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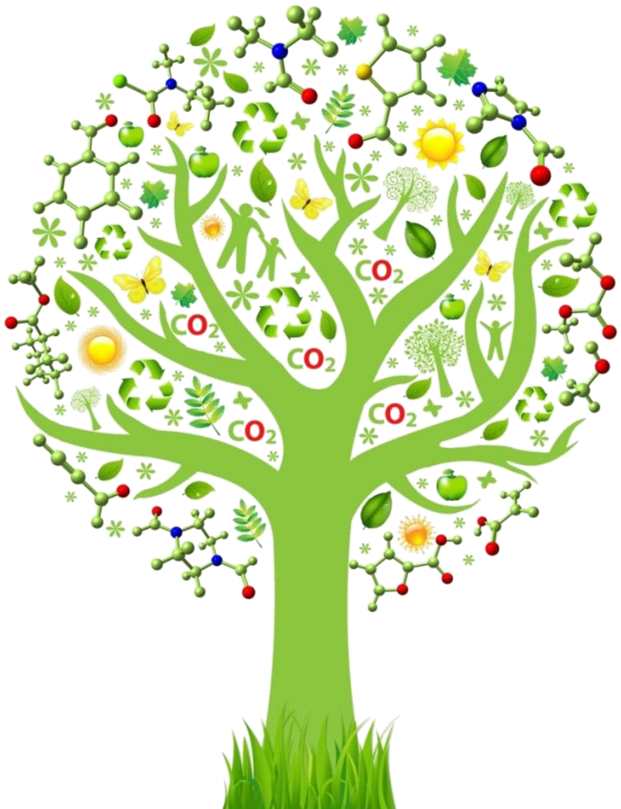
CO_2 RECYCLING, A DIAGONAL APPROACH

CEA / DSM / IRAMIS | Thibault Cantat

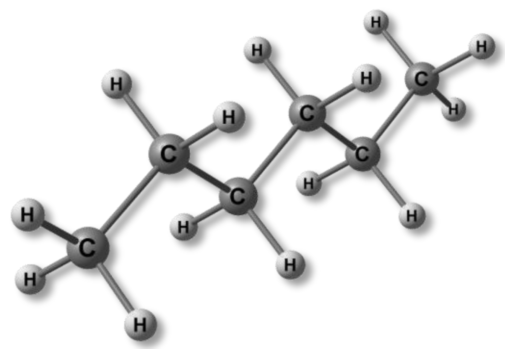


FONDATION TUCK

MAY 26 – 2014

FROM THE CONTEXT TO THE CHALLENGES

A widespread use of fossil resources: fuels and chemistry



Hydrocarbons, gas, coal

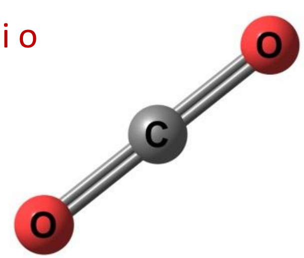
10%

Fuels

80% of the world energy portfolio

Chemicals

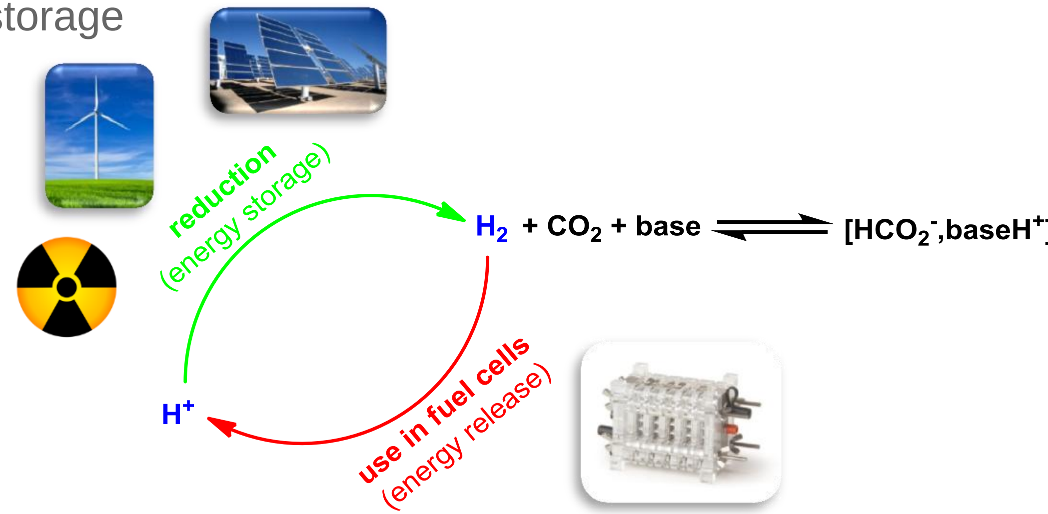
95% of organic chemicals derive from fossil feedstocks



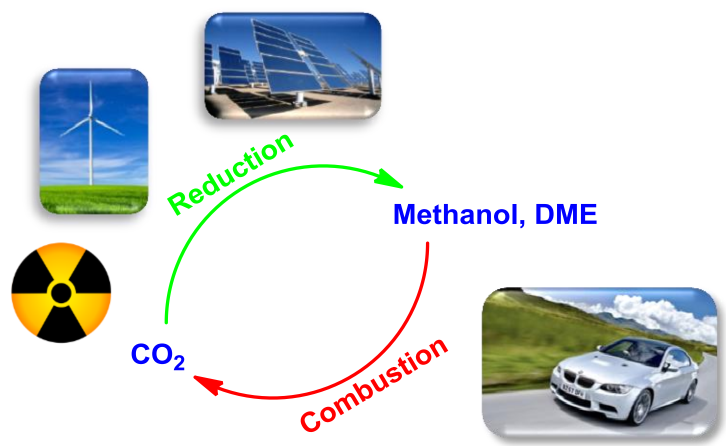
CO_2 AS AN ENERGY VECTOR

CO_2 reduction: recycling to fuels

- CO_2 hydrogenation for hydrogen storage
  - CO_2 to formic acid HCOOH
  - CO_2 to methanol CH_3OH



- CO_2 electro- and photoelectro-catalytic reduction to CO, formic acid, methanol, etc.



