

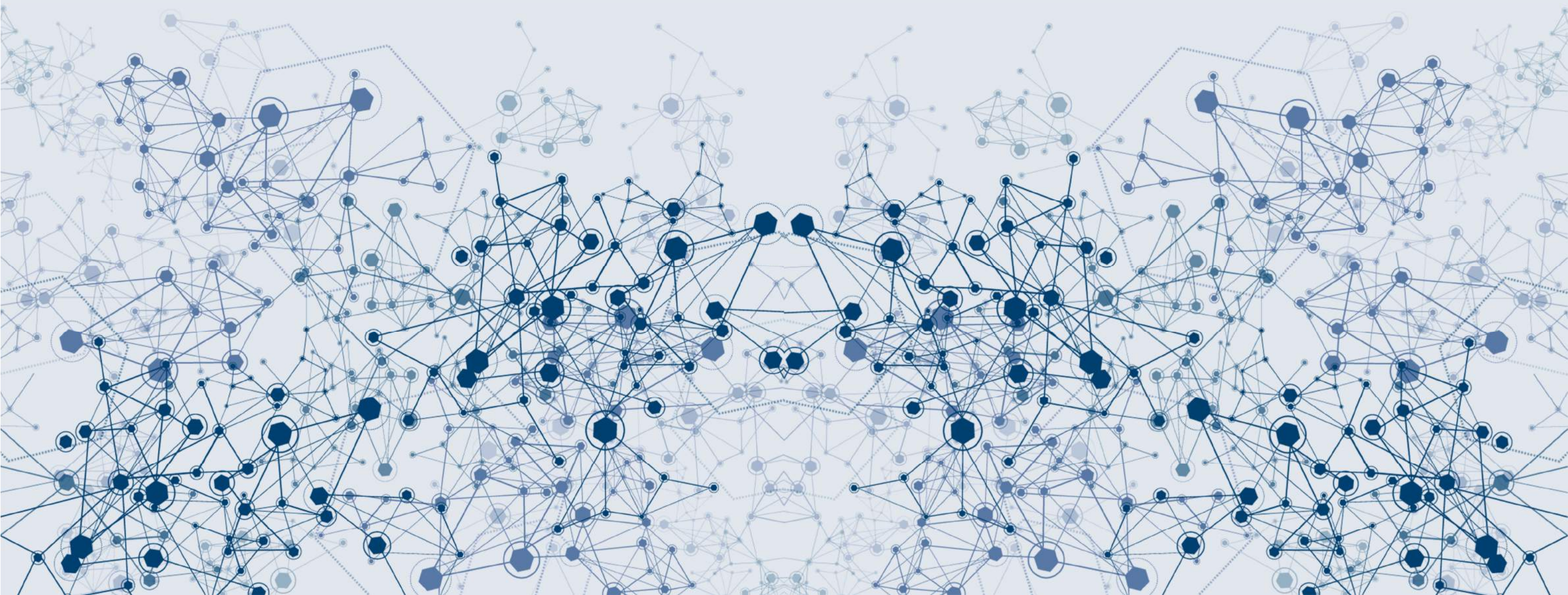
SCIENCE AND TECHNOLOGY ROADMAP ON CATALYSIS FOR EUROPE

A PATH TO CREATE A SUSTAINABLE FUTURE

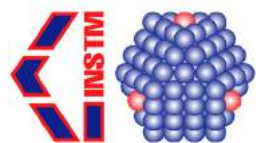
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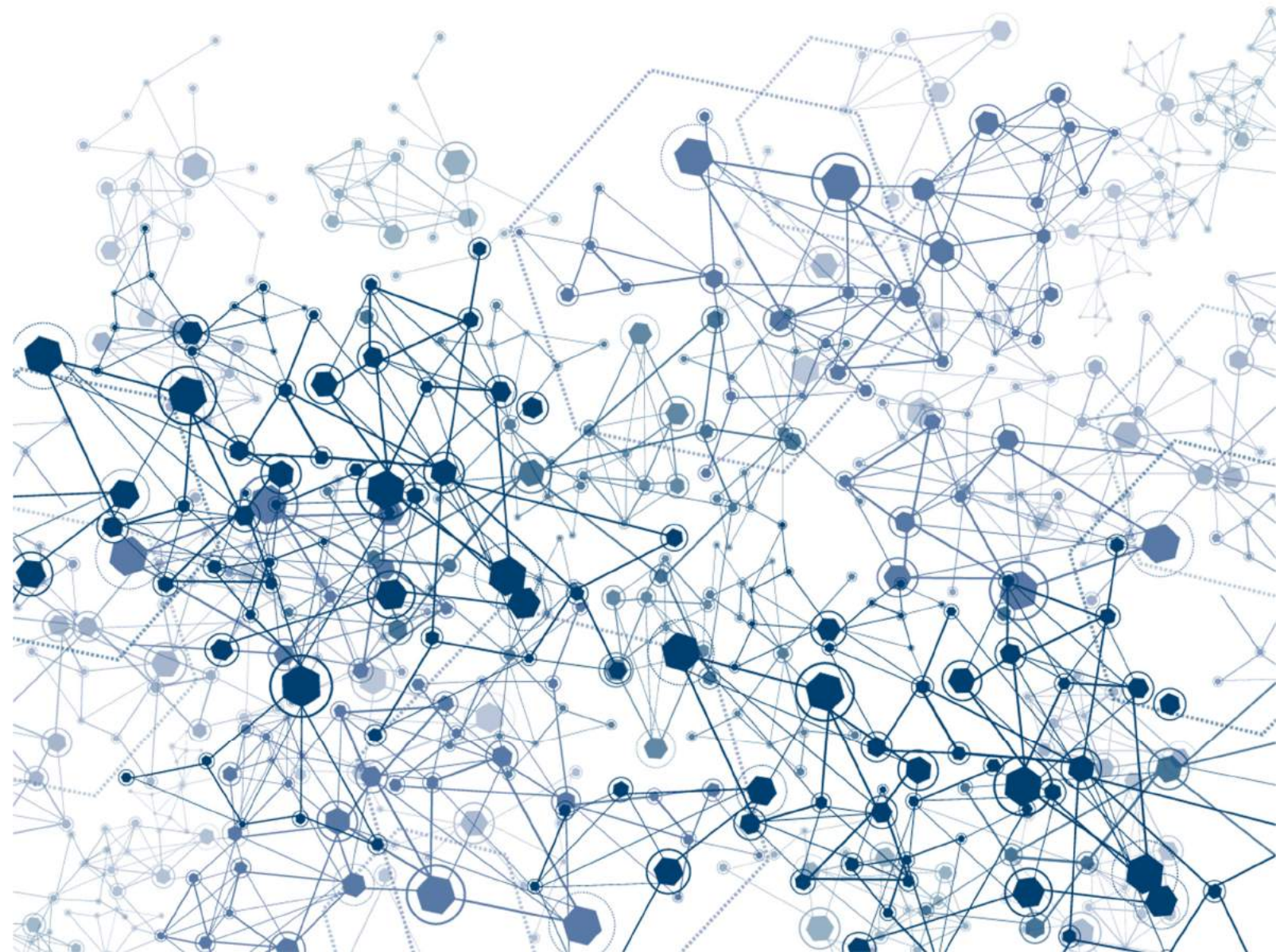
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CONTENTS

Contributors list (in alphabetical order) **1**
 Acronyms list **4**
 Foreword of the European Commission **6**
 Preface **7**
 The methodological approach for roadmap **10**

THE VISION AND SCENARIO ANALYSIS 13

- 1. Catalysis, setting the scene for an evolving scenario 13**
 - 1.1 The Energy-Chemistry Nexus **15**
 - 1.2 Moving to a new sustainable energy scenario **16**
 - 1.2.1 Energy storage: from smart grids to chemical storage of energy **16**
 - 1.3 A new vision for refineries **17**
 - 1.3.1 Renewable H₂ as key building block for sustainable chemistry and energy production **19**
 - 1.4 Bio-refineries and bio-factories **19**
 - 1.4.1 CO₂ a key carbon source element **22**
 - 1.5 Methanol: at the crossover of new energy-chemistry nexus **23**
 - 1.6 Exploiting shale-gas **24**
 - 1.7 Bio-gas-based chemistry **27**
 - 1.8 Solar-driven chemistry **27**
 - 1.8.1 Catalysis for sustainable energy **28**
 - 1.9 Structured catalysts for process intensification **28**
 - 1.9.1 Process intensification by molecular catalysis **29**

Conclusions 29

HIGH LEVEL GOALS 31

2. Grand challenges for catalysis 31

- 2.1 Catalysis to address the evolving energy and chemical scenario **34**
- 2.2 Catalysis for a cleaner and sustainable future **35**
- 2.3 Addressing catalysis complexity **35**
 - 2.3.1 Advanced design of novel catalysts **35**
 - 2.3.2 Understanding catalysts from molecular to material scale **36**
 - 2.3.3 Expanding catalysis concepts **36**

**THE STRATEGIC RESEARCH AGENDA AND IMPLEMENTATION
PLAN 39**

3. Catalysis to address the evolving energy and chemical scenario 39

- 3.1 Challenges and Opportunities for Catalysis 42
 - 3.1.1 Fossil raw materials 42
 - 3.1.2 Bio-mass and Renewable Resources 45
 - 3.1.3 CO₂ Conversion and Solar Energy Storage 50
 - 3.1.4 Energy storage and conversion 54
- 3.2 Research needs and expected outputs 57

