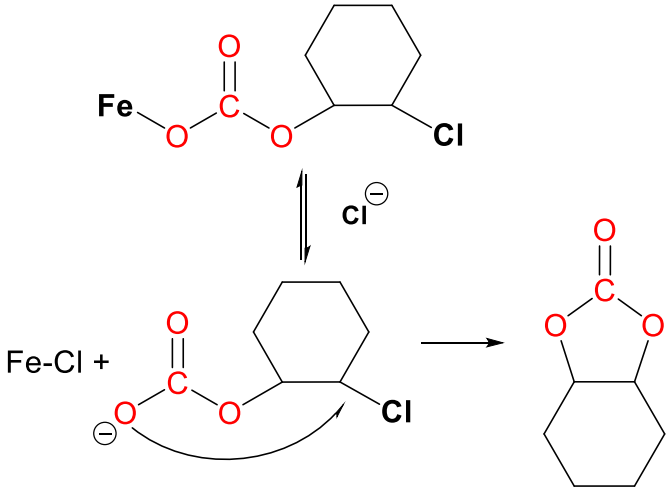
Chem. Comm., **2011**, *47*, 212



Impact of the bimetallic structure, see:

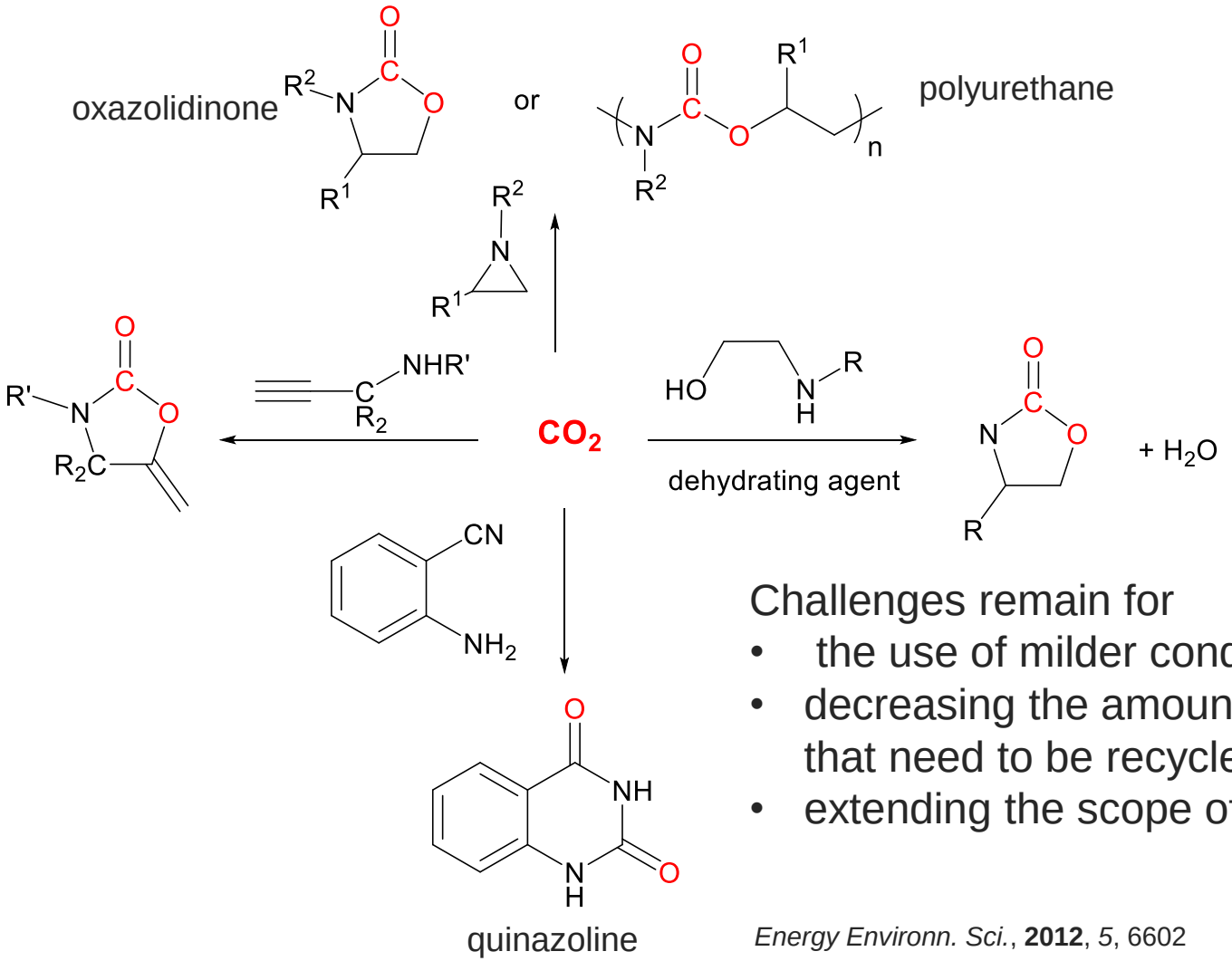
Chem. Commun., **2011**, 47, 212-214
J. Am. Chem. Soc. **2011,** *133*, 17395

Role of the chloride salt



C-N bond formation from CO_2

CO_2 reactivity with amines and aziridines



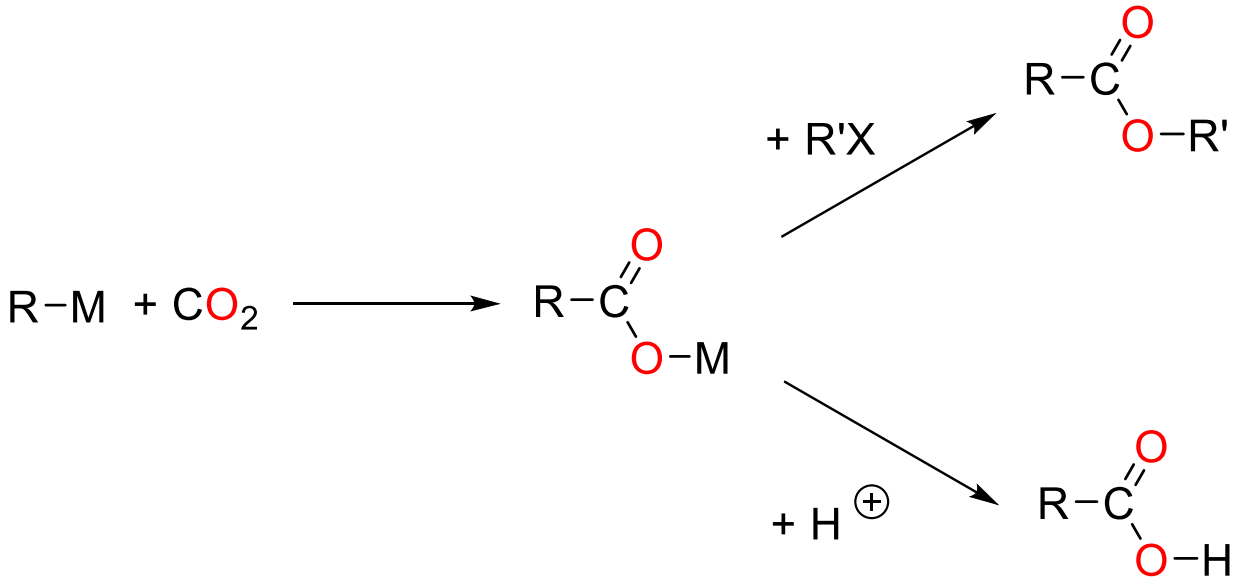
Challenges remain for

- the use of milder conditions
- decreasing the amount of wastes that need to be recycled
- extending the scope of products

Energy Environ. Sci., **2012**, *5*, 6602

C-C bond formation from CO_2

Different strategies based on the carbon nucleophile

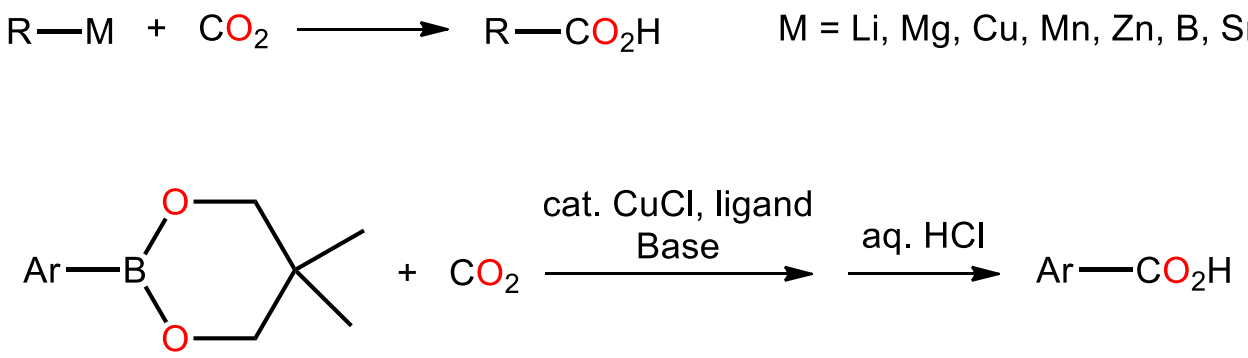


- Use of an organometallic reagent (C-M bond)
- Generation of a carbon nucleophile by oxidative addition in a C-X bond
- Generation of a carbon nucleophile by C-H activation
- Use of electron rich C=C bonds

