PILLAR 1 – NANO for ENERGY (PARALLEL SESSION 1.1) Nanotechnologies and Advanced Materials for a Carbon-neutral Society by 2050 Bucharest (Romania), June 12th, 2019

Possible scientific/ technological solutions

Challenges in energy nanomaterials to substitute the use of fossil fuels

 $\rightarrow$  the crucial factor: solar fuels and chemicals







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## Why solar fuels and chemicals

- Materials & technologies for solar fuels and chemicals are the missing & limiting factor to accelerate the rate of introduction of renewable energy in the EU energy mix, the necessary factor to meet climate change targets AND realize an innovative competitiveness & sustainable growth
  - Already today there are the economic bases for this transition, but the **limiting factor** is the still **too slow** progress in the development of the related technologies and energy materials.
  - There is the need to accelerate the scientific and technological progress in this area by
     developing the necessary large initiative, to realize an integrated and coherent wide TRL approach on short-, medium/long term perspective
    - Catalyze synergies and critical mass, not only identify priorities





## How to meet GHG targets in EU

AND industrial competitiveness, EU innovation, energy security, etc.



## The limiting (missing) factors

To increase the rate of RE introduction in the energy mix

#### Import RE from remote area

- develop effective chemical energy vectors (e.g. solar fuels) which are the equivalent to actual fossil-based vectors AND which can be introduced in the actual energy infrastructure without major (costly) changes; they should be easily stored and transported
- Stabilize grid (from fluctuations) and exploit "excess" (not used) RE sources
  - $\rightarrow$  seasonal / yearly storage ( $\rightarrow$  chemical energy vectors)
- Defossilization (rather than decarbonization) of the chemical production
  - nexus between chemistry and energy, bases for manufacture
  - electrify production, use alternative C-sources to fossil fuels
    → change in the model of production (distributed)





In spite of a decade of intensive research, only a small decrease in the overpotential, a measure of the energy loss in the process, has been obtained Most materials have properties that are well off the optimum value where the overpotential is lowest. We need to discover new classes of materials with completely new surface chemical properties.

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#### New scientific developments

#### New paradigm in materials discovery

- New synthesis with molecular scale precision
- New advanced characterization methods
- Theoretical/computational materials design
- Data-driven methods and machine leaning





## BUT science development should be linked to technology development & to demo units

In these critical areas still underdeveloped

#### Transport fuels

 complementary to the electrification, offering solutions where batteries are generally less effective, like e.g. for *long-distance transport* or for freight transport, energy transmission and grid stabilization services.

#### Chemicals and decentralised production

 production of chemicals by applying renewable electricity, decentralized production





## A timeline of energy nanomaterials

Solar fuels and chemicals

#### On short term

- Increase rate of RE share in energy mix:
  - Nanomaterials and technologies for chemical energy storage, to transport RE from long distance (& seasonal/yearly RE storage)
    - Green H<sub>2</sub> (higher performance, noble-metal free, nanostructured electrodes, scale-up electrodes) and CO<sub>2</sub>-energy vectors as CH<sub>3</sub>OH (higher productive cat., less sensible to deactivation, integration with electrolyzers)
- Defossilize chemical production:
  - Develop novel **waste to chemicals** technologies (with RE integration)
  - Power-to-X materials & technologies, to reuse CO<sub>2</sub> industrial emissions (with novel materials to recover CO<sub>2</sub>)
  - Energy valorisation of *low temperature streams*
- Develop the background **knowledge** for more efficient energy nanomat.
  - Comprehensive theoretical modelling of reaction systems, prediction of materials and processes, synthesis, kinetics, functional analysis
  - Understanding electro- and photo-catalysts & plasma-catalysis interaction

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## A timeline of energy nanomaterials