4. Catalysis for a cleaner and sustainable future 61

- 4.1 Challenges and Opportunities for Catalysis **63**
 - 4.1.1 Catalysis for eco-technologies **63**
 - 4.1.2 Catalysis to improve sustainability of chemical processes **67**
- 4.2 Research needs and expected outputs **79**
 - 4.2.1 Catalysis for eco-technologies **79**
 - 4.2.2 Catalysis to improve sustainability of chemical processes **81**

5. Addressing catalysis complexity 87

- 5.1 Challenges and Opportunities for Catalysis **89**
 - 5.1.1 Advanced design of novel catalysts **89**
 - 5.1.2 Understanding catalysts from molecular to material scale **92**
 - 5.1.3 Expanding catalysis concepts **94**
- 5.2 Research needs and expected outputs **98**
 - 5.2.1 Optimal control over chemical systems and reactions **98**
 - 5.2.2 Predictive modelling **98**
 - 5.2.3 Understanding complex and real systems **99**
 - 5.2.4 Integrated Multi-Catalyst/Multi-Reactor Systems **100**
 - 5.2.5 Fundamentals and Methodology **101**

Appendix A - Standardization, Regulation, Safety Issues **102**

Appendix B - International Cooperation **106**

Appendix C - Training & Education, Dissemination, Popularisation in the field of catalysis **107**

KEYWORDS 109

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ACRONYMS LIST

3G	Third generation	HOZ	Hierarchically organised zeolite
AIPO	Aluminophosphate	HSE	Health, safety and environment
APR	Aqueous phase reforming	HT	High-throughput (experimentation)
APU	Auxiliary power unit	IL	Ionic Liquid
ATR	Autothermal reforming	IR	Infrared
CAPEX	Capital expenditure	KET	Key enabling technologies
CCS	Carbon capture/subsequent sequestration	LA	Levulinic acid
CHA	Chabasite	LCA	Life Cycle Assessment
CO₂-eq	Carbon dioxide equivalent	LOHC	Liquid Organic Hydrogen Carriers
COF	Covalent organic framework	LPG	Liquefied petroleum gas
CRM	Critical raw materials	MIEC	Mixed ionic–electronic conducting ceramic
CSF	Catalytic Soot Filters	MOF	Metal organic framework
CWA	Chemical Warfare Agents	MTA	Methanol to aromatics
DES	Deep eutectic solvent	MTBE	Merhyl tert-butyl ether
DFT	Density functional theory	MTH	Methanol to hydrocarbon
DMC	Dimethyl carbonate	MTD	Methanol to olefin
DME	Dimethyl ether	MTP	Methanol to propylene
DMFC	Direct alcohol fuel cell	NG	Natural gas
DOC	Diesel Oxidation Catalysts	NMR	Nuclear magnetic resonance
EJ	Exajoules	OCM	Oxidative coupling of methane
EMCC	European Materials Modelling Council	OME	Oxymethylene ethers
EPR	Electron paramagnetic resonance	PAH	Polyaromatic hydrocarbon
FCC	Fluid Catalytic Cracking	PCET	Coupled transfer of multiple electrons and proton
FDA	Food and drug administration	PEC	Photoelectrochemical or photoelectrocatalytic (PECa)
FFR	Furfural	PEG	Polyethylene glycol
FT	Fischer Tropsch	PEM	Proton exchange membrane (fuel cell)
GDP	Gross Domestic Product	PGM	Platinum group metals
GHG	Greenhouse Gases	PHA	Polyhydroxyalkanoate
Gt	Giga Tons	PI	Process intensification
HDO	Hydro-deoxygenation	PM2.5	Particulate matter below 2.5 microns
HGO	Heavy gasoil	PO	Polyolefin

R&D	Research and Development
RCL	Rich-catalytic lean-burn combustion
RE	Renewable energy
REACH	Registration, evaluation, authorisation of chemicals
rH₂	Renewable H ₂
RWGS	Reverse Water Gas Shift
SAPD	Silicoaluminophosphate
SARA-ATRP	Supplemental Activator and Reducing Agent Atom Transfer Radical Polymerization
SCR	Selective Catalytic Reduction
sc-CO₂	Supercritical carbon dioxide
SET-LRP	Single-Electron Transfer Living Radical Polymerisation
SOFC	Solid oxide fuel cells
SR	Steam Reforming
syngas	Mixture of CO and H ₂
TOF	Turnover frequencies
TON	Turnover numbers
VFA	Volatile fatty acid
VOC	Volatile organic compound
XAS/XES	X-ray absorption / emission spectroscopy
XFEL	X-Ray free-electron laser
WGS	Water Gas Shift

FOREWORD OF THE EUROPEAN COMMISSION

Our society is profoundly influenced by advanced materials and technologies. Materials have helped to raise our standard of living, but new challenges steadily emerge and novel materials and properties are demanded, representing a key element of the success of tomorrow's industrial products and competitiveness of European industry. Complexity permeates more and more our world and simple mechanical technologies are increasingly being replaced by invisible and intelligent materials with tailor-made properties. An integrated approach is needed and materials have to be developed and used taking into account the entire life-cycle of resulting products and processes as well as the corresponding raw materials and the carbon footprint, while technical efficiency and economic rationality will continue being essential issues.

In this respect, catalysis is one of the utmost cross-cutting and key enabling discipline in chemical industry. Catalytic materials are crucial to reduce today's and future environmental burdens and can help to make products greener and more sustainable, to reduce CO₂ emissions or to address future energy challenges.

All this represents a considerable challenge for research policy-makers who are called upon intervening through legislation and administration: research financing, technological investments, regulation, industrial policy and many more.

financing, technological investments, regulation, industrial policy and many more.

The first **'Science and Technology Roadmap on Catalysis for Europe'** can provide valuable input for the elaboration of future research policies which are oriented towards technical efficiency and economic rationality but which also considers the social and ecological consequences of the introduction of specific technologies and novel materials.

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PREFACE

The **European Cluster on Catalysis** (www.catalysiscluster.eu) has been created in January 2015 by the European Commission with the aim to develop a **European Roadmap on Catalysis** which provides a long term vision and action plan to support catalysis research in the EU. The project was initially based on existing EU-funded projects with a significant catalysis signature and later extended to several institutions, organisations and companies, all supporting this initiative to promote catalysis research. The Cluster is conceived as an **open and dynamic platform** accessible to all players and stakeholders, both from academia and industry, whose activity is focused on catalysis and its applications. This **Science and Technology Roadmap on Catalysis for Europe** is the result of the efforts within the European Cluster on Catalysis and a public consultancy of all stakeholders. A major theme of interest was to promote the central role of catalysis as key technology to a sustainable future.

Further input to this process were *recent national roadmaps* from the Netherlands and Germany (*Science and Technology Roadmap for Catalysis in the Netherlands* - Jan. 2015, and *Roadmap of Catalysis Research in Germany*, March 2010), Important stakeholders in the roadmapping process, besides the Cluster participants were ERIC aisbl, the European Research Institute of Catalysis, ENMIX, the European Nanoporous Materials Institute of Excellence, ERA-NETs (Acenet and Capita), SusChem and CEFIC ([European Chemical Industry Council](http://EuropeanChemicalIndustryCouncil.org)). In addition, the recent position paper on "Catalytic oxidation as a key technology", prepared in October 2015 by the German

German Catalysis Society, has been also considered in writing the present Roadmap.

The broader perspective was safeguarded by considering roadmaps where catalysis also plays a role, in particular, the SPIRE (*Sustainable Process Industry through Resource and Energy Efficiency*) Roadmap (2012), the *Technology Roadmap on Energy and GHG Reductions in the Chemical Industry via Catalytic Processes* (Dechema/IEA/ICCA, 2013) and the roadmap on *Chemical Sciences and Engineering Grand Challenges* in UK (EPSRC/ICHEME/RSC, 2009). Finally, it includes indications from the EuChemS and DFG initiative on "Solar-driven Chemistry" (2015), related to the vision for chemistry in 30 years from now, and from "Solar Fuels and Artificial Photosynthesis - Science and innovation to change our future energy options" report produced by the Royal Society of Chemistry (2012).

Other reference materials are the book edited by Robert Davis "International Assessment of Research and Development in Catalysis by Nanostructured Materials" (World Scientific Pub., 2011), and the Vision Paper 2025 "Chemistry & Physics: Fundamental for our Future" (The Netherlands, 2013).

A particular aim of the present roadmap is to *harmonise, merge and update these roadmaps and put forward a more general common vision for Europe*, shared by both companies and research Institutions, entailing fundamental and applied research on catalysis. Derived from this, this roadmap aims to better define the priorities and objectives for future research on catalysis and to underline its impact on society and sustainable industrial production in Europe. This shared roadmap will form the basis to identify ac-

tions needed to promote the role of catalysis as *key enabling discipline for a sustainable future of our society. A specific goal is to define* topics relevant for H2020 calls aimed at creating the path for this sustainable future.

This effort, as for all roadmap activities, is dynamic and the aim is to continue to periodically update the Roadmap, to include new emerging aspects, and to follow closely the evolving scenario present in energy vectors and chemicals industrial production. A related objective of this Roadmap is to *maximise the social and environmental impact through the development of improved catalytic material & processes*, as extensively outlined in the introduction of chapter 1. To cope with these challenges, it is essential to *foster and tighten the synergy between fundamental research and technological applications*. Relevant aspects here include the integration of new materials, molecular chemistry and biosciences.

All of these aspects should preferably be addressed in an *integrative manner*. A key characteristic of catalysis as a scientific discipline is its **interdisciplinary** nature. Successful realisation of new catalytic solutions and technologies requires to integrate knowledge and expertise from fundamental (chemistry, physics, biology, mathematics, etc.) areas to engineering (chemical and material engineering) and applied (industrial chemistry, etc.) aspects. Integration of *a priori* theoretical modelling with *in-situ/operando* studies to understand the reaction mechanism, science of catalyst preparation at nanoscale level, advanced micro-kinetics and reactor modelling are examples of the current trends in catalysis. Another challenge is to reach a **unified approach** for homogeneous, heterogeneous and bio-catalysis. All these aspects are elements of the generic challenge

of "catalyst by design".