CO_2 to chemicals: C-C bond formations

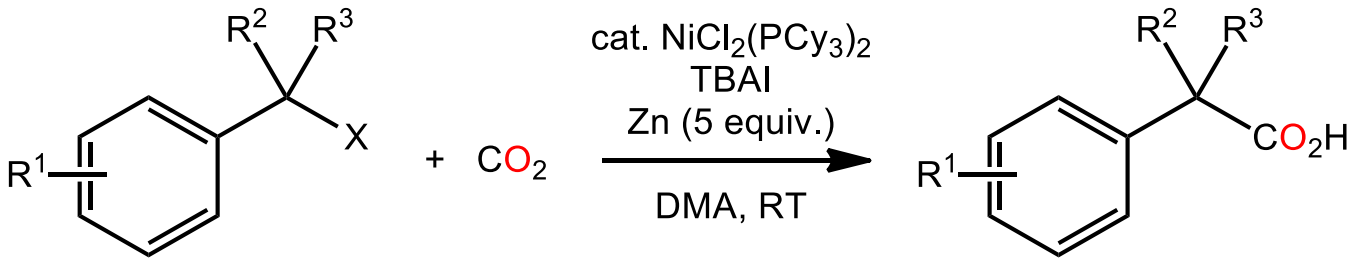
Carboxylation reactions

- Carboxylation of organometallic compounds



Iwasawa, 2008
Hou, 2008

- Reductive carboxylation of benzyl halides

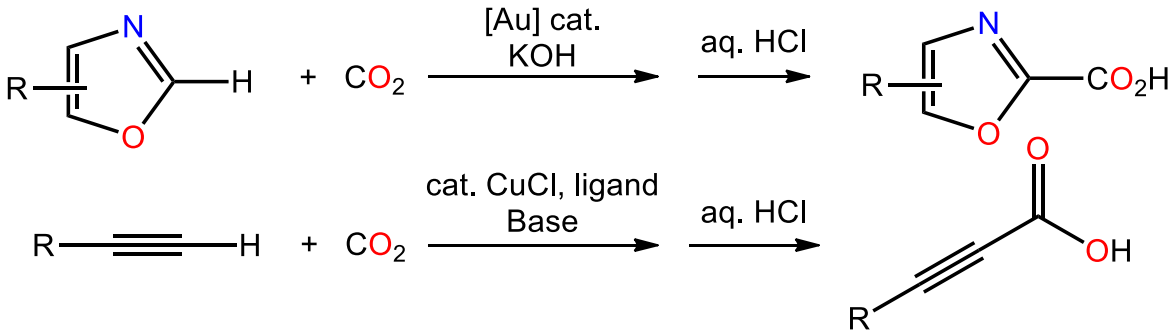


Martin, 2013

CO_2 to chemicals: C-C bond formations

Carboxylation of C-H bonds

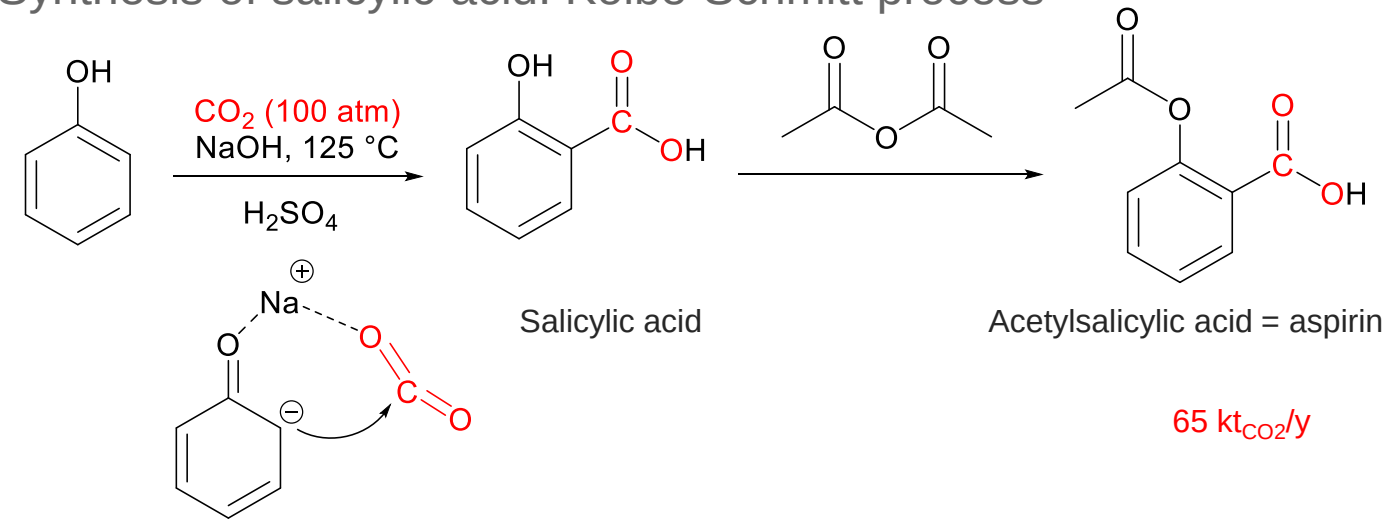
- CO_2 insertion into activated C-H bonds