Solar fuels and chemicals

#### From short to medium term

- Develop pilot technologies to use science developments in electro- and photo-catalytic as well as plasma-catalytic processes
  - Low P (& T) ammonia synthesis (and materials for the *direct* electrocatalytic production of fertilizers)
  - Materials/processes for e-(bio)refineries
  - Advanced design of electrode (selectivity, high productivity) and novel methodologies for their (low cost, scalable) preparation
  - Use of non-critical raw materials in electrodes (and energy nanomat.)
- Technologies & processes to produce novel low-carbon fuels and chemicals (using energy vectors)
  - CO<sub>2</sub> (from biogas) and RE to biofuels (jet fuels, heavy tracks and ships)
  - Base raw materials for chemical production (olefins, aromatics) from energy vectors (as methanol)
- Novel **PEC** approaches (& related materials)
  - Effective photo/electro integration, robust design, scalable and industrially exploitable, higher T/P operations (for intensification)

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## **BACKUP SLIDES**

#### How integrate **RE** in chemical production

- Plasma (@catalysis)
- Microwave
- Photocatalysis
- Electrocatalysis (and photo-electro catalysis)

All these technologies are particularly suited for small-size (distributed) devices, i.e. systems which can be used up to a regional or district level, and for a circular economy

All above options are relevant to develop novel routes for a solar-driven chemistry, **electro-catalysis** is perhaps the **most advanced** presently for industrial implementations.

More advanced on crucial aspects such scalability to larger-size devices, which is actually the major limit of the other technologies.





## **Challenges and opportunities**

for electrocatalysis

- Identify disruptive processes for the new solar-driven chemistry scenario
- Creating an innovative landscape
- Pushing development of ground-breaking catalysts and catalysis concepts
- Process Intensification by electrocatalysis
- Opening of new value chains
- New reaction paths for the electrocatalytic conversion
- The role of surface confinement in the electrocatalytic conversion





#### The case of ammonia synthesis

The direct electrocatalytic ammonia (NH<sub>3</sub>) synthesis decreases by 93% the carbon footprint (e.g.  $CO_2$  emissions) from 1.83  $t_{CO2}/t_{NH3}$  in the actual ammonia production scheme to 0.12  $t_{CO2eq}/t_{NH3}$  in the direct synthesis, besides the *advantages* in terms of

- large reduction in the process steps,
- milder operations,
- elimination of the use of fossil fuels,
- suitability for distributed production (avoiding impact of large-scale) processes and relevant local impact, cost and impact of transporting ammonia),
- use for the chemical storage of excess renewable energy





#### Nature of iron species (Operando EXAFS)

A ferrihydrate (FeOOH) is present rather than a  $Fe_2O_3$  phase under working conditions, with the ferrihydrate nanoparticles located predominantly at the carbon defect sites.



Nature Comm. 2018, 9 (1), 935.



- **strained-FeOOH** nanorods exhibited enhanced catalytic water oxidation and FeOOH shows high electrocatalytic oxygen reduction activity. (Park et al., Nanoscale, 9 (2017) 4751; Luo et al., J Mater Chem A, 5 (2017) 2021
- In both cases, the behavior was associated to the specific surface configuration, able to give **multielectron transfer** in water oxidation and oxygen electrocatalytic reduction.

## A multielectron transfer

- To develop low temperature (and pressure) active electrocatalysts for direct NH<sub>3</sub> synthesis the direct hydrogenation of N<sub>2</sub> rather than first dissociation is a preferable route, because N<sub>2</sub> dissociation would be hardly realized under mild conditions where the catalytic chemistry is dominated from the strongly bounded species.
- However, the direct hydrogenation of N<sub>2</sub> would generate high-energy intermediate (N<sub>2</sub>H, N<sub>2</sub>H<sub>2</sub>). The reduction potential of

 $N_2 + H^+ + e^- \rightarrow N_2 H$ 

is -3.2 V vs. NHE, while -1.83 V vs. NHE in the 2-e reduction process

 $N_2 + 2H_2O + 4H^+ + 2e^- \rightarrow 2NH_3OH^+$ 

#### For multi-electron reduction process, for example

$$N_2 + 5H^+ + 4e^- \rightarrow N_2H_5^+$$
$$N_2 + 8H^+ + 6e^- \rightarrow 2NH_4^+$$