CO_2 TO FUELS

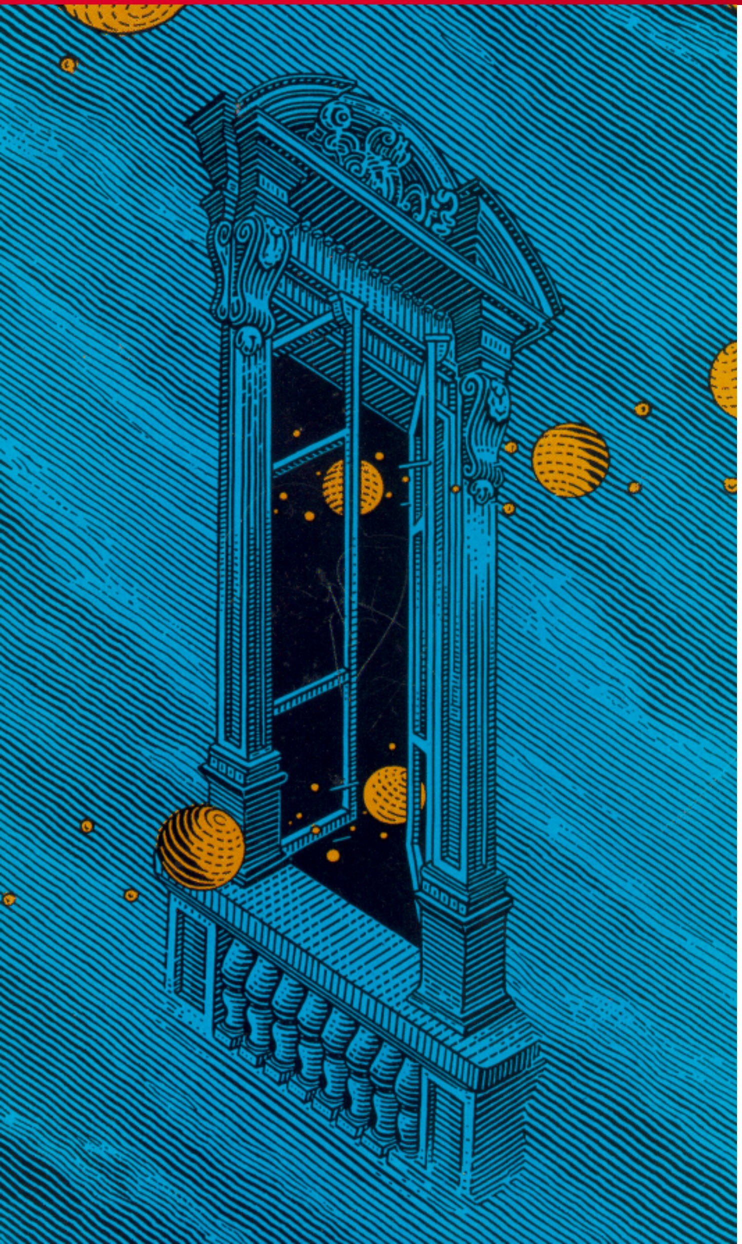
Limited short terms opportunities

$$H_2O \longrightarrow H_2 + {}^{1}/_{2}\, O_2$$

$$H_2 \xrightarrow{+\ CO_2} CH_3OH + H_2O$$

methanol

DESIGN UNDER CONSTRAINT



The problem

Reduce CO_2 using a carbon-free energy input while carbon fossil resources are the cheapest and more abundant energy source

The solution

Catalysis

The strategy

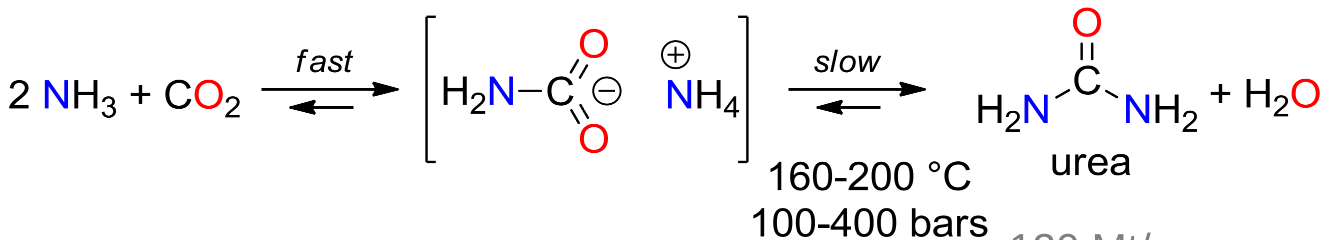
CO_2 to chemicals:

- develop efficient catalysts for CO_2 reduction
- avoid the fuel sector
- convert CO_2 to high value products

INDUSTRIAL PROCESSES UTILIZING CO_2

Industrial routes from CO_2

- Bosch-Meiser process for urea production



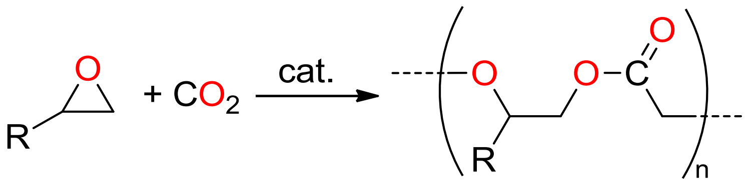
120 Mt/y

- Inorganic carbonates

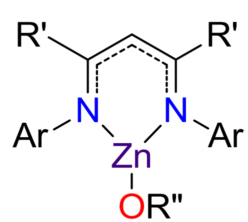
$CO_2 \xrightarrow{\text{brines}}$ inorganic carbonates (M-CO_3) for CCS applications