Nolan, 2010

Zhang, 2010

- Synthesis of salicylic acid: Kolbe-Schmitt process



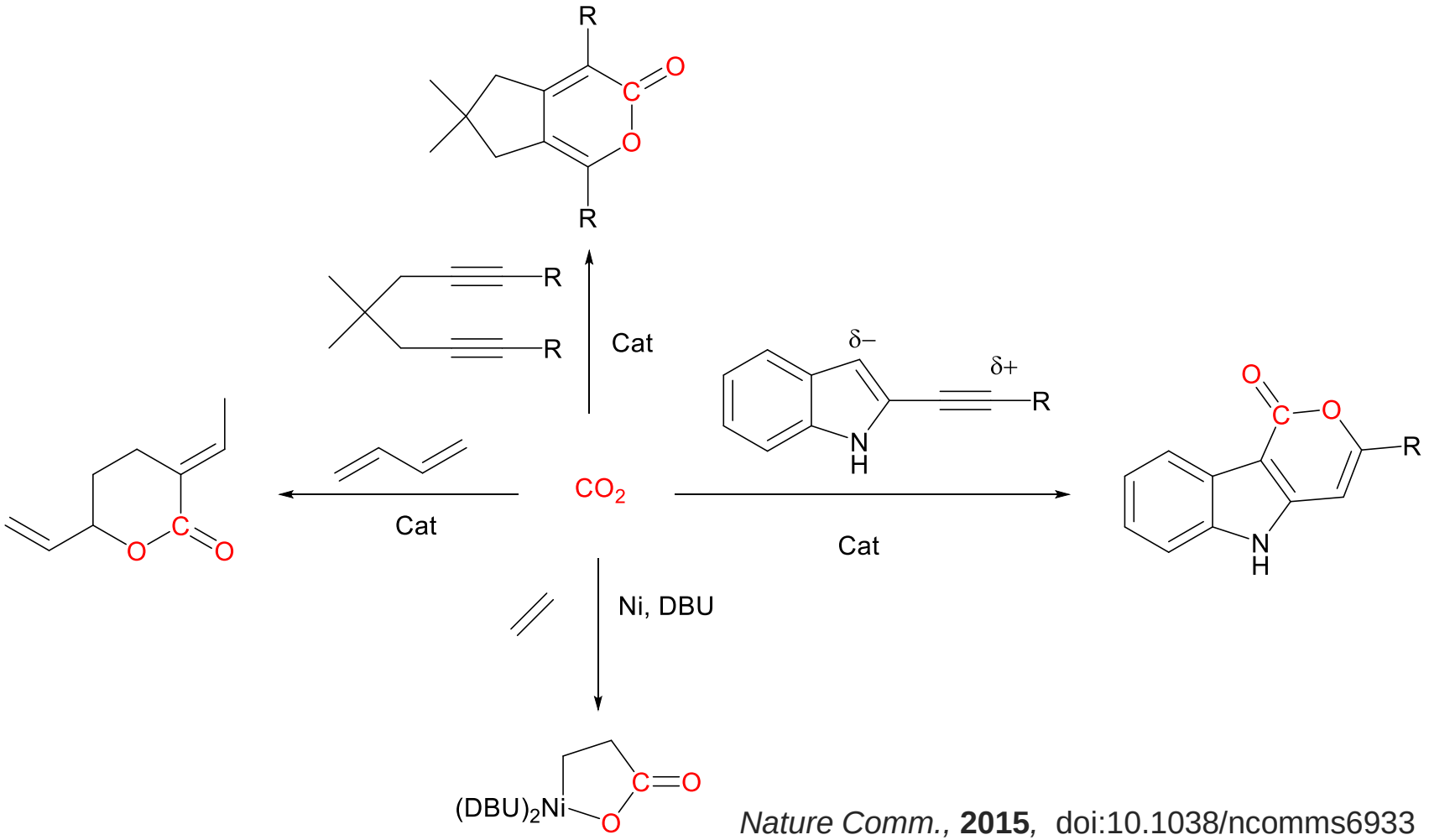
Salicylic acid

Acetylsalicylic acid = aspirin

65 kt_{CO2}/y

C-C bond formation from CO_2

Carboxylation of unsaturated compounds



Nature Comm., **2015**, doi:10.1038/ncomms6933

CO_2 conversion using catalysis: reduction and functionalization

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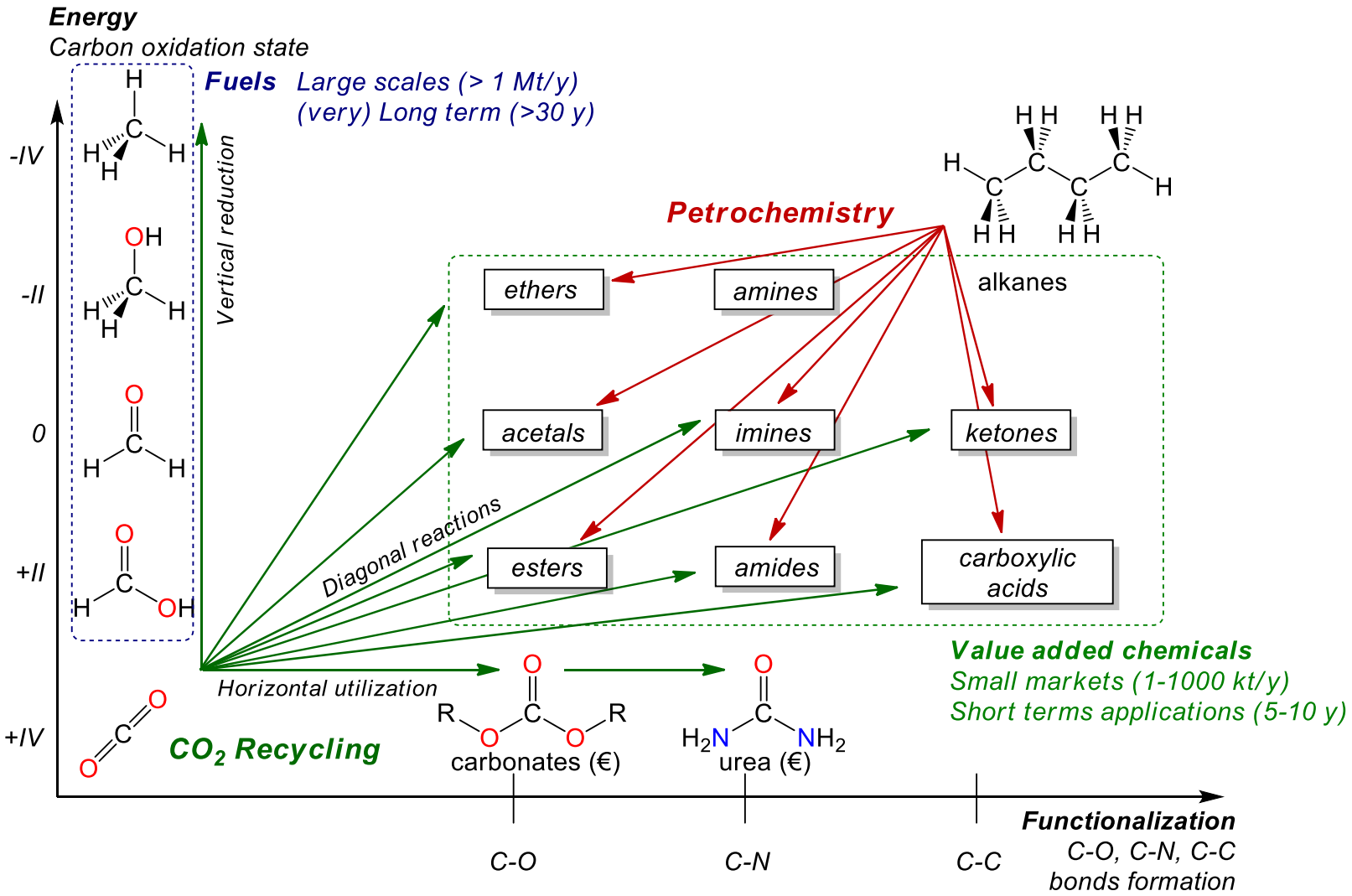
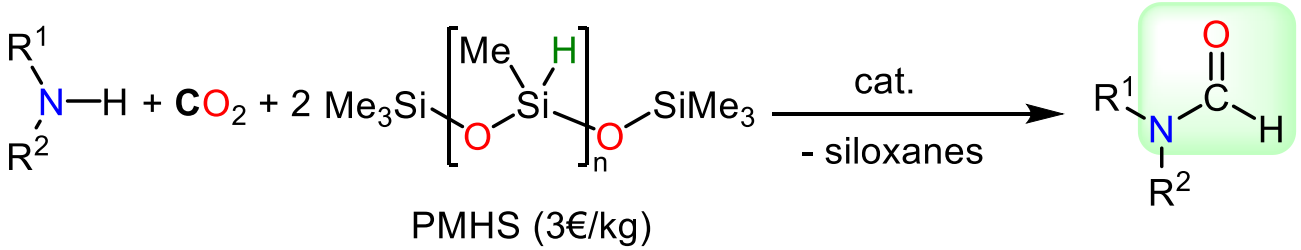
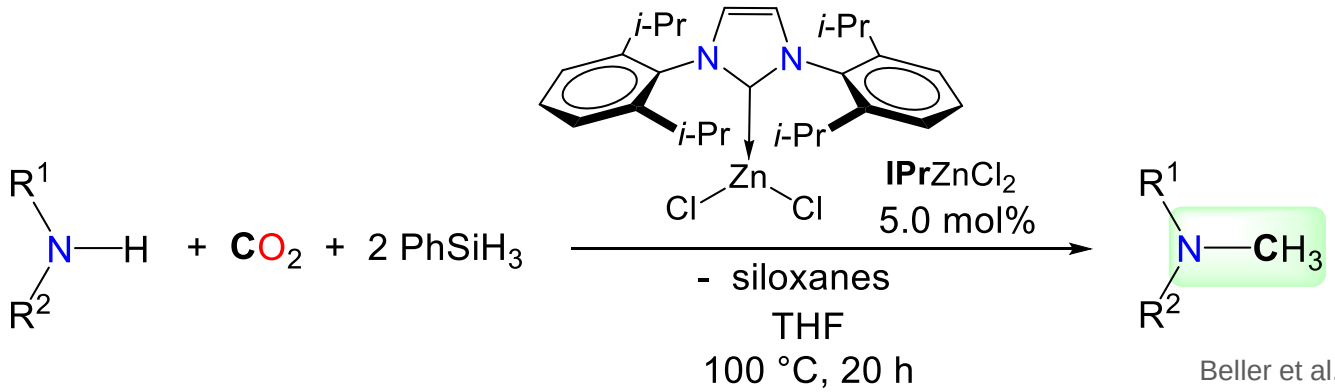


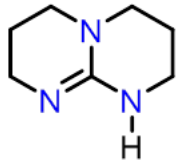
Cantat et al., *Angew. Chem. Int. Ed.* **2012**, *51*, 187

New diagonal transformations for CO_2 utilization

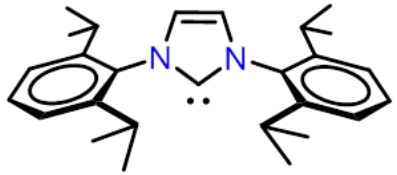




Catalysts:



TBD

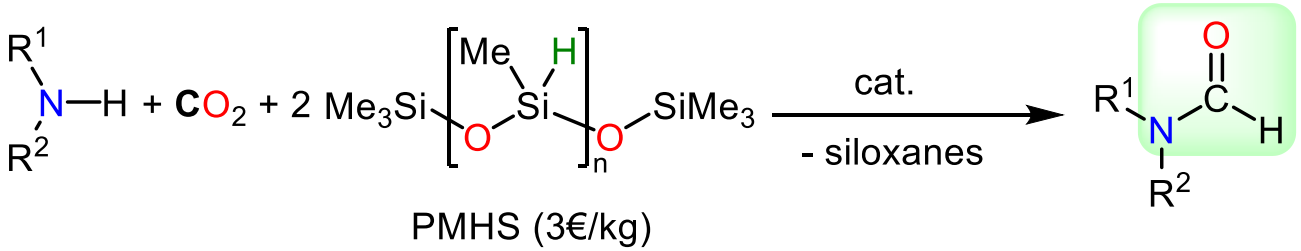


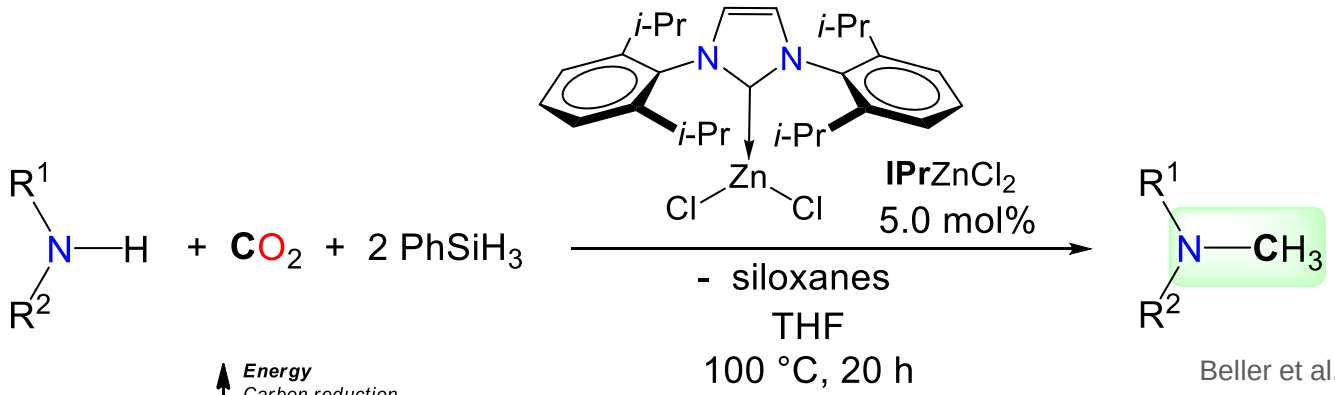
IPr

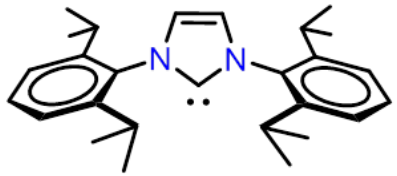
For a Ru cat., see:
Beller et al. *Angew. Chem. Int. Ed.* **2013**, *52*, 9568

