TUCK TOTAL PAU 20 JUNE 2008

Valorisation du CO_2 par l'industrie chimique

CO_2 as building block in the chemical industry

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Where we are….


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Cernihiv
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Rzeszow
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le Mans
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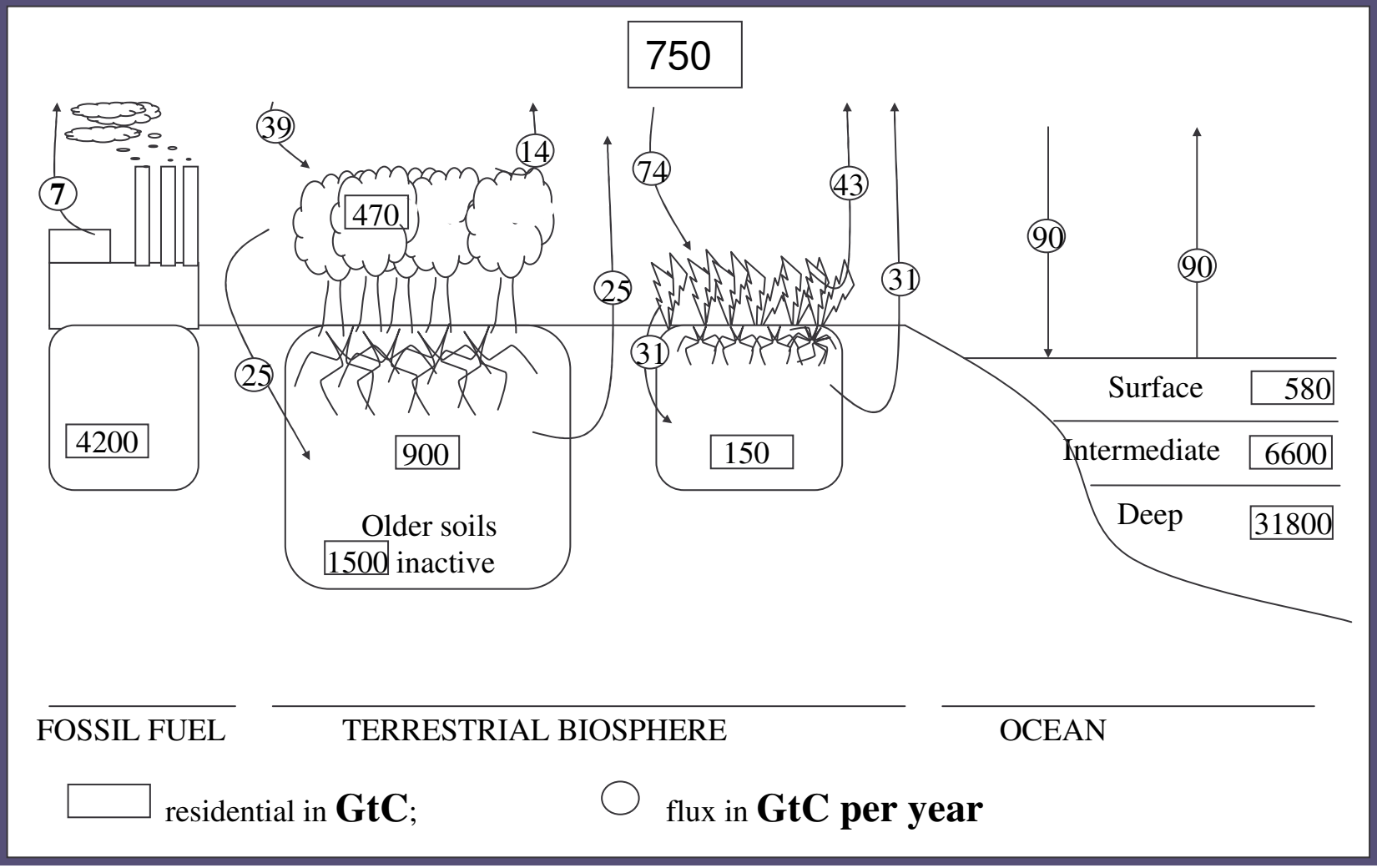
Outline

- The Carbon Cycle
  - The anthropogenic carbon dioxide
- The Origin of Anthropogenic CO_2
  - How we can use CO_2
- Industrial Utilisation of CO_2
  - **Chemical**
  - **Technological**
- The Must in the Utilisation of CO_2
  - Used vs avoided CO_2
- Sustainability and CO_2 Utilisation
  - Process innovation
  - Tandem chemical-biological
  - Conversion of biomass
- **Classes of Compounds of Industrial Interest**
- LCA as a Tool for Quantifying the Avoided CO_2
- Perspective in CO_2 Utilisation
  - Opportunities and Challenges

The Carbon Cycle and the Excess Anthropogenic CO_2



The origin of anthropogenic CO_2

90 % Use of fossil carbon and biomass for energy production

10 % from chemicals

How can we use CO_2 ?

Fuels:
HCs require hydrogen
De-oxygenation to C
requires energy

Chemicals:
Bulk chemicals
Specialties

The Utilization of CO_2 in the Chemical Industry

Compound	Date	Amount Mt/y	Catalyst
Urea	1870	70	No cat
Salycilic acid	1869	20 E-3	Group 1 metals
Methanol	1970	6	TM oxides
Carbonates			
Organic	1972	Few kt	Various systems
Inorganic	1860	30	No cat

The Technological Utilization 18 Mt/y

- **Additive to beverages**
- **Food packing/conservation**
- **Cereals preservation (bactericide)**
- **Fire estinguisher**
- **Water treatment**
- **Mechanicl industry (moulding,…)**
- **Dry-washing**
- **Air-conditioning**
- **Extraction (scf and EOR)**

The MUST in the utilisation of CO_2

The new process (conversion or technological use) or product (substitute of existing ones) must minimize