the reduction potential becomes -0.23 V and 0.274 V vs. NHE, respectively

## How realize a multi e<sup>-</sup>/H<sup>+</sup> transfer

- Common approach: realize biomimetic analogous (of nitrogenase Fe-Mo) metal complexes 

   how synchronize the simultaneous transfer
  - LIMITS: stability and productivity (per electrode area), loading on the electrode, …
- Alternative possibility:
  - localized electrons in oxygen vacancies are active to adsorb N<sub>2</sub> by electron donation
  - tightly bound excitons can capture additional electrons to form charged excitons (such as trions, i.e. e<sup>-</sup>h<sup>+</sup>e<sup>-</sup>)
    - These charged excitons with two or more electrons in one bound state, may act as electron-rich species to facilitate a multi-electron reduction process of molecular N<sub>2</sub>.



## **LONG-TERM: artificial leaves**

Combine H<sup>+</sup>/e<sup>-</sup> solar production with direct use to produce fuels/chemicals





#### Engineering of the photoanodes based on ordered TiO<sub>2</sub>-nanotube (TNT) array

as a function of NtTiO<sub>2</sub> thickness and characteristics

- The best tested photo-catalyst was the one-hour TNT
  - 1.60 % STH efficiency (solar-to-hydrogen efficiency)
  - 99.2 % Faradaic efficiency
  - 65 % IPCE (λ=330 nm): incident photon to current conversion efficiency
- Between the best reported for PECa cells using undoped TiO<sub>2</sub> photoanodes & absence of external bias or sacrificial agents.



#### Solar-to-hydrogen efficiency (STH) H<sub>2</sub> production rate **STH efficiency Photoanode Incident light** $(mmol h^{-1})$ (%) TNT Open spectrum 85.5 1.68 Solar (AM 1.5G) TNT 7.8 0.24 **CuO-TNT** 2.04 **Open spectrum** 104.3 0.53 **CuO-TNT** Solar (AM 1.5G) 17.4

## CO<sub>2</sub> reduction in a PEC full cell

current generated during this experiment  $\rightarrow$  0.2 mA

GDL/Cu<sub>2</sub>O-Cu as cathode and NtTiO<sub>2</sub>/CuO as photoanode



- formate in this case is not the preferential product formed
- after 24 h the concentration of acetate and formate are similar, reaching 0.027 and 0.020 mmol L<sup>-1</sup>, respectively



 We are moving to a new scenario for chem. and energy production, which requires to develop new route and technologies



- Solar-driven chemistry and energy represents the vision of the future
- smaller, cleaner, safer and more energy efficient technologies: the next revolution of the chemical industry to significant increase the resource and energy efficiency.
  - there is the need to develop the catalysts, technologies, processes able to use directly photons, electronics, etc. for chemical synthesis or energy storage
    - we need to develop the knowledge to make possible this change which drivers, however, are external









## Outline

#### Why beyond fossil fuels

- The new scenario for energy and chemistry
- Motivations and outlooks

#### The use of alternatives feedstocks

- short-term: MSW to urea and methanol (motivations, economics)
- *medium-term:* CO<sub>2</sub> as C-source and energy-vector (to enhance RE use)
- Iong-term: artificial-leaf

#### Conclusions

While different technologies will be necessary in a longer term (electro-, photo- ...), there is the need of also short-term technologies to start transition

) PRODUCTION

LONG

MEDIUM

SHORT

## Oil peak and energy transition

forecast for oil demand over the next 25-30 years from a variety of public and private sector organizations 135



#### **BP Energy Outlook 2018**

wide range of estimates of the point at which oil demand is likely to peak

 "there is little reason to believe that once it does peak, that oil demand will fall sharply. The world is likely to demand large quantities of oil for many decades to come."

#### BUT

- these predictions catch the real trend in a complex economy with an on-going transition ?
- it is the correct way to analyse timing for the transition, and to prepare the related technologies?