44 Mt/y

- Synthesis of polycarbonates from CO_2/epoxide copolymerization

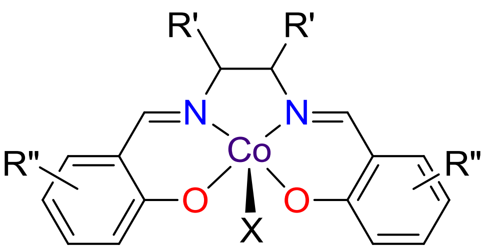


76 kt/y



Bimetallic mechanism

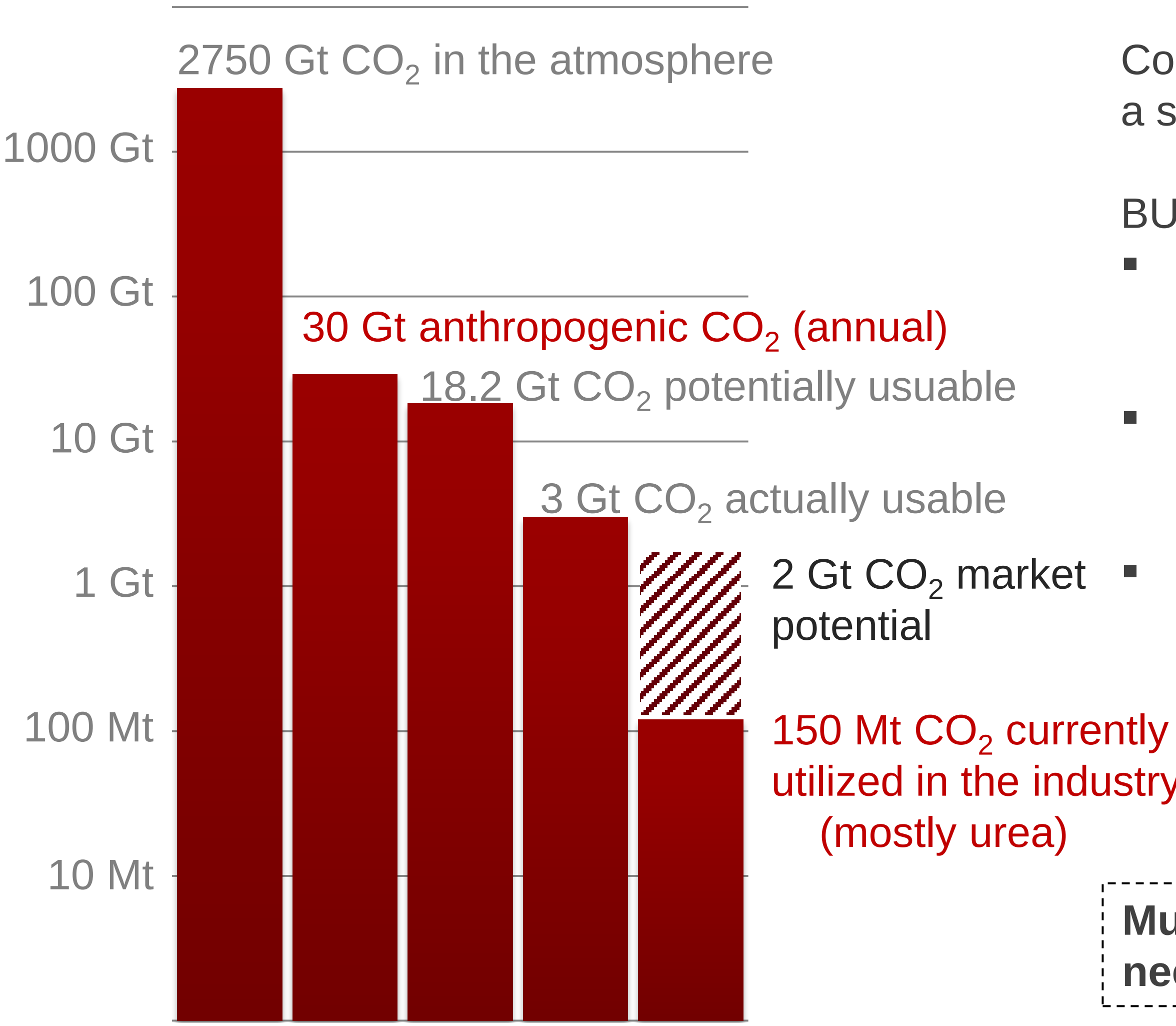
Coates



Darensbourg

CO_2 TO VALUE ADDED CHEMICALS

Market opportunities with no significant impact on CO_2 emissions



Conversion of CO_2 to chemicals is NOT a solution to the greenhouse effect

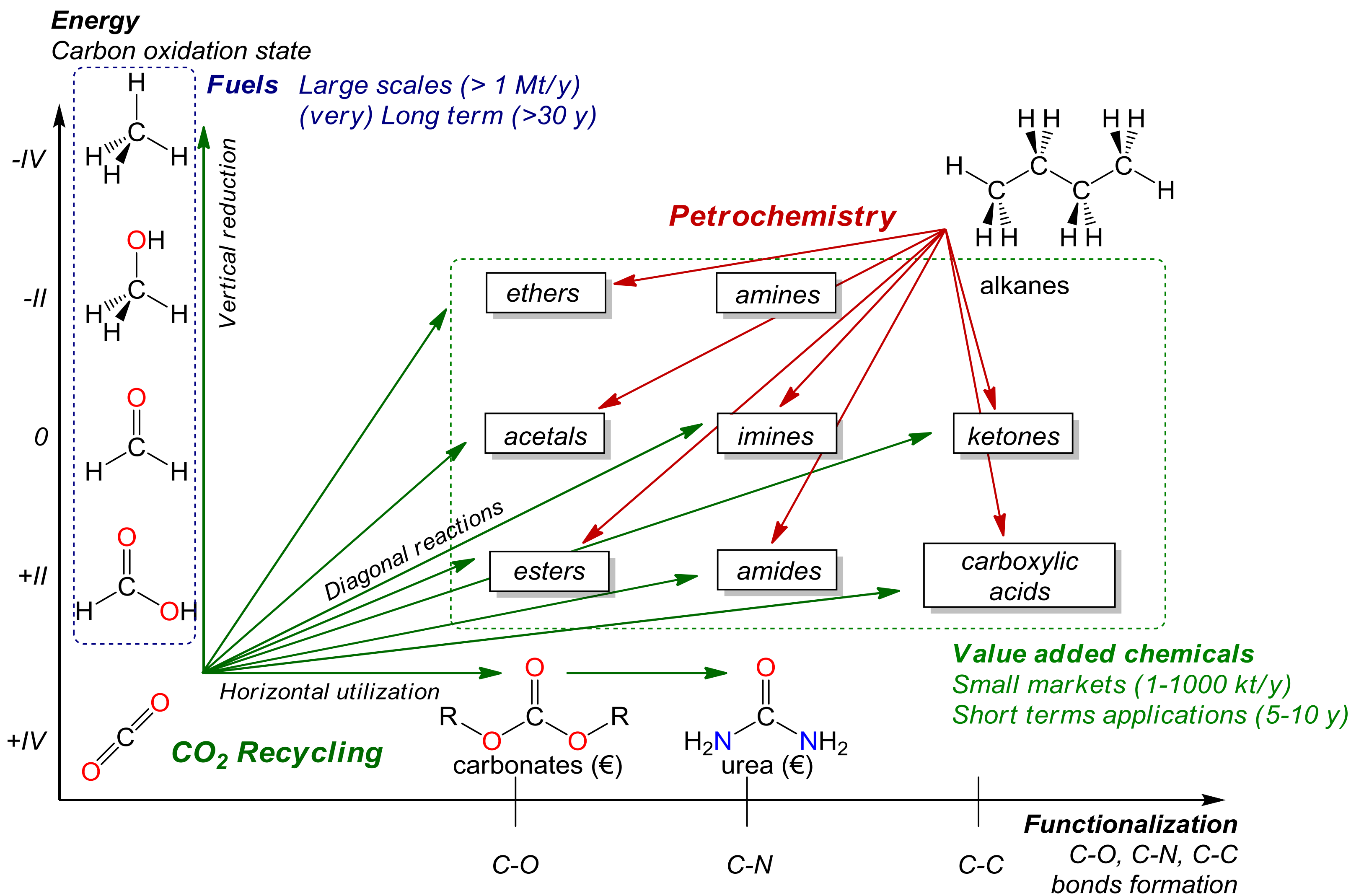
BUT:

- CO_2 is a cheap, secured, renewable and well-distributed carbon feedstock
- CO_2 can replace toxic reagents (phosgene, isocyanates, etc.)
- Short terms opportunities in bulk chemicals to fine chemicals

Multiple markets, multiple targets: need for multiple new processes