Angew. Chem. Int. Ed. **2012**, *51*, 187
J. Am. Chem. Soc. **2012**, *134*, 2934
Chem. Sci. **2013**, *4*, 2127
ChemCatChem **2013**, *5*, 117

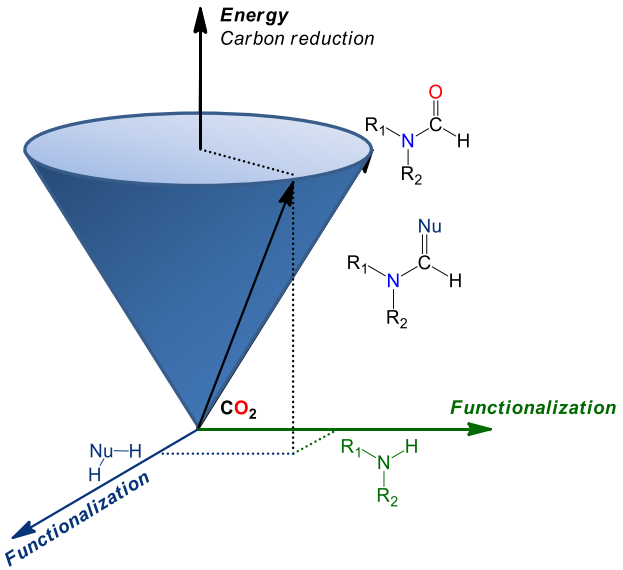
New diagonal transformations for CO_2 utilization

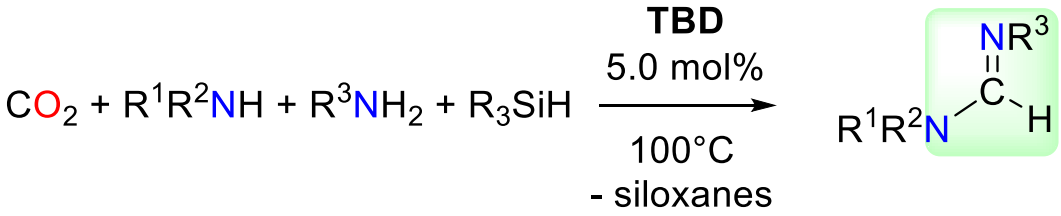






For a Ru cat., see:
Beller et al. *Angew. Chem. Int. Ed.* **2013**, *52*, 9568

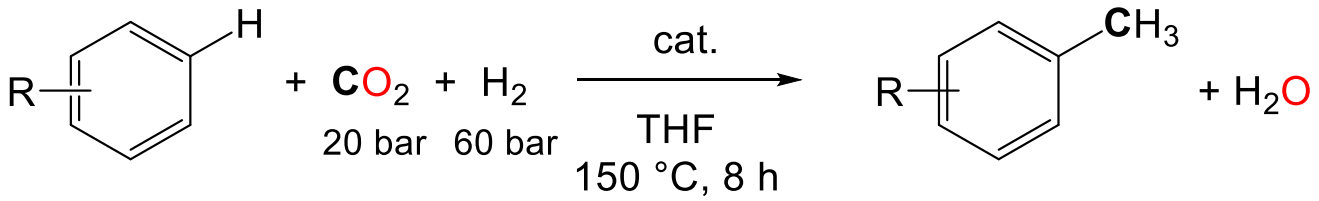




ChemCatChem **2013**, *5*, 117

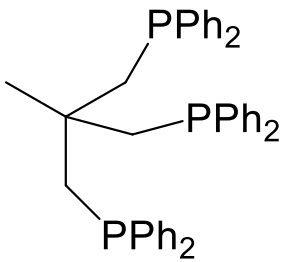
CO_2 conversion alkyl compounds

- Methylation of C-H bonds with CO_2

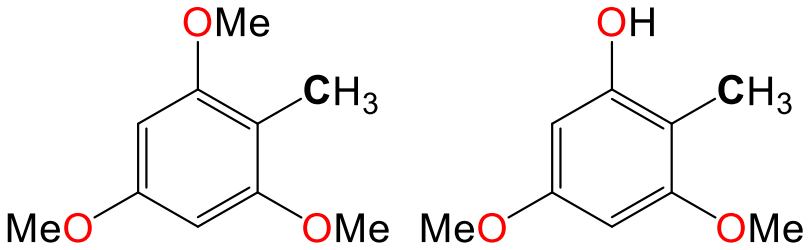


cat. : $Ru(acac)_3$ (2 mol%)
triphos (3 mol%)
$Al(OTf)_3$ (5 mol%)

triphos =



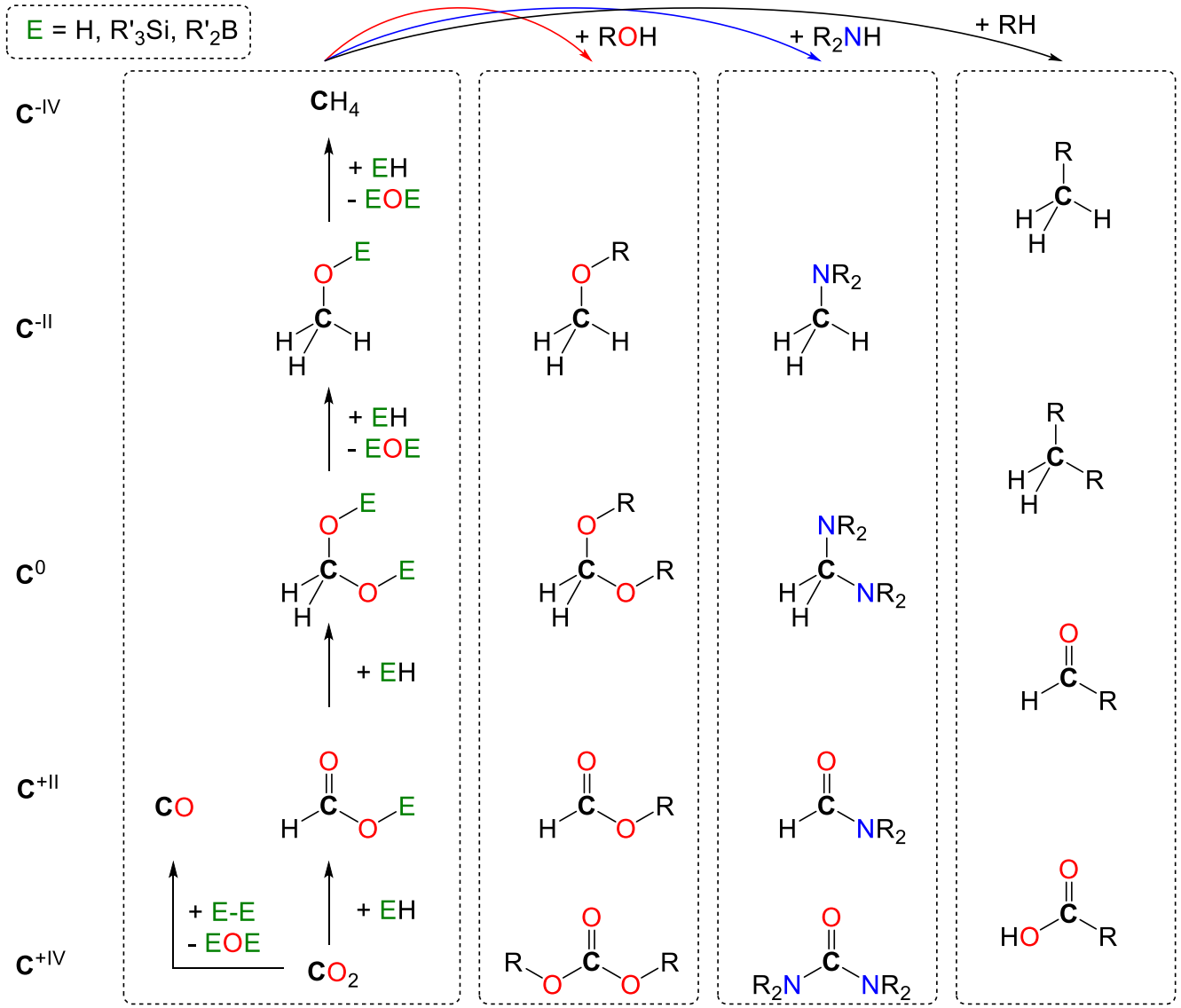
examples:



Beller *et al. Angew. Chem. Int. Ed.* **2014**, *53*, 10476

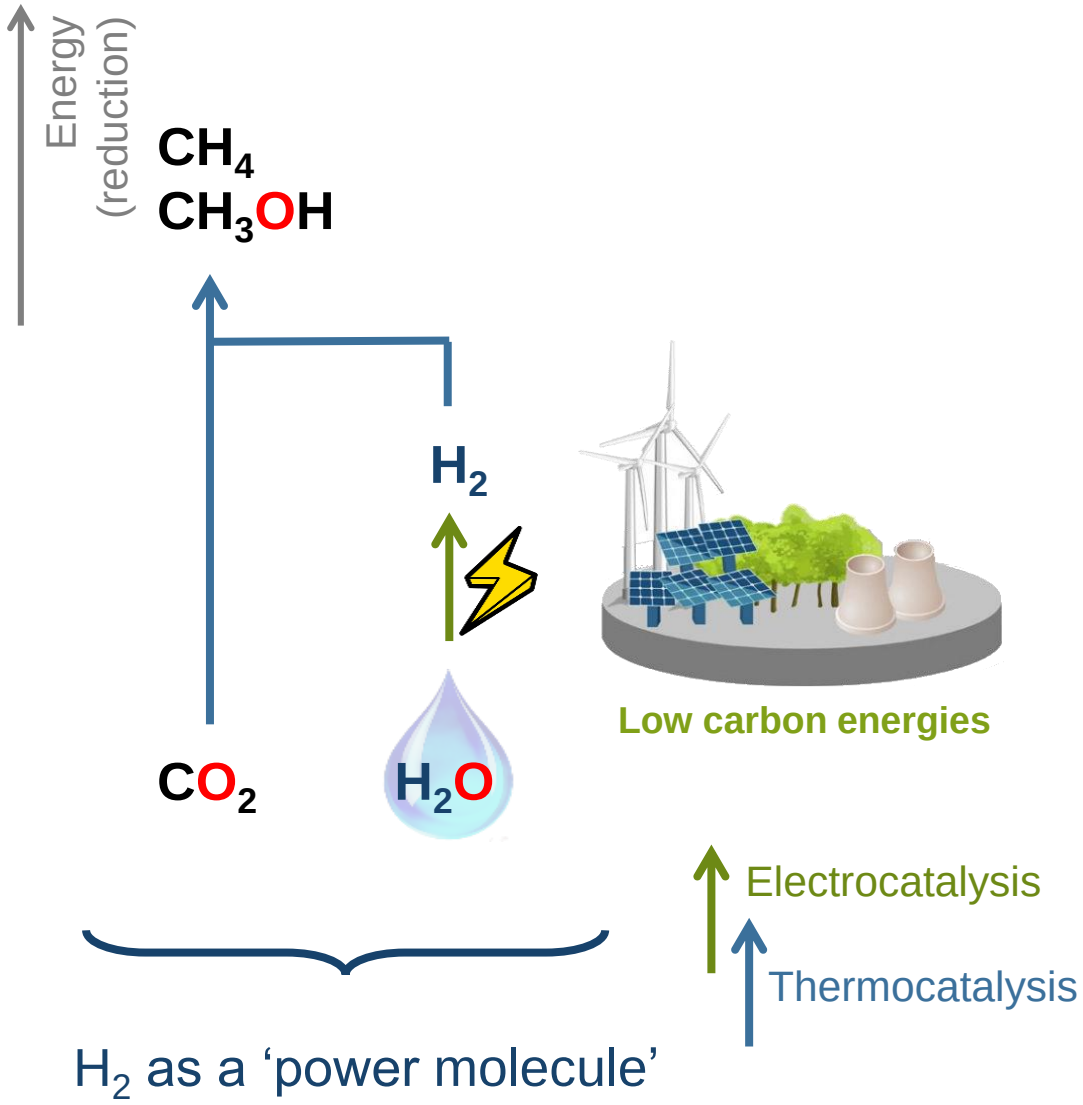
Conclusions

Multiple pathways available depending on the reagents and the catalyst

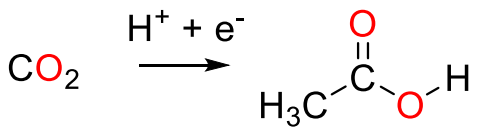


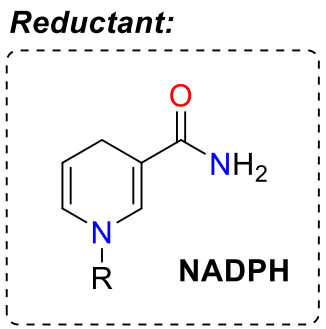
Conversion of CO_2 Coupling electrocatalysis and thermocatalysis

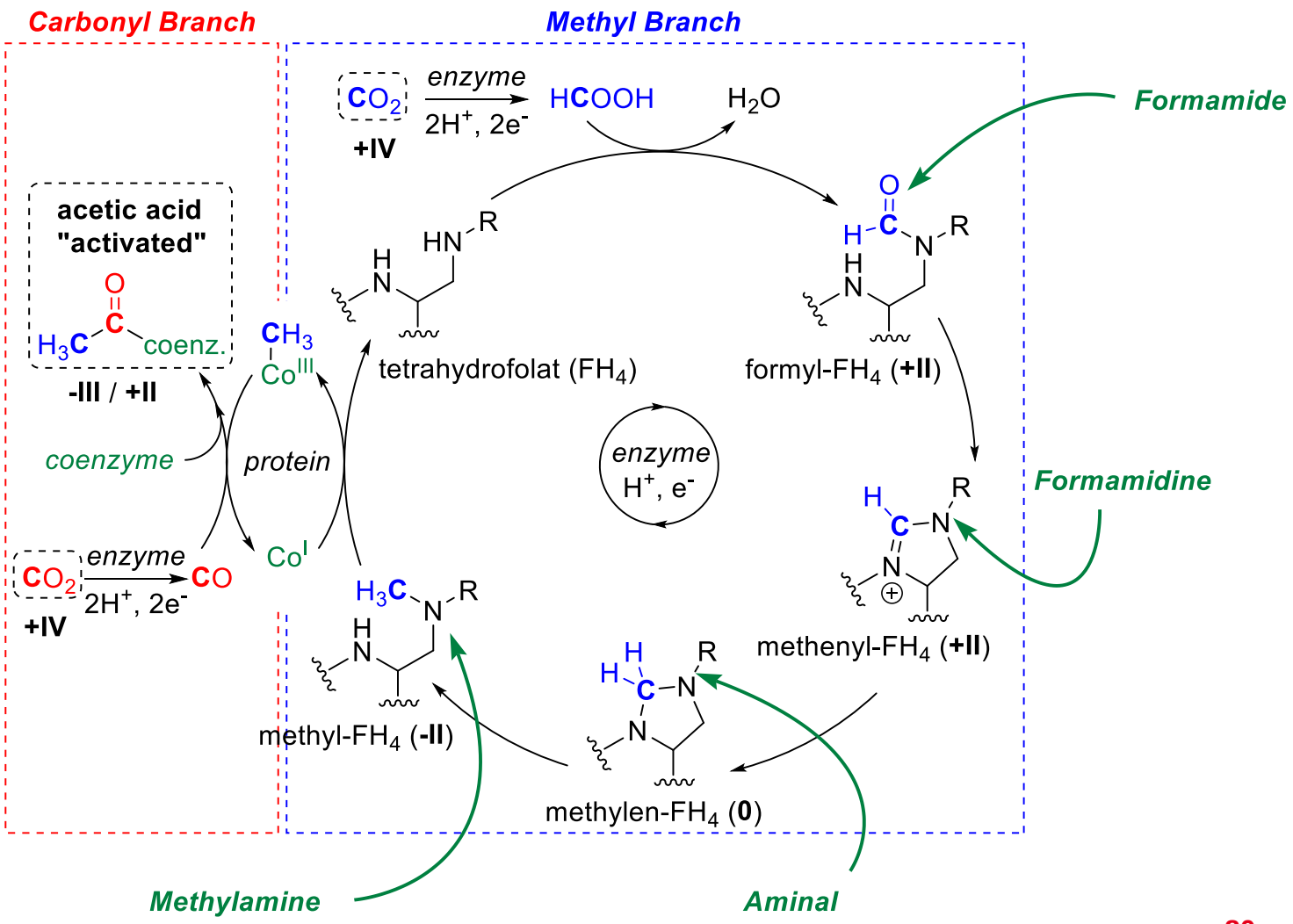
H_2 as a ‘power molecule’



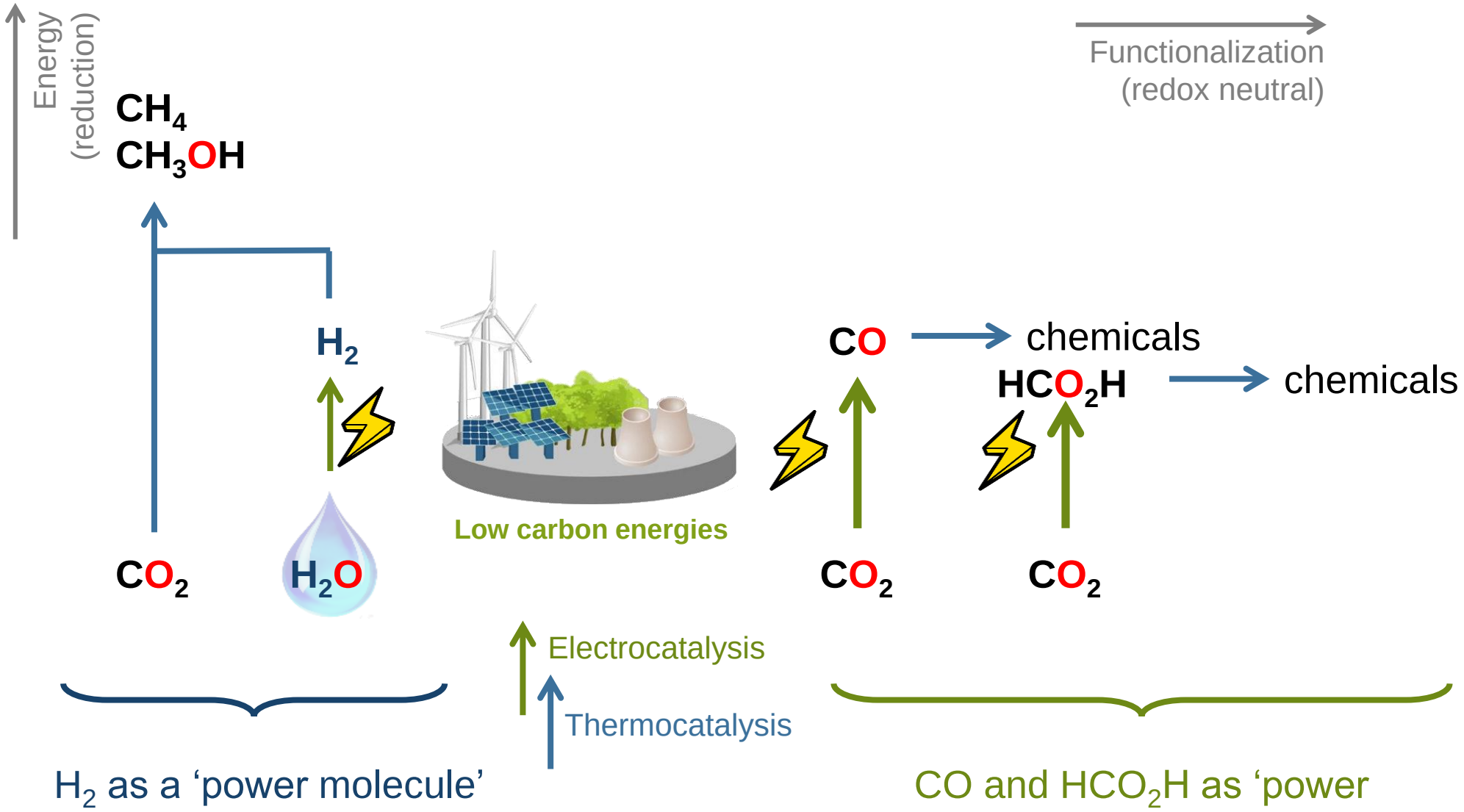
CO and HCO_2H: key molecules for the construction of C-C bonds