Currently, the field of catalysis is moving from description to prediction. A *more rational approach to the development of new catalytic materials* for chemical processes is in demand. Important elements of such an approach are computational modelling of catalytic processes at various length- and time-scales and advanced synthetic approaches aimed at delivering materials with improved catalytic performance, preferably starting from cheap, earth-abundant and easily accessible raw building blocks. A representative example of this concept are carbon-based nanomaterials doped with light heteroelements, which represent a class of catalytic (noble) metal-free systems promising to catalyse a number of key chemical transformations at the heart of renewable and environmental technology. The last few years have witnessed an impressive number of applications of these metal-free systems in catalysis.

The **catalysis by design approach** mostly refers to model/ideal systems. There is a great need to apply these methods also to the synthesis of materials so that the concept of the ideal active site can be realised in scalable production of catalysts. Vice versa, it is highly desirable to understand the operation of relevant technical catalytic solids for which *in-situ/operando* spectroscopy/microscopy are ideally suited. Together, these approaches can lead to a real *bottom-up approach to the catalyst by design* by *merging the gap between theory and experiment*. These goals can only be met by joining expertise in synthetic (organic and inorganic) chemistry in the context of materials science, theoretical modelling, physical chemistry and engineering.

Although heterogeneous (solid) catalysis will likely still dominate future industrial uses of catalysis, it is evident that many of the new challenges facing catalysis, from the use of solar energy to the use of bio-mass,

bio-mass, require **integrating homogeneous, heterogeneous and bio-catalysis**. It is thus of critical relevance to foster this integration and develop a common vision between these scientific areas and overcome the remaining barriers.

In line with remarks made in the position paper of the German Catalysis Society on **catalytic oxidation**, it is emphasised that there is a desire to support research efforts also in the more consolidated areas (e.g., catalytic selective oxidation) from the perspective that **a knowledge-driven realisation of a sustainable future will be largely based on the capacity to rationalise the current developments**. A case in point is the ability of industrial catalysts to perform extremely complex reactions with high selectivity, e.g., the 14 electron oxidation of n-butane to maleic anhydride. Understanding better such complex aspects may represent the key to realise other single-stage catalytic transformations, which is the core element for process intensification and reduction of energy/process costs. For instance, understanding how to selectively activate the C-H bond in alkanes is a key to develop selective methane upgrading, a long-standing challenge to the chemical industry. *Looking into the future requires rationalising better the past*. There are no mature areas in catalysis, but only mature ways to look at catalysis.

To summarise: The importance of a *tailored* approach to materials design is stressed with a view of understanding the way catalytic solids operate at the atomic level in the reactive cycle. This will allow moving faster toward the development of designed catalytic systems capable to perform more efficiently specific energy- and environmental-demanding catalytic transformations. This requires systematic feedback between theoretical modelling, in-situ/operando characterisation and

experimental kinetics to progress beyond the "trial-and error" approach toward rational catalyst design.

Among the **emerging issues in catalysts design**, it is worth to highlight:

- Cooperativity in catalysis,
 - * the interaction between transition metal centres and the surrounding ligands (e.g., non-innocent organic moieties in homogeneous catalysts, supports and ligands in heterogeneous catalysts) and their role in the catalytic cycle.
 - * synergies between the main-group chemistry and transition metal chemistry leading to novel reactivity concepts, e.g., by unusual bonding modes.
- Combining molecular catalysts with other areas of catalysis: for example, tandem catalysis combining a homogeneous or heterogeneous catalyst and an enzymatic catalyst.
- Address structured/hierarchical catalysts including bifunctional catalysts and complex reactor design.
- Tailoring innovative nanocomposite catalysts and electro-catalysts by exploiting 2D active layers (beyond graphene). Herein chalcogenides, 2D oxides, monolayer catalysts and nanocarbons can be included.
- Novel synthetic strategies to break, in a specific substrate, strong bonds in place of weaker ones.
- Developing life cycle assessment (LCA) to orient design in catalysis.
- Developing heterogeneous (sub) nanocatalysts prepared with atomic-scale precision.

In the context of **resources**, there will be a greater diversity of feedstocks and related

processes used by the chemicals and fuel industry (gas & oil remote fields, bio-mass gasification/pyrolysis, fermentation). As a consequence, the availability and purities of building blocks can vary drastically depending on the location. The processes to concentrate and purify these building blocks to acceptable levels for state of the art catalytic processes usually penalises their energy efficiency and significantly increases investment costs.

Advances in the development of **nano-architected catalysts** and other nanostructured materials have opened new possibilities to reach these objectives, by developing innovative solutions in order to realise in one stage complex multi-step separation/concentration and reaction processes, to selectively convert raw materials while preventing other components and impurities to react and eventually degrade catalytic performances. **Catalyst design** shall combine different functions of separation, concentration and reactions at different length scales. The separation/concentration could be carried out by selective transport through a permeable (protective) shell or membrane which allows selectively the transport of reactants and products and limit/prevent the diffusions of unwanted substrates toward the catalytic centres.

In conclusion, this roadmap and the activities of the European Cluster of Catalysts have the ambitious objective to define the **new path to create a sustainable future through catalysis**. The process is bottom-up as it started with national roadmaps and inputs from across all Europe involving academia, industry and different organisations. The aim is to develop a common broad vision and highlight strategies to reach the challenges facing industry and society in a transitional period to a new economic cycle.

THE METHODOLOGICAL APPROACH FOR ROADMAP

An effective roadmap requires **combining bottom- and top-down elements** and to **integrate the industrial needs with fundamental aspects and more long-term visionary elements**. This is the approach used in this roadmap which started from the identification of the needs to create a sustainable, innovative and competitive development and of the role of catalysis to realise these challenges. For this reason, we have also preferred to not discuss specific reactions (for example, the C-H activation), being this an element of the general challenge of using alternative raw materials such as shale-gas. There are, however, general methodologies in catalysis, such as a better theoretical modelling or improved techniques for *in-situ/operando* studies which are critical to enable the possibility of a step-change in developing new catalysts for the identified challenges. **The closer link of these methodologies to practical catalysis is the element to remark and the valley to overcome**. In spite of the relevant advances in the ability to prepare nanomaterials and in their characterisation, there is still limited capability to transfer the results to conceptually new catalysts, while there are progresses in current catalysts. There is thus a **methodological issue** in the development of catalysts and for this reason this is one of the three identified grand challenges, while the other two are related to societal objectives.

Catalysis is at the interface of fundamental and applied research, and naturally oriented towards industrial production. Therefore, all aspects of **catalyst scale-up and engineering**, as well as the relation between **catalyst design and reactor/process engineering** are very relevant to the catalysis discipline. It should be emphasised that we can only highlight those developments taking place in the open literature, yet it is evi-

dent that many academic groups working in catalysis have teamed up with industry in competitive research, re-emphasising the close cooperation between academia and industry in valorising fundamental research efforts into real applications.

Roadmaps are naturally oriented towards future needs in terms of novel processes, yet it should be realised that catalysis is the **key enabling technology** of the current chemical industry, that is in the the production of all energy vectors and all chemicals. It is thus **imperative to continue to support catalysis R&D for current industrial chemical processes** to maintain competitiveness and innovation in this vital sector of the European chemicals manufacturing area.

A final comment regards the selection of the priority elements, which are identified especially in the section on the vision of the future production of energy vectors and chemicals. In the transition to a new economy, as we are likely experiencing already, there are always contrasting idea between those who believe in change and those who don't. A particular case in point is the *role of CO₂ in future scenarios* – mitigating CO₂ will be a key element, yet it can also be considered a raw material in the future. CO₂, bio-mass and renewable energy are thus three interconnected elements to progressively substitute oil (fossil fuels) with a target of a 30% substitution by year 2030. There is no consensus on this issue and various researchers consider this substitution not feasible. Interestingly, at the start of the current economic cycle with oil being dominant – roughly 60 years ago, a similar debate ensued on the substitution of acetylene by olefins as raw materials.

This lesson, even with its intrinsic limitations, teaches us about the difficulties in roadmapping the future. It is evident

that the current approaches that rely on fossil fuels are not sustainable. This document discusses the main elements and options for a more sustainable future for society.

At the end of this Roadmap, appendices have been included, dealing with specific topics such as "Standardisation, regulation and safety issues in the scientific and technological fields related to catalysis" (Appendix A), on "Internationalisation" (Appendix B) and on "Dissemination and training in the field of catalysis" (Appendix C).

THE VISION AND SCENARIO ANALYSIS

«THIS INITIAL CHAPTER INTRODUCES THE VISION OF THE ROADMAP, BASED ON THE ANALYSIS OF THE SCENARIO FOR SUSTAINABLE PRODUCTION OF CHEMISTRY AND ENERGY VECTORS. IT PROVIDES THE LONG-TERM STRATEGIC GOALS IN RELATION TO THE EXPECTED CHANGED SCENARIO. AFTER INTRODUCING THE ROLE AND RELEVANCE OF CATALYSIS, THIS SECTION DISCUSSES SHORTLY THE ASPECTS IDENTIFIED TO DOMINATE (FROM THE CATALYSIS PERSPECTIVE) THE FUTURE PRODUCTION OF CHEMICALS AND ENERGY VECTORS LANDSCAPE, AS WELL AS THAT OF THE OTHER AREAS OF CRITICAL USE OF CATALYSIS»



1 CATALYSIS, SETTING THE SCENE FOR AN EVOLVING SCENARIO

The production of chemical and energy vectors in Europe is rapidly changing with the aim to improve competitiveness and to

address the societal challenges, the foremost being the effort to make the transition to a clean and sustainable future. Traditional raw materials have to be substituted with more sustainable resources, new cleaner and intensified processes have to be developed, new production concepts should be implemented to couple high efficiency with changing and more variable feedstocks, flexible production (i.e. the

possibility of adapting plant to variable outputs in terms of volume and type of products - see, for example, the F3 Factory EU project) and new ways to use energy in chemical transformations have to be realised. There is thus an **evolving scenario to move to a new economic cycle**. Many economic indicators confirm the reality of this transition and it is therefore critical to intensify research and development to enable it and deal with the energy-chemistry nexus.