A DIAGONAL APPROACH

VARIOUS OPPORTUNITIES TO CO_2 RECYCLING…



Objective: develop efficient and viable catalytic processes

DESIGN UNDER CONSTRAINT

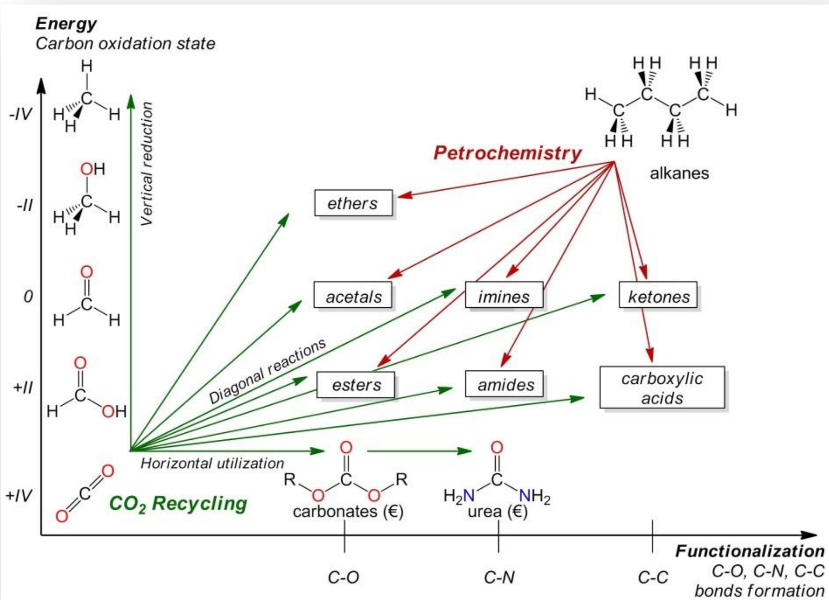
Two strong constraints: energy and resources availability

- carbon-free energy inputs
- high selectivity
- large kinetics
- low pressure, low temperature
- high selectivity

- use of earth abundant materials
- use of non-toxic materials
- tolerant to impurities (NO_x, SO_x, M, etc.)
- atmospheric pressure of CO_2
- high temperature (niche app. with cogeneration)

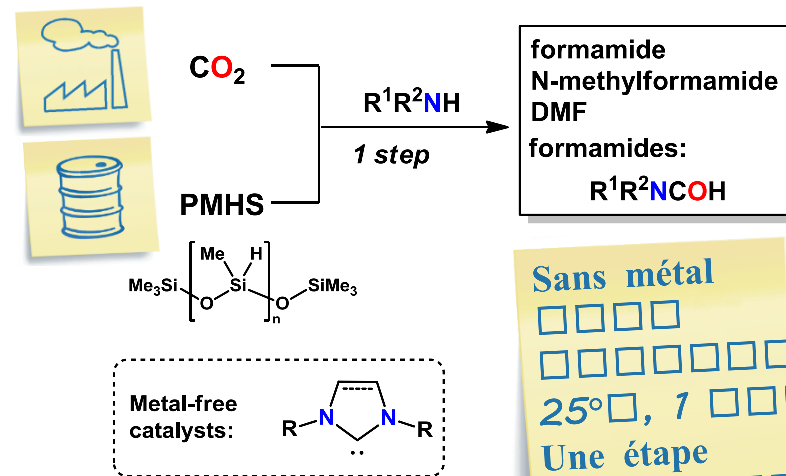
PROOF-OF-CONCEPT: NEW CATALYTIC PROCESS

Proof-of-concept for the diagonal approach



Co-recycing CO_2/PMHS (CEA/DSM technology)