the energy consumption

and the emission of

CO_2

Used CO_2 *versus* Avoided CO_2

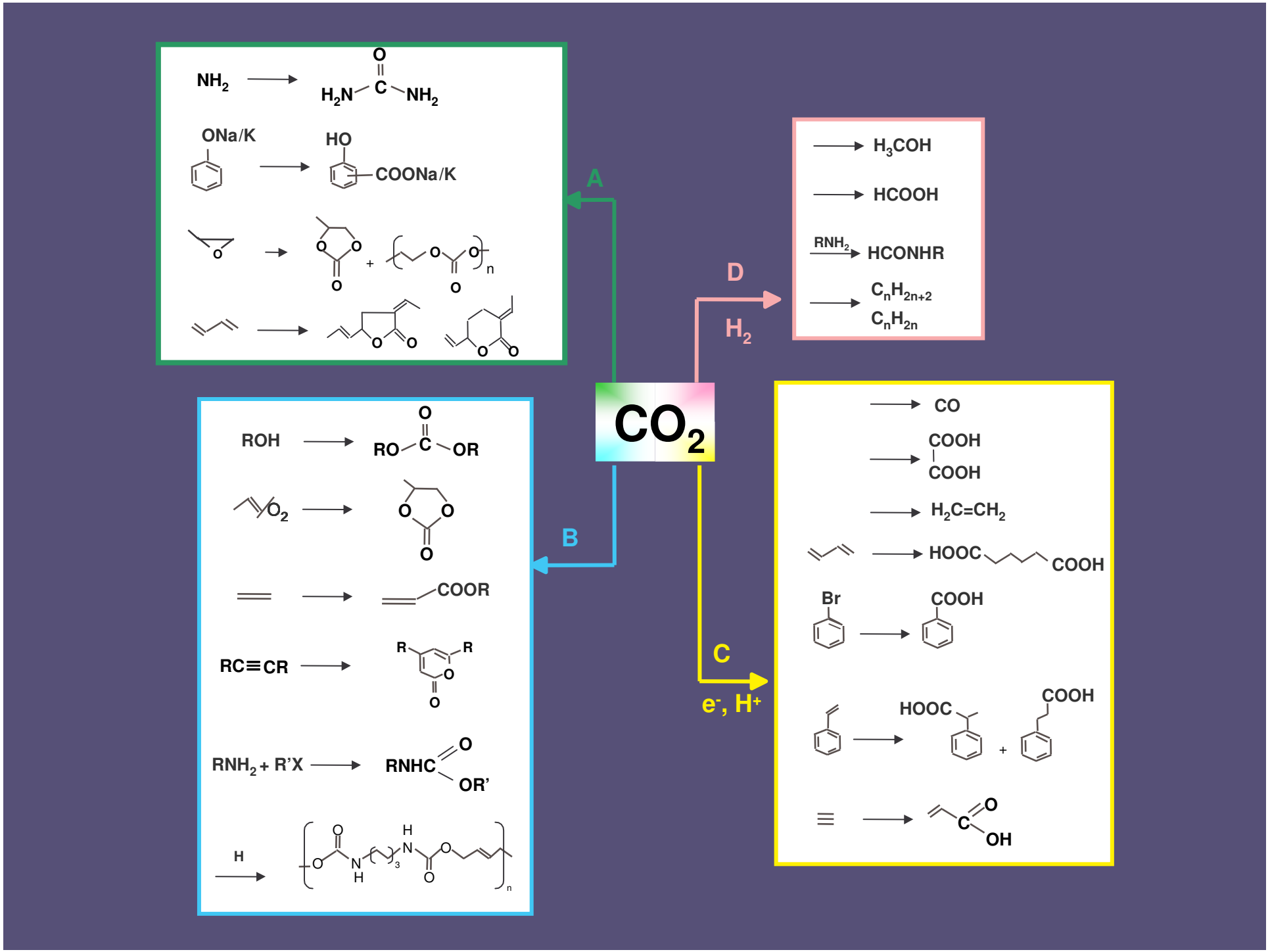
- **The lifetime of chemicals**
  - **Storage of carbon: limited potential**
- **Recycling of carbon**
  - **Innovative processes**
- **Rate of formation and fixation**
  - **Combustion processes vs conversion**
- **Reducing fossil-C extraction**
  - **Efficient conversion processes**
  - **Optimized C-utilization efficiency**

Avoid the extraction of CO_2

- Use of recovered CO_2
  - Purity (food industry)
    - Better exploitation of sources of pure CO_2
      - Fermentation industry
        - » Seasonality
- Replace extracted CO_2
  - EOR

Sustainability and CO_2 Utilisation

- **Process Innovation**
  (use of concentrated CO_2-flows):
  - Reduce the Carbon and Energy dependence
  - Recycling Carbon
  - Raw material diversification
- **Tandem Chemical-Biological**
  - Coupling Chemistry and Biotechnology
- **Intelligent use of Biomass**
  (exploitation of atmospheric CO_2)
  - Nature makes, Man re-shapes

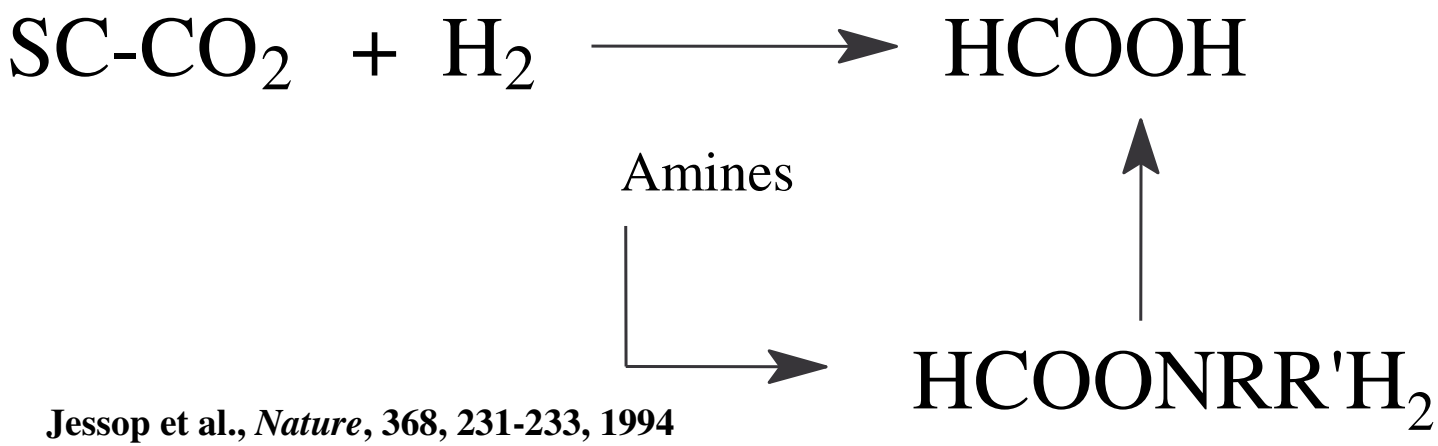

CO2
A
B
C
D
H2
e-, H+
NH2
H2N
C
NH2
ONa/K
HO
COONa/K
n
ROH
RO
C
OR
O2
COOR
RC≡CR
R
R
RNH2 + R'X
RNHC
OR'
H
n
H3COH
HCOOH
RNH2
HCONHR
CnH2n+2
CnH2n
CO
COOH
COOH
H2C=CH2
HOOC
COOH
Br
COOH
HOOC
COOH
C
OH

Classes of compounds of industrial interest: opportunities and challenges

- Carboxylates:
  - Formic acid
  - Long chain acids, lactones, pyrones
- Carbonates
  - Molecular (linear and cyclic) and polymeric
- Carbamates
  - Molecular and polymeric
- Acrylic acids and their esters
- Energy products