#### What is the cost of oil barrel



70-80 US\$

cost associated to sustain the economies of the extracting countries

Diesel 10.04 **Other Distillates** 1.24 Jet Fuel **Other Products** Heavy Fuel Oil (Resid Liquified Petroleum Gases (LPG) 1.72 Gasoline 19.36

cost of production

even considering market expansion, there is a decrease in request for mobility and residential / industrial due to progress in renewable energies

an increasing cost

## Energy Return On Investment (EROI)



Solar PV EROI	<i>2013</i>	<i>2018</i>	<i>2025</i>
Increase effic.	6	12-15	> 20-25
Coal EROI	<i>2013</i>	<i>2018</i>	<i>2025</i>
incl. env. costs	8.7	~5	< 2



EROI will be soon not longer advantageous for fossil resources



- Bottom-up method: modification of synthesis
- Top-down method: post-synthesis treatment (demetallation, delamination)

#### Drawbacks

- o Acidity loss
- o Defects insertion
- Valid for an optimal Si/Al range (in other cases, need to add pore directing agents)
- Time consuming/larger volumes



Ni/Beta-75 before and after pyridine adsorption

Ni/Beta-75 Des before and after pyridine adsorption

quantimeation of Brønsted and Lewis dela sites				
Brönsted sites [µmol/g]	Lewis sites [µmol/g]			
19.5	257.6			
162.8	17.8			
153.5	49.1			
145.7	83.1			
	Brönsted sites [μmol/g] 19.5 162.8 153.5 145.7			

#### quantification of Brønsted and Lewis acid sites

Amorphous silica-alumina, presents the highest acidity with a major contribution of the Lewis sites and a very low Brönsted acidity (19.5 μmol/g), while for the other supports Brönsted acidity drastically increase. FT-IR data confirm that the **desilication** treatment leads to a slight increase of the total acidity, introducing **prevalently Lewis acidic** sites.



- Strong influence of the acidity and apparently no correlation with MSA;
- The conversion of MP shows a max for an intermediate number of acidic sites;
- The low conversion with the Ni/SBA-15 confirms that the prevailing mechanism for production of n-C15 and n-C16, in presence of acidic sites, goes through PA as intermediate (the HDO reaction thus requires an acid function together with the hydrogenation one).

## Conclusions (zeolies for algal oil)

#### HDO and selective hydrocracking of methyl palmitate

- the localization of Ni particles, when located inside the zeolite channels show lower performances;
- the acidity of the zeolite (Brønsted acidity is necessary together with the hydrogenation function related to Ni);
- the presence of mesoporosity is necessary to provide a mechanism of selective cracking, via likely a pore mouth reaction mechanism.

#### > Hydroisomerization/hydrocracking of n-hexadecane

 the introduction of controlled mesoporosity increases the activity and the selectivity to most valuable cut (C11-C15) and leads to the formation of carbon species easily oxidable.



#### Hydroisomerization/hydrocracking of nhexadecane

- The results, although limited to n-hexadecane, indicate that Ni/Des H-Beta has good characteristics for the combined production of green jet fuels and diesel.
- The use of Beta rather than MFI (ZSM-5) **reduces** significantly the **rate of coke formation**, which is further decreased by the **introduction of mesoporosity** (desilication). In addition, the latter treatment **reduces the hardness of carbon** and thus facilitates its removal by oxygen treatment.
- The acidity of the catalyst has a major effect on hydro-reactions.
  - The deposition of Ni on ASA (higher number of total acid sites, with negligible Brönsted and high Lewis acidity), leads to a catalyst with much lower activity than its **zeolitic** counterparts.
  - The better catalytic performance are obtained with H-MFI, which exhibits mainly Brönsted acidity, but with an unacceptable gas formation and very low hydroisomerization activity
  - A high catalytic activity is also observed for H-Beta which possess a concentration of Brönsted sites similar to H-MFI. The performance of Beta catalysts is enhanced after *desilication*, although Brönsted acidity is only slightly modified.
  - The introduction of mesoporosity by desilication enhances the activity, while still maintaining an acceptable gas formation and good hydroisomerization properties.

behaviour is likely related to both acid strength and proximity between acid sites and hydrogenation functions within the zeolite crystals; reducibility of Ni seems not a critical parameter



## **SHORT-TERM:** THE VALORIZATION OF WASTE RESOURCES

#### WASTE TO CHEMICALS

It is techno-economic and environmental feasible?