Metal-free catalysts, room temperature, single step



Sans métal □□□□
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25°□, 1 □□□
Une étape
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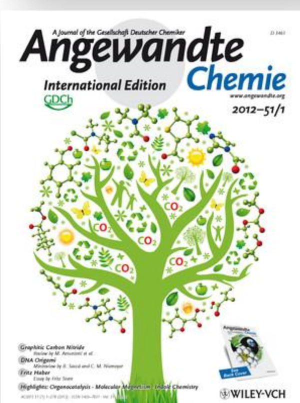
World production: 500 kt/y from oil
Utilization as solvents and reactants



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

- CO_2 as an alternative to petrochemistry
  Utilization of an energy vector (H, Si) coupled with a functionalizing reactant

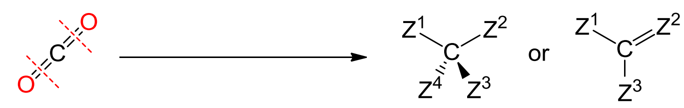
Angewandte Chemie *2012*, ***JACS*** *2012*, **WO2012137152**

A DIAGONAL APPROACH

NOVEL PROCESSES

CHALLENGE: CO_2 DEOXYGENATION

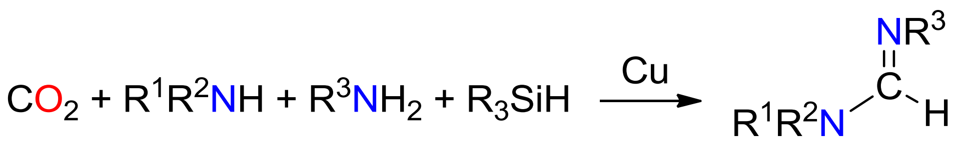
Complete deoxygenation of CO_2



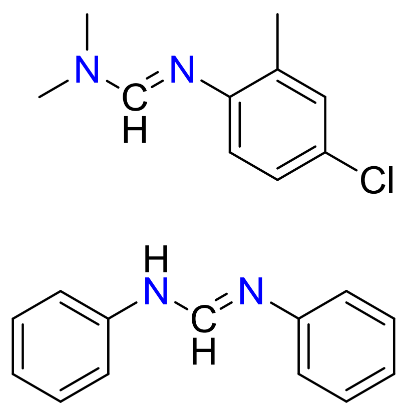
"cut-and-paste" reaction for CO_2 recycling

CO_2 as a C_1 building block

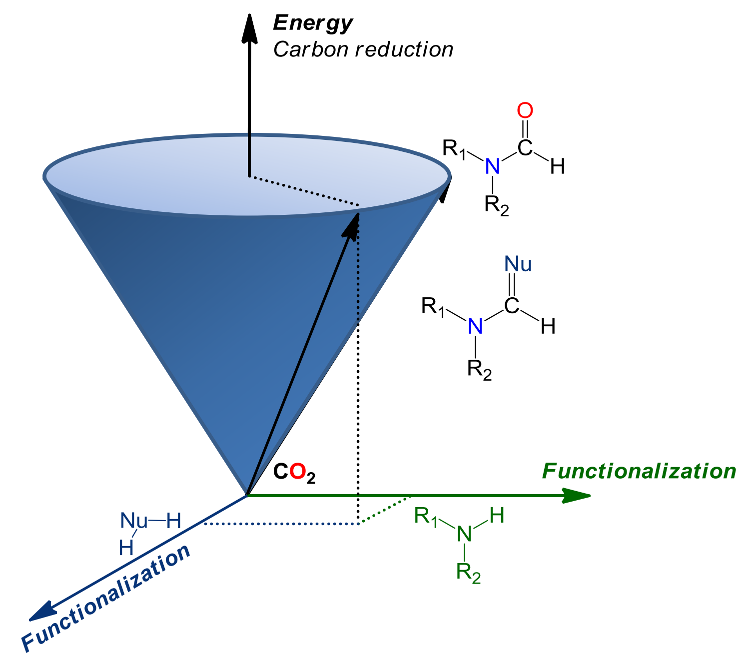
- Complete deoxygenation of CO_2 to formamidines



Formamidines



Fertilizers, pesticides, fongicides



ChemCatChem *2013*, ***ChemCatChem*** *2013*, **PCT/IB2013/054601, PCT/IB2013/059304**

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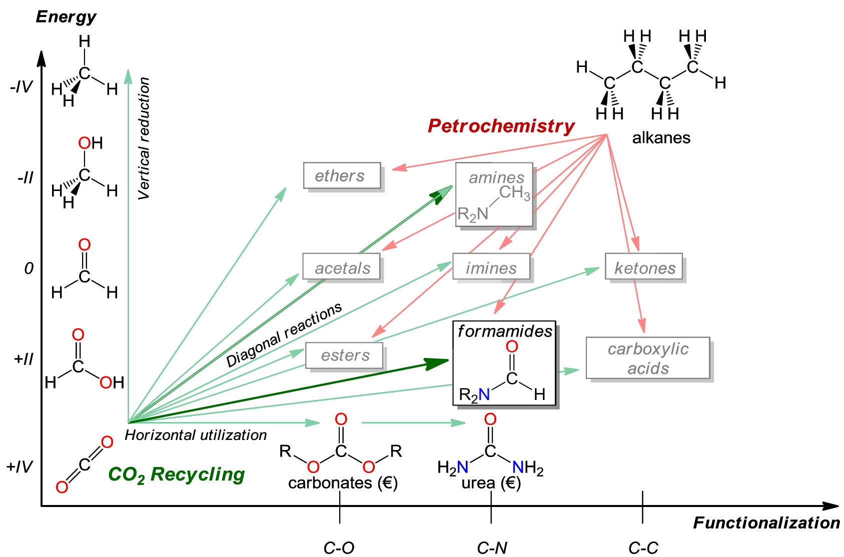
NEW PROCESS FOR THE CONVERSION OF CO_2 TO METHYLAMINES