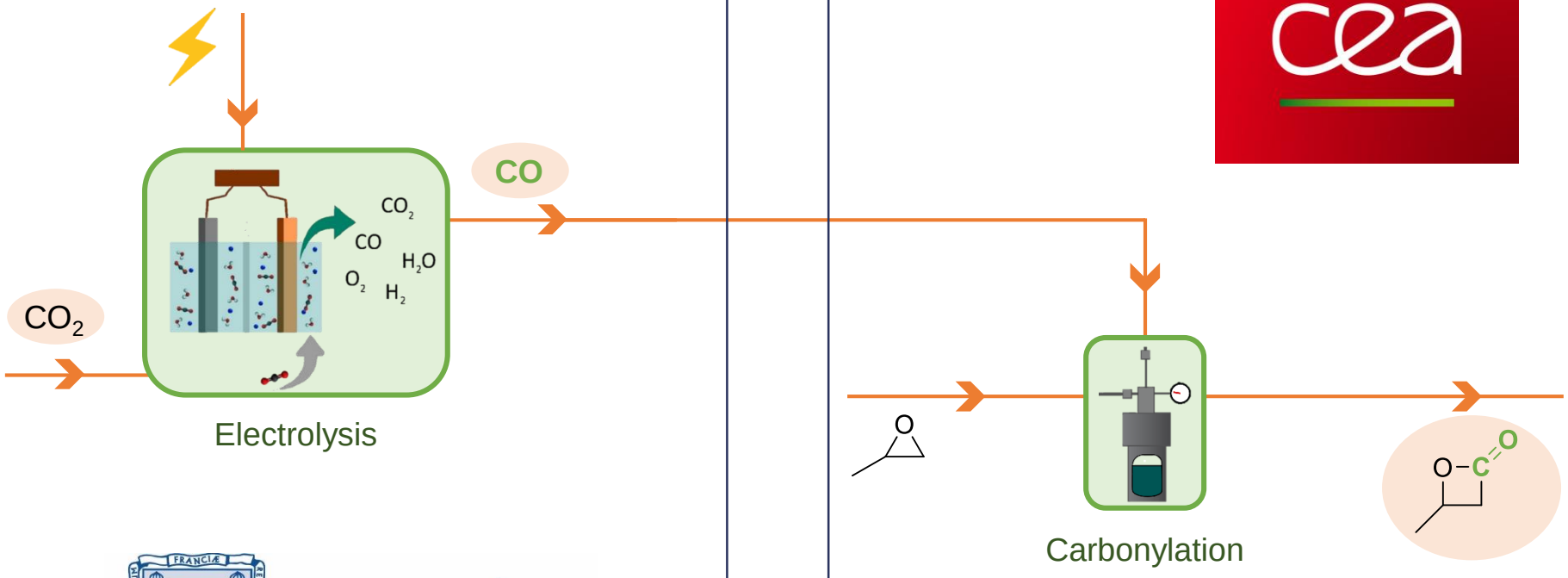




H_2, CO and HCO_2H as 'power molecules'

