Modern Methods in
Heterogeneous Catalysis Research
Berlin(Germany), Oct. 17, 2014

Future Challenges in Heterogeneous Catalysis Research

LECTURE SERIES
HETEROGENEOUS CATALYSIS

Gabriele CENTI

University of Messina, CASPE-INSTM and ERIC aisbl,
Dept. DIECII, Sect. Industrial Chemistry, Italy

centi@unime.it

Univ. Messina
European Research Institute of Catalysis
INSTM

Look at the future *(of energy, chemistry)*

What will be the future scenario for energy & chemistry and related challenges for catalysis ?

A preamble

Industrial Chemical Production: *evolution*

Chemical production evolution is the result of different forces

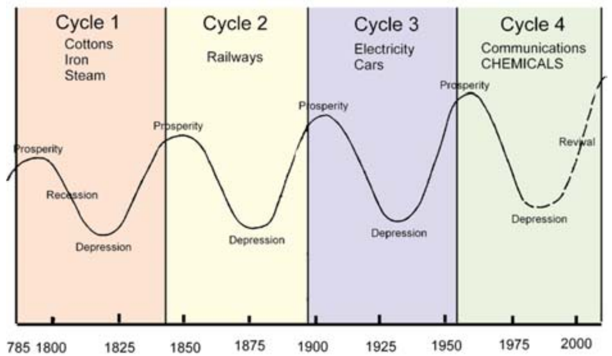
- **Push:** raw materials, technology
- **Pull:** social demand (market demand, security, environment, quality of life)

a cyclic evolution

Macro-economic cycles of Kondratieff

Nikolai Kondratieff was an economist that predicted the existence of cycles in economy

- The economic cycles (renewal, prosperity, recession, depression) of various industries become synchronized and mutually reinforce. Historically, cycles of about 55 years have been observed in the last two centuries.



C. Gent, CHEM. COMMUN. , 2002, 2927

New "green" Kondratieff cycle

- This new "green" Kondratieff cycle will be characterized by global structural changes in the economy with a crucial reorganisation of the energy infrastructure, where the switch to renewable energies will largely influence the market.

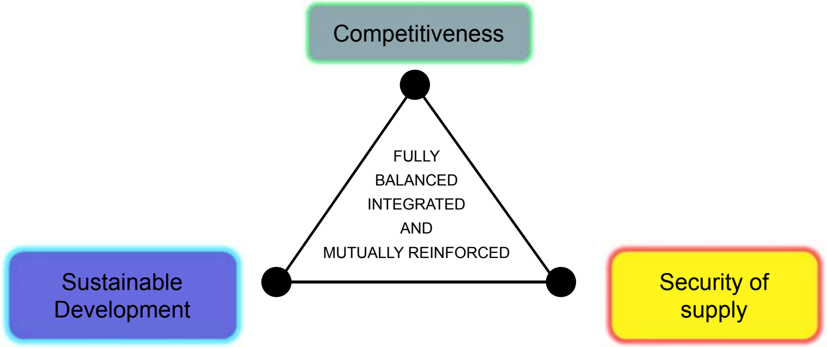
- *We are now on the turning edge of a new major change in the structure of chemical & energy production, with the increasing need to find* ***new raw materials*** *substituting fossil fuels for the production of chemicals and polymers (and energy), and* ***new production methodologies*** *which decouple production from the scale-economy.*

A changing scenario

Towards a low-carbon economy

- Increase **competitiveness** in a global market whilst drastically **reducing resource and energy inefficiency and environmental impact** of industrial activities.

Responding to the triple challenge



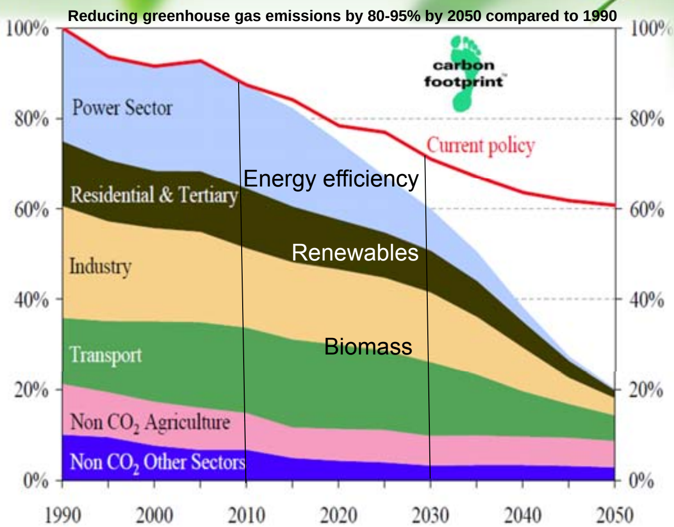
Roadmap 2050: cost-efficient pathway and milestones

80% domestic reduction in 2050 is feasible

- If all economic sectors contribute to a varying degree & pace.

Efficient pathway:

-25% in 2020
-40% in 2030
-60% in 2040



http://ec.europa.eu/clima/roadmap2050/

Towards a green & sustainable energy/chem.

- Even if large progresses in this direction have been made over the last two decades,
  - a systemic change in the way energy and raw materials are used is necessary in a world with finite resources and a rapidly growing population.

- The novel aspect is that chemical industry is realizing now that this approach could be
  - a winning opportunity for increasing competitiveness and innovation in the chemical industry

Towards a low carbon economy

- biomass as chemical feedstock, (re)use of CO_2, waste valorization and use of *renewable energy*
  - at the **core of strategies** of chemical/ energy industries for a *resource and energy efficient* sustainable future.

Sustainable Process Industry through Resource and Energy Efficiency

Components for resource efficiency

- **Feedstock**
  - Bio-feedstock
  - Waste as a feedstock
  - The conversion of CO_2 into feedstock for the chemical/process industry
  - Fossil feedstock (Increasing resource efficiency in using)
- **Process**
  - Process Intensification, Introduction of renewable energy in chemical industry, Chemical Energy storage and Transformation, End of life Waste Management and Recycle, ...
- **New Materials**
  - Material Innovation, ..

SPIRE ROADMAP

Moving to a sustainable energy & chem. prod.

New raw materials and energy sources:

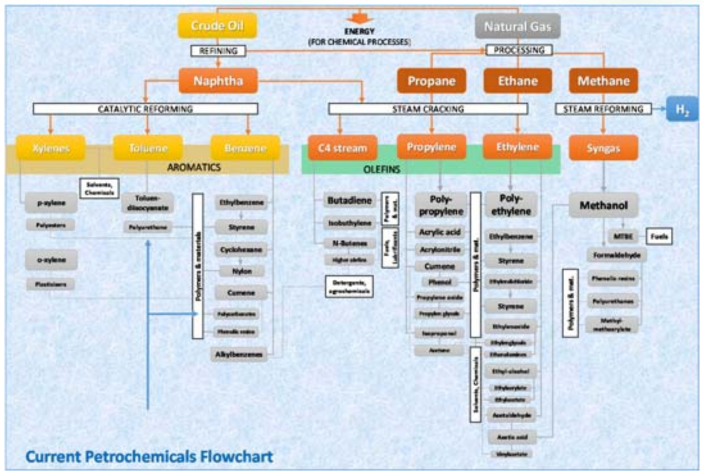
opening new scenarios for the chemical & energy industry

A New Scenario for Green & Sustainable Chemical Production

61 (2014) 719

New scenario for sustainable chem. prod.

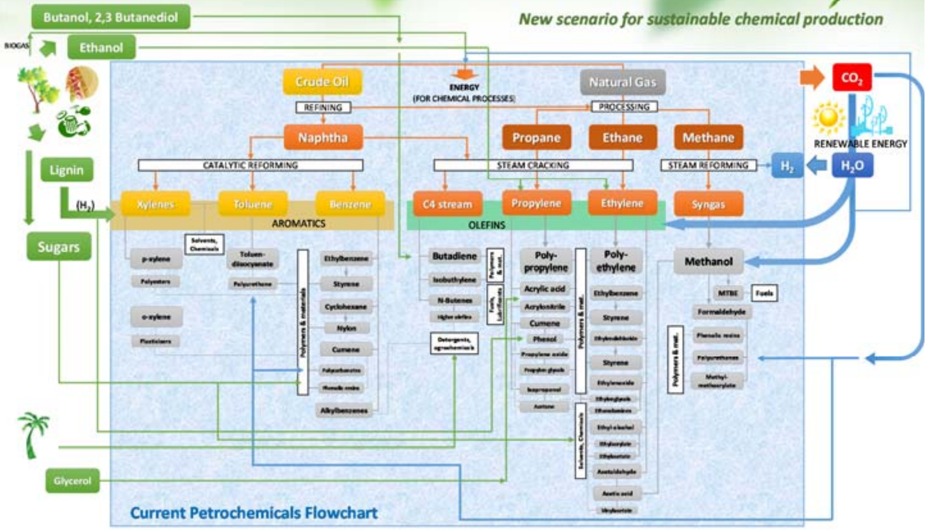
New raw materials and green energy for chemical production value chain



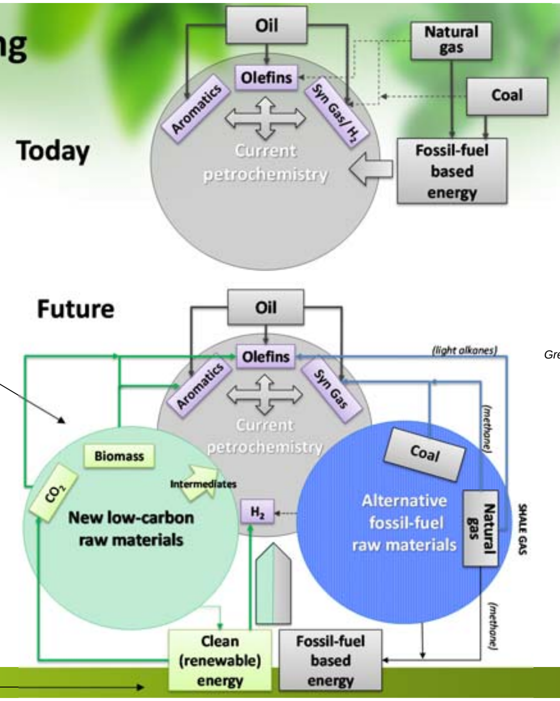
G. Centi, S. Perathoner, *ChemSusChem* 2013 (subm.)

New scenario for sustainable chem. prod.

New raw materials and green energy for chemical production value chain



A changing scenario



Catalysis for biomass and CO_2 use through solar energy

Chem. Soc. Rev., DOI: 10.1039/C3CS60396B

CO_2 Recycling and renewable energy

ChemSusChem, DOI: 10.1002/cssc.201300926

Introduct. renewable energy in chem. prod.

Energy Environ. Sci., 2013,6, 1711

Green Energy series (De Gruyter)

Catalysis to address this changing scenario

- grand challenges for catalysis
- *some examples*
  - expanding NG utilization
  - utilization of CO_2 (and solar energy)
  - evolving scenario for biorefineries
  - (disruptive type of catalytic materials)

A view of grand-challenges for catalysis

1. **Catalysis to address the evolving energy and chemical scenario**
   - *new raw materials* (from natural gas to biomass and CO_2, including non-conventional fossil fuels)
   - use of *renewable energy* in integration with catalysis
   - *energy-saving* processes through catalysis
   - process *intensification* by catalysis and integration of catalysis with other technologies (e.g. membrane technologies) to reduce the number of process steps
   - new catalytic technologies for *energy storage and conversion* (including fuel cells, H_2 production and storage)
   - catalysis for *novel polymer* materials and *intermediates*

GRAND CHALLENGES

A view of grand-challenges for catalysis

2. Catalysis for a cleaner and sustainable future

- catalysis for *eco-technologies* (from air to water and waste; stationary and mobile; including photocatalysis)
- towards *100% selectivity*
- catalysts in *novel process design* for resource and energy efficiency
- *cleaner fuels* in refining
- novel catalytic processes to *reduce eco-impact* of fine and specialty chemicals production (including asymmetric catalysis, organocatalysis and enzymatic process, tandem process)
- *eco-conception* (LCA) of catalysts and processes

GRAND CHALLENGES

A view of grand-challenges for catalysis

3. Addressing catalysis complexity

- catalyst design for *multistep reactions*, for bulky molecules
- catalysis for *materials with specific properties* (electronic, photonic, magnetic)
- synthesis of *advanced and hybrid catalytic systems* with tailored reactivity:
  - functional nanoarchitectures in catalysts
  - novel preparation methods
  - integrating homo-, hetero- an bio-catalysis
  - novel nanoparticles
  - organometallic complexes, organocatalysts,
  - biomimetic catalysts and enzymes,
  - catalysis with immobilized or single site complexes

GRAND CHALLENGES

A view of grand-challenges for catalysis

4. Understanding and design catalyst from molecular to material scale

- from deductive to *predictive* catalysis
- theory and modelling of catalysis
- new approaches in catalysts and *reaction mechanism* (including in-situ and operando methods)
- model systems (including *surface science* approach)
- bridging *molecular to reactor engineering* aspects in designing new processes
- *kinetics* and reaction engineering

5. Expanding catalysis concepts

- catalysis with electrons, photons and energy sources other than heat
- catalyst design to operate under non-conventional or extreme conditions
- use of non-conventional solvents in catalytic processes
- novel catalytic materials

GRAND CHALLENGES

Moving to a sustainable energy & chem. prod.