Synthesis of Formic Acid

Leitner et al., *J. Chem. Soc. Chem. Commun.*, 1465-1466, 1993

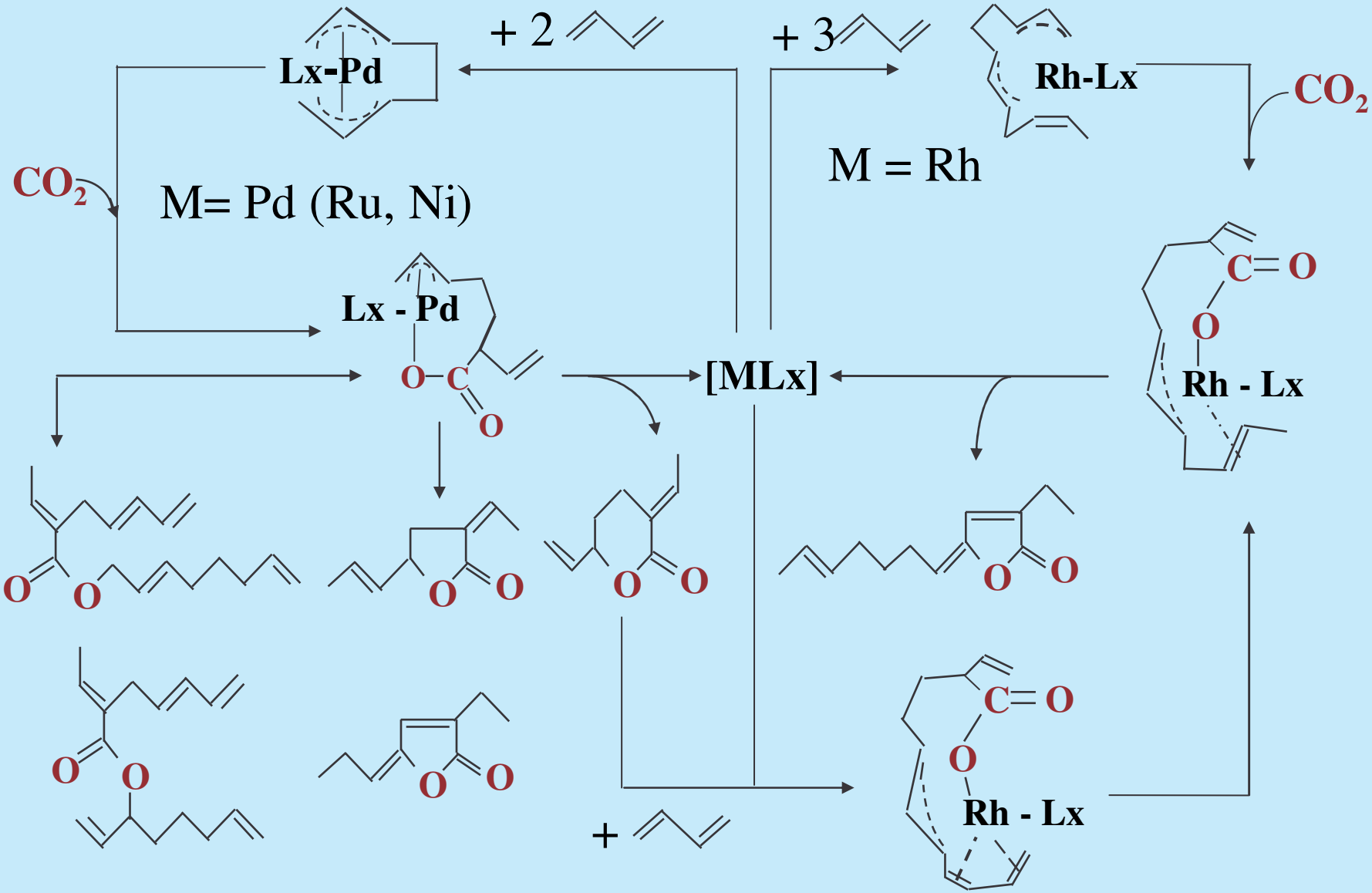


Jessop et al., *Nature*, 368, 231-233, 1994

TOFh ~ 10000 at 80 °C and 1364 at room temperature

High pressure: **Laurenczy et al.** *Appl. Catal. A: Gen.*, **2003**; *Chem. Eur. J.* **2007**

Lactones, Pyrones, Long Chain Carboxylic Acids or Esters



Musco, 1978; Behr, 1984; Braunstein, 1998; Dinjus, 2002

M.Aresta, New J. Chem, 1994, 18, 133

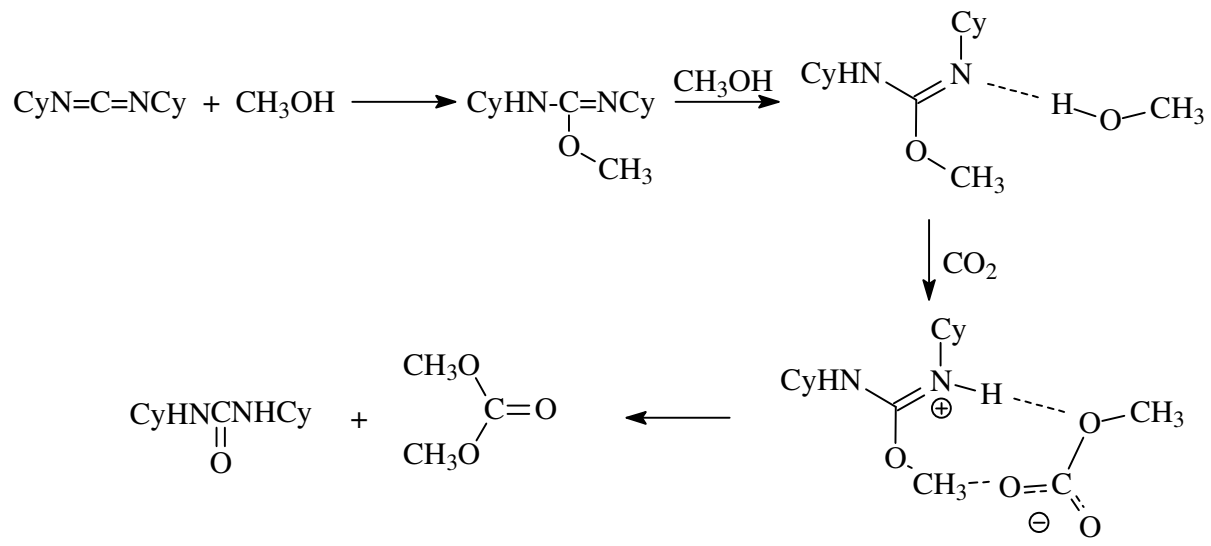
Carboxylation of Alcohols

$$2ROH + CO_2 \rightleftharpoons ROC(O)OR + H_2O$$

- **Thermodynamics says that the reaction is "quasi-neutral": the equilibrium concentration of the carbonate is reported to be close to 1-2%**
- **Water is formed that should be eliminated for displacing the equilibrium to right and avoid that catalysts are modified**
- **The reaction mechanism: in principle an alcohol should undergo an acid-activation (to generate –R) and a base-activation (to generate –OR): bi-functional catalysis**