Catalysis has a pivotal role in current chemical and energy vectors production. Catalysis is the **single most important and pervasive interdisciplinary technology in the chemical industry**, and perhaps one of the disciplines having the largest societal impact, although often hidden or underestimated. Catalysis, enabling the production of fertilisers, makes it possible to feed a world population of 7 billion humans. Catalysis allows producing fuels from oil in the quality and

quantity necessary for the modern use of energy. Catalysis is the key enabler to combine vast use of cars with good air quality, and environmental catalysis for car, van, ship and train exhaust gas after-treatment and other mobile applications should deserve increasing at-

tention. In the production of many healthcare, pharmaceutical, and agrochemical products, catalysis is a core technology, thereby increasing our living standards. Catalysis is a **key enabling technology** for most of the seven societal challenges in Horizon 2020.

Catalysis and catalytic processes account directly or indirectly for about 20-30 % of world GDP. Also the manufacture of catalysts in Europe has a large economic impact, of about 3-4 B€ (global market for catalysts: US\$ 16.3 billion in 2012, chemical processing accounting ~ 75%, petroleum refining ~ 25%). Of the 50 largest volume chemicals currently produced, 30 are produced via catalytic routes. These 50 highest volume processes account for more than 20 billion tons of carbon dioxide emitted to the atmosphere each year. The manufacture of 18 products (among thousands) accounts for 80% of energy demand and 75% of greenhouse gas (GHG) emissions in the chemical industry. **Technical improvements in catalyst and related process** could reduce energy intensity for these products by 20% to 40% as a whole by 2050 combining all scenarios. In absolute terms, improvements could save as much as 13 EJ (exajoules) and 1 Gt of carbon dioxide equivalent (CO₂-eq) per year by 2050 versus a "business-as-usual" scenario. Catalysis is thus crucial to reduce this environmental burden.

More than 85 % of all today's chemical products are produced using catalytic processes, and catalytic processes enable the modern refining of fuels. Nevertheless, *catalysis goes beyond the chemical industry and petroleum refinery*. It has a critical role in enabling a sustainable use of energy, for example in fuel cells and batteries, in the production of bio-fuels, as well as to protect our environment and climate. *Catalysis is thus at the core of the European process industry, one of the economic roots of the European economy* (by transforming raw materials into intermediate and end-user products), as well as of many processes for environmental protection. It is necessary to **place catalysis among the core enabling elements to achieve the strategic goals** defined by the European Commission in the Europe 2020 strategy and *across its various flagship initiatives*.

As evidence for global climate change continues to grow, catalysis has moved to the front lines of the struggle to obtain new, sustainable technologies for the future. *Catalytic technology is intimately intertwined with new and emerging solutions* for our current and future supply of energy sources. A clean and sustainable future is tightly dependent upon discoveries in the field of catalysis, either to improve energy efficiency, enhance and open up new pathways for energy conversions and storage, and mitigate adverse environmental impact.

The magnitude of the societal challenges to which catalysis is of strategic importance and the relevance of the challenges catalysis itself is facing have demonstrated that it is necessary to *revise catalysis roadmap and harmonise the current different indications in a single vision* that consider the evolving scenario for the production of chemicals and energy vectors, as well as the other areas of critical use of catalysis, such as devices for sustainable

production, use and storage of energy, technologies for greenhouse gases emission control and reuse, processes and devices for environment protection.

To better understand this change it is necessary to begin to analyse briefly some of the major aspects which may be identified to dominate (from the catalysis perspective) the future production of chemicals and energy vectors landscape, as well as that of the other areas of critical use of catalysis. This *scenario analysis* will allow setting up the **grand challenges of catalysis** to address our sustainable future, and discuss then in a more specific manner the research topics which are the parts of this roadmap.

1.1 THE ENERGY-CHEMISTRY NEXUS

Energy and chemistry are at the core of our current society, but the nexus between them is evolving in parallel to the changing scenario for a sustainable energy and chemistry. New technologies, focused on the use of renewable resources and energy, are emerging and will constitute the backbone of the future economic cycle, even if fossil fuels are and will be still for at least the next two-three decades available at relatively low costs.

However, it is the push for innovation and competitiveness, combined with other driving factors (socio-environmental motivations, greenhouse gas – GHG – reduction, resource security and related motivations, creating new value chains and further aspects) that will drive change. **Enabling the transition** requires inserting new technologies/ processes within the current economic and productive infrastructure, in order to reduce investments that otherwise would be too large. In a longer term, this transition will **change the current energy-chemistry nexus**. *Defining a path to the future* requires thus to identify the elements driving the change, but at the same time to determine the conditions

making possible their realisation and the transition to the future. A *closer integration between energy and chemistry* is needed in many areas, to develop, for example, new effective models of integrated bio-refineries. It is necessary to overcome through chemistry the use of energy mainly as thermal energy, including in chemical processes, with related thermodynamic limitations, and exploit instead potentially more efficient routes such as the *direct use of electrons and photons*.

In other words, **energy intensification** to parallel the better known concept of **process intensification** should be emphasised in future developments. Deeper integration of solar energy in the energy-chemistry value chain going beyond the exclusive use of photovoltaic cells is a required step, and this necessitates the development of *new advanced materials for energy*. Extending the use to other renewable energy (RE) sources is another relevant element, whose implementation also requires chemistry-based solutions, for example to *store and transport over long distances RE through suitable chemical energy vectors*. Catalysis plays a key role in all the technologies and processes to address these issues, for example to catalyse electro- and photo-induced processes, and to produce the energy vectors necessary to store and transport energy.

An effective transition to a sustainable energy and chemistry future requires *extending also the clean and efficient use of alternative raw materials going beyond the current oil-centric vision*. These and other aspects are changing the energy-chemistry nexus and the future of sustainable energy and chemical production.

1.2 MOVING TO A NEW SUSTAINABLE ENERGY SCENARIO

As outlined, catalysis is a critical technology to move to a new sustainable energy scenario. In order to progress towards a *sustainable energy production and use*, it is imperative to increase progressively the use of **renewable (regenerative) energy** (solar, wind, hydro, etc.), and in the transition to increase smarter use of bio-mass (e.g. use of bio-mass in more eco-efficient processes than simple combustion). There is the need to move to a *new vision of production and use of energy*, to contrast the natural trend in the expansion of demand related to the increasing population accessing to a large fruition of energy itself. *Catalysis is a key enabling technology to realise this new sustainable energy scenario*, being involved both in the processes of production of bio-fuels and efficient bio-mass transformation, and in many of the technologies for energy conversion and storage, for example in fuel cells and electrolyzers.

1.2.1 ENERGY STORAGE: FROM SMART GRIDS TO CHEMICAL STORAGE OF ENERGY

Energy needs to be stored to match demand. Smart grids use a combination of different devices and regulatory tools to meet this goal requiring creating a hierarchy of storage solutions, which will necessarily depend on energy storage capacity and time. Smart grids are a key element in the future energy infrastructure and will form the backbone of the future decarbonised power system.

The transition to a **smart grid system** constitutes one of the main limits to the further expansion in the production and use of RE in developed countries. In a long term perspective, it is necessary to enable a system to trade, distribute and store RE on a world scale, as currently occurs with oil and derivate energy vectors. This objective requires developing new technologies

of **chemical energy storage**, with the production of energy vectors which preferably integrate within the actual energy infrastructure, with minimisation of the costs for the transition. Catalysis is a critical element to implement this objective.

Converting electrical to chemical energy by producing suitable energy vectors allows a more flexible use of energy in different applications (transport, residential, industry, etc.). Suitable energy vectors can be used also as base raw materials for the chemistry sector enabling a new low-carbon economy. Within the next two decades, about 10 PWh/y of additional RE could be exploited by enabling an effective route for electrical to chemical energy conversion to store and transport RE, and by integrating this possibility into an extended smart grid.

1.3 A NEW VISION FOR REFINERIES

The future scenario will be based on the progressive substitution of fossil fuel-derived products, both as raw materials and energy vectors. In part, this replacement will stem directly from biomass-products, but with constraints related to the cost and complexity of their transformation, which likely will limit large-scale use as bio-fuels to only a few platform products derived from biomass. The use of energy vectors which can be easily stored and distributed (thus equivalent of those derived from oil) will remain a key element of energy infrastructure, but substituting those deriving from oil from those deriving from renewable energy sources. Even if different opinions exist, the transition to a more sustainable and low-carbon future for these energy vectors will be likely characterised from:

- I. the reduced use of energy vectors deriving from fossil fuels;

- II. the use of bio-fuels;
- III. the integration of solar fuels in energy vectors production;
- IV. the progressive introduction of 3rd generation fuels, for example deriving from algae processing.

Regarding the use of **bio-fuels**, the cost and complexity of transforming biofeedstocks not in competition with food and their impact on environment (land use, water cycle) indicates the need to intensify research on high efficient processing and utilisation of sustainably produced bio-mass. However, likely the share of bio-fuels to the total energy demand will not go beyond 20% and will involve simple production processes.