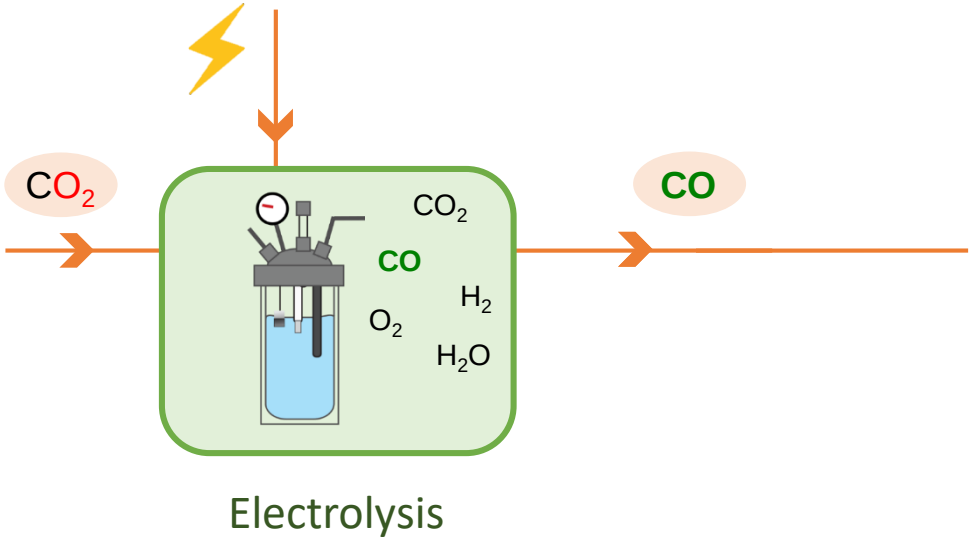


Coupling electrocatalysis with thermocatalysis

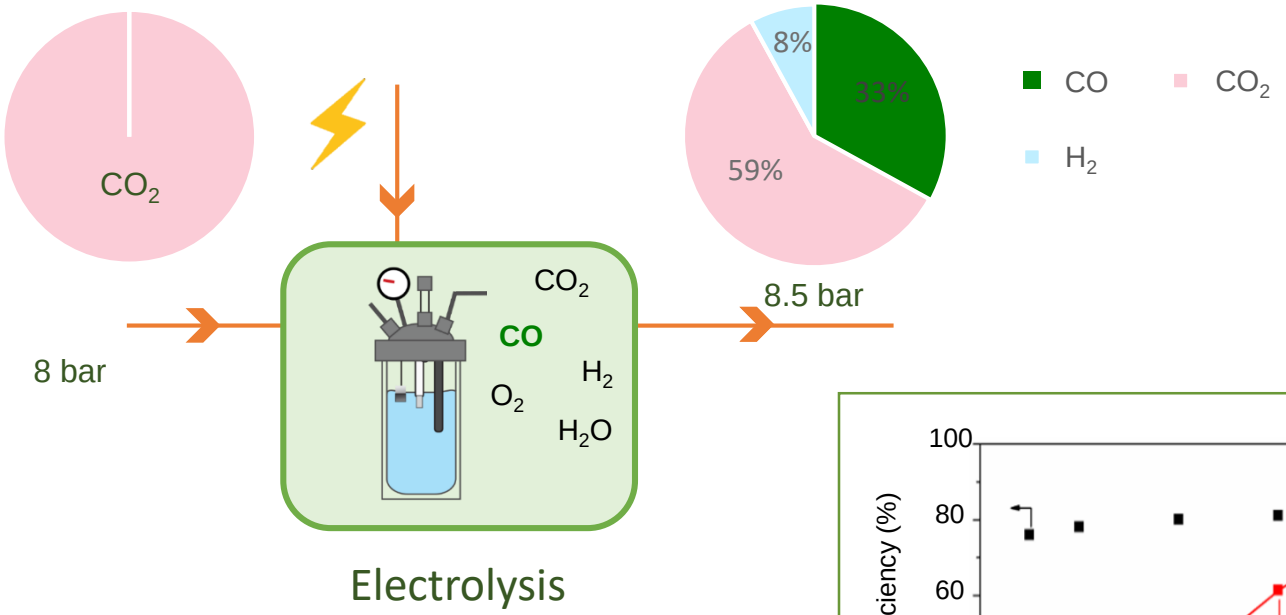


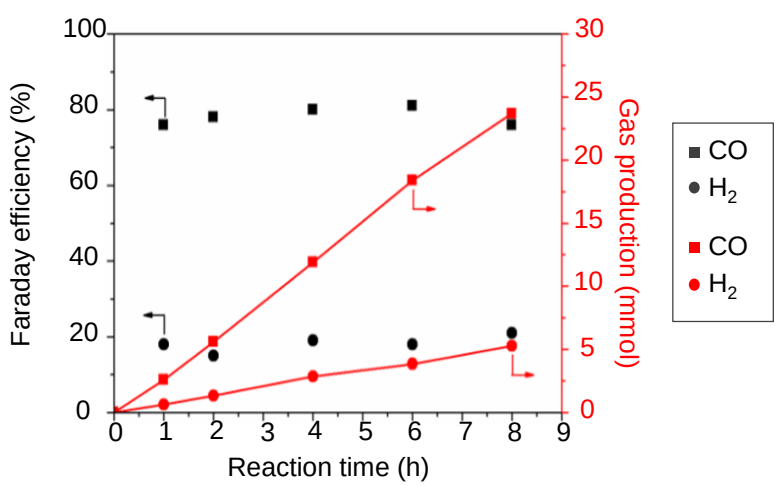
Marc Fontecave's group

CO production by electrocatalysis



Coupling electrocatalysis with thermocatalysis



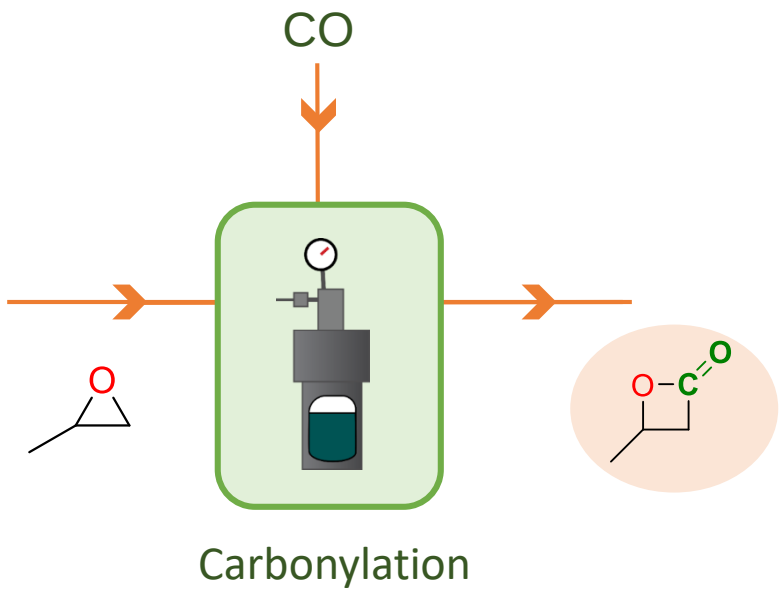


Constant current -0.2 A.cm^{-2}. 0,1 M $CsHCO_3$ under 8 bar CO_2

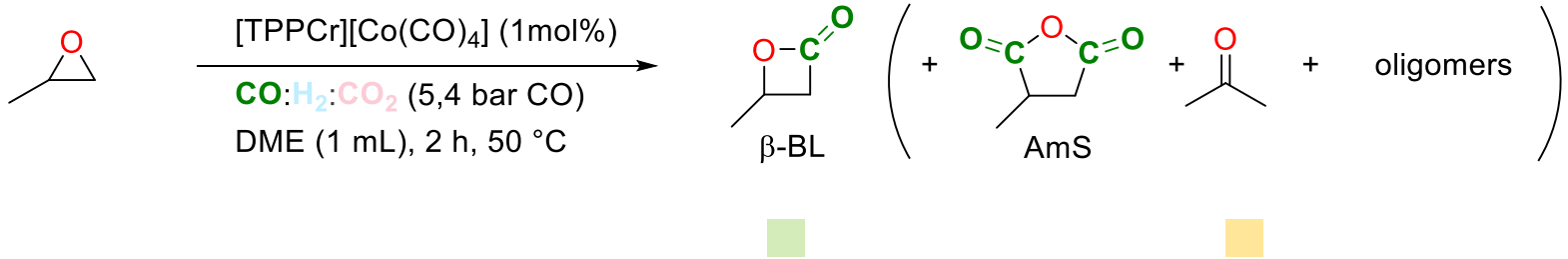
- Cathode : Zn dopped with 9,4 % Ag
- Anode : Graphite
- Electrolyte : 0,1 M $CsHCO_3$

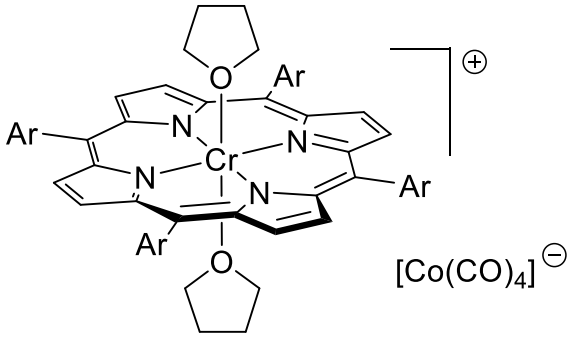
Lamaison, S.; Wakerley, D.; Blanchard, J.; Montero, D.; Rousse, G.; Mercier, D.; Marcus, P.; Taverna, D.; Giaume, D.; Mougel, V.; Fontecave, M. *Joule* **2020**, *4* (2), 395–406.

Thermocatalytic carbonylation of propylene oxide



Thermocatalytic carbonylation of propylene oxide



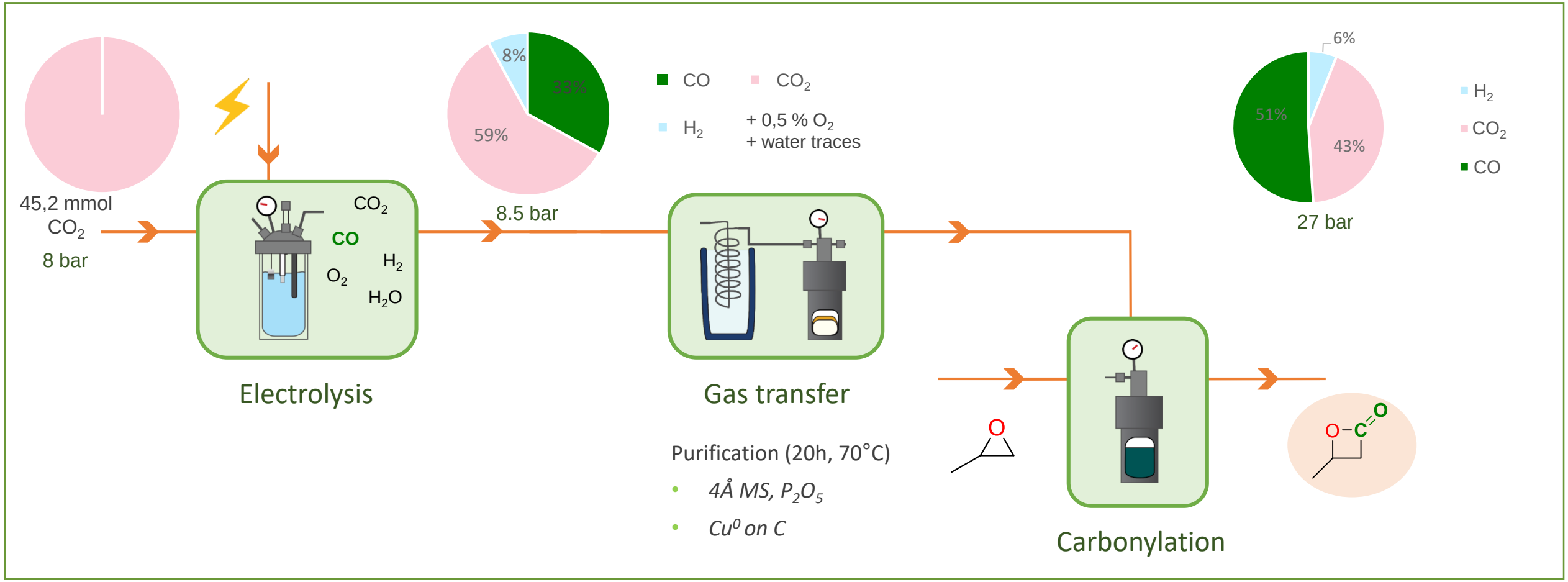


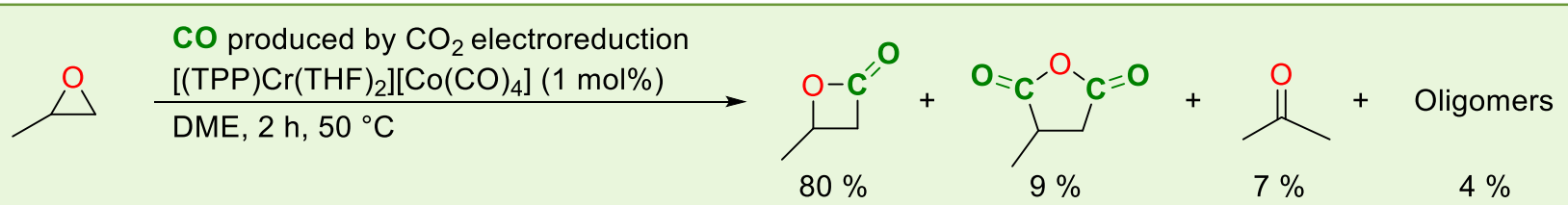
[TPPCr][Co(CO)$_4$]

ChemSusChem, **2021**, 14, 2198

Schmidt, J. A. R.; Mahadevan, V.; Getzler, Y. D. Y. L.; Coates, G. W. *Org. Lett.* **2004**, *6* (3), 373–376