Double base-activation of methanol

DCC + 2MeOH + CO_2 → DMC + urea

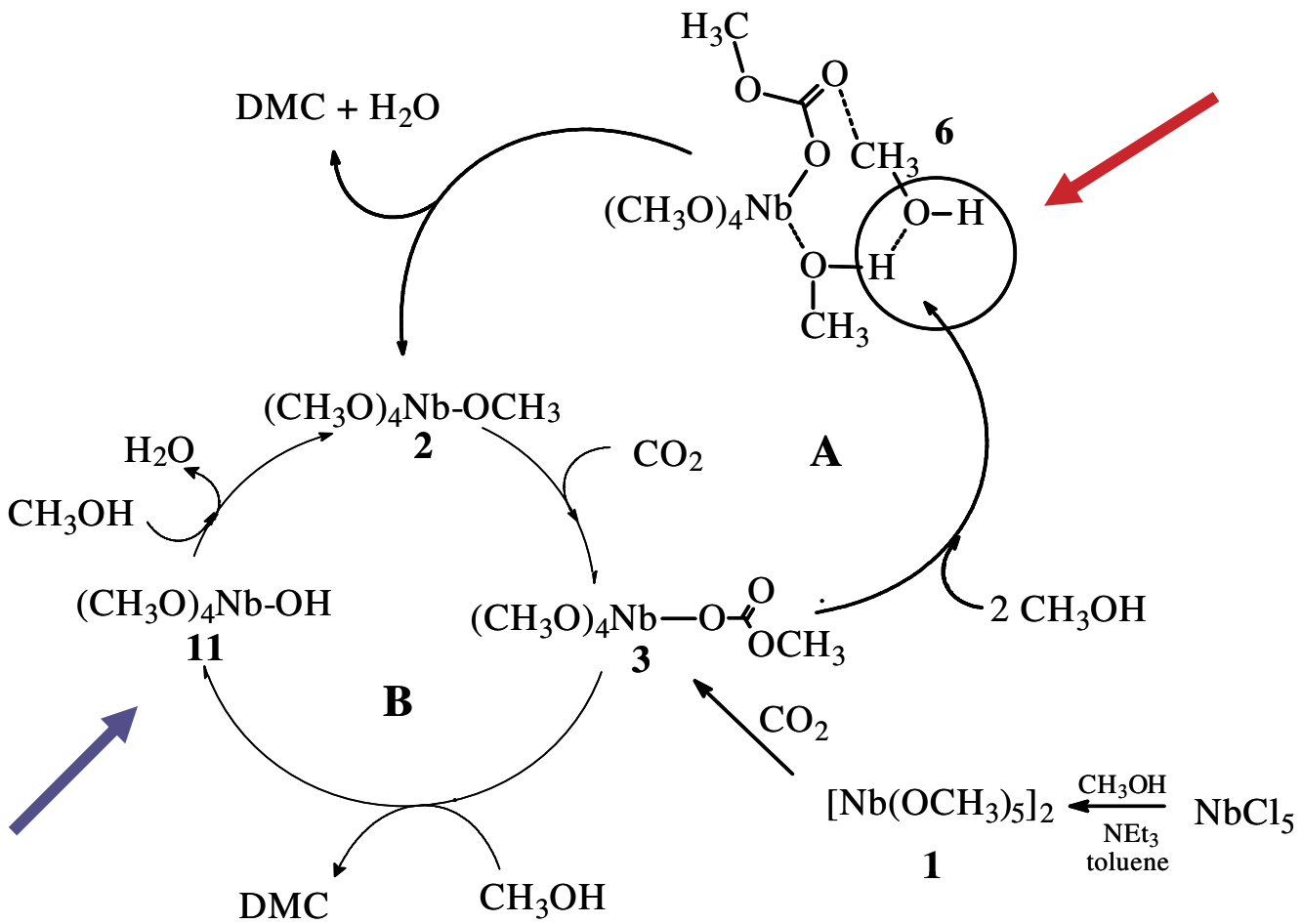


Aresta et al, JOC 2005

Transition metal system

$nBu_2Sn(OMe)_2$ + CO_2 = DMC + 1/n $[nBu_2Sn{=}O]n$

T. Sakakura, 1998-2000; D. Ballivet, 2002



Aresta et al., 2003, 2005, 2006, 2007

Reaction mechanism of formation of DMC from methanol and CO_2 under $[Nb(OCH_3)_5]_2$ catalysis: the case of the base-plus-acid activation of methanol

Use of heterogenized catalysts

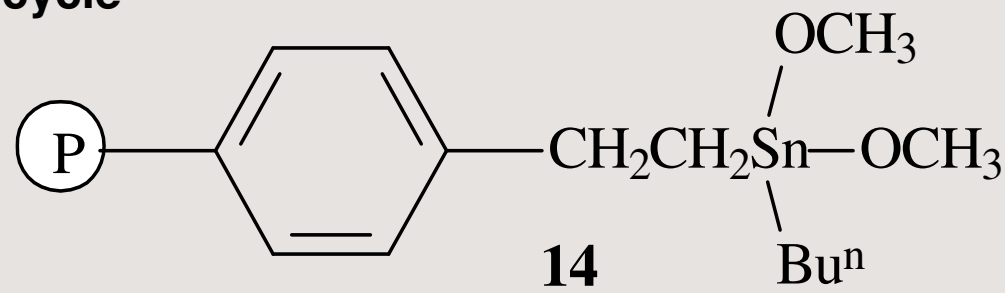
Grafted Sn-complexes

$$PS\text{-}C_6H_4\text{-}CH_2CH_2Br + {}^{n}BuLi \xrightarrow[-\ LiBr]{193\ K} PS\text{-}C_6H_4\text{-}CH{=}CH_2 + {}^{n}BuH$$

$PS\text{-}C_6H_4\text{-}CH_2CH_2Li$

Catalyst recycled ten times with a DMC/Sn ratio equal to 1.2-1.6 per cycle

$Bu^{n}SnCl_3$
2 $NaOCH_3$



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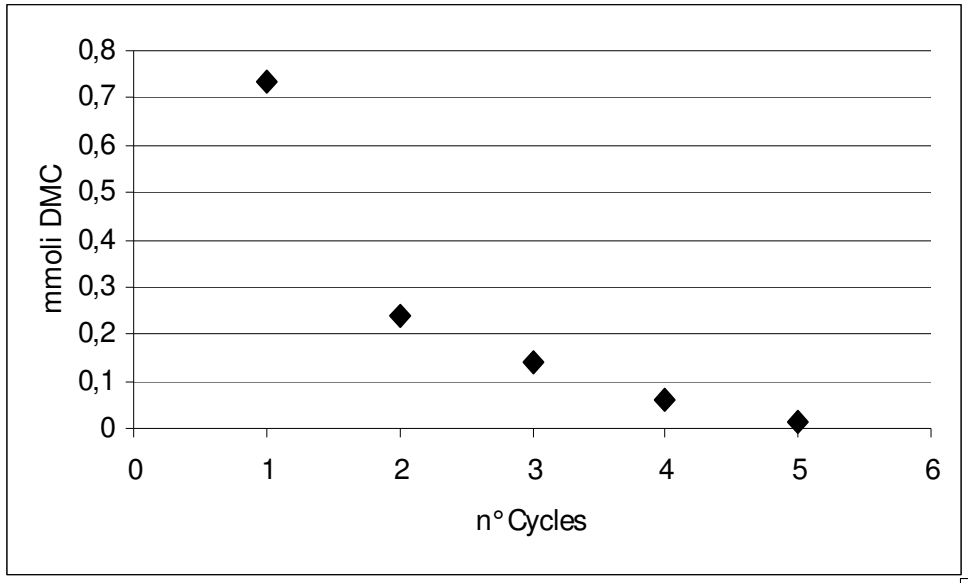
M. Aresta et al, ICA, 2007

