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.
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

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

Roadmap 2050: cost-efficient pathway and milestones

- 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 CO₂, waste valorization and use of renewable energy
  - at the core of strategies of chemical/energy industries for a resource and energy efficient sustainable future.

Components for resource efficiency

- Feedstock
  - Bio-feedstock
  - Waste as a feedstock
  - The conversion of CO₂ 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, ...

Moving to a sustainable energy & chem. prod.

New raw materials and green energy sources: opening new scenarios for the chemical & energy industry
A changing scenario

Today

Future

New raw materials and green energy for chemical production value chain

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

Green Energy series (De Gruyter)

Catalysis for biomass and CO$_2$ use through solar energy


Introduct. renewable energy in chem. prod.

Energy Environ. Sci., 2013, 6, 1711

- 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
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

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- and bio-catalysis
     - novel nanoparticles
     - organometallic complexes, organocatalysts, biomimetic catalysts and enzymes,
     - catalysis with immobilized or single site complexes

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
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.

NEW OPPORTUNITIES TO USE NG FOR CHEMICAL PRODUCTION

Direct and indirect routes for CH₄ 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

- 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

- O₂-activation
  - change in geometry (new peak at 8987 eV), but no change in oxidation state
  - CH₄-loading
    - Cu²⁺ 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

- ZSM-5: -164 kJ/mol
- MOR: -291 kJ/mol
- Cu⁺, CuOH⁺, CuO⁺, H⁺
- 2x CuO⁺
- 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)

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- ZSM-5
- MOR
- Cu trimer cluster
- Cu⁺, CuOH⁺, CuO⁺, H⁺
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 (H₂O₂ as oxidant)

Novel MMM for methane select. conv.
**Zn modified H-ZSM-5 zeolites**

- solid-state NMR and theoretical calculations

\[ \text{CH}_4 \rightarrow \text{CH}_3^+ \rightarrow \text{CH}_3\text{O}^- \rightarrow \text{methanol} \]

- 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

**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\(_2\)C or MoO\(_x\)C\(_y\) species)**

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

A Density Functional Theory Study

\[ 2\text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \]

**Methane aromatization on Mo/ZSM-5**

- DFT: Mo\(_x\)(CH\(_3\))\(_y\)/ZSM-5 is the effective active center for methane activation
- The C–H bond dissociation occurs on the \(\pi\) orbital of Mo=CH\(_2\) with an activation energy of 106 kJ/mol

**Mechanism of reaction:** conversion of CH\(_4\) to C\(_2\)H\(_4\) (C\(_3\)H\(_2\)) on molybdenum carbide or oxycarbide and further conversion of C\(_3\)H\(_4\) (C\(_4\)H\(_2\)) 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

- zinc sites efficiently activate CH₄ to form zinc Me species (-Zn-CH₃), the Zn-C bond of which is further subject to the CO₂ insertion to produce surface acetate species (-Zn-OOCCH₃).
- 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

- 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.
**CO₂ and renewable energy (RE)**

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

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**CO₂: a sustainable renewable feedstock**

*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 CO₂-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)

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**CO₂: a valuable source of carbon**

- **Realize resource efficiency**
  - CO₂-based polymers
    - at pilot plant scale: polycarbonate, polyurethanes, ...
  - Base raw materials and chemicals for chemical industry
    - via product, renewable H₂ (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
    - CO₂-based acetone, higher alcohols, succinic acid, fragrances, ...

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**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, \(\approx 60\%\))

![Graph showing global ethylene + propylene market, Mtons](image)

Light olefin produc. and impact on CO₂

- On the average, over 300 Mtons CO₂ are produced to synthetize light olefins worldwide

Specific Emission Factors (Mt CO₂/Mt Ethylene) in ethylene production from different sources in Germany.

<table>
<thead>
<tr>
<th>Process</th>
<th>Fuel</th>
<th>Electricity Indirect</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>from gasoil</td>
<td>0.24</td>
<td>1.58</td>
<td>1.88</td>
</tr>
<tr>
<td>from LPG</td>
<td>0.03</td>
<td>1.27</td>
<td>1.32</td>
</tr>
<tr>
<td>from naphtha</td>
<td>0.02</td>
<td>1.47</td>
<td>1.53</td>
</tr>
<tr>
<td>from refinery off-gases</td>
<td>0.03</td>
<td>1.19</td>
<td>1.24</td>
</tr>
</tbody>
</table>

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 CO₂ as carbon source

Flowsheet for the CO₂ to olefin process

- renewable energy (wind, solar, etc)
- rWGS (from carbon capture)
- stranded H₂ (CSP or semiconductors)
- CO₂ single stage possible modified FT
- thermal recovery
- separation methane, light alkanes and >C₅
**CO₂ to light olefins - catalysts**

- Ethylene and propylene have a positive standard energy of formation with respect to H₂, but water forms in the reaction (H₂O(g) = -285.8 kJ/mol) and the process do not need extra-energy with respect to that required to produce H₂.