Figure 1 outlines, as an example, a schematic diagram of a possible future integrated scheme of production of energy vectors (refinery). This scheme outlines the integration between bio-refineries on one side and solar refineries on the other side. Natural (shale) gas is indicated as the main source of H_2 production, whose use may be expanded to upgrade heavy oil fractions and should in future especially also utilise bio-mass/algae as feedstocks, e.g. via gasification of bio-mass.

Solar fuels integration, besides bio-refinery integration within refineries schemes, is likely an important element of future scenarios to lower carbon footprint, whilst at the same time reducing dependence on fossil fuels. **Solar fuels indicate those energy vectors which are produced using renewable energy** (not only limited to solar direct use) and thus utilised to store and transport renewable energy. **Figure 2** illustrates briefly the concept of solar (bio)refineries and the integration with the energy infrastructure.

The flow chart of key components of a “solar (bio)refinery” indicates how hydrogen generation options can be combined with molecular precursors to form a limited number of platform molecules. These can

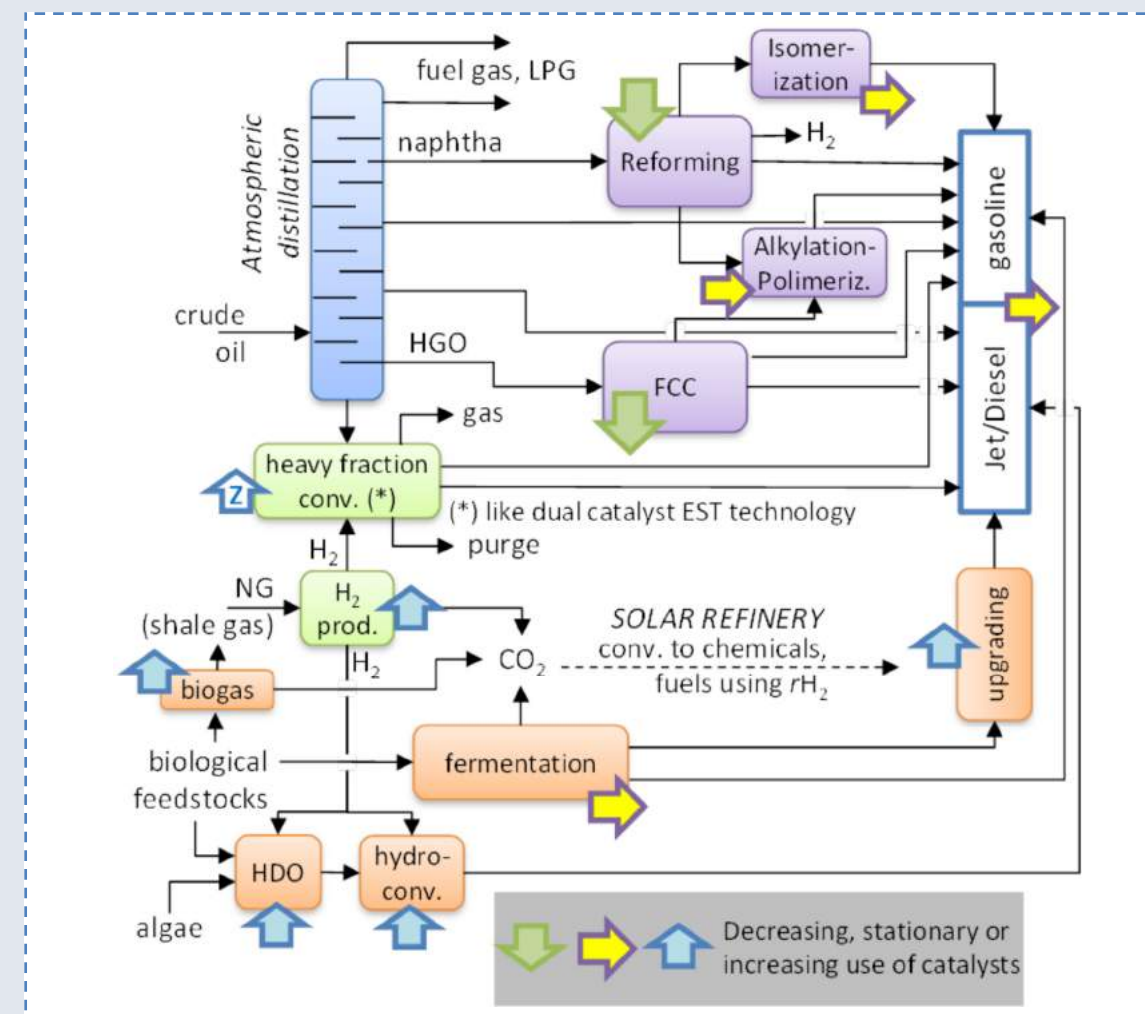


Fig. 1 Schematic diagram of possible future integrated scheme of energy vectors production (refinery). Solar refinery deals with the conversion of CO_2 to chemicals using renewable H_2 (see figure 2). *Source. Catal. Science & Technol.*, 2016, 6, 2485.

be further converted into useful classes of energy carriers in a similar way as present refineries produce a range of petrochemicals. This diagram exemplifies the systemic character of **chemical energy storage**, the integration with biomass use, the need of tight integration between fuels and chemicals production, and the interrelation with the energy systems. Enabling this vision for the future of a sustainable energy system requires to progress in many important scientific areas.

CO₂ use, from the perspective of a **circular economy**, is one of the critical elements in the integration of bio and solar

-refineries in the energy infrastructure (within an advanced refinery scheme as outlined in Fig. 1) when the goal is to move to a new low-carbon economy. Lowering GHG emissions, in addition to other motivations (energy security, promote rural living, etc.), is a major motivation for regulations and incentives for **bio-fuels utilisation**. The possibility to expand **the use of bio-mass** will be helpful as large amounts of CO₂ are produced in fermentation processes to produce bio-fuels. Therefore, the integration of renewable (solar) energy and CO₂ reuse within bio-refineries provides a means of maximising liquid yields from sustainably produced bio-mass. The transformation of CO₂ to fuels

facilitates incorporating renewable energy into the fuel and possibly chemicals pool. There are several possible options to realise this objective, as described in the following.

1.3.1 RENEWABLE H₂ AS KEY BUILDING BLOCK FOR SUSTAINABLE CHEMISTRY AND ENERGY PRODUCTION

A key element to enable solar fuels is the availability of **renewable H₂**, e.g. avoiding the use of fossil fuels for the industrial production. Different possible routes can be envisaged: bioprocesses based on enzymes or bacteria, solar thermal energy or using photon-absorbing semiconductors, advanced electrolysis coupled with renewable electrical energy, catalytic systems either in gas or liquid phase using waste or by-products streams from bio-mass transformation, and microbial electrolysis.

There are significant efforts underway globally, particularly in Japan, to produce renewable H_2 at low cost at large scale, and integrate this renewable hydrogen in CO_2 valorisation. A technical limitation for the integration of renewable H_2 in the current catalytic processes is the cost of compression since almost all processes operate at medium to high pressure.

1.4 BIO-REFINERIES AND BIO-FACTORIES

The chemical industry is currently making an effort in using in the future less fossil fuels and more renewable resources (bio-mass). Catalytic processes can be conveniently used to convert bio-mass, as renewable resource, into chemicals and fuels. Many processes have been proposed (e.g. gasification, pyrolysis, steam/dry reforming, etc.)