Use of heterogeneous catalysts

CeO_2 (Tomishige 2006)	Short-living
ZrO_2 (Tomishige 1999)	Short-living
CeO_2/ZrO_2	(Tomishige 2000)
Tl_2CO_3 (Aresta, 2006)	Long-lasting, slow
CeO_2-Al_2O_3 (Aresta, 2008)	Long-lasting, fast
$CeO_2 – M_xO_y$ (Aresta, 2008)	Long-lasting, fast

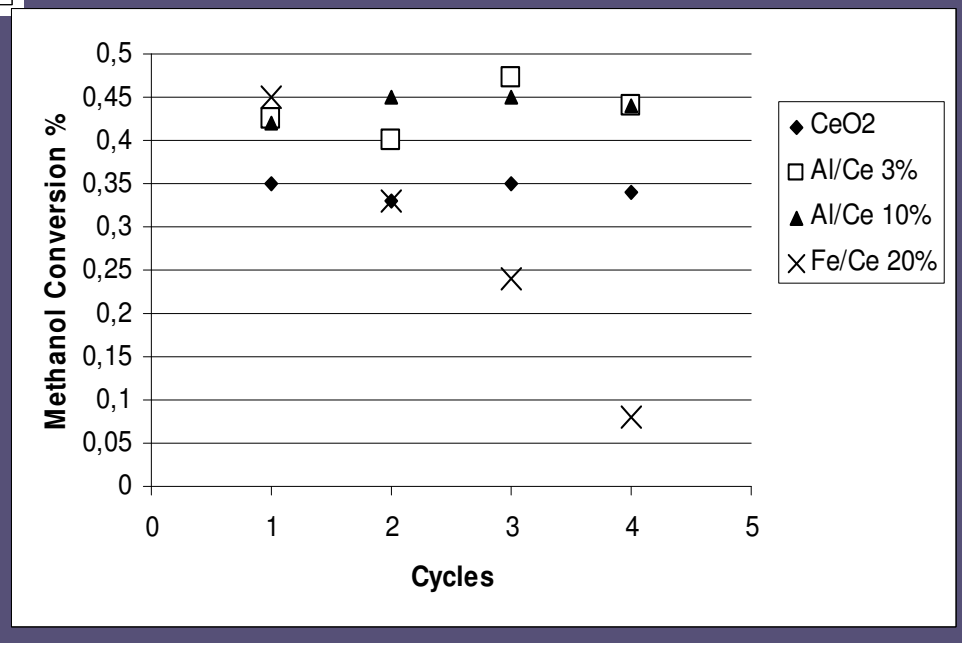
Effect of catalyst modification on its performance



Commercial CeO_2
Size of particles: µm

Each cycle 5 h

CeO_2 nano-particles synthesised and loaded with Al and Fe
Each cycle 3 h



Aresta et al, CatTod 2008

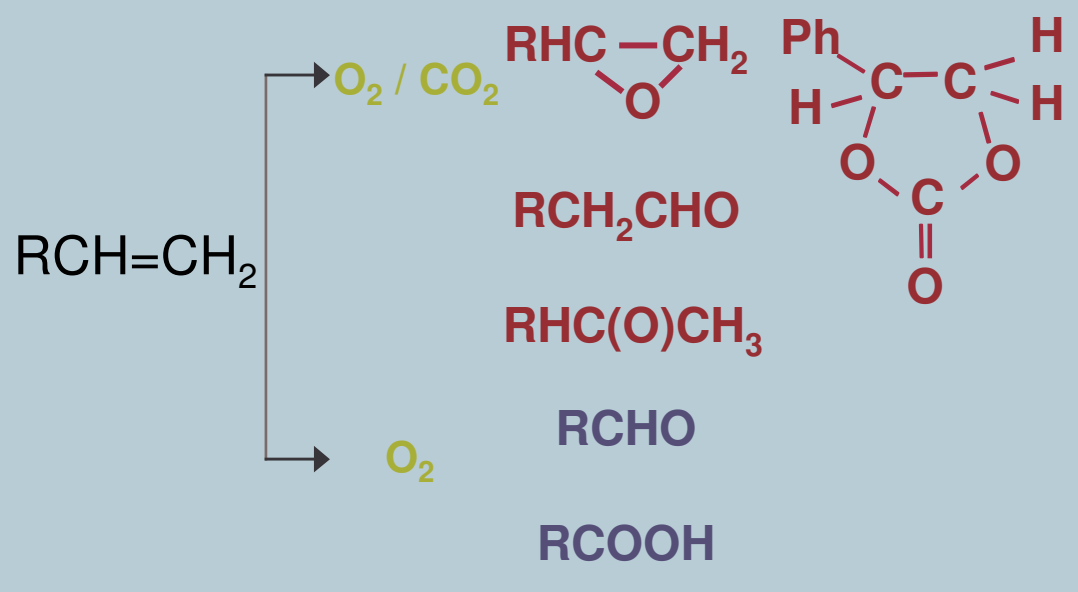
Cyclic carbonates

- Epoxides plus CO_2
  - Several catalysts are used
  - IL are optimal reaction media as they fasten the reaction

- Olefins plus CO_2 and O_2 (oxidative carboxylation)

  One-pot synthesis avoiding the isolation of epoxides

Direct carbonation of olefins. Several issues….



"two oxygen" transfer to the olefin"

"one oxygen" transfer to the olefin"

1. The oxidation products distribution is mediated by CO_2

2. An aldehyde is formed that promotes the formation of the epoxide

3. The latter is converted into the carbonate

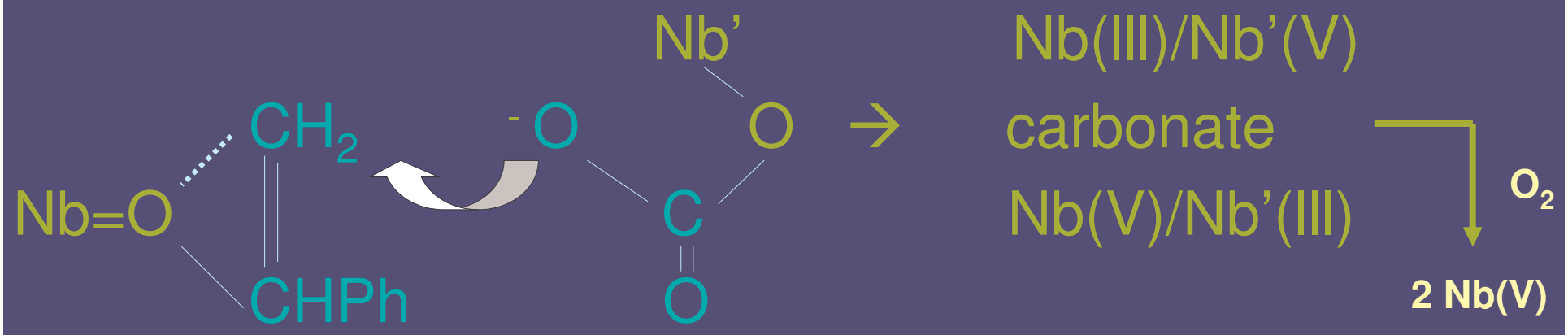
4. Is it possible to avoid the double bond cleavage?