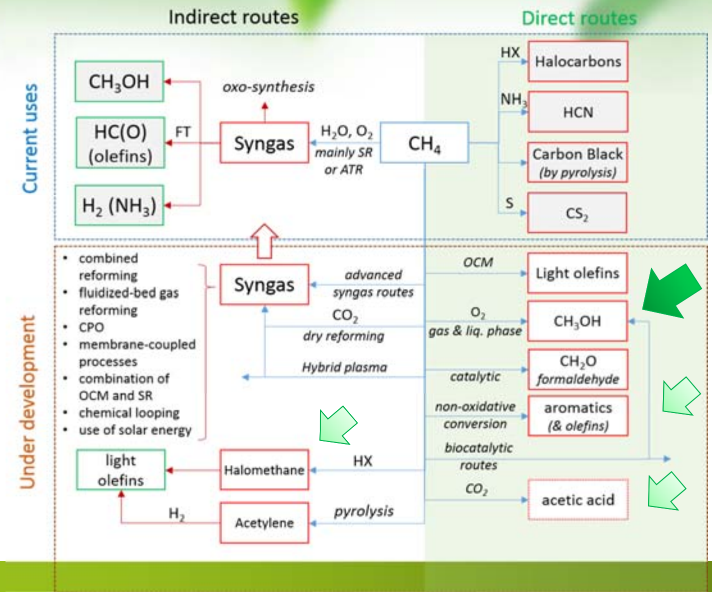
expanding use of NG

Gas is Green

Drivers to expand use of NG

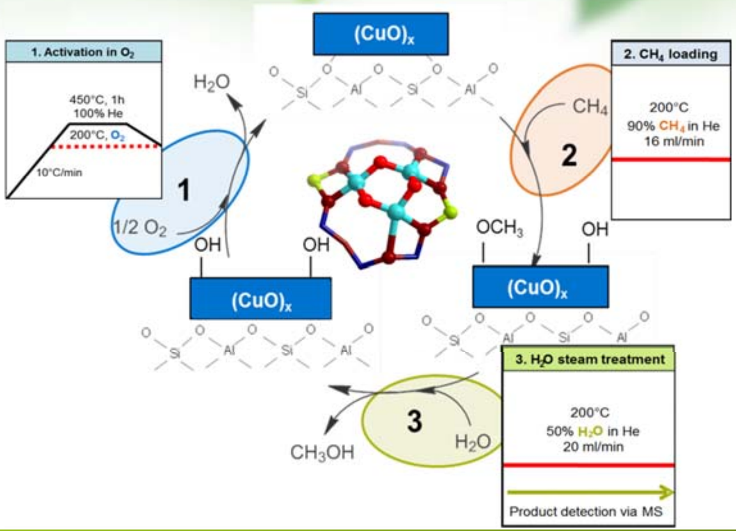
- large NG reservoirs in the world
  - BUT with about one third of them (**stranded** NG resources) not directly exploitable (via pipeline, or liquefaction /regasification).
- discovery and rapid proliferation of **shale gas** basins
  - Unconventional gas (gas shales, tight gas sands and coalbed methane) represents a potential of about 330 Tcm (Trillion cubic meters).
- scientific advances in both homogeneous and heterogeneous catalysts, and bio-catalysts as well
  - opened the doors to the development of new innovative solutions at scientific level, in some cases already tried to be exploited from companies.

Direct and indirect routes for CH_4 conv. to chemicals

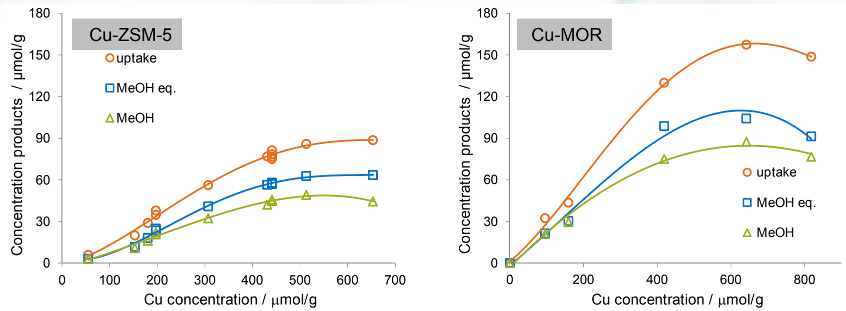


Cu-exchanged zeolites

Three step reaction sequence allows yielding methanol



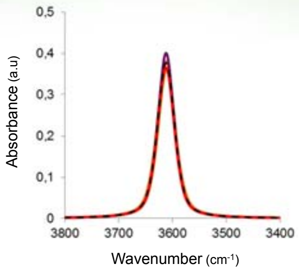
Methanol production vs Cu concentration MOR vs. ZSM-5



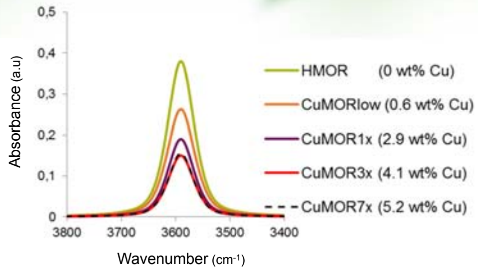
- Cu-MOR is almost two times better than Cu-ZSM-5.
- For Cu-MOR the ratio of converted methane to copper is 1:3 for Cu/Al ≤ 0.3 under saturation conditions.
- For over-exchanged catalysts (Cu/Al ≥ 0.5) the yield of methanol equivalents is decreasing.

Cu clusters in MOR - IR spectroscopy of BAS

BAS in main channel ($3612\ cm^{-1}$)



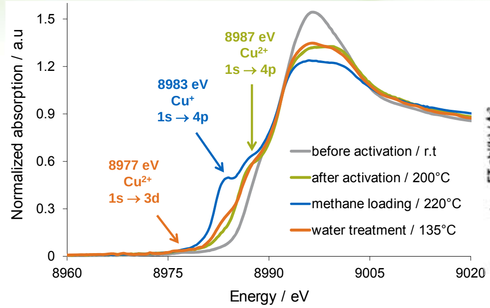
BAS in side pockets ($3590\ cm^{-1}$)

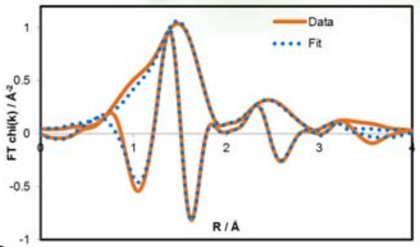


- Concentration of BAS in the main channel is unchanged by Cu- or Co-exchange
- 2/3 of the BAS(framework Al is located in the side pockets of MOR
- Upon Cu-exchange 2/3 of framework Al in side pockets is coordinated by Cu for Cu/Al ≥ 0.35 for MOR with Si/Al=11 and Si/Al=21

→ **Cu is located in the side pockets of MOR.**

In-situ XAFS characterization





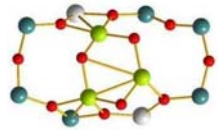
- **O_2-activation**

- change in geometry (new peak at 8987 eV), but no change in oxidation state

- **CH_4-loading**

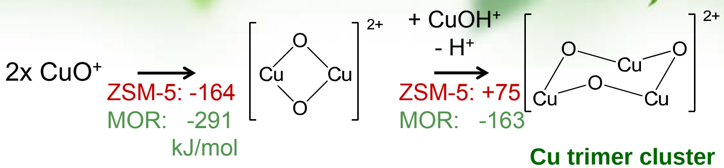
- Cu^{2+} is partially reduced to Cu^{+} (new strong peak at 8983 eV)

- EXAFS fitting suggests a **Cu trimer cluster** being the active site.

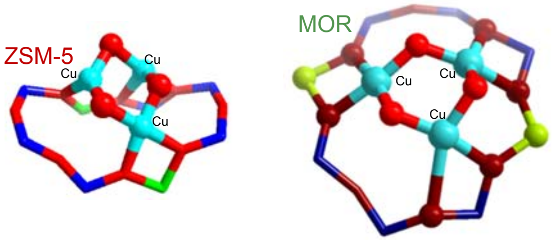


Multinuclear Cu sites in MOR vs. ZSM-5

Zeolite
Cu^{+}
$CuOH^{+}$
CuO^{+}
H^{+}



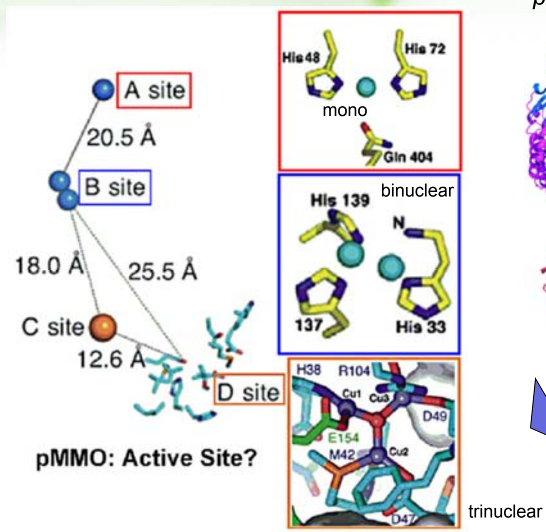
Cu trimer cluster

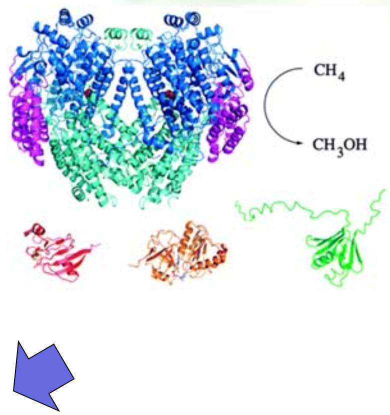


MOR side-pocket: unique stabilization of multinuclear complexes

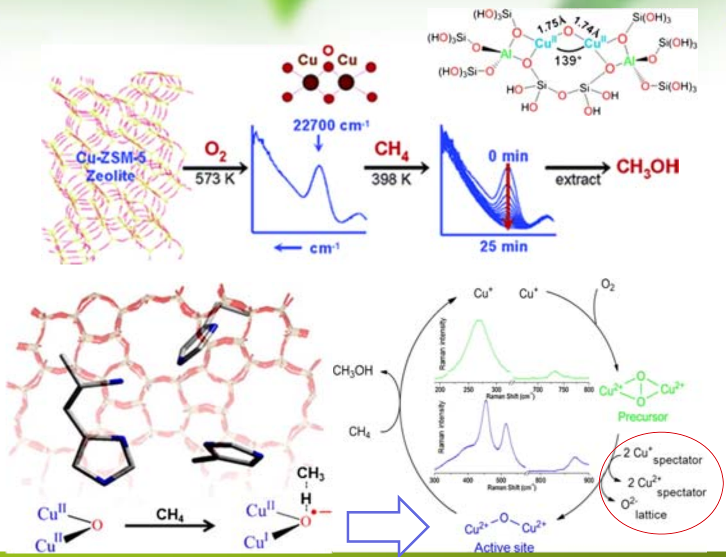
Tri-Cu sites also those active in enzymes (for methane to methanol - pMMO)

particulate methane monooxygenase

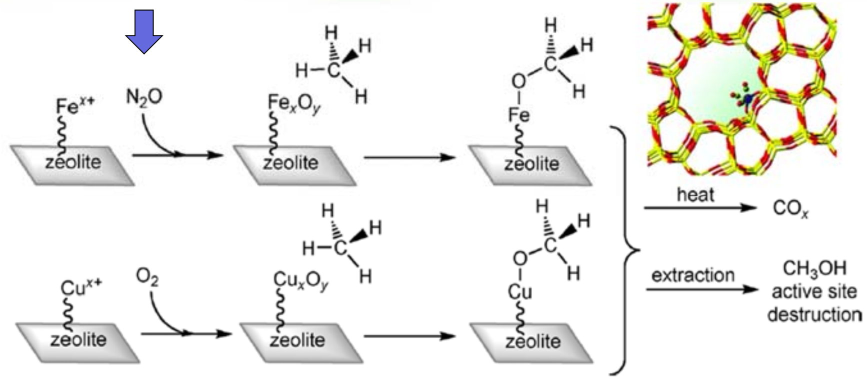




Bi-nuclear copper sites in ZSM5 for methane to methanol conversion



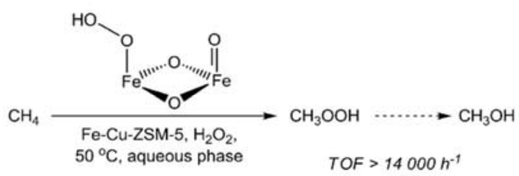
Methane to surface-bound methoxy species over Fe- or Cu-exchanged zeolites