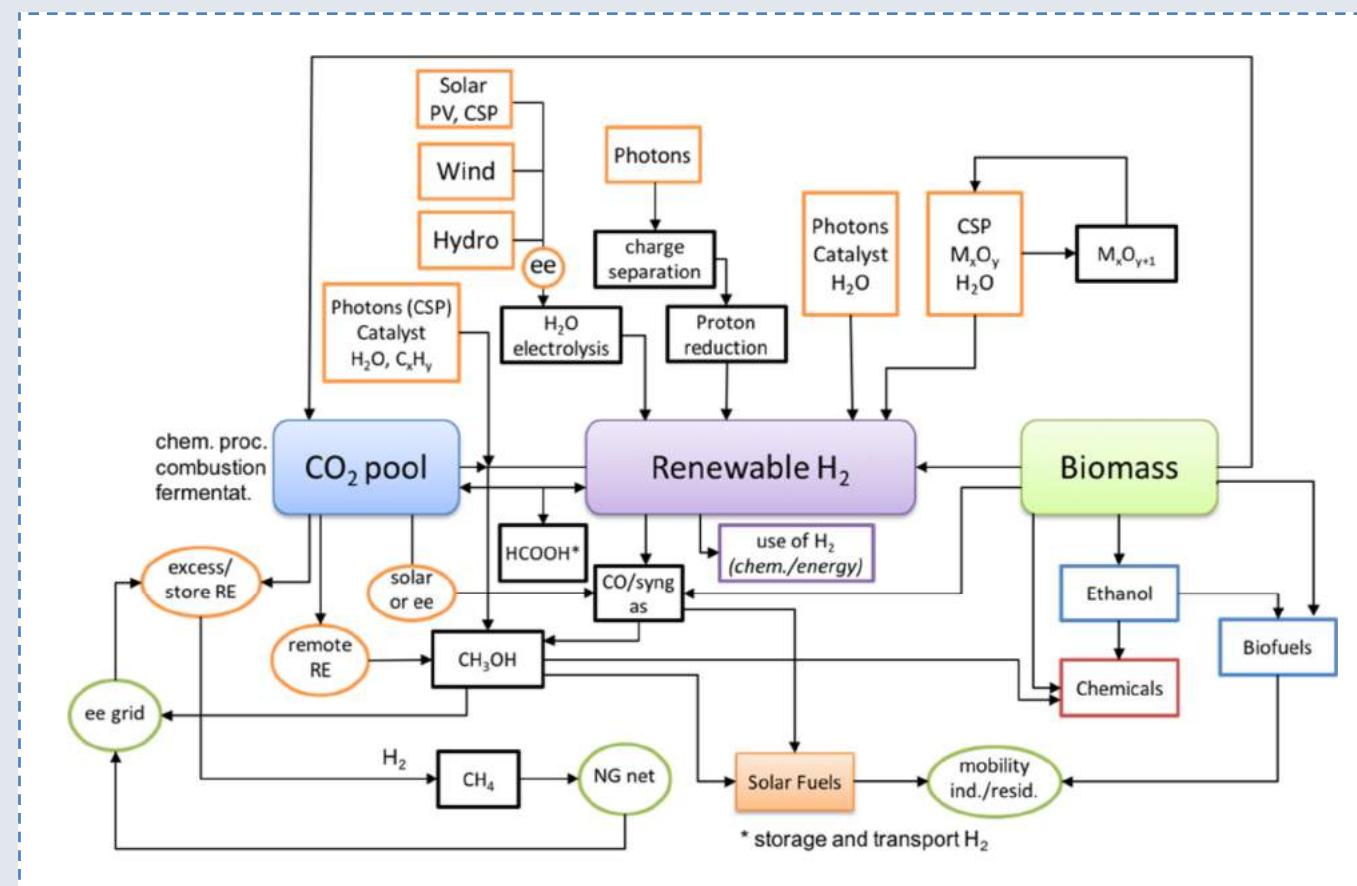


Fig. 2 The solar (bio)refinery concept for chemical energy storage science and technologies. Modified from the original presented by Schlögl¹.

-and some of the examples are in pre-competitive stage or early commercialisation. However, the economic sustainability of these processes has to be carefully optimised in order to make them viable alternatives for private investments. Therefore, process integration, materials and process optimisation, energy intensification and economic assessment of the systems should be carefully revised. The concept of the bio-refinery is growing but requires the development of new high-performance catalysts compatible with these new sources of raw materials. The idea of what bio-refineries represent has changed in time as does their envisioned role in the future energy-chemistry scenario. **Figure 3** illustrates this concept.

¹(a) Schlögl R, Schlögl R ed, In: Chemical Energy Storage, Berlin (Germany): De Gruyter, 2013, Ch. 1.1, p. 1. (b) Schlögl R, Green 2013, 2: 233.

With respect to the current situation, largely based on 1st generation (1G) bio-refineries and some petrochemical sites with individual biotech plants, the future trend is to move to 2nd generation (2G) bio-refineries (not based on raw materials in competition with food, like lignocellulosic and waste raw materials) or possibly, on the longer term, to 3G bio-refineries, and to fully integrated biotechnological and chemical production sites.

The transition to 2G bio-refineries is underway, admittedly at a much slower rate as supposed a decade ago; the future of biobased production will also require development and/or integration of other **new advanced concepts**, for example a) solar bio-refineries, b) bio-factories (characterised by small-size process intensification (PI) and chemi-

-and chemical production at the core of plant design), and c) symbiosis bioproduction, e.g. highly integrated with surrounding products in terms of raw materials and output.

The new integrated plant concept in **moving from the current to the future bio-refinery** models will be based on the following key elements:

- expansion of raw material basis,
- improvement of sustainability, efficiency of use of resource and energy, and lower impact on the environment
- expansion of product range.

At the core of this strategy is the development of **new process intensification concepts**, and the development of **highly efficient small-scale and flexible processes**, adapted to operate with **a broader range of input raw materials and type of products**. Full use of bio-mass and **symbiosis** with other industries at regional level are further critical aspects of the future of bio-refineries, with a consequent high degree of *regional specialisation* of bio-refineries schemes. This would require developing **process technologies easy to be adapted at different process schemes**. The development of new catalysts which fit to these new requirements and process operations, as well optimally integrate with biocatalytic operations, is a **key element** to realise this future vision.

The concept of **bio-refinery** already includes the idea of bio-mass processing into a spectrum of products (food, feed, chemicals, fuels, biosurfactants and materials), but it is still strongly linked with the oil refinery concept: i) large scale, ii) relatively limited range of products with low added-value, and iii) limited flexibility in terms of products. The new model of bio-refinery indicated as **bio-factory** underlines instead the aspect that chemical production is becoming the main target, with en-

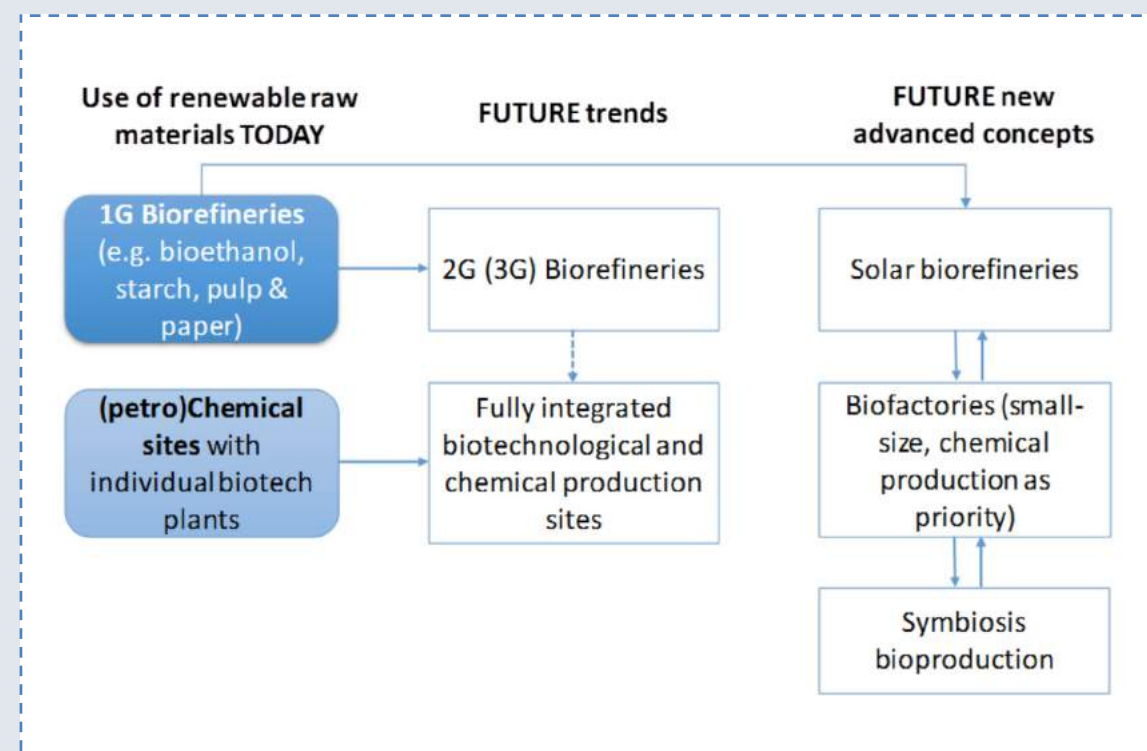


Fig. 3 Simplified scheme of the status and future trends in integration of fossil- to biobased refineries.

ergy products (mainly higher-value additives rather than directly components for fuel blending) as side-product stream. This model focuses at integrating bio-factories within the current oil-centered refinery and chemical production, rather than replacing it. Oil will be still abundant in the next half century and successful transition to a more sustainable economy will require lowering the barrier to change by

- decreasing the economic investments, thus minimising the extent of change in the value production chains
- reduce the elements which delay the introduction of new products to the market, for example by regulatory normative

This requires that the new processes/technologies can be inserted readily (or with minor changes) within the current infrastructure (drop-in products and processes/ technologies), but also

that the innovation path is accomplished by a series of measures which facilitates the introduction of new technologies:

- easier access to venture capitals; the CAPEX (i.e. CAPITAL EXpenditure, i.e. a business expense incurred to create future benefit) values are often not compatible with the amount of cash of the companies in Europe – low credit value helps but are not decisive here;
- help societal acceptance; citizens are very often very concerned with the constructions of large chemical complexes. It results in heavy and long administrative paths whose outcomes depend on ever changing political context;
- develop suitable politics to incentive high-risks companies, including reducing burden to construct the demo plants.

Keywords characterising the new models of

bio-refinery will be: **i)** small-scale, **ii)** flexible/modular production, **iii)** high added value products, and **iv)** chemicals production as core element. The reason is the need to (i) integrate better the production at regional level, (ii) have a production more suited to follow a fast evolving scenario, (iii) require low investment of capital, thus allowing also a large platform of investors, (iv) allow more efficient intensification of the processes, and (v) reduce overall the impact on the environment.

This has clear consequences also in terms of catalysis needs to enable these new models of bio-refinery to be adopted and implemented. Not only better catalysts but also more robust catalysts are needed that withstand different reactor workloads due to decentralised operation and variable availability of the feedstocks. To be competitive in that race and decrease the time-to-market delay, High-Throughput (HT) technologies can also contribute to provide a decisive answer².

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²The combination of HT experiments with statistical experimental design is actually an outstandingly efficient approach. An example is the REALCAT (Advanced High Throughput Technologies Platform for Biorefineries Catalysts Design) platform, founded by the French government in the frame of the Investment for the Future Plan. Its aim is to catalyse the innovation in all the fields of industrial catalysis with an emphasis on emergent biorefinery catalytic processes. REALCAT represents the first and unique in the world laboratory combining HT synthesis, characterisation and measurement of catalyst performance in heterogeneous, homogeneous, or bio- catalysts and their combination under the ultra-efficient very novel concept of hybrid catalysis. The access to such outstanding equipment could be decisive to make the European research in catalysis more competitive at the international level.