Detailed study on solvent, pressure of O_2 and CO_2, co-catalysts

Carbonate formation without the intermediacy of the radical path. Surface chemistry on metal-oxides!

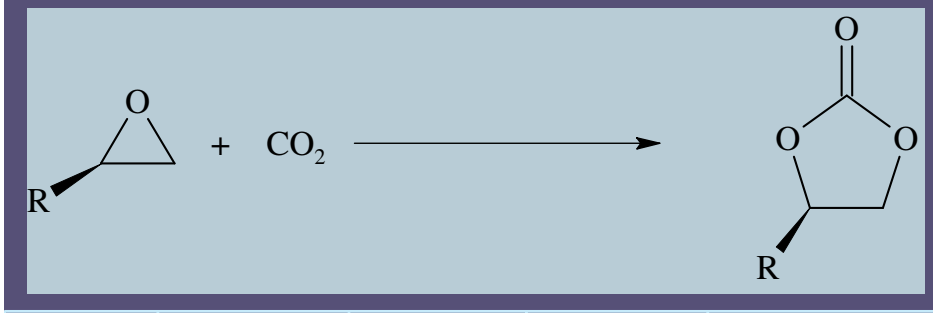
A two-step process based on molecular oxygen

- $Nb_v{=}O$ + CO_2 → $NbCO_3$ *(FTIR, literature)*
- Lattice-oxygen (M_yO_x) can be transferred to the olefin → "$O_{x-1}M_yOCH_2CHPh$". (***CatTod, 2006; CatTod, 2008***)
- $NbCO_3$ can react with oxidized styrene → Nb(III) + carbonate



Asymmetric syntheses

Enantiomer R



R	Catalyst	Yield*	TON	e.e.
CH_3	Nb_2O_5	77 %	17	> 98% (R)
Ph	Nb_2O_5	80 %	29	> 98% (R)

Enantiomer S

R	Catalyst	Yield*	TON	e.e.
CH_3	Nb_2O_5	65 %	15	> 98% (S)
Ph	Nb_2O_5	65 %	25	> 98% (S)

* **Isolated yield**

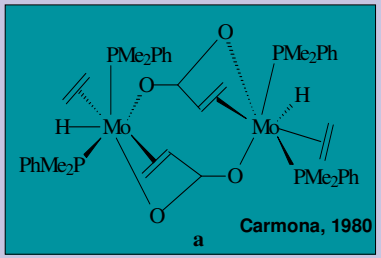
CO_2 as co-monomer

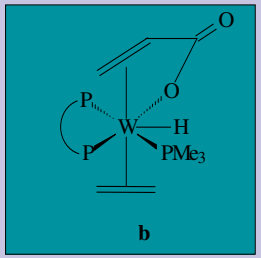
- Co-polymerisation with propene-epoxide
  - Al-porphyrins (on stream in CH)
- Co-polymerisation with cyclohexene-oxide
  - Cr-catalysts
  - Zn-catalysts

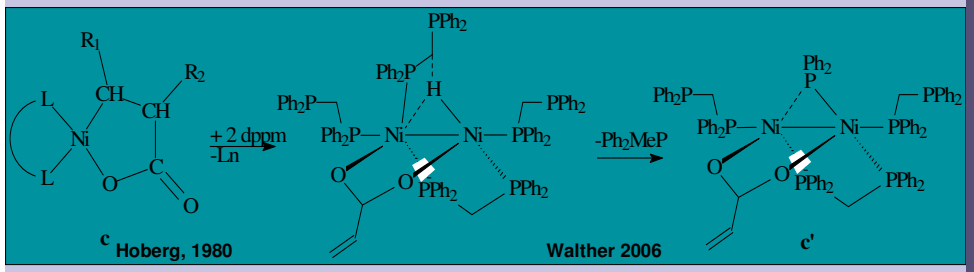
Coupling of ethene with CO_2

$RCH{=}CH_2 + CO_2 \rightarrow RCH{=}CHCOOH$

Aresta & Papai, Organometallics, 2004, Papai, JACS, 2003

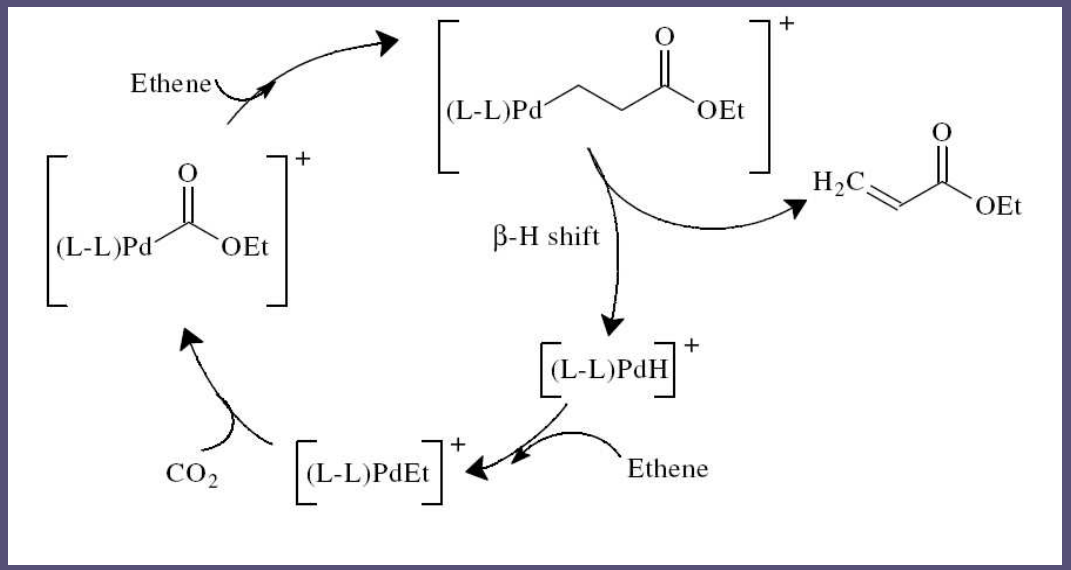






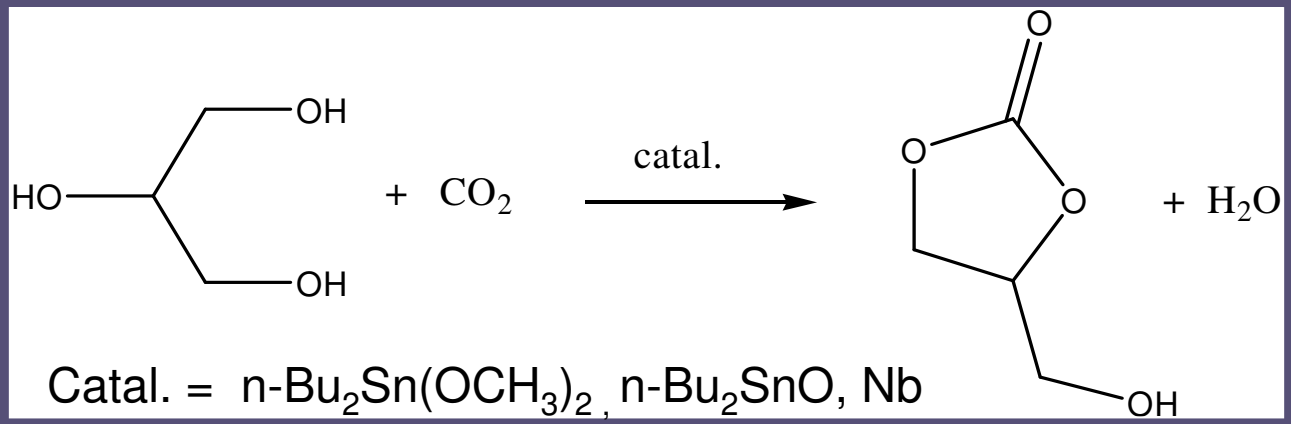
The elimination of acrylic acid is not observed although the thermodynamics is favourable: The kinetic barrier is too high. Energy of the M-O and M-H bonds

Avoiding the formation of the M-H bond favours the elimination of the acrylate: the mechanism of formation of the ester from CO_2 and ethene is still under investigation.