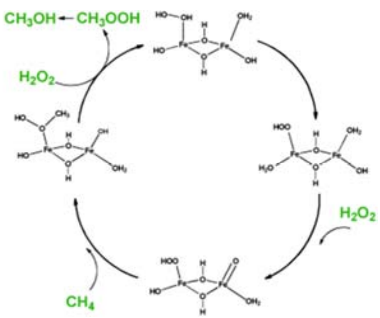


Methane to methanol in liq. phase (H_2O_2 as oxidant)

selective oxidation of methane over Fe-Cu-ZSM-5

unique diferric active site formed upon the heterolytic activation of H_2O_2 at 50°C





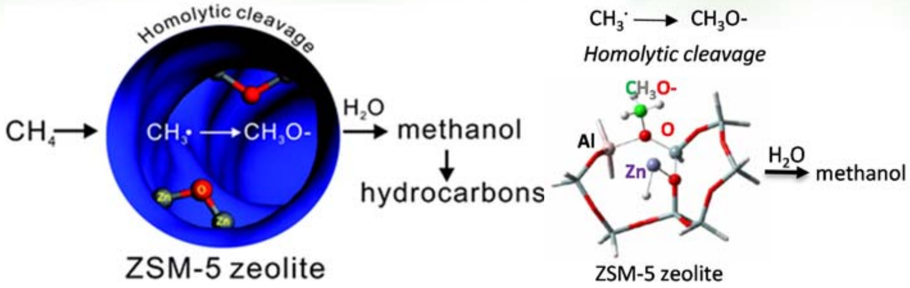
P_{CH4} 30 bar, 0.5M H_2O_2 (very large excess H2O2), 50°C
productivity : 7 mmol/g catal. [conv < 1%, Sel. 85% with respect to product, unknown respect H_2O_2)

Novel MMM for methane select. conv.

- Direct methane to methanol oxidation at quite low temperatures (about 150°C), but with very low productivities.
- Best productivities (extracted products), for a 5% Ni-ZSM5 after activation at 650°C in pure O_2 and reaction at 175°C, are about **6 μmol/g**, but with formation of similar amount of formic acid and about 3 μmol/g of ethylen glycol.

Zn modified H-ZSM-5 zeolites

solid-state NMR and theoretical calculations



- oxygen-containing dizinc cluster center in an open shell ⇨ **homolytic** cleavage of the C–H at room temperature ⇨ formation of methyl radicals.
- methyl radicals form then surface methoxy intermediates
- **heterolytic** dissociation of methane on isolated Zn^{2+} ions ⇨ zinc methyl species.

BUT not further demonstrated experimentally

Chem. Sci., 2012,3, 2932

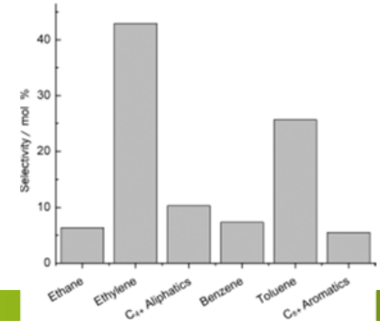
Methane conversion over Zn-Mo/H-ZSM-5 catalysts in the presence of methanol

- CH_4 conv. 30.7 %, 3 % Zn-Mo/H-ZSM-5 catalyst
- major reaction products were ethane, ethylene, C4+ aliphatic hydrocarbons, and aromatic hydrocarbons.

Methane activation and conversion in presence of **bifunctional** catalyst (M=Ga, Zn, or In; *X*=Mo_2C or MoO_xC_y species)

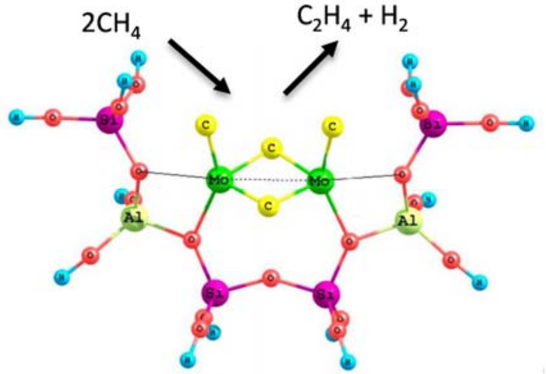
3 % Zn-5 % Mo/H-ZSM-5 catalyst

Temp. 650-850°C



Dehydrogenation and Coupling to Ethylene over a Mo/HZSM-5 Catalyst

A Density Functional Theory Study

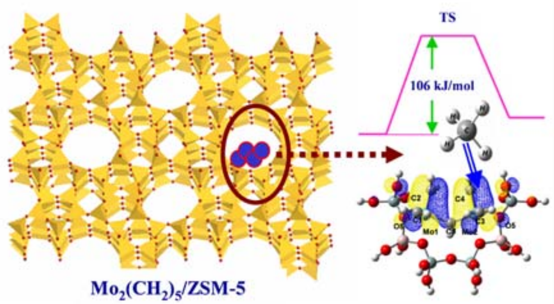


J. Phys. Chem. C **2012**, *116*, 4060

Methane aromatization on Mo/ZSM-5

DFT: $Mo_2(CH_2)_5$/ZSM-5 is the effective active center for methane activation

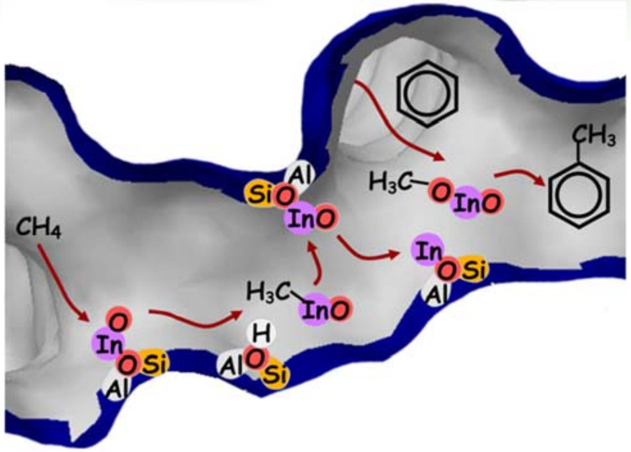
The C-H bond dissociation occur on the π orbital of Mo=CH_2 with an activation energy of 106 kJ/mol



Mechanism of reaction: conversion of CH_4 to C_2H_4 (C_2H_2) on molybdenum carbide or oxycarbide and further conversion of C_2H_4 (C_2H_2) to aromatic products over the acidic sites within the channels of the zeolite.

In/ZSM-5 for methane aromatization

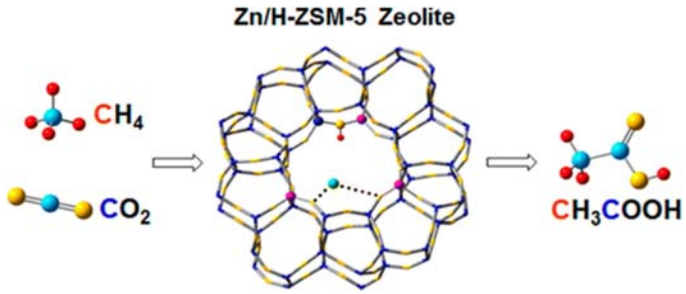
solid-state NMR and XPS



Methane to acetic acid over Zn/H-ZSM-5

solid-state NMR spectroscopy

- zinc sites efficiently activate CH_4 to form zinc Me species (-Zn-CH_3), the Zn-C bond of which is further subject to the CO_2 insertion to produce surface acetate species (-Zn-$OOCCH_3$).
- Bronsted acid sites play an important role for the final formation of acetic acid by the proton transfer to the surface acetate species.



Methane conv. on Me-containing zeolites

SUMMARY

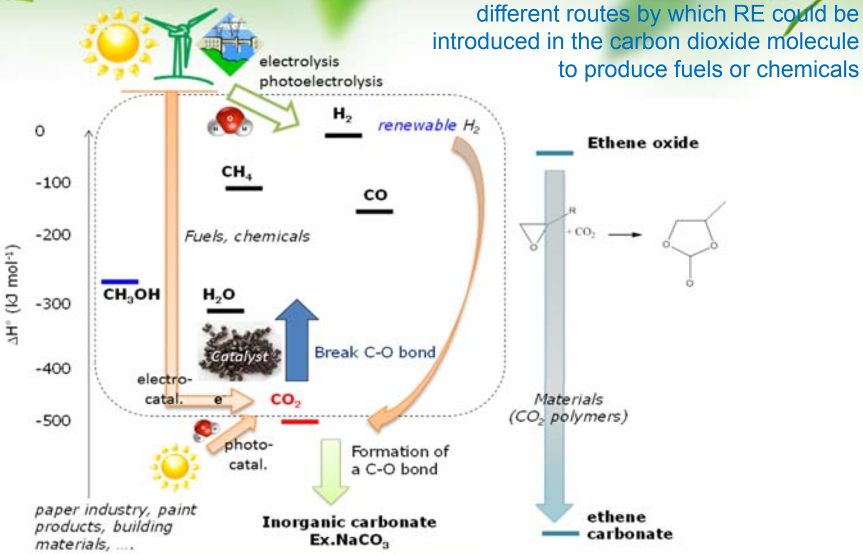
- a fast growing area, although often not demonstrated the technical feasibility
- various type of transition metals show interesting "potential" possibilities
- *better results*: Cu/Zeolite for methane to methanol conversion
  - still under discussion the type of sites, probably trinuclear
  - excellent selectivity (> 95%)
  - still two steps at different temp. necessary to close cycles (may be used a circulating reactor)
  - main problem productivity, need to be increase by a factor 10-20 to make possible industrialization

Moving to a sustainable energy & chem. prod.

the role of CO_2

CO_2 and renewable energy (RE)

different routes by which RE could be introduced in the carbon dioxide molecule to produce fuels or chemicals



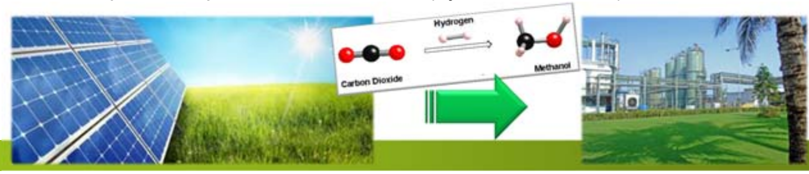
CO_2: a sustainable renewable feedstock


Wiley
ISBN: 978-1-118-59088-1

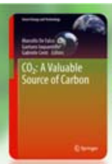
NEITHER A POLLUTER NOR A WASTE

- *a valuable source of carbon to produce*
  - raw materials *(basic chemicals)* for the chemical industry (light olefins, methanol, etc.)
  - fine and specialty chemicals
  - high-value CO_2-cont. polymers (polycarbonate, polyurethanes, etc.)