<table>
<thead>
<tr>
<th>Sample</th>
<th>FTY (1kPa)</th>
<th>Selectivity (%C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/NF</td>
<td>2.98</td>
<td>CH₂ = C₂ = C₃</td>
</tr>
<tr>
<td>Fe-NiO₂</td>
<td>8.48</td>
<td>CH₂ = C₄ = C₅</td>
</tr>
<tr>
<td>NiO₂</td>
<td>8.48</td>
<td>CH₂ = C₆ = C₇</td>
</tr>
<tr>
<td>Fe-NiO₂</td>
<td>3.95</td>
<td>CH₂ = C₈ = C₉</td>
</tr>
<tr>
<td>W-Cu/Co</td>
<td>1.62</td>
<td>CH₂ = C₁₀ = C₁₁</td>
</tr>
<tr>
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</tr>
</tbody>
</table>

20 bar, 340°C, H₂/O₂=1:64 h on steam

**CO₂ to olefin (CO₂TO) 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 CO₂TO process the feedstock cost is related to renewable H₂
  - CO₂ is a feedstock with a negative cost (avoid C-taxes)

- Current ethylene and propylene prices range on the average between 1200-1400 US$/ton
  - for a renewable H₂ cost ranging in the 2-3 US$/kg H₂ range, the CO₂TO process may be economically competitive to current production methods, in addition to advantages in terms of a better sustainability.

**H₂ from renewable energy sources**

- CH₄ steam reforming: 8.9 kg CO₂/kg H₂
- H₂ from biomass: average 5-6 kg CO₂/kg H₂ (depends on many factors)
- Wind/electrolysis: < 1 kg CO₂/kg H₂
- Hydroelectric/electrolysis or solar thermal: around 2 kg CO₂/kg H₂
- Photovoltaic/electrolysis: around 6 CO₂/kg H₂ (but lower for new technol.)

**CO₂ to light olefins - catalysts**

- via conversion of methanol/DME on multifunctional catalysts
  - Fe-Cu-K catalysts supported on ZSM-5 (Si/Al = 25) to improve the selective olefin production

- 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-

**H₂ from renewable energy sources**

- Natural gas reforming
- Ethanol reforming
- Electrolysis
- Central wind electrolysis
- Biomass gasification
- Nuclear
**PEM water electrolysis (for H₂ product.)**

- **PEM water electrolysis**
  - Safe and efficient way to produce electrolytic H₂ and O₂ 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 led 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 H₂ generation

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

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**Hydrogen Production Cost Analysis**

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**CO₂ re-use scenario: produce CH₃OH using cheap ee in remote areas**

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

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**Hydropower potential**

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

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**NREL (actual data, April 2012)**

- **Hydropower potential**

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**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)**

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

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**North America**

- **Europe**
- **Asia**
- **Africa**
- **Latin America**
- **Oceania**

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**An alternative (and more effective for chem. ind.) way to CCS**
Simplified block diagram of different material flows participating into the process of methanol synthesis from CO$_2$ and renewable H$_2$.

Cost of CH$_3$OH 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.

Comparison of the CO$_2$/RE path with CCS and biofuels

- 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

CO$_2$ current vs. potential future chem. use

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Comparison of the CO₂/RE path with CCS and biofuels

- **CCS**
  - average 60€/ton captured
  - tot. cost in year 2050 per 1Gt CO₂ 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 CO₂ removed ⇒ 35 B€

- **CO₂/RE**
  - considering 20€/ton subsidies to make methanol cost eq. to fuel projected cost
  - tot. cost in year 2050 per 1Gt CO₂ removed ⇒ 20 B€

- CO₂/RE is the cost-effective solution for GHG emission reduction

New routes for producing renewable H₂

- bio-route using cyanobacteria or green algae
- high temperature thermochemical one using concentrated solar energy
- phot(oelectro)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**

Solar fuels (energy vectors)

- SNG
- Fuel cells
- CH₄
- CH₃OH
- CH₃OCH₃
- CO + H₂
- HCOOH ⇔ Fuel cells
- Chemical routes:
  - FT: Fischer Tropsch
  - DR: Dry reforming
  - RWGS: Reverse water gas shift
  - SR: Sabatier reaction
- Electrochemical routes
- Solar thermal routes