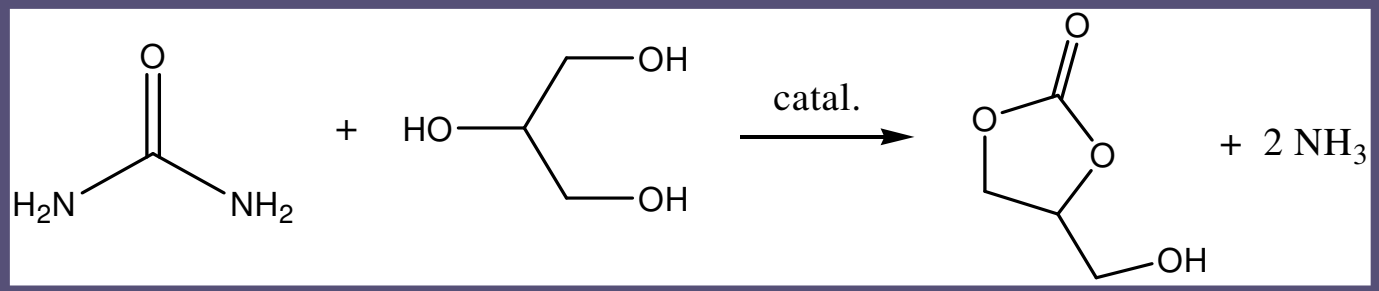


Aresta et al, Chem Eu J, 2007

The carboxylation of glycerol: a valuable product from two wastes



M. Aresta, A. Dibenedetto, F. Nocito, C. Pastore, *J. Mol. Catal.*: A, 2006



Catalyst fully recovered and reused; ***90 % isolated*** in 2 h at 140 ℃
Molar ratio Urea : Glycerol = 1:1 weight ratio Catalyst : Glycerol 0.03

M. Aresta, A. Dibenedetto, F. Nocito, Patent Application

CO_2 as mild oxidant

$$C_6H_5CH_2CH_3 + \mathbf{CO_2} \xrightarrow{\text{cat1}} C_6H_5CH{=}CH_2 + CO + H_2O$$

$$CO + H_2O \xrightarrow{\text{cat2}} \mathbf{CO_2} + H_2$$

$$C_6H_5CH_2CH_3 \rightarrow C_6H_5CH{=}CH_2 + H_2$$

Methane Tri-Reforming Plasma technology

$CH_4 + ½ O_2 \longrightarrow CO + 2 H_2$	$\Delta H^0_{298} = -36$ kJ mol^{-1}
$CH_4 + H_2O \longrightarrow CO + 3 H_2$	$\Delta H^0_{298} = 206$ kJ mol^{-1}
$\mathbf{CH_4 + CO_2 \longrightarrow 2\ CO + 2\ H_2}$	$\mathbf{\Delta H^0_{298} = 247}$ **kJ mol^{-1}**

The methane dry-reforming may contribute to the implementation of the GTL technology with a direct conversion at the extraction well of LNG into liquid fuels

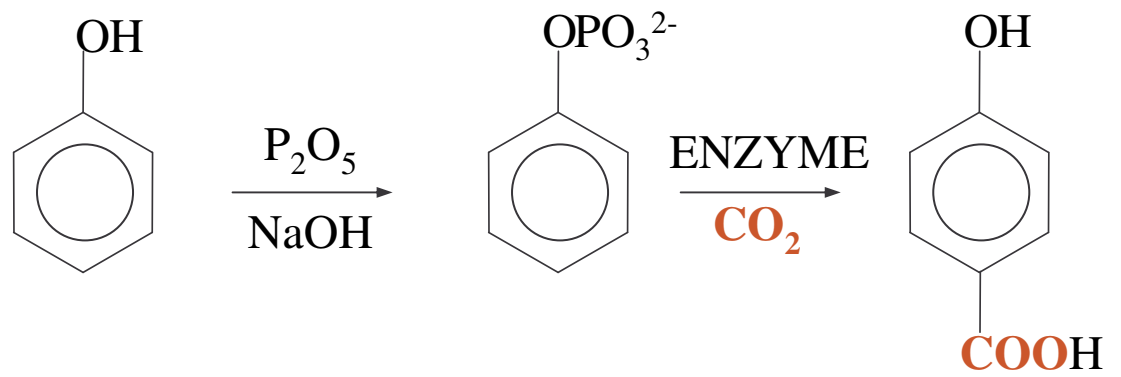
Coupling Chemistry and Biotechnology:
From CO_2 and H_2O to CH_3OH at rt

- $CO_{2\ aq} \rightarrow HCOO^-$ **Formate dehydrogenase**
- $HCOO^- \rightarrow H_2CO$ **Formaldehydedehydrogenase**
- $H_2CO \rightarrow CH_3OH$ **Methanoldehydrogenase**

- **NAD^+/NADH is the source of energy.**
- **Key issue: how to reverse the NAD^+/NADH couple after oxidation?**
- **Use of TM systems for solar light harvesting-utilisation**