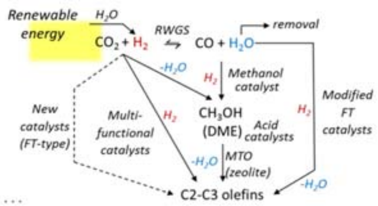
- *a key element to* ***introduce renewable energy*** *(RE)*
  - a resource & energy efficiency chemical production
  - to import unexploited RE resources (hydro, solar, wind)



CO_2: a valuable source of carbon


Springer
ISBN 978-1-4471-5119-7

- **Realize resource efficiency**
  - CO_2-based polymers
    - *at pilot plant scale*: polycarbonate, polyurethanes, ...
  - Base raw materials and chemicals for chemical industry
    - via product. renewable H_2 (water electrolysis)
      ⇨ methanol *(extension current ind. process from syngas)*,
      ⇨ light olefins *(R&D scale)*
      ⇨ acrylic acid, acetic acid, formic acid, aromatic carboxylic acids, ... *(R&D scale)*



  - Fine and specialty chemicals
    - Carbamate, isocyanate, carbonate, ...
  - As C-source for industrial biotechnology
    - CO_2-based acetone, higher alcohols, succinic acid, fragrances, ...

Resource and Energy Efficiency

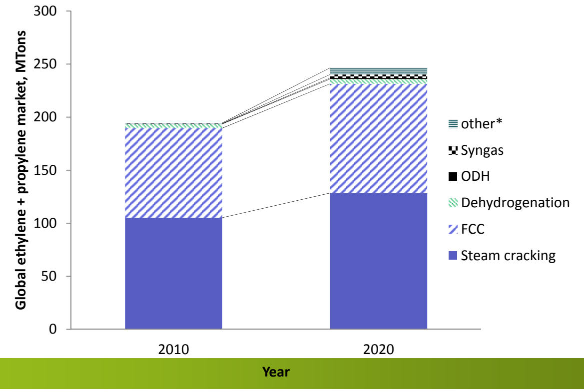
in process industry

- **How to introduce renewable energy in the energy and chemical production chain** ***(30% target ?)***
  - *a major issue not well addressed, but a critical element to decrease the carbon and environmental footprint*
  - all methods based on the use of renewable energy source produce electrical energy as output (except biomass) in a discontinuous way
  - Electrical energy does not well integrate into chemical production, except as utility.
    - *chemical processes:* based on the use of heat as the source of energy for the chemical reaction, apart few processes
    - In the chemical sector, on the average only 20% of the input energy is used as electrical energy (including that generated on-site) to power the various process units and for other services.

To introduce renewable energy in the chemical production chain it is necessary to convert renewable to chemical energy and produce raw materials for the chemical industry

Current methods of light olefin product.

- Building blocks of petrochemistry
  - but their production is the single **most energy-consuming** process
- Steam cracking accounted for about 3 ExaJ (10^{18}) primary energy use (inefficient use of energy, ≈ 60%)



Light olefin produc. and impact on CO_2

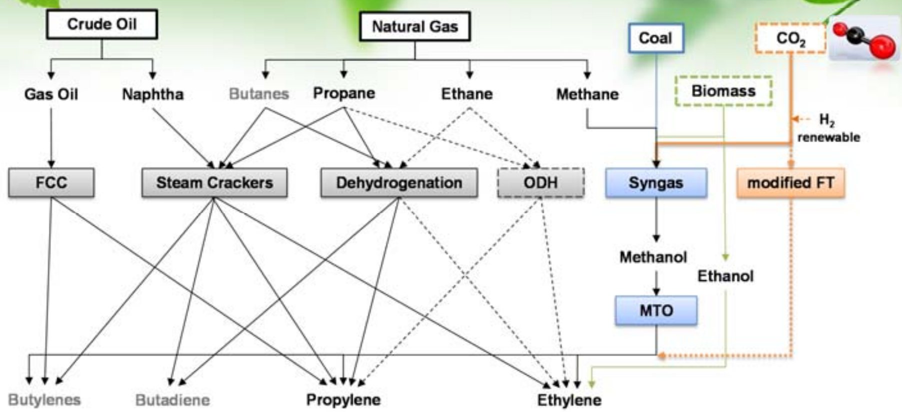
- On the average, over 300 Mtons CO_2 are produced to synthetize light olefins worldwide

Specific Emission Factors (Mt CO_2 /Mt Ethylene) in ethylene production from different sources in Germany.

	Process	Fuel	Electricity Indirect	Total
from gasoil	0.24	1.58	0.04	1.86
from LPG	0.03	1.27	0.03	1.32
from naphtha	0.02	1.47	0.03	1.53
from refinery off-gases	0.03	1.19	0.93	1.24

Centi, Iaquaniello, Perathoner, *ChemSusChem*, 2011

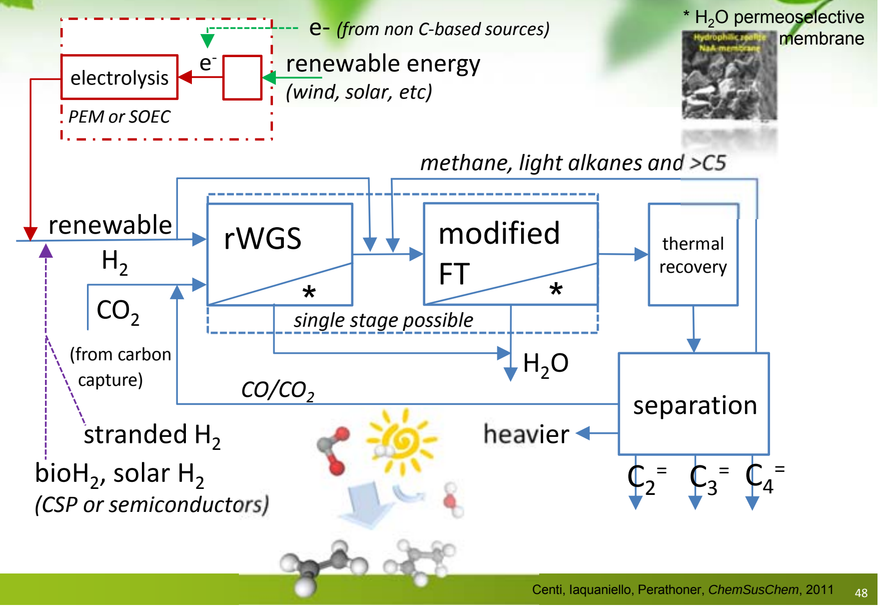
Current methods of olefin production



- widen the possible sources to produce these base chemicals (moderate the increase in their price, while maintaining the actual structure of value chain)
- In front of a significant increase in the cost of carbon sources for chemical production in the next two decades, there are many constrains limiting the use of oil-alternative carbon sources ⇨ **use CO_2 as carbon source**

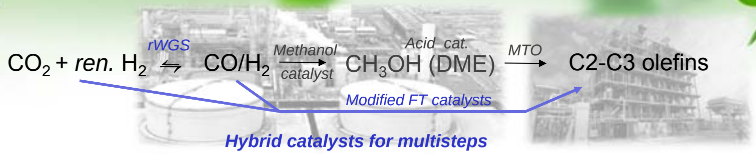
Centi, Iaquaniello, Perathoner, *ChemSusChem*, 2011

Flowsheet for the CO_2 to olefin process



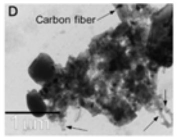
Centi, Iaquaniello, Perathoner, *ChemSusChem*, 2011

CO_2 to light olefins - *catalysts*



- Ethylene and propylene have a positive standard energy of formation with respect to H_2, but water forms in the reaction (H_2O(g) = -285.8 kJ/mol) and the process do not need extra-energy with respect to that required to produce H_2.

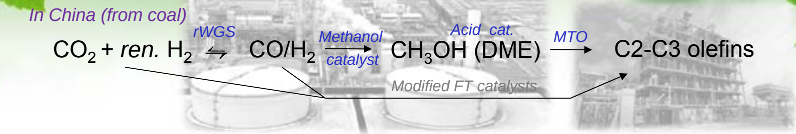
Sample	FTY (10^{-5} $mol_{CO}/g_{Fe}.s$)	Selectivity (%C) CH_4	C_2–C_4 olefins	C_2–C_4 paraffins	C_{5+}	Oxygenates
Fe/CNF	2.98	13	52	12	18	5
Fe/α-Al_2O_3 (6 wt % Fe)	8.48	24	35	21	10	10
Fe/α-Al_2O_3 (12 wt % Fe)	2.66	17	39	19	14	11
Fe/α-Al_2O_3 (25 wt % Fe)	1.35	11	53	6	21	9
Fe/β-SiC	6.38	35	19	39	4	3
Fe/γ-Al_2O_3	0.25	49	33	11	1	6
Fe-Ti-Zn-K	0.49	24	28	29	10	9
Fe-Cu-K-SiO_2	1.12	26	36	12	18	8
Bulk Fe	0.57	30	32	18	14	6



20 bar, 340°C, H_2/CO=1; 64 h on stream

Science 335, 835 (2012)

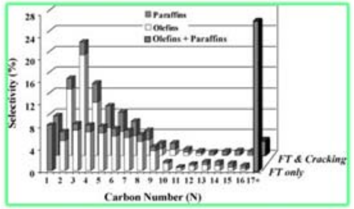
CO_2 to light olefins - *catalysts*



- via <u>conversion of methanol/DME on multifunctional catalysts</u>
  - Fe-Cu-K catalysts supported on ZSM-5 (Si/Al = 25) to improve the selective olefin production
    - Kang et al. *Fuel Proc. Techn.*, 91(2010), 399

Si/Al ratio	CO conv.	CO_2 sel.	Selectivity in hydrocarbons C_1	C_2–C_4	C_5+
25	80.7	37.7	18.3	24.9	56.8
40	78.9	37.1	17.5	23.7	58.8
140	61.6	29.1	12.6	16.5	70.9

  - dual-bed reactor: (1) Fe-Cu-Al based FT catal.; (2) ZSM-5 cracking catalysts.
    - 52% selectivity to C2-C4 hydrocarbon rich in olefins (77% selectivity).
      - Park et al. *Ind. Eng.Chem.*, 15(2009),847-.

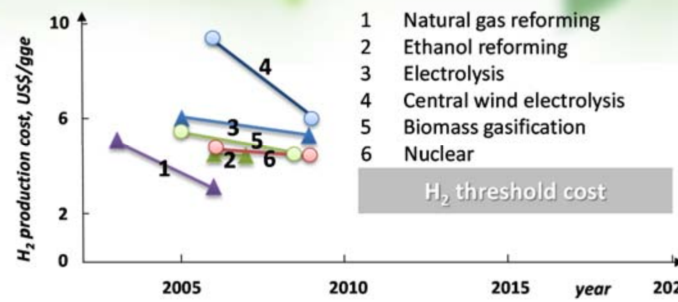


None optimal, but space for improvements

CO_2 to olefin (CO_2TO) process

- Feedstock costs accounts for 70-80% of the production costs
  - the difference to 100% is the sum of fixed costs, other variable costs (utilities such as electricity, water, etc.), capital depreciation and other costs.
- In the CO_2TO process the feedstock cost is related to renewable H_2
  - CO_2 is a feedstock with a negative cost (avoid C-taxes)
- Current ethylene and propylene prices range on the average between 1200-1400 US$/ton
  - for a renewable H_2 cost ranging in the 2-3 US$/kg H_2 range, the CO_2TO process may be **economically competitive** to current production methods, in addition to advantages in terms of a better sustainability.