A CO₂ roadmap

- 2012: excess electrical energy (discont., remote,...)
- 2020: PEC H₂ prod. (Conc. solar, bioH₂,...)
- 2030: Artificial leaves

- Diesel
- CH₃OH, DME, olefins, etc.
- Catalysis
- Distributed energy

- In chemical industry to increase use of renewable energy
**Toward artificial leaves**

1st generation cell

- Assembly of subcomponents with the solar assistance

- Light

- CO2 reduction

- ORR

- Water reduction

- Electrocatalyst for H2 evolution in CO2 reduction

2nd generation cell

- Light

- CO2 reduction

- ORR

- Water reduction

- Electrocatalyst for H2 evolution in CO2 reduction

**Moving to a sustainable energy & chem. prod.**

**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 dehydration 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 CO2 and renewable (solar) energy

**New routes of production of olefins from biomass**

- Bioethanol
- Ethylene
- Butadiene
- Butanol
- Biooil
- Syngas

- High performance weak acidity Zeolite catalysts to be developed

- Where MMM play a role

- Already commercial
Dehydration of ethanol to ethylene

Acidity should be controlled

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 FAIc (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)

Lewis acidity
transfer hydrogenation from the alcohol to HMF

weak Brønsted acidity

strong Brønsted acidity

Etherification of HMF

LOW PRESSURE (60 bar)

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

 Etherification of 5-HMF on \( \text{NH}_4^+ \) zeolites

SiO\(_2\)/Al\(_2\)O\(_3\) = 25
BET surface area = 380 m\(^2\)/g

High yield to EMF for \( \text{NH}_4^+\)-BEA → synergy of acidity and channel structure


ChemSusChem, 7 (2014) 2255

Effect of silanols to products selectivity

Silicalite-1

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

Integrated solar biorefinery approach

- Ethanol production
- H₂ photo production
- CO₂ fixation to ethanol
- Algal oil processing

Algal oil processing

- Conventional algal oil process
- Advanced algal oil processing

- Transesterification
- CO₂ fixation to ethanol
- H₂ production from waste
- Lipids & free fatty acids
- Methanol
- Water
- Purification
- Glycerol
- Biodiesel

Ecofining™ Process for Green Diesel Production

- Eni/Honeywell UOP for the HDO of vegetable oils to produce “green” biodiesel
- HYDROG./HDO
- ISOMERIZ.
- ISOMERIZ.
**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/Decarboxylation
    - \( C_6 COOH \rightarrow \text{Catalyst} \rightarrow C_6 CO + \text{H}_2 \)
    - \( C_6 COOH + \text{H}_2 \rightarrow \text{Catalyst} \rightarrow C_6 CH + \text{H}_2 \)
  - Water Gas Shift
    - \( \text{CO} + \text{H}_2 \text{O} \rightarrow \text{Catalyst} \rightarrow \text{CO}_2 + \text{H}_2 \)

- **Hydrodeoxygenation**
  - \( C_6 COOH \rightarrow \text{Catalyst} \rightarrow nC_{18} + 2\text{H}_2 \)

- **Hydroisomerization**
  - \( nC_{18} + iC_{18} \rightarrow \text{Catalyst} \rightarrow iC_{18} + nC_{18} \)

- **Hydrocracking**
  - \( H_2 \rightarrow \text{Catalyst} \rightarrow \text{isomerization} \)

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

- **Triglycerides**
  - \( \text{MW} = 700-900 \)
- **Fatty Free Acids**
  - \( \text{MW} = 200-300 \)

**Hydrocracking and Selective Hydroisomerization**

- **Isomerization versus cracking**
  - nC18 conversion

Pores and pore mouths for several combinations of zeolite types and molecules:
- Molecules have access to cavities or interrupted channels.
- Molecules are branched in pore openings.
- Key-lock catalysis.
- Molecules are converted in the intracrystalline space.
Hierarchical zeolites
Avoid mass transfer limitation by increasing mesoporosity

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: sp³, sp², and sp¹.
  • 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 nearby C atoms, they play a role in various reactions, from ORR to hydrochlorination, epoxidation, etc.
Active sites in nanocarbons

- Edge sites and defects
- Functional groups (Carbonyl groups)
- Doping atoms

From 1st to 3rd generation nanocarbons
- Fullerene
- Graphene
- Carbon nanotubes

Take home message

Green energy/resources

A game changer
(for chem./energy industry)

But a vision to identify the priority paths is necessary