1.4.1 CO₂ A KEY CARBON SOURCE ELEMENT

One of the key elements in the new models of bio-refineries is also the need to integrate CO₂ valorisation and renewable energy in the bio-refinery value chain and maximise yields from limited, sustainably produced bio-mass resources. It is possible to increase bio-mass to fuel conversion, when CO₂ utilisation is integrated in bio-refinery. In bio-factories, the scope is instead different and the target is the optimal integration of CO₂ utilisation within the value chain. Symbiosis with near lying factories is another emerging element characterising the new models of bio-economy. There are different possibilities of efficient symbiosis, but an interesting option is the use of waste from other productions (wastewater and CO₂, for example, in advanced microalgae processes) to enhance the energy efficiency and reduce environmental impact and CO₂ emissions of a productive district.

There are various interesting new models for advanced bio-refineries/bio-factories, two of which are emerging as a new opportunity:

- bio-production of olefin and other base raw materials;
- development of flexible production of chemicals and fuels.

The first is centred on the production of base raw materials for chemical production, while the second focuses attention on intermediate and high-added-value chemical products, including monomers for polymerisation, but with flexible type of production for a rapid switch to produce eventually fuel additives, depending on the market opportunities. Two of the elements characterising both models are the full use of the bio-mass and process intensification (for efficient small-scale production).

An example of the possible future sustainable and low-carbon chemical produc-

tion, deriving from the progressive substitution of fossil fuels (30% as target for 2030 indicated by SPIRE initiative) with alternative raw materials (bio-mass and CO₂) is shown in **Figure 4**. This scheme does not cover all the possibilities, but outlines a possible realistic scenario to reach the target indicated above, which requires a very intense and synergic cooperation between academia and companies.

1.5 METHANOL: AT THE CROSSOVER OF NEW ENERGY-CHEMISTRY NEXUS

Methanol, DME and OMEs are at the crossover of the new energy-chemistry nexus, because their production and use show unique features of flexibility, one of the main requirements for the future energy-chemistry scenario. Methanol can be used both as (1) chemical and raw material for large-volume chemicals, and (2) fuel, both as blending component or to produce a range of other components for fuels. With respect to bioethanol, methanol shows a larger spectrum of uses and production paths. Dimethyl ether (DME) and oxymethylene ethers (OMEs) are considered important clean fuels in the future.

It may be produced both from (i) fossil fuels (methane, and from coal, the latter in rapid expansion in China) and (ii) non-fossil-fuel sources (residue/bio-mass/renewable + CO₂). Methanol is thus *one of the most important and versatile platform chemicals* for the chemical industry, but also a key element in the transformation to a sustainable energy future, for example to trade renewable energy on world scale.

Methanol/dimethyl ether (DME) may be converted to olefins (MTO - metha-

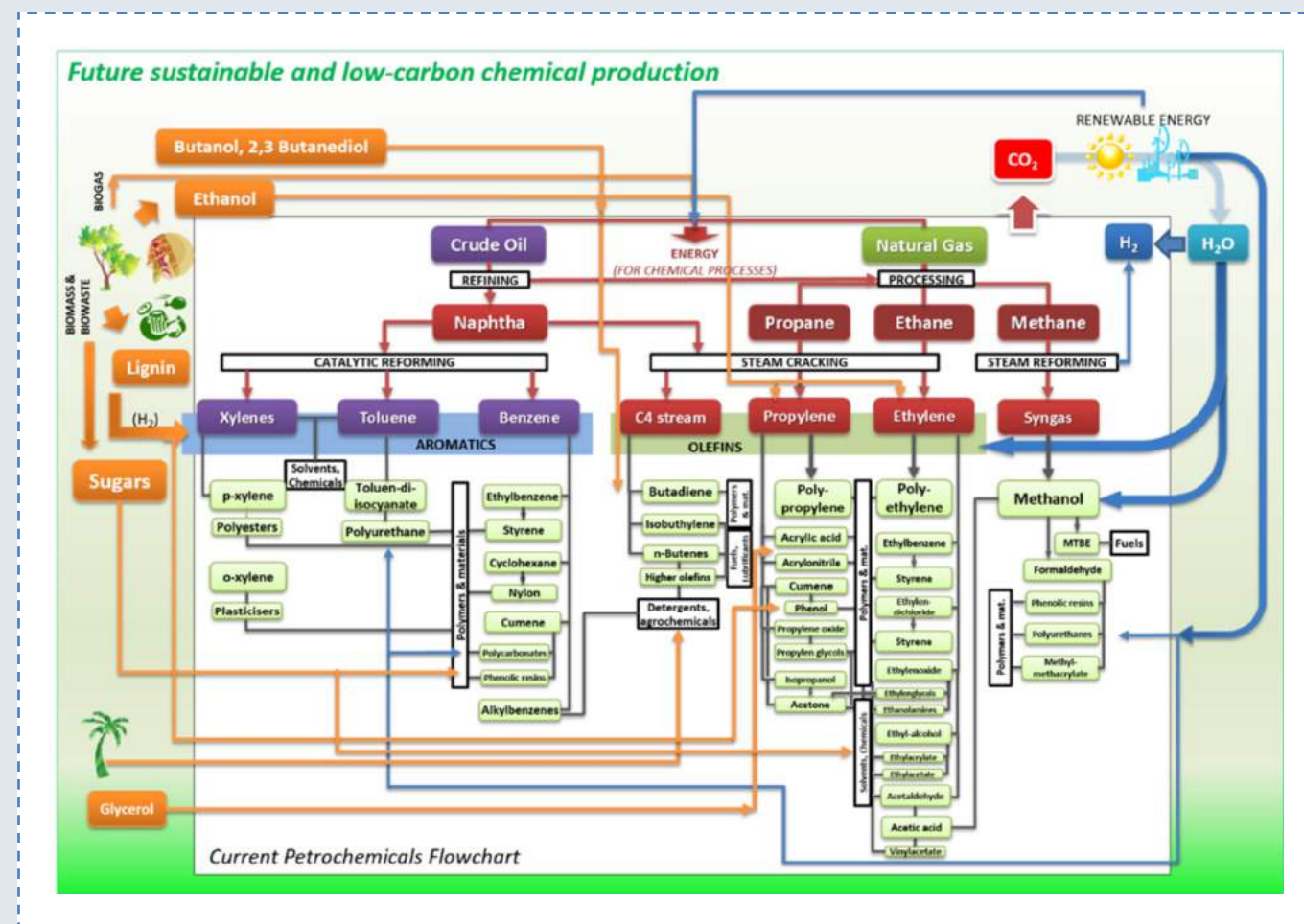


Fig. 4 Simplified flowchart of current petrochemical production with an outline of the possible new scenario for a sustainable chemical production based on the reuse of CO₂ and of bio-mass to produce both raw materials (building blocks) and specific intermediates. Source: *Chem. Soc. Rev.* 2014, 43, 7562.

nol to olefin/MTP - methanol to propylene and related processes) or aromatics (MTA - methanol to aromatics) over zeolite-based catalysts, besides to be raw materials for other large-volume chemicals (acetic acid, formaldehyde and others). Olefins and aromatics deriving from refinery fractions will be progressively substituted from these alternative raw materials, and in part also from shale-gas.

Figure 5 outlines schematically a possible future integrated scheme for chemical production. The availability of alcohols at low cost from bio-mass fermentation processes stimulates their use as raw materials to produce other chemicals (especially ethylene deriving from ethanol). In addition, CO₂ emitted from bio-refineries and

other processes (biogas production, for example), and thus 100% fossil-fuel-free, is an excellent C-source to produce the raw materials for chemistry (olefin, especially, via conversion to methanol or dimethylether - DME).

1.6 EXPLOITING SHALE-GAS

Widespread availability and low cost of shale-gas is another element in the future energy and chemicals scenario discussion. As customary with novel feedstocks, price volatility is high and it appears that the future will bring a drastic reduction in the price advantage. Exploitation of natural gas (NG) (as such or as hydrogen source,

for energetic purpose and also as raw material for chemical production) is often indicated as relevant to lower the global warming emissions, but leakage of methane during drilling and extraction of NG from wells and its transportation in pipelines should be drastically minimised.

Heterogeneous catalysis plays an important role as many methane conversion processes, yet not all, are catalytic in nature. Significant efforts are being made to develop novel catalysts for preferably direct routes for the conversion of methane into building blocks (ethylene, benzene, methanol being the most important ones), as summarised in **Figure 6**. In this framework, direct methane valorisation (i.e. without passing from the energy-intensive intermediate formation of syngas) to liquid fuel by efficient conversion to methanol or hydrocarbons is a strategic target to widen the use and sources of NG. Reducing energy use and costs of the production of syngas, for example by introducing new process schemes based on the integration of membranes, is a critical intermediate objective (i.e. when direct conversion is not feasible), particularly for small-medium size applications.

Although some of the routes summarised in Fig. 6 are known from several years (oxidative coupling of methane, OCM, for example), **i.** the changing landscape in methane cost due to availability of shale-gas, **ii.** the competitiveness push to develop new solutions to enter into a highly competitive market (particularly for venture capital companies) and **iii.** novel scientific advances in both homogeneous and heterogeneous catalysts, and biocatalysts as well, have re-invigorated both scientific and industrial interest in this area. OCM, and the alternative route via halo-methanes, are among the *potential routes to produce chemicals from methane*.