H_2 from renewable energy sources



but strong dependence on local costs

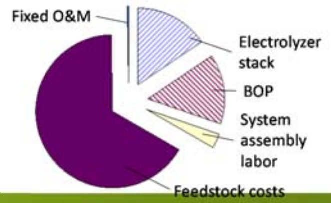
Carbon footprint (LCA analysis) for H_2 production

- CH_4 steam reforming: 8.9 kg CO_2/kg H_2
- H_2 from biomass: average 5-6 kg CO_2/kg H_2 (depends on many factors)
- Wind/electrolysis: < 1 kg CO_2/kg H_2
- Hydroelectric/electrolysis or solar thermal: around 2 kg CO_2/kg H_2
- Photovoltaic/electrolysis: around 6 CO_2/kg H_2 (but lower for new technol.)

PEM water electrolysis (for H_2 product.)

preferable current technology

- PEM water electrolysis
  - Safe and efficient way to produce electrolytic H_2 and O_2 from renewable energy sources
  - Stack efficiencies close to 80% have been obtained operating at high current densities (1 A·cm^{-2}) using low-cost electrodes and high operating pressures (up to 130 bar)
  - Developments that leaded to stack capital cost reductions:
    - (i) catalyst optimization (50% loading reduction on anode, >90% reduction on cathode), (ii) optimized design of electrolyzer cell, and (iii) 90% cost reduction of the MEAs (membrane-electrode assembling) by fabricating
    - Stability for over 60,000 hours of operation has been demonstrated in a commercial stack.
  - Electricity/feedstock is the key cost component in H_2 generation



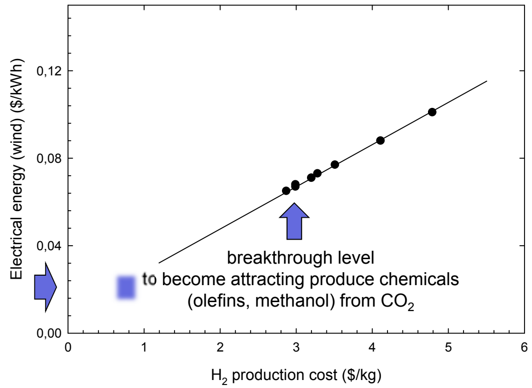
Still space for electrode improvement, but cost is depending on electricity cost

Hydrogen Production Cost Analysis

ee + PEM electrolyzers

NREL (actual data, April 2012)

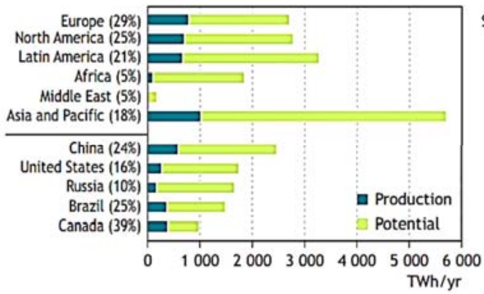
cost of producing electrical energy in some remote area



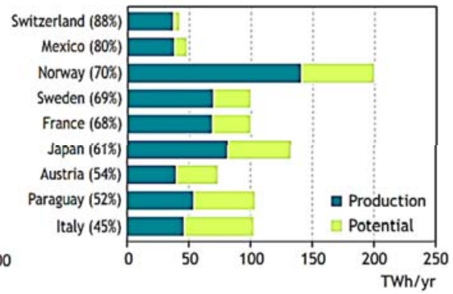
For a cost of ee of 0,02 $/kWh (estimated production cost in remote areas which cannot use locally ee, neither transport by grid) estimated production CH_3OH cost is <300 €/ton (current market value 350-400 €/ton)

Hydropower potential

Hydropower development ratio for world regions and top five countries with the highest potential



Countries with largest developed proportion of their hydro potential (countries with hydropower prod. > 30 TWh/yr)

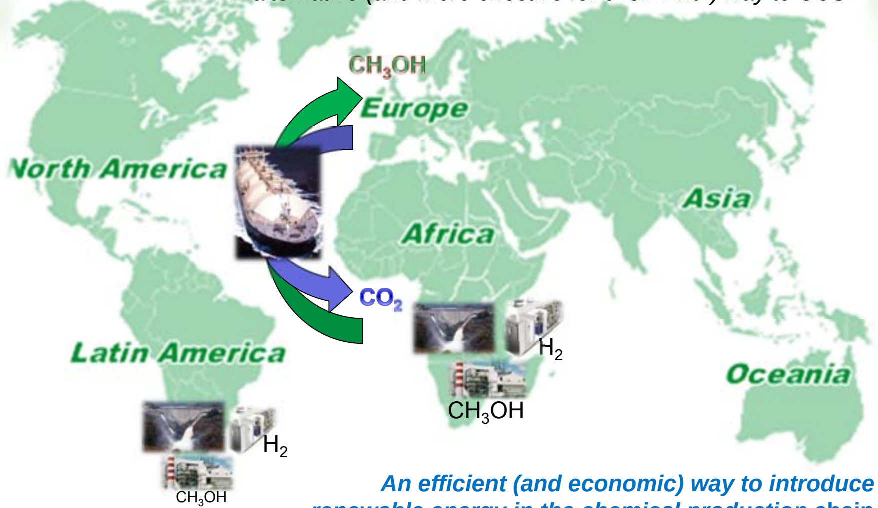


Much larger potential of hydropower, but to <u>fully enable</u> these possibilities it is necessary to <u>transport energy at long distance</u>

Data source: WEC Survey of Energy Resources 2007, IEA Renewables Information 2010

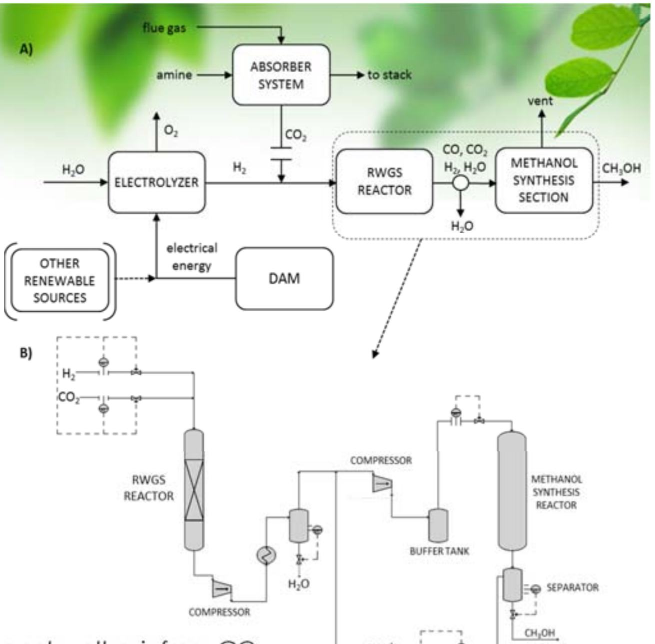
CO_2 re-use scenario: produce CH_3OH using cheap ee in remote areas

An alternative (and more effective for chem. ind.) way to CCS



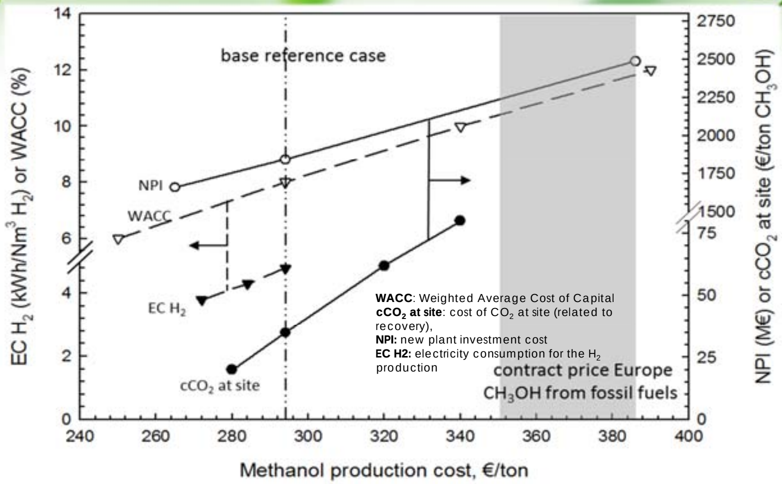
An efficient (and economic) way to introduce renewable energy in the chemical production chain

Simplified block diagram of different material flows participating into the process of methanol synthesis from CO_2 and renewable H_2.



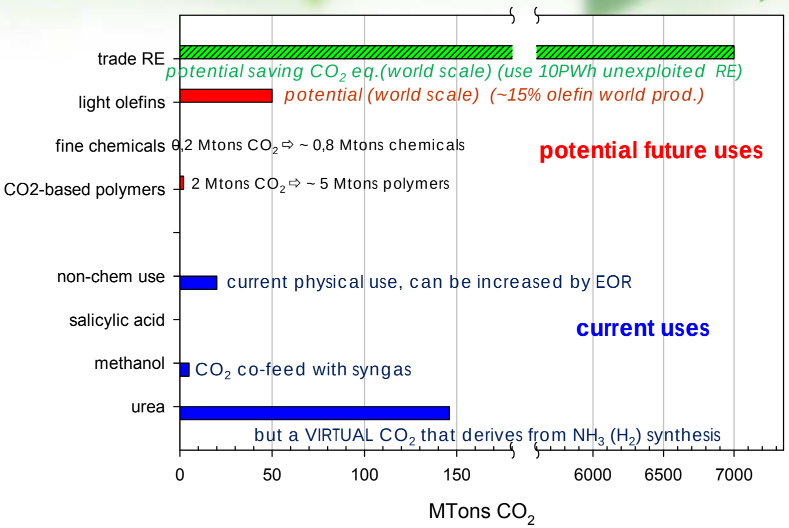
two stages methanol synthesis from CO_2

Cost of CH_3OH from CO_2 (remote ee/ren. H_2)



Sensitivity analysis of the methanol production cost from CO_2 and renewable H_2 as a function of four main parameters. The cost estimated for the base reference case and the actual range (Aug. 2013) for contract price of methanol in Europe are also indicated.

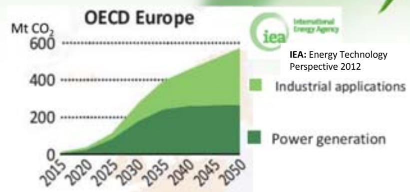
CO_2 current vs. potential future chem. use



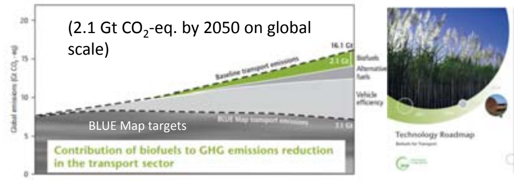
Comparison of the CO_2/RE path with CCS and biofuels

estimation for Europe, by 2050

- **CCS** ~ 600 Mt CO_2
  - effective contribution nearly half
    ⇨ energy need for CO_2 capture, transport and storage



- **biofuels** ~ 700 Mt CO_2
  - lower if considering land change use & other aspects



- **CO_2/RE:** potential impact > 800 Mt CO_2
  - 15% of unexploited RE, includes about 0.2 tons CO_2 per ton CO_2 eq. of energy for the conv. to methanol; the impact is related to avoided CO_2 by introducing RE in the energy chain

- CO_2/RE is an effective solution to contribute to mitigate on climate change

Comparison of the CO_2/RE path with CCS and biofuels

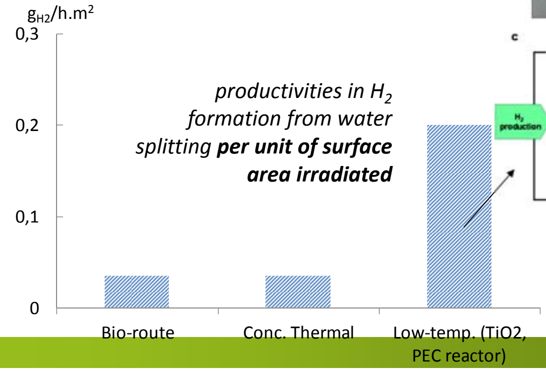
estimated costs (Europe)