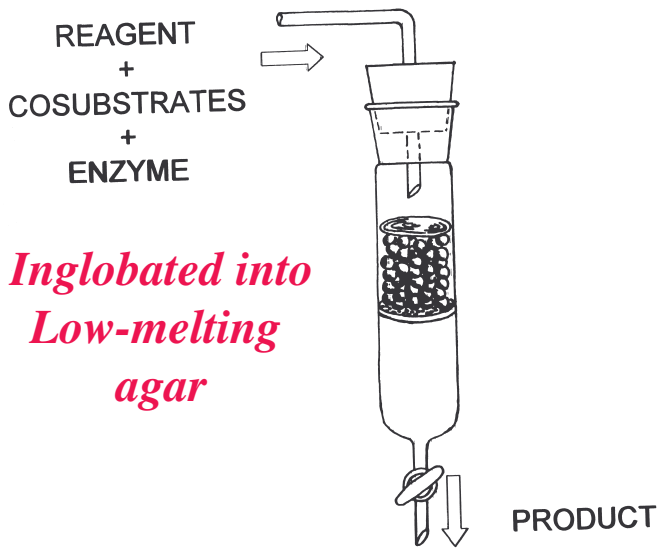
Enzymatic Phenol Carboxylation

Biotechnological synthesis of 4-OH benzoic acid also in sc-CO_2

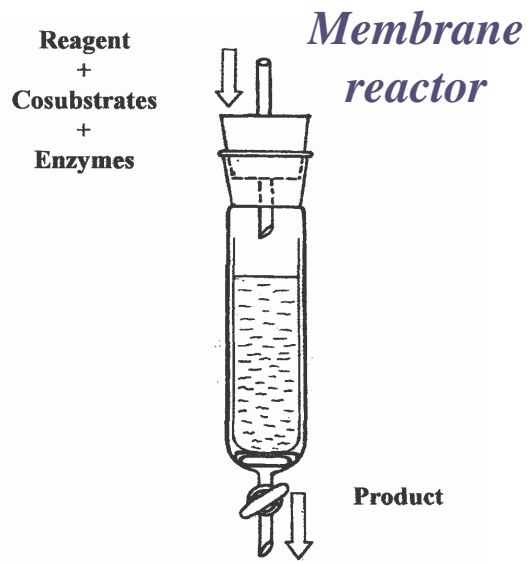


TON = 1600

TOF = 60



Aresta, M., Tommasi, I., Dileo, C. *Tetrahedron*, 54(1998), 8841 - 8846



Aresta M., Dibenedetto A. *Rev. Mol. Biotech.*, 90, 113-128, 2002

Biomass exploitation: Nature makes, Man re-shapes

Non-destructive

- Extraction of chemicals with complex molecular structure, icluding triglycerids for biodiesel (Product Entropy)

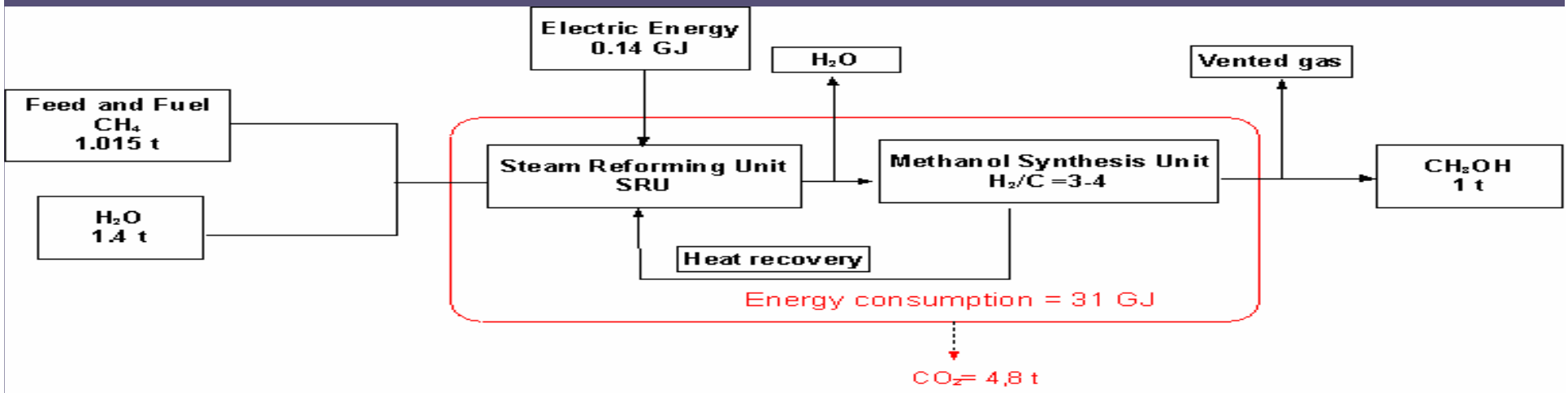
Partially destructive

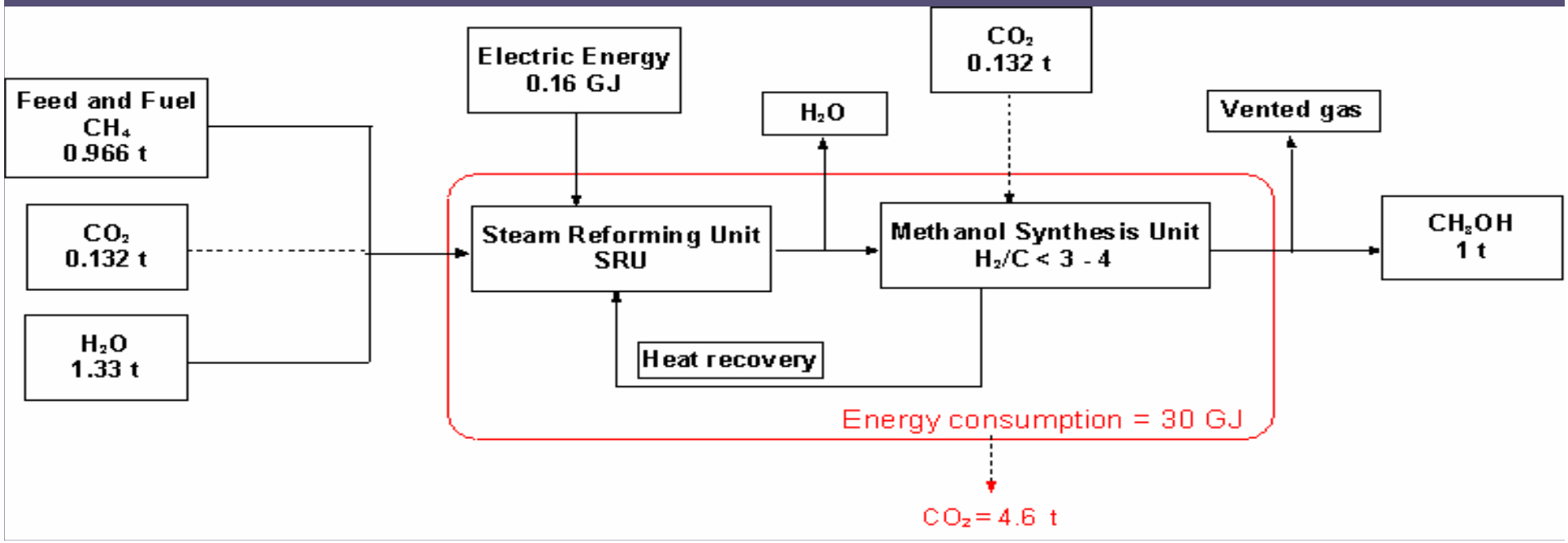
- Exploitation of the lignine structural features
- Enzymatic conversion of lignine and cellulosic materials

Destructive

- Biogas production
- Conversion of biomass into Syngas
- Use of Syngas for the synthesis of methanol
  - Bio-methanol for FAME
  - Bio-hydrogen (bacterial or chemical production)
- Use of Syngas for the synthesis of gasoline and diesel

Quantifying the avoided CO_2





Opportunities and challenges

over 1 Mt/y

- Carbonates
- Acrylic acids and their esters
- Fuels
- Polymers
- Olefins oxidative carboxylation

- Water elimination
- Avoid the formation of hydrido-acrylates
- Source of hydrogen
  - **Water splitting**
  - **Reduction of CO_2 in water**
- Production of epoxides and azetidines/aziridines
- Suppression of the radical path

Catalyst life