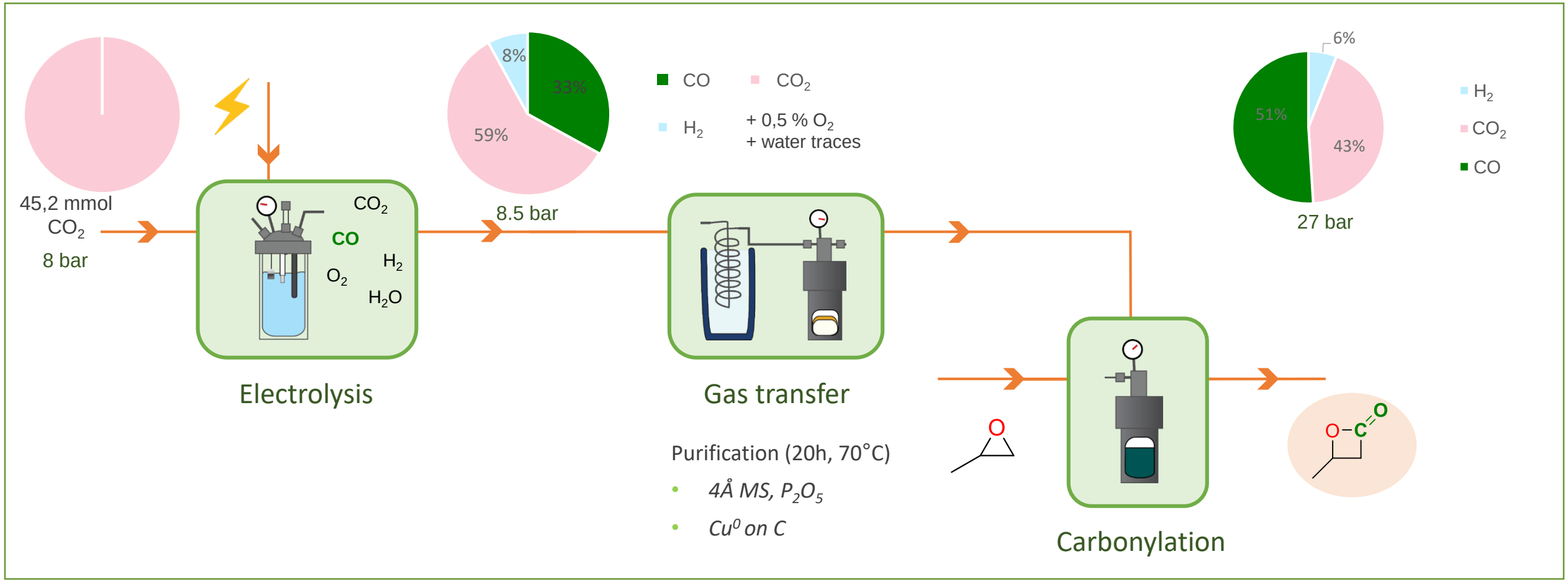
Coupling electrocatalysis with thermocatalysis

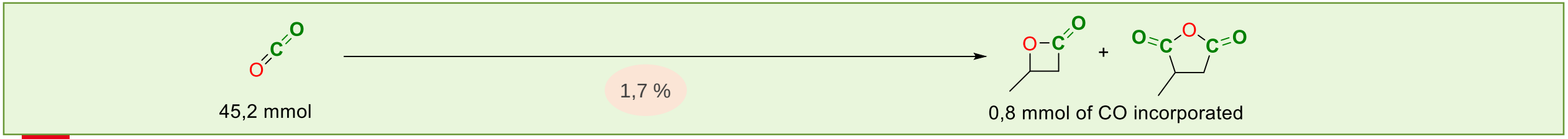




Ponsard L. *et al.*, *ChemSusChem*, **2021**, 14, 2198

Coupling electrocatalysis with thermocatalysis

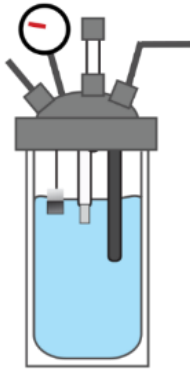




Ponsard L. *et al.*, *ChemSusChem*, **2021**, 14, 2198

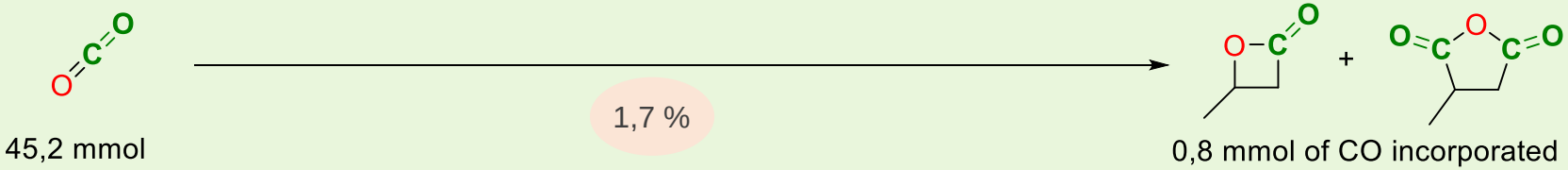
Coupling electrocatalysis with thermocatalysis:

Lessons learned, what is needed?



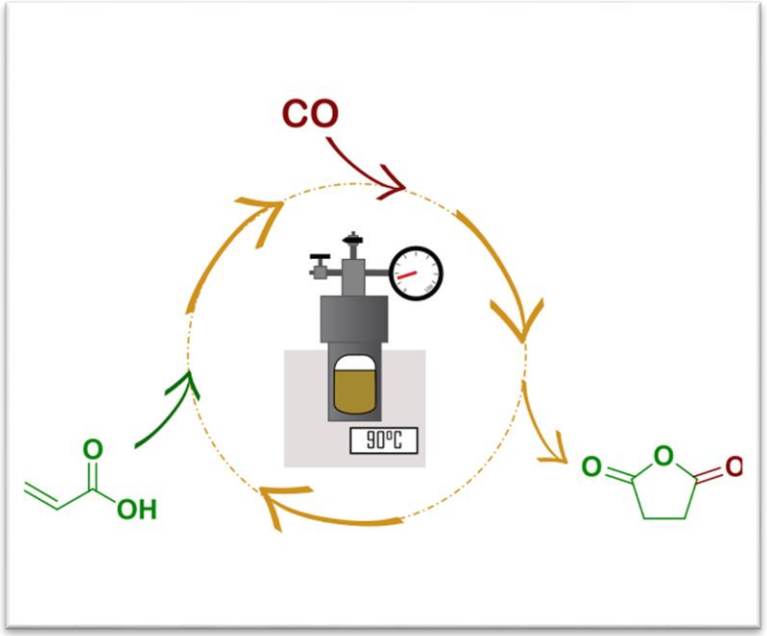
- Better CO_2 conversions
- Devices for high pressure electrolysis
- Suppress O_2 pollution in the output gas

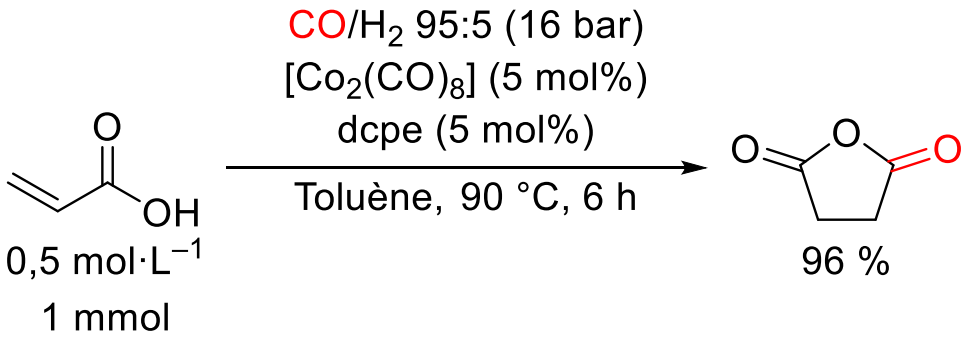
- Robust catalysts, able to work with pollutants
- Low pressure carbonylation catalysts
- New carbonylation reactions



Ponsard L. *et al.*, *ChemSusChem*, **2021**, 14, 2198

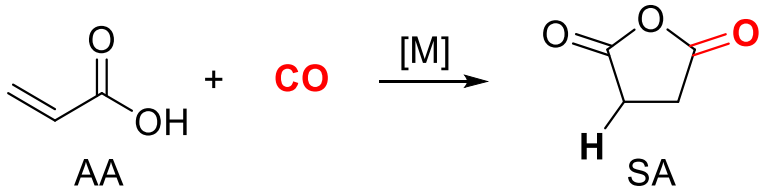
A new carbonylation reaction



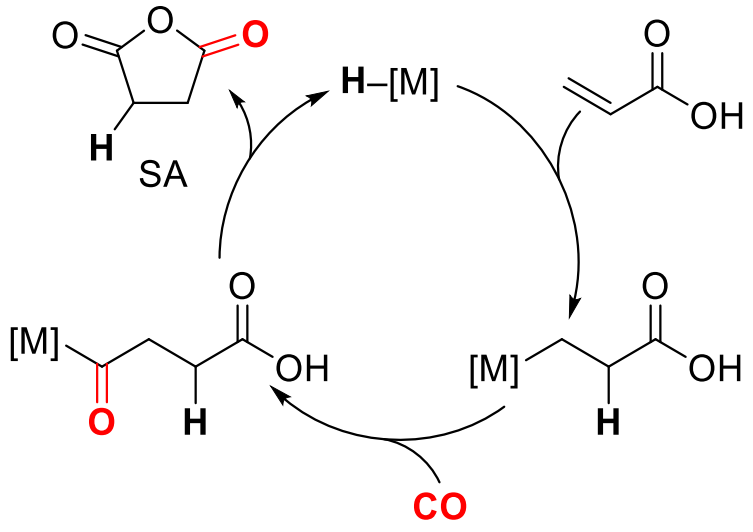


Patent filed 2021 - n°FR2111996

(a) Synthetic approach



(b) Envisioned mechanism



Pietraru M.-H. *et al. ChemCatChem* **2023**, *15*, e202300720

Thank you!

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