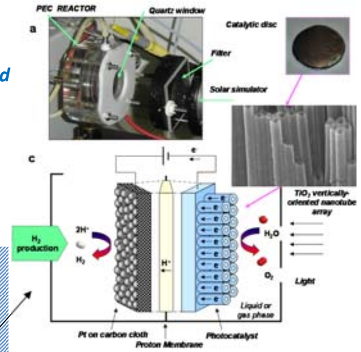
- **CCS**
  - average 60€/ton captured
  - tot. cost in year 2050 per 1Gt CO_2 removed EU ⇨ 60 B€
- **biofuels**
  - IEA (BLUE Map Scenario): "... Between 2030 and 2050, total incremental costs for biofuels are around US$ 330 billion in the high-cost scenario..." (oil at US$ 120/bbl in 2050)
  - tot. cost in year 2050 per 1Gt CO_2 removed ⇨ 35 B€
- **CO_2/RE**
  - considering 20€/ton subsidies to make methanol cost eq. to fuel projected cost
  - tot. cost in year 2050 per 1Gt CO_2 removed ⇨ 20 B€
  - CO_2/RE is the cost-effective solution for GHG emission reduction

New routes for producing renewable H_2

- bio-route using cyanobacteria or green algae
- high temperature thermochemical one using concentrated solar energy
- photo(electro)chemical water splitting or photoelectrolysis using semiconductors

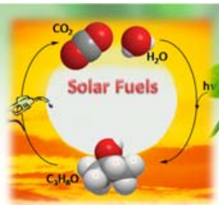
The low temperature approach (PEC solar cell) has a greater potential productivity in solar fuels per unit of area illuminated AND may be used also for C-based energy vector

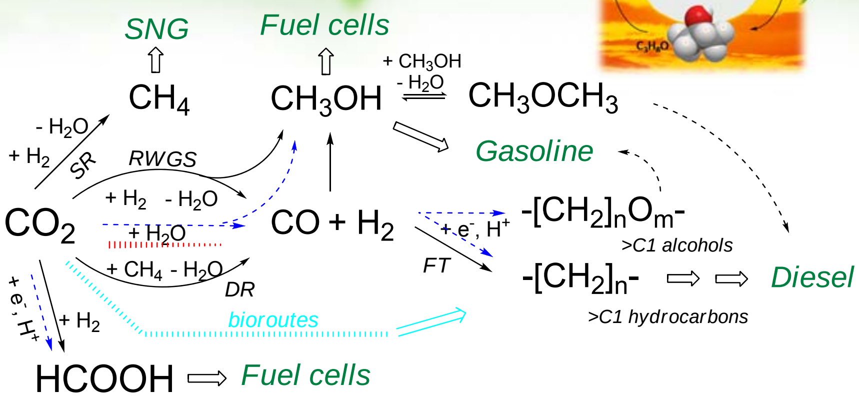




Centi., Perathoner, *ChemSusChem*, 3 (2010) 195.

Solar fuels (energy vectors)





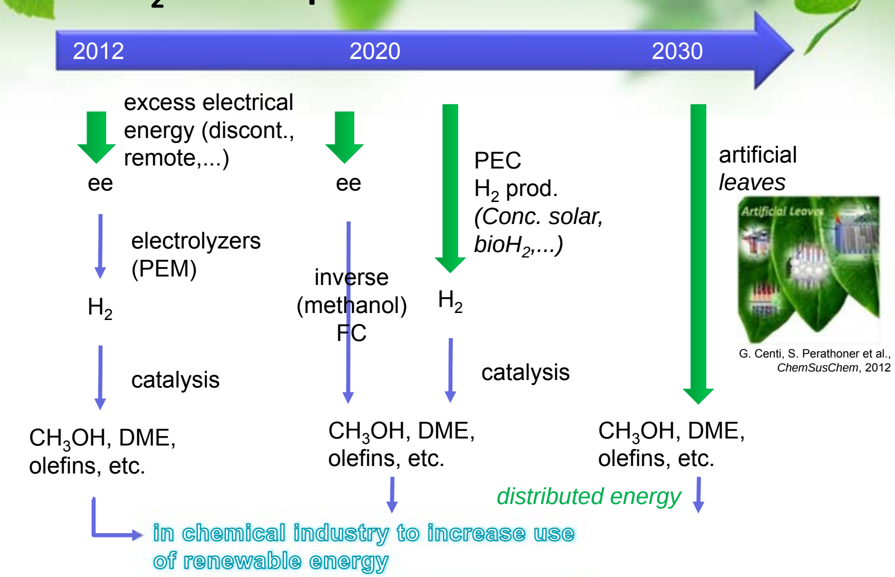
Chemical routes : (catalytic)

FT : Fischer Tropsch
DR: Dry reforming
RWGS: Reverse water gas shift
SR: Sabatier reaction

Electrochemical routes
Solar thermal routes

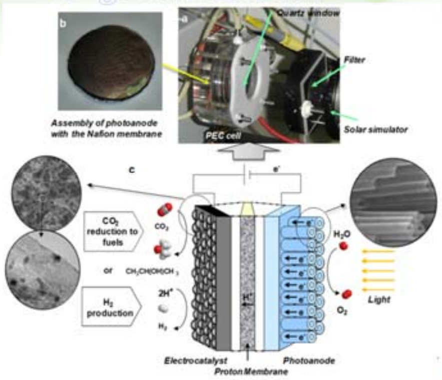
Greenhouse Gases: Science and Technology (CO_2-based energy vectors for the storage of solar energy) Vol 1, Issue 1, (2011) 21

A CO_2 roadmap



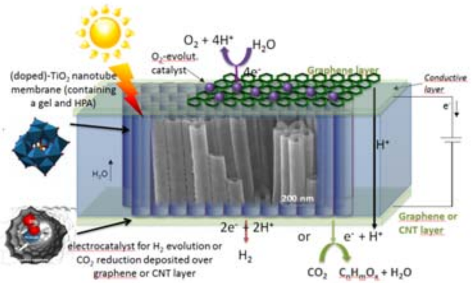
Toward artificial leaves

- 1st generation cell



G. Centi, S. Perathoner et al., *ChemSusChem*, 2012

- 2nd generation cell



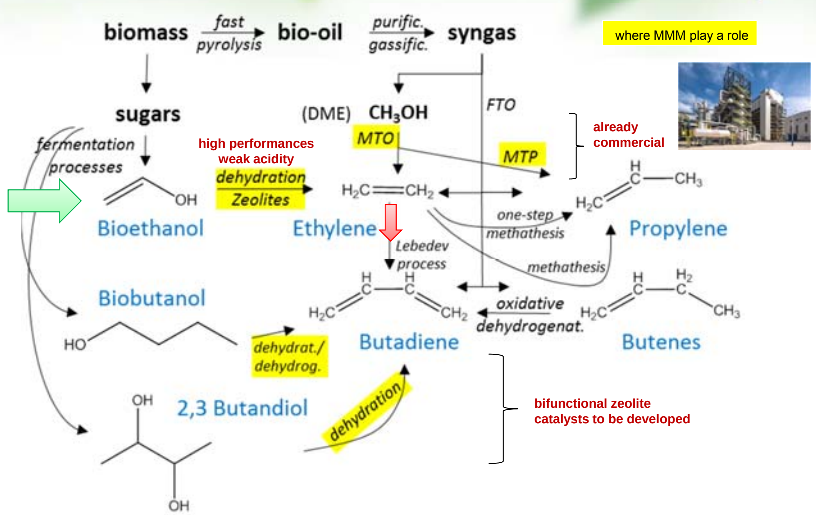
Moving to a sustainable energy & chem. prod.

evolving scenario in biorefineries

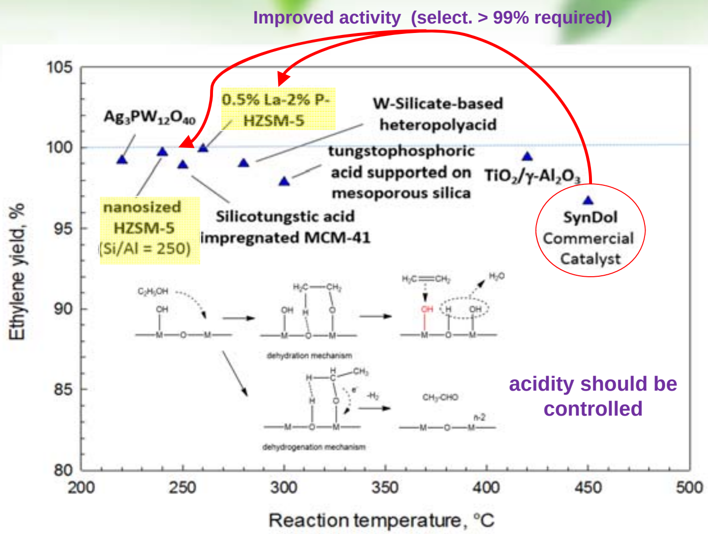
Advanced concepts for biorefineries

- **Olefin biorefineries**
  - dehydration of ethanol produced from biomass fermentation
  - methanol via syngas from biomass, then MTO/MTP or olefins from syngas by FTO
  - C3 or C4 alcohols or diols via fermentation, then dehydrat. or other conv. routes
- **Biorefineries for sustainable chemical/energy production**
  - platform chemicals for chemicals/energy: furfurals (also called furanics), succinic acid, (glycerol)
- **Integrated solar biorefineries**
  - use of CO_2 and renewable (solar) energy

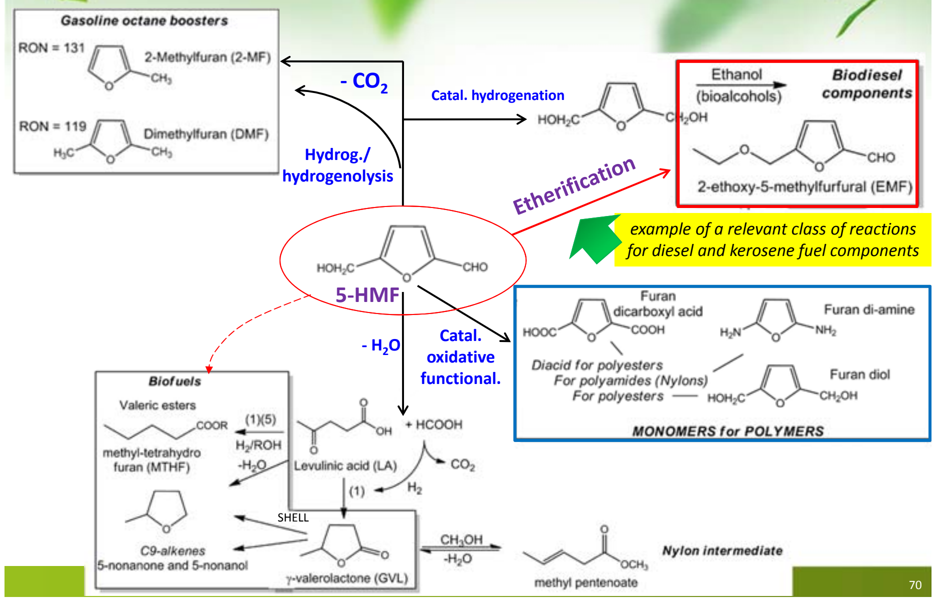
New routes of production of olefins from biomass