# Waste-to-chemicals for a circular economy ⇒ waste-to-urea

#### Urea: Nitrogen product of choice representing 60% of total N fertilizer use



## **Urea production cost**

Urea price variation in the last ten years



*To great variability and dependence on NG costs, Price advantage of countries with NG reserve* 

## Municipal Solid Waste (MSW): a diffused, underused, C source

Rapid urban population growth has resulted in a number of challenges, including municipal solid-waste management. National and municipal governments often have insufficient capacity or funding to meet the growing demand for solid-waste management services. Solid-waste management is the single largest budget item for many cities





ChemSusChem, 2016 10 (5), 912-920

## Population density to feed the plant

#### RdF feed of 700 ton/d

- average MSW annual production per habitant (475 kg) ⇒ 40% of RdF production from MSW ⇒ about 1.1 Million persons would be necessary to produce a RdF feed of 700 ton/d.
- considering that transport of RdF should be limited ≤ 100 km ⇒ population density of about 35 persons/km<sup>2</sup>



#### **Economics assessment**

Cost of production and income per ton of urea, estimated cost (**COP**) for the production of urea from waste in a 500 MTPD plant starting from RdF

Category		M€ per year		
COSTS				
Power		9,7	The estimated profit per ton	
Slag disposal		0,9	of urea is in the range of	
Maintenance		7,0	90€; <b>IRR</b> (Internal rate of	
Depreciation		30,4	return) of the project is in	
Other costs (well demiwater)		2,0	the range of 11-12%, which	
Labor		4,0	profitability of the waste-to- urea approach.	
TOTAL COSTS		54,0		
INCOMES				
RdF (avoided disposal)		24,5		
CO <sub>2</sub> avoided		1,95	15€ per ton of CO <sub>2</sub>	
Excess CO <sub>2</sub> for Bio-CSS		3,85	25€ per ton of CO <sub>2</sub>	
TOTAL INCOMES		30,3 M€ per year		
Yearly urea production		175000 MTPY		
СОР		135 € per ton of urea		
	The largest part of the cost of production in the waste-to-urea			

technology is associated to the depreciation + maintenance term, constituting almost 70% of the overall costs 2/2

#### **Environmental impact analysis**

#### comparison of the conventional vs. waste-to-urea – WtU

- CO<sub>2</sub> is produced in an amount about three times higher in the WtU technology with respect to the conventional, but in a form easy usable for other applications (in liquid form), while is present diluted in the flue gases (together with other pollutants as NOx) in the conventional technology.
- Around 190 MTPD of methane should be fed in the conventional process instead of about 700 MTPD of RdF in the WtU approach
  - RdF is a waste produced anyway which should be thus disposed ⇒
    WtE (waste to energy) ⇒ net effect is thus conventional + WtE WtU



a saving of about 0,113 tons  $CH_4$  and about 0,78 tons  $CO_2$  per ton urea produced



#### Waste to Chemicals for a Circular Economy Syngas Purification Gasifier $+ CO_{y}/H_{2}$ Adjustment MSW (RDF) gas FT FTO fermentation WGS urea $\stackrel{CO_2}{\longleftarrow}$ NH<sub>3</sub> $\stackrel{N_2}{\longleftarrow}$ H<sub>2</sub> hydrocarbons Ethanol CH<sub>3</sub>OH CH<sub>4</sub> (olefins) (methatesis) DME Polyolefins MTO/MTP (LDPP)

Cost of production of various chemicals via the waste-to-chemical concept				
	Cost of	Average product		

Chemical	Cost of production, €	Average proauct value, €
Urea, €/t	135	225
Methanol, €/t	150	325
Low density polypropylene, €/t	550	1000
H₂, €/Nm³	0,07	0,12
CH₄, €/Nm³	0,16	0,25

# CO<sub>2</sub> as a waste resource

## CO<sub>2</sub> to SNG (catalysis)



## 100% fossil-free Denmark

100% Renewable Power and Heat by 2035, 100% Renewable Energy in All Sectors by 2050

- Danish Energy Agency report: Energy Scenarios for 2020, 2035 and 2050
  - Different scenarios, but the most likely will be a mix of about 50% from wind and 50% of SNG from biogas
  - Nov. 2017: signed an agreement that 100% of the gas in the gas grid will be green by 2035.