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

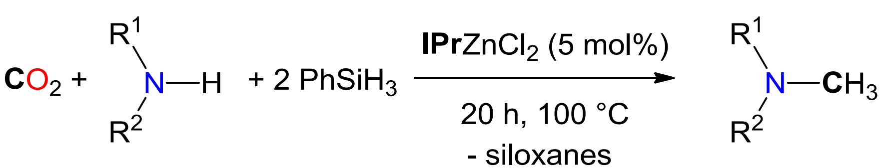


Methylamines are basic reagents in nitrogen chemistry

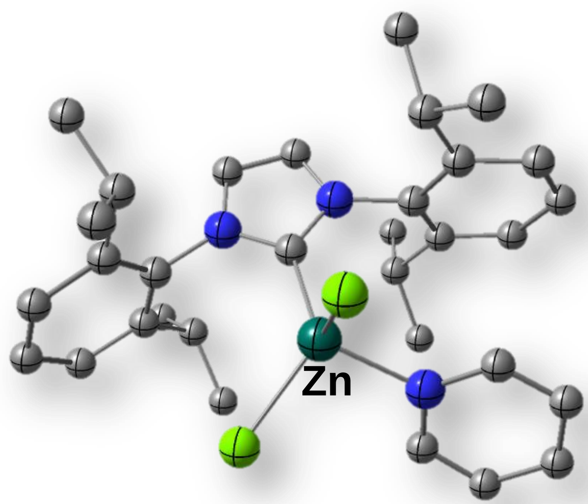
Production of $MeNH_2$, Me_2NH and Me_3N reaches 600,000 tons/year

CEA technology

Novel catalytic reaction (2012)



Zinc catalysts designed @ CEA/DSM



Chemical Science 2013, ***Catal. Sci. Tech.*** 2014, **PCT/IB2013/054599**

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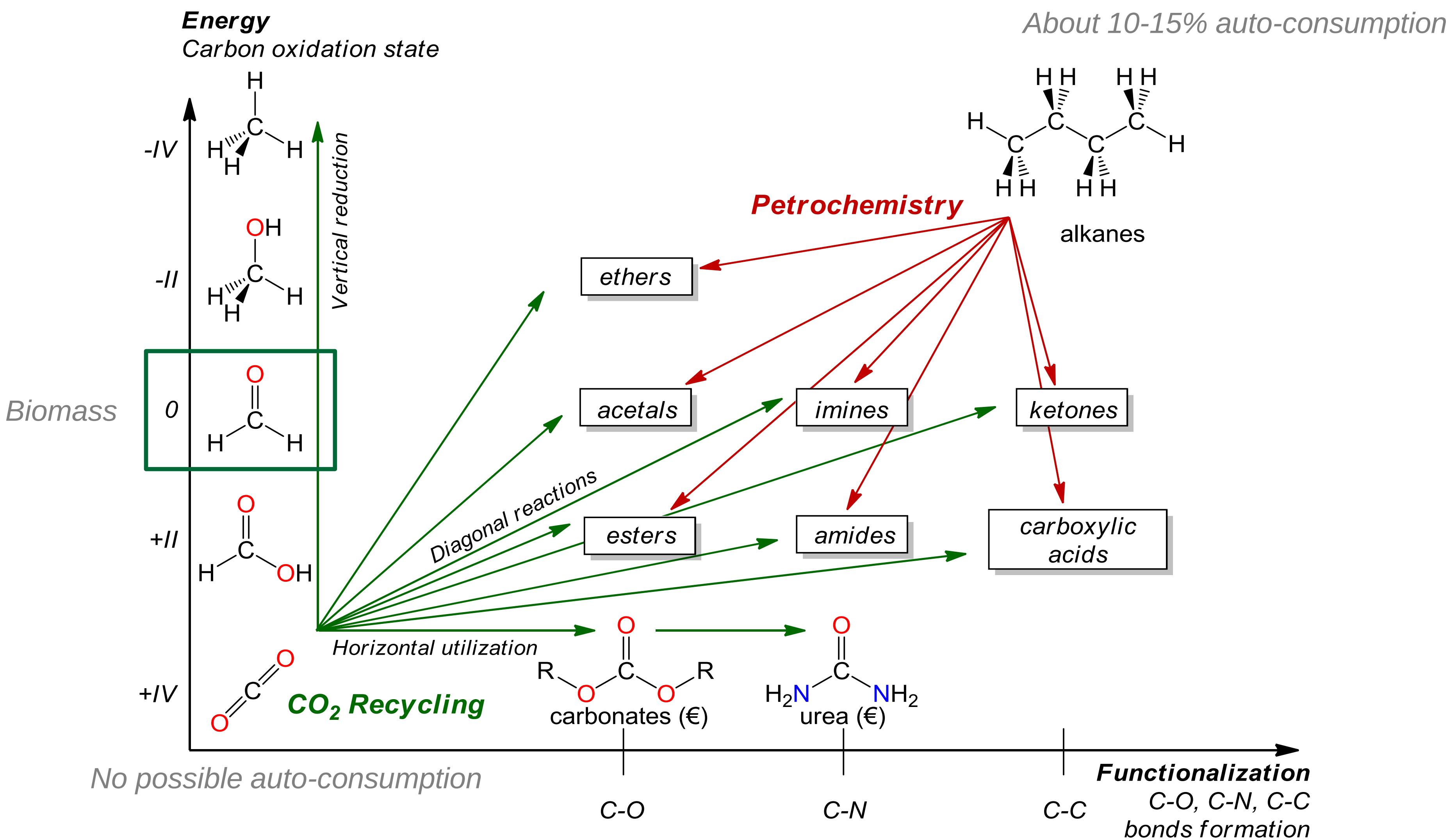
SEVENTH FRAMEWORK PROGRAMME
INSTITUT DE FRANCE