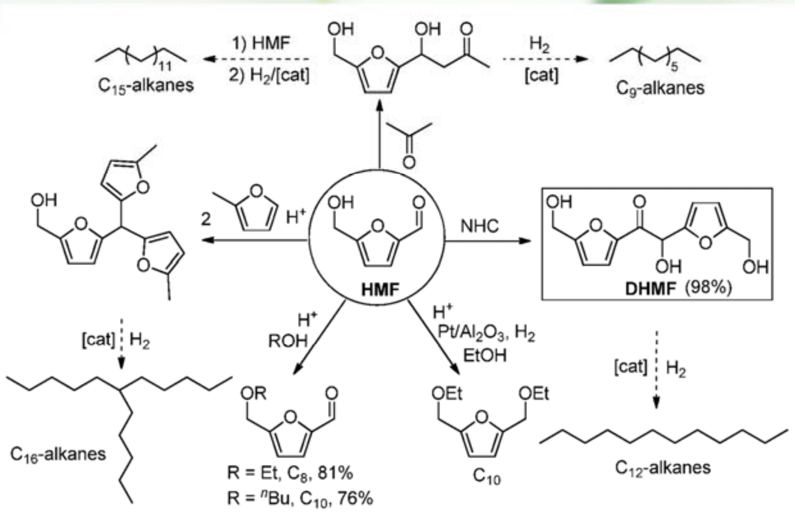
Dehydration of ethanol to ethylene



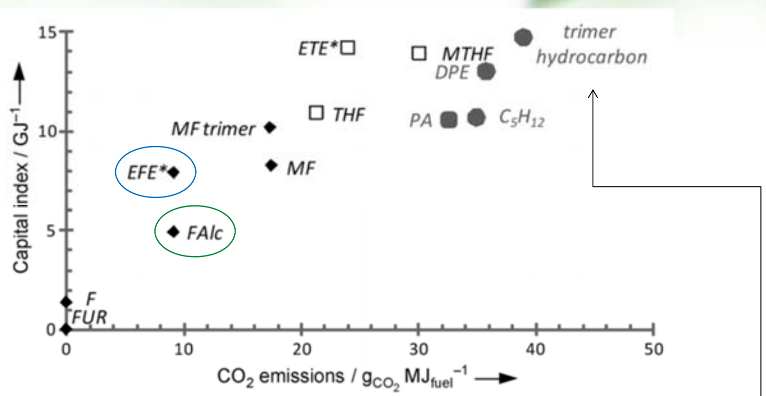
Biorefineries for sustainable chemical/energy production
5-HMF as platform molecule



Routes to upgrade HMF to diesel/gasoline fuel components



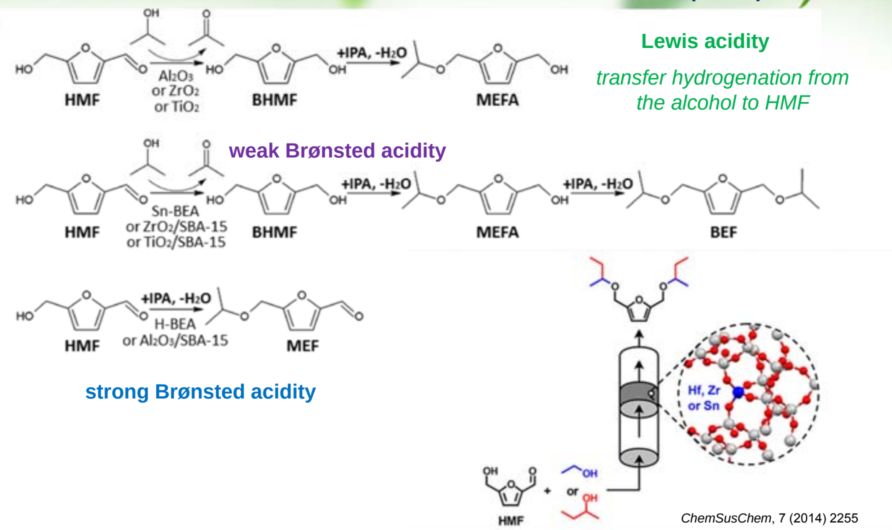
Manufacture footprint



- *limited footprint for the conversion of the aldehyde group of furfural to alcohol*, ether or methyl groups in **FAlc** (furfuryl alcohol) or **EFE** (ethylfurfuryl ether), *but larger footprint when ring opening and/or hydrogenation*

Behavior greatly depending on acidity and reaction conditions

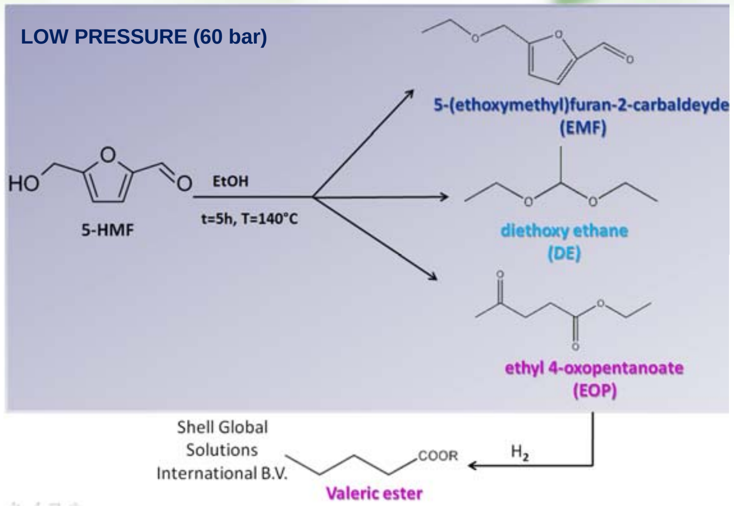
UNDER PRESSURE (60 bar)



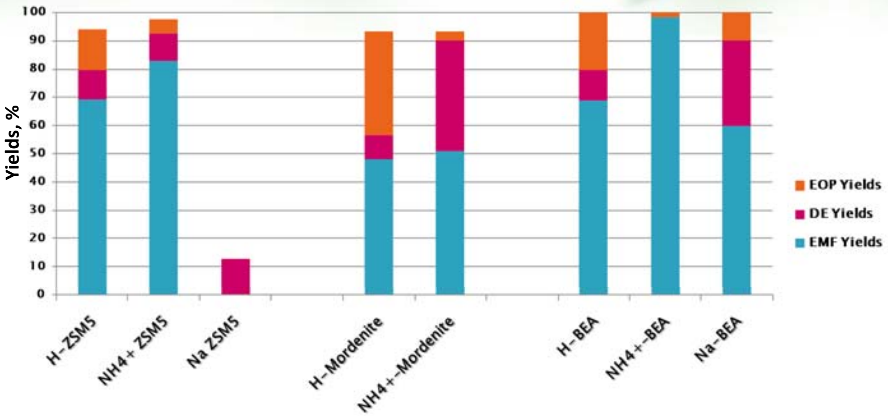
ChemSusChem, 7 (2014) 2255

Etherification of HMF

biodiesel components

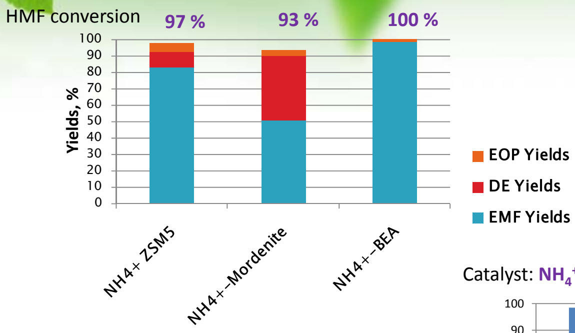


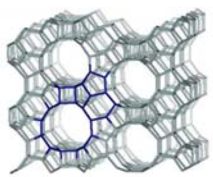
Etherification of 5-HMF on different zeolites: influence of channel structure



➢ High yield to EMF for NH_4^+-BEA → sinergy of acidity and channel structure

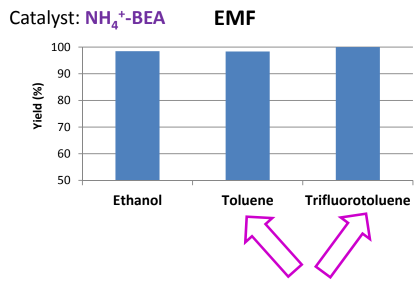
Etherification of 5-HMF on NH_4^+ zeolites





SiO_2/Al_2O_3 = 25

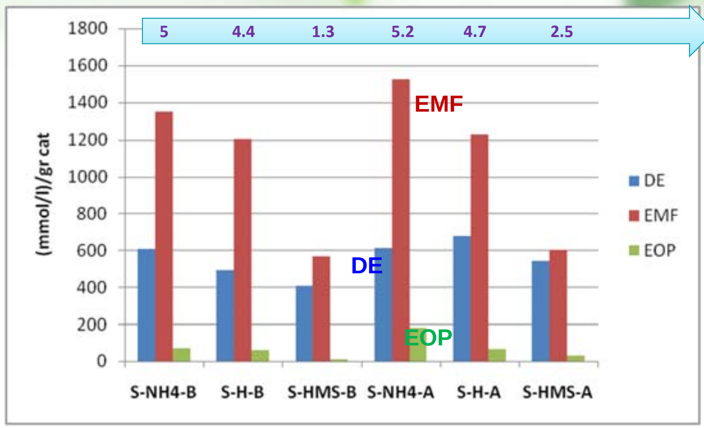
BET surface area = 380 m^2/g

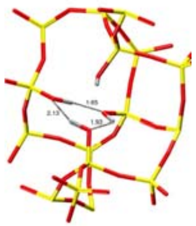


5-HMF and Ethanol = 1 : 1 molar ratio

Effect of silanols to products selectivity

Silicalite-1

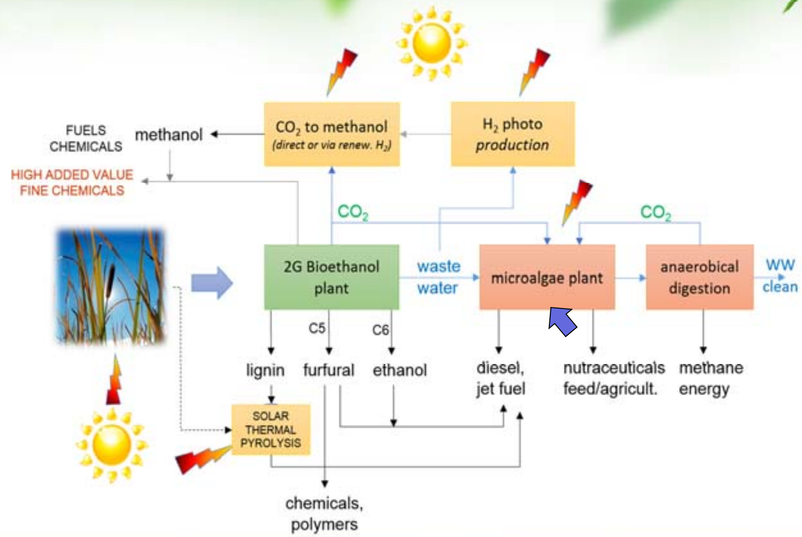



Silanol nest

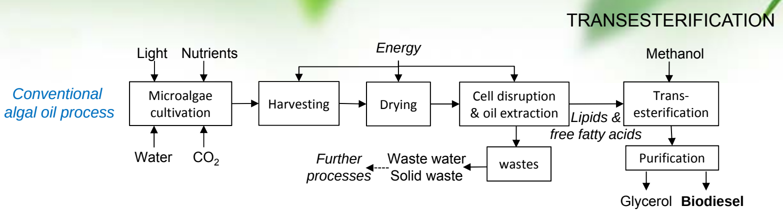
- decrease of n° of silanols → *decrease of EMF productivity*
- loss of silanol group after calcination (decrease of Brönsted acidity) → *corresponding decrease of EOP productivity*
- Sylilation decreases the amount of free silanols → *low catalytic activity*

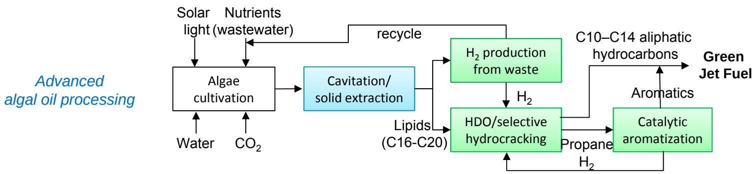
Integrated solar biorefinery approach

a possible model



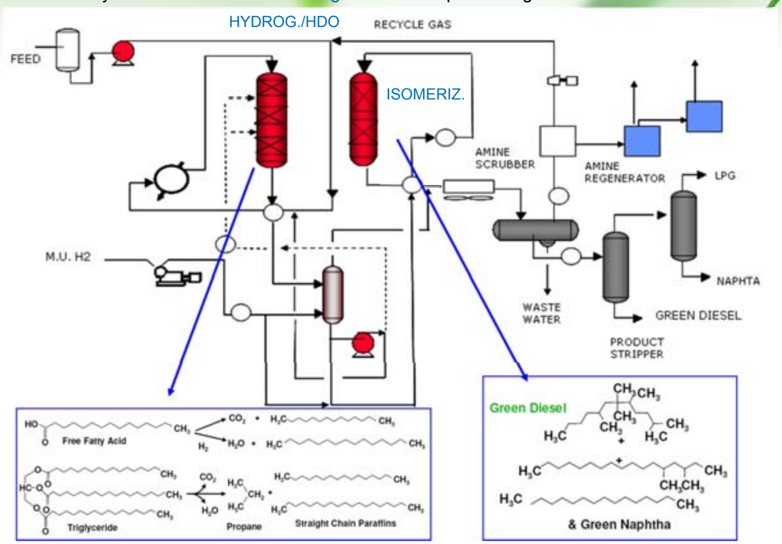
Algal oil processing





Ecofining™ Process for Green Diesel Production

Eni/Honeywell UOP for the HDO of vegetable oils to produce "green" biodiesel



Needs of catalysts improvements

- catalysts should not contain non noble metals
  - reduce the use of critical raw materials
- catalysts should be optimized for the specific application to convert lipids from microalgae
  - different fatty acid composition, free fatty acids, impurities (salts, P)
- realize (preferably) one-step process
  - reduce process cost
- introduce selective hydrocracking functionalities
  - improve yield more valuable cuts, such as jet fuel