#### High CO<sub>2</sub> gas fields offshore

- Exploitation of high CO<sub>2</sub> NG fields is one of the new challenges for E&P companies worldwide
  - High CO<sub>2</sub> content gas reservoirs make most of the gas field development uneconomical and it has remained undeveloped.
- Methanation of CO<sub>2</sub> offers new possibilities to increase economics of these high CO<sub>2</sub> fields and at the same time to meet the increasing gas demand.



## **CO<sub>2</sub> catalytic methanation**

THE SCIENTIFIC CHALLENGE

- The Sabatier reaction known from a century
- A reversible exothermic reaction

 $\text{CO}_2 + 4\text{H}_2 \leftrightarrows \text{CH}_4 + 2\text{H}_2\text{O}$ 

#### • The scientific issue:

To meet in one-pass through reactor the SNG specifications (for grid injection) H<sub>2</sub> (residual) < 5%, CO<sub>2</sub> < 3%, ....), taking into account that it is a reversible exothermic reaction, it is necessary to operate at a maximum temperature (reactor outlet) of about 320°C</p>

• MOST of the literature data are at HIGHER temperatures

- These low-temperature of operation induce also problems of longterm stability, because due to high chemisorption of CO<sub>2</sub> & H<sub>2</sub>O at these temperatures, *reconstruction* of the catalyst may occurs
- "Commercial" catalysts, derives from syngas methanation catalysts, contain very high (up to 70-80%) amounts of Ni (potential critical raw material, due to high economic importance)

#### Ni-based nanosheet-type catalysts

Ni nanoparticles (11-12 nm) on Fe-doped MgAIO<sub>x</sub> nanosheets



SEM images of (a) 25%Ni-Al<sub>2</sub>O<sub>3</sub>-NS and (b) 25%Ni-**2.5%Fe**-Al<sub>2</sub>O<sub>3</sub>-NS.

nanosheet-type catalyst

#### CO<sub>2</sub> methanation catalysts: stability at low temperature



- stabilization of small Ni nanoparticles on a highly accessible surface, associated to the nanosheet structure, leads to higher specific activity per Ni amount;
- enhanced stability associated to the fact that at these low temperatures, due to the water formed during methanation, Ni particles tend to form **Ni-hydroxide**, reducing thus availability of metallic Ni for the methanation reaction.

#### How integrate **RE** in chemical production

- Plasma (@catalysis)
- Microwave
- Photocatalysis
- Electrocatalysis (and photo-electro catalysis)

All these technologies are particularly suited for small-size (distributed) devices, i.e. systems which can be used up to a regional or district level, and for a circular economy

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More advanced on crucial aspects such scalability to larger-size devices, which is actually the major limit of the other technologies.



#### Solar fuels and chemicals

Solar is the most abundant (and environmental clean) energy source



**Solar fuels (& chemicals)** represent the **bridging element** to connect solar (& related) energy to the products (and current infrastructure) at the basis of our life

## Transformative chemistry and energy

- Main impact on economy: a sustainable model '
  - change the production model: from fossil fuels as and energy-source to the use of alternative C-sources in strong symbiosis with the use of renewable energy

⇒FOSTER INNOVATION:

– current production model (*low rate of new processes*),
 because based on the economy of scale → large plant sites (environ. & societal issues) → need of heat integration

⇒INDUSTRIAL IMPACT:

- to a **distributed** model, with easy scalable (parallelized approach), faster time to marked and high flexible processes
- a distributed model will favor new investors and create a positive impact on innovation → new economic model





#### Solar Fuels and Chemicals



Economics evolve faster than predicted

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PhotovoltaicElectricity in Power Purchase Agreements



#### Solar fuels and chemicals

#### Bridging the transition to a new solar economy



## **Challenges and opportunities**

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![](_page_60_Picture_9.jpeg)