EFFICIENT REDUCTION OF C-O BONDS

ORGANOCATALYTIC REDUCTION OF LIGNIN MODEL COMPOUNDS

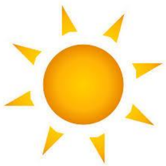
LIGNIN AS A RENEWABLE CARBON FEEDSTOCK

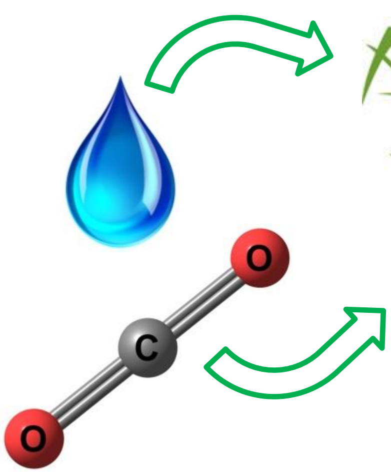
Biomass to chemicals

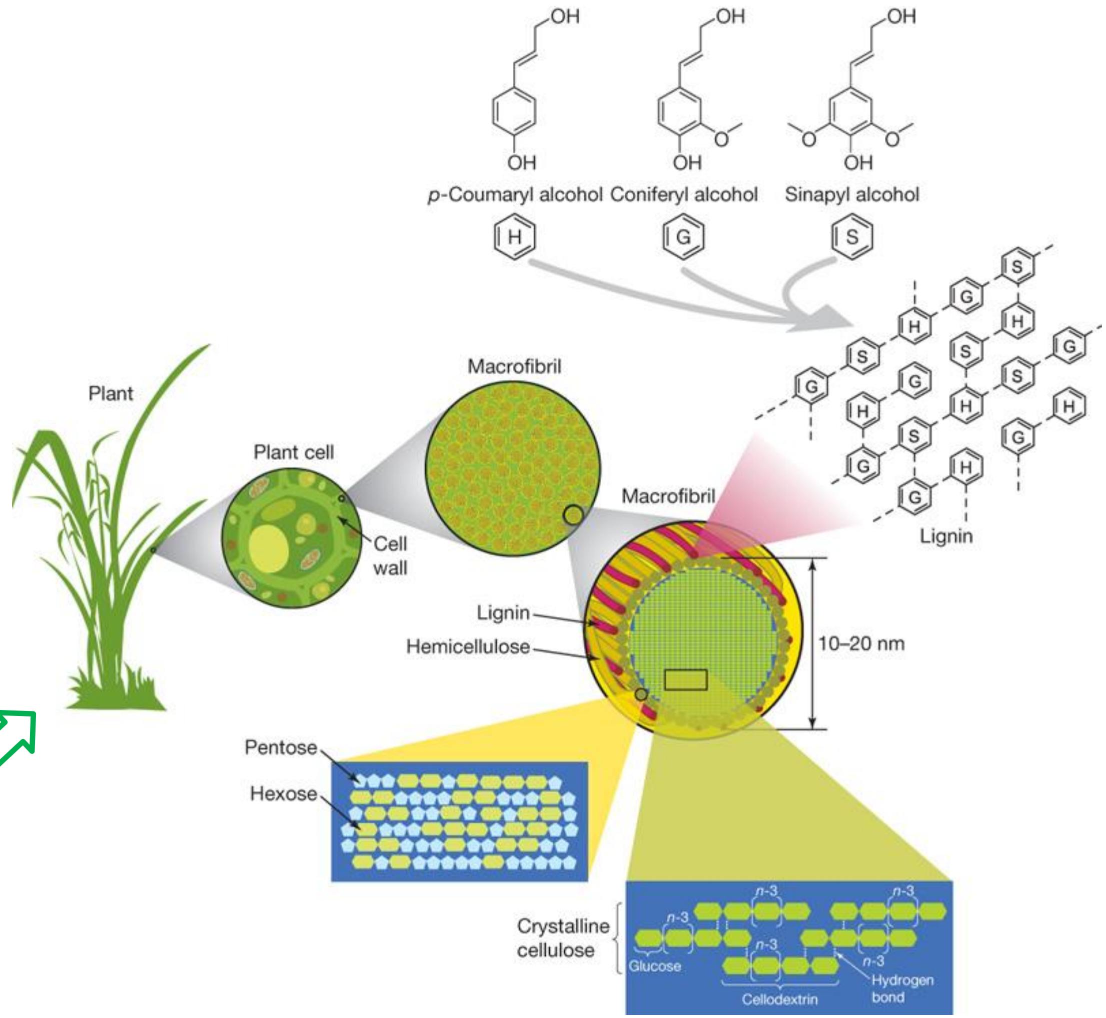


LIGNIN AS A RENEWABLE CARBON FEEDSTOCK

Lignin a source of aromatics







From EM Rubin *Nature*, **2008**, *454*, 841

CHALLENGES

Lignin depolymerization to chemicals

- Avoid the fuel market and develop short term applications in the conversion of lignin to chemicals (higher added value)
- Increase the energy content of lignin
- Promote lignin depolymerization
- Lack of efficient technologies for the reduction of lignin
- Isolation of functional products: molecular phenols, alcohols, aromatics
- Constraints: presence of impurities (H_2O, O_2, etc.), no noble metals