Green Jet Reactions

Olefin Saturation

Decarboxylation/Decarbonylation

$C_n COOH \xrightarrow{Catalyst} C_n + CO_2$

$C_n COOH + H_2 \xrightarrow{Catalyst} C_n + CO + H_2O$

$CO + H_2O \rightleftharpoons^{Catalyst} CO_2 + H_2$ *Water Gas Shift*

Hydrodeoxygenation

$C_n COOH \xrightarrow[Catalyst]{+3H_2} nC_{n+1} + 2H_2O$

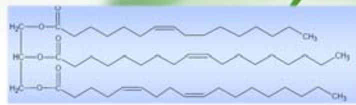
Hydroisomerization

$nC_{n+1} + nC_n \xrightarrow[Catalyst]{H_2} iC_{n+1} + iC_n$

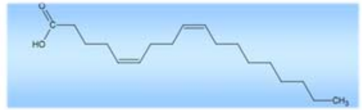
Hydrocracking

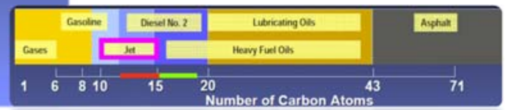
$iC_n \xrightarrow[Catalyst]{H_2} iC_{n-y} + iC_y$

Triglycerides MW = 700-900



Fatty Free Acids MW = 200-300

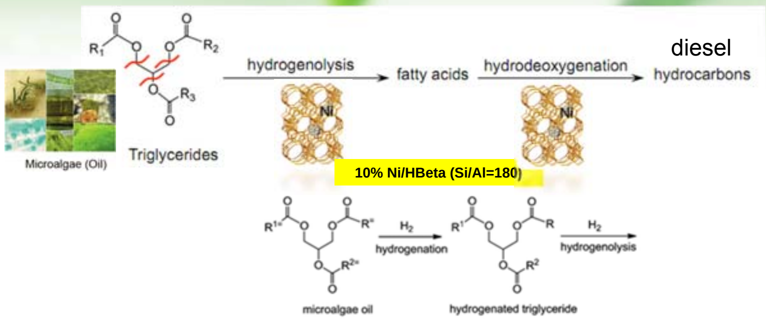




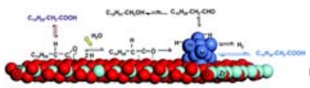
Oil → Deoxygenation → Isomerization → Green Diesel

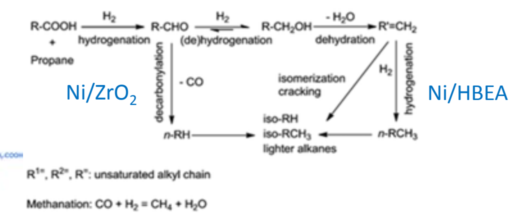
Oil → Deoxygenation → Selective Cracking/ Isomerization → Green Jet ← Aromatics (<25%)

Biofuel production from lipids (by a single-step route)



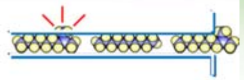
the H coverage on the active sites selects either hydrogen.– decarbonylation or self-condens. (ketonization) pathways



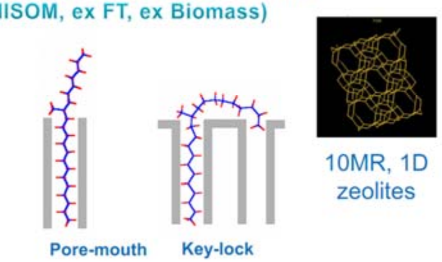


Hydrocracking and Selective Hydroisomerization

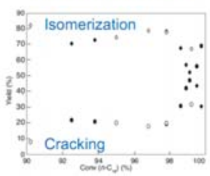
- isomerization versus cracking

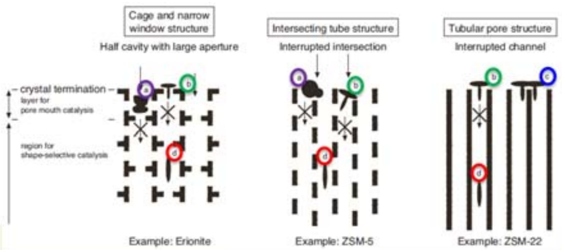


Hydroisomerization of long paraffins (HISOM, ex FT, ex Biomass)



nC18 conversion

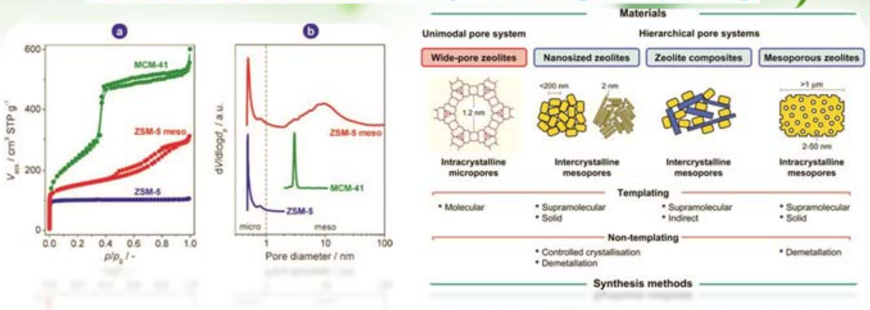


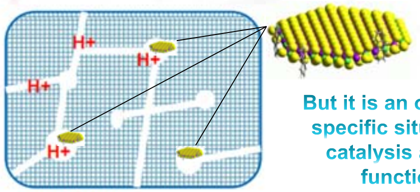


Pores and pore mouths for several combinations of zeolite types and molecules:
a) molecules have access to cavities or interrupted channels,
b) molecules are «branched» in pore openings,
c) key-lock catalysis,
d) molecules are converted in the intracrystalline space

Hierarchical zeolites

Avoid mass transfer limitation by increasing mesoporosity





Zeolite cristal

But it is an opportunity (largely unexplored) to create specific situations to enhance pore-mouth/key-lock catalysis and to incorporate hydrogenation/HDO functionalities or metal particles (Ni, etc.)

Chem. Soc. Rev., 2008, 37, 2530–2542

Moving to a sustainable energy & chem. prod.

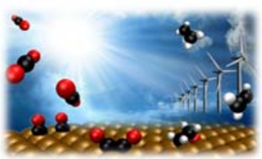
disruptive catalysts

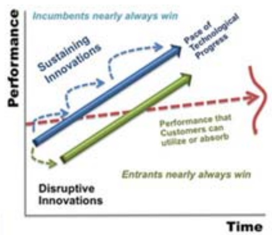
Disruptive catalysis

- when create a new market and value network, and eventually disrupts an existing market and value network (over a few years or decades), displacing an earlier technology.

  ⇨ transformational or revolutionary

- In contrast to disruptive catalysis
  - a sustaining catalyst evolves existing ones with better value ⇨ evolutionary

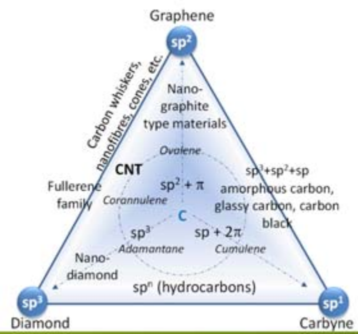




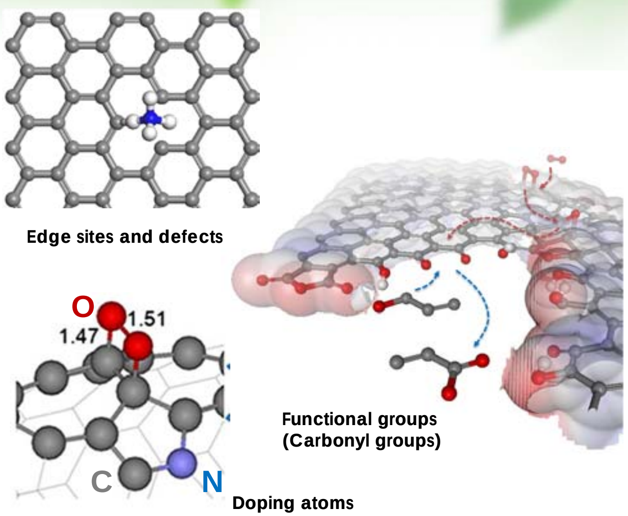
Nanocarbons as catalysts

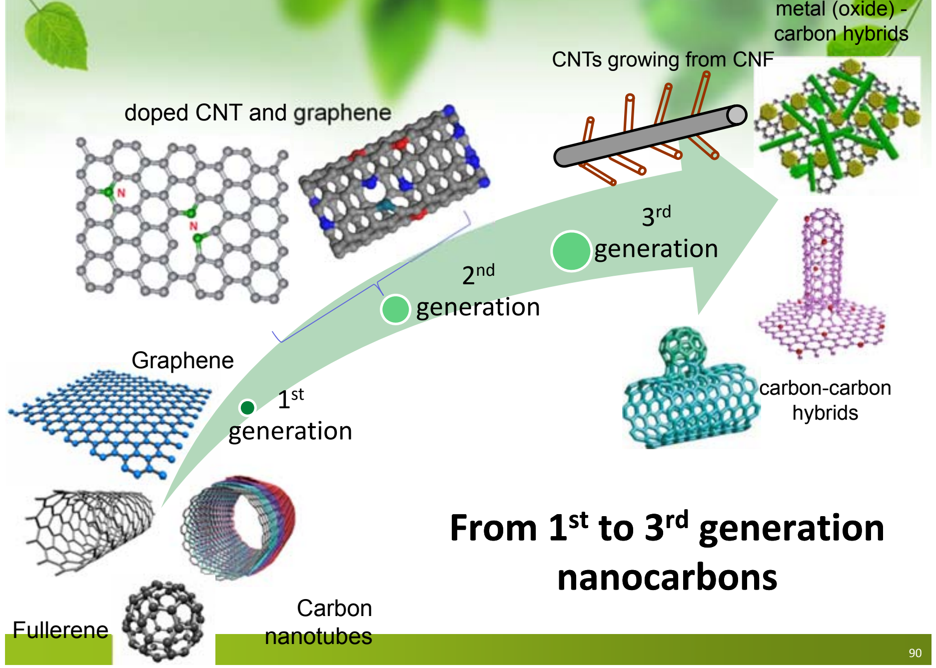
- a new type of catalyst family
  - carbon, differently from the other catalytically active elements, forms a great variety of crystalline and disordered structures because it can exist in three different hybridizations: sp^3, sp^2, and sp^1.
  - new type of active centers and catalytic functionalities

- *Functional groups,* either with acido-base or redox character: they are active in various classes of reaction such as dehydrogenation, oxidation, hydrogenation, etc.
- *Edge sites and defects:* active for example in decomposition reactions.
- *Doped atoms:* by influencing the properties on near-lying C atoms, they play a role in various reactions, from ORR to hydrochlorination, epoxidation, etc.



Active sites in nanocarbons





From 1st to 3rd generation nanocarbons

Take home message

Green energy/resources

A game changer

(for chem./energy industry)

But a vision to identify the priority paths is necessary