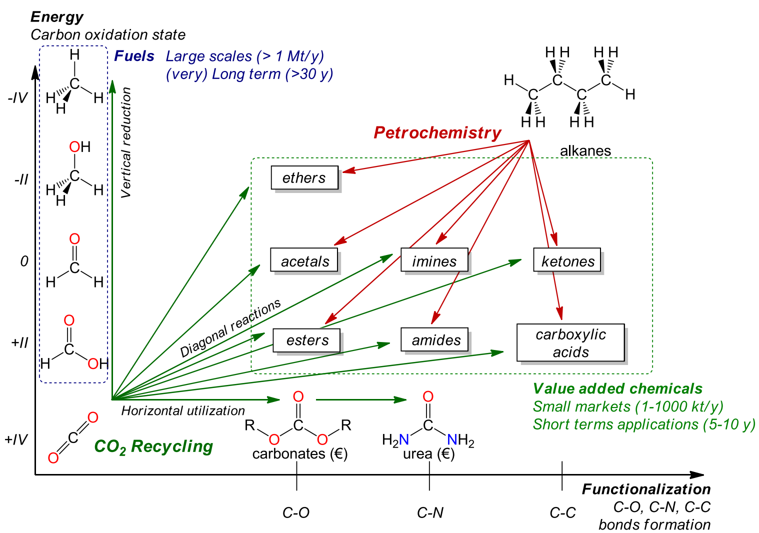
Need for metal-free reductive cleavage of ethers

Chem. Commun. ***2014***, *50*, 862

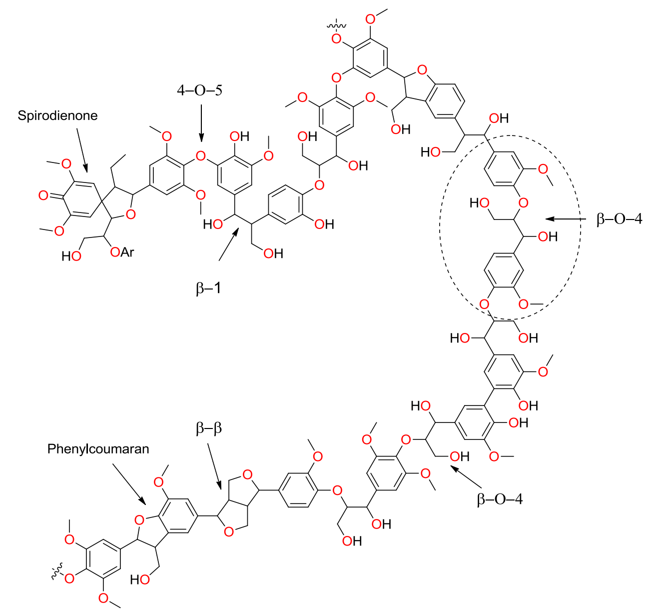
LIGNIN REDUCTION TO CHEMICALS

Lignin reductive depolymerization

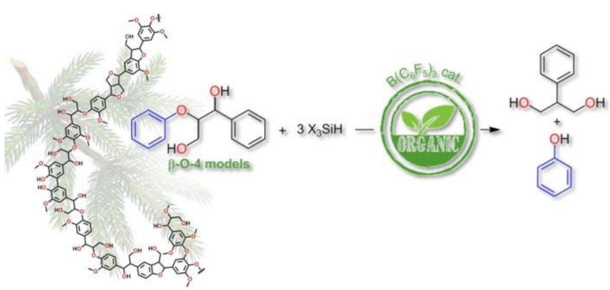
- Biomass enables autoconsumption



- Idea: convergent reduction of lignin



- Proof-of-concept on molecular models:



Sans métal

25°, 16

Chem. Commun. **2014**, 50, 862

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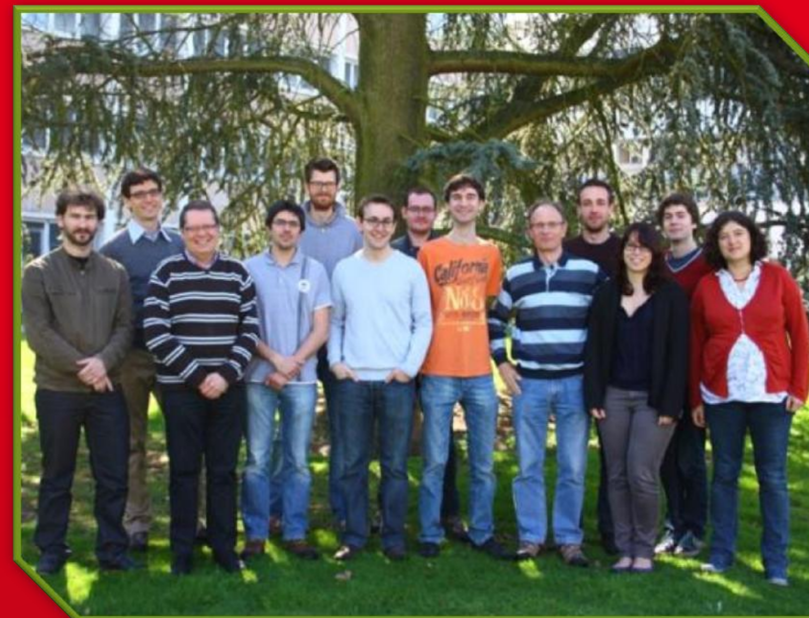

PhD Students:

F. Dulong
C. Gomes
X. Frogneux
E. Feguali
E. Blondiaux
S. Savourey
N. von Wolff
C. Chauvier
J. Charr

Postdocs:

Dr. O. Jacquet
Dr. J. Pouessel
Dr. A. Tlili
Dr. G.Lefèvre

Researchers:
Dr. P. Thuéry
Dr. J.-C. Berthet
Dr. C. Genre

Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Saclay | 91191 Gif-sur-Yvette Cedex
T. +33 (0)1 69 08 43 38 | F. +33 (0)1 69 08 66 40

Direction des Sciences de la Matière
Institut IRAMIS
UMR CEA/CNRS 3299 – SIS2M