Other processes related to the utilisation of methane are the production of syngas by reforming and by catalytic partial oxidation. Nowadays, the industrial application

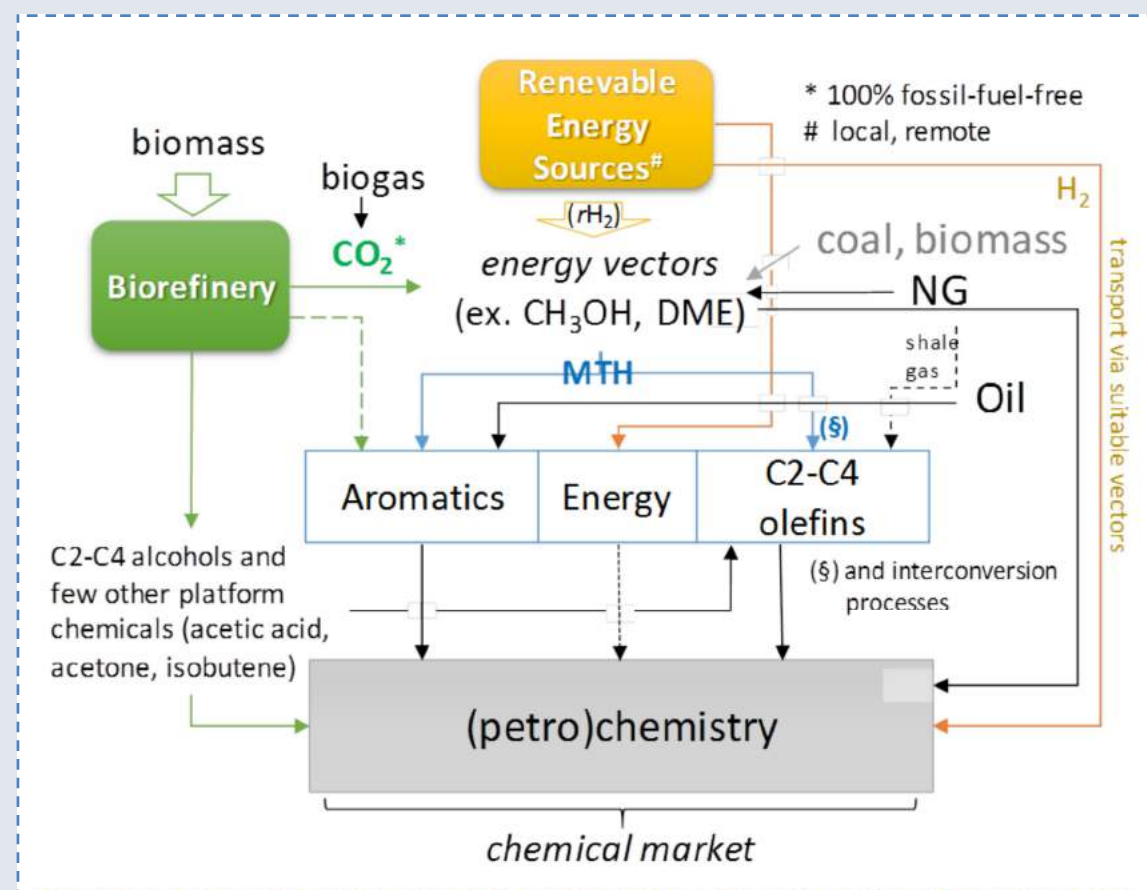


Fig. 5 Simplified schematic diagram of a possible future integrated chemical production. Source: *Catal. Science & Technol.*, 2016, 6, 2485.

privileges the reforming processes due to a better established technology, in spite of the high endothermicity of the involved reactions making the processes quite energy demanding, when intense energy recovery is not realised (requiring very large plants). The catalytic partial oxidation of methane represents a possible alternative to the reforming processes, in virtue of its exothermicity and also of the produced syngas with $H_2:CO$ ratio of 2:1, suitable for methanol and Fischer Tropsch synthesis. Driven by the current interest of the industry, new catalytic systems for the selective partial oxidation of methane should be developed which should be resistant to carbon deposition on the surface and exhibiting high methane conversion at low temperature and high hydrogen selectivity. Such objectives can be tackled by ap-

propriate choices of the carrier and by the loading procedure of the active metal, mainly nickel. Modification of the active ensemble size is also pursued by addition of appropriate dopant elements.

The growth in shale-gas as a feedstock creates new investment opportunities for converting methane to methanol, ethane to ethylene and propane to propylene (and possibly butanes to C4 olefins/diolefins), therefore improved efficiency in these conversions though novel catalytic technologies would be valuable. There is an abiding opportunity for better dehydrogenation or oxy-dehydrogenation technology for C2-C4 alkanes, and investment opportunities for methanol to olefins. These opportunities have existed for many years, but shale-gas and stranded NG offer increased opportunities.

All oxidative conversions of hydrocarbons

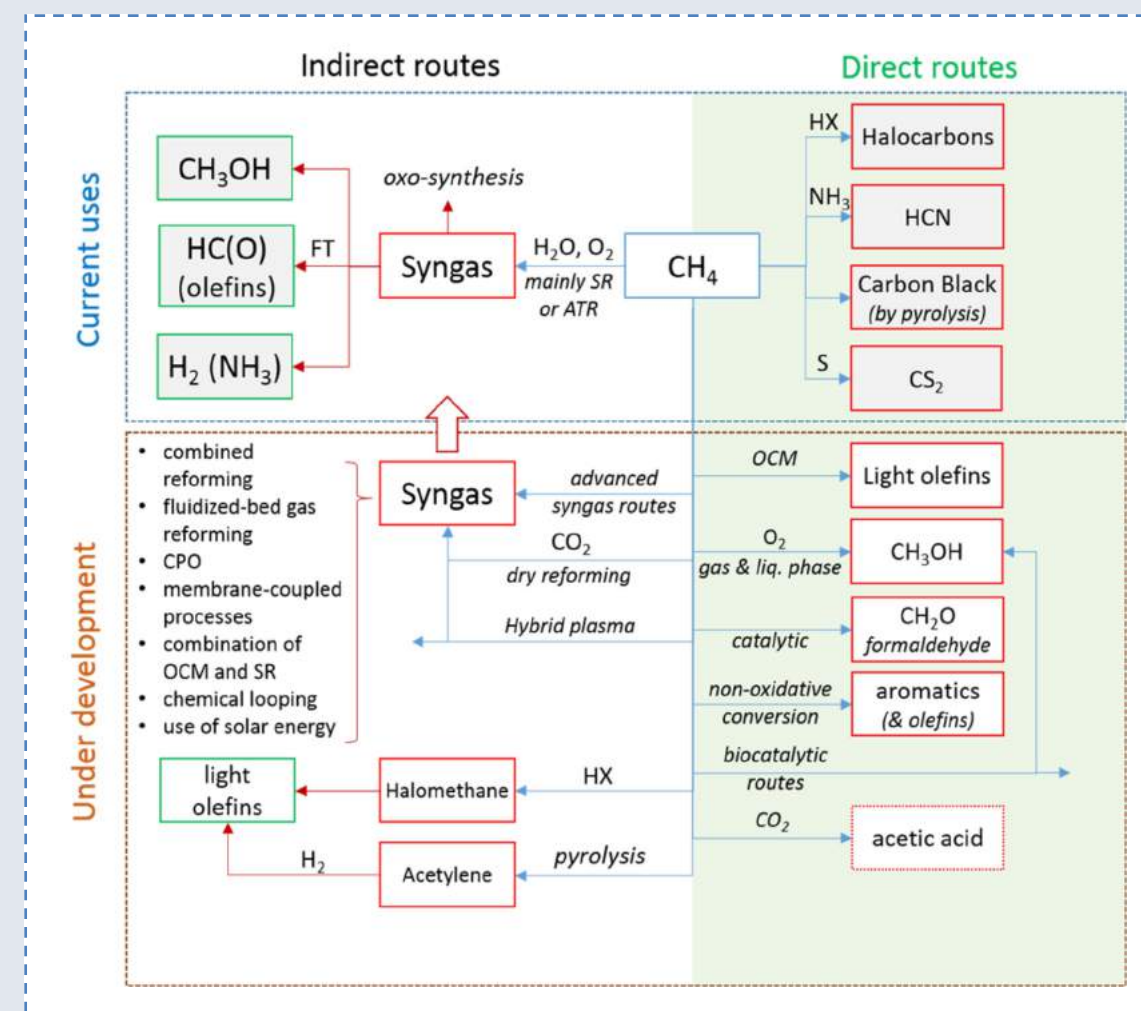


Fig. 6 Scheme of the current and under development catalytic routes for indirect and direct conversion of methane. Source: *Nat. Science Rev.* 2015, 2 (2), 143-145.

like oxidative coupling or oxidative dehydrogenation suffer for substantially decreasing selectivity with increasing conversion of the feedstock. This is either caused by consecutive reactions of the more reactive products of the involvement of different oxygen species of different reactivity. Such challenges cannot be solved by catalyst development alone. These reactions are typical examples for problems that can only be solved in joint interdisciplinary efforts considering all phenomena from the molecular to the process level.

Another emerging route in this broad scenario is related to the use of *non-thermal plasma*; this technology option includes different ways to generate the

plasma. This approach presents a conceptual change of paradigm, from the issue of methane activation (or simultaneous CO_2 and/or H_2O activation) to the control of selectivity in the pathway of further catalytic conversion.

The use of transition and main groups metals in zeolites (Zn, Cu, Ga, etc.) is opening new interesting possibilities for *new gas and liquid phase transformations of methane* to products such as methanol, olefins etc. New processes of methane conversion based on homogeneous or bio-catalysts show interesting prospects, although process economics are still an issue. The combination with solid (photo)catalysts to enhance the rate of reaction and/or close the cycle is another emerging area.

1.7 BIO-GAS-BASED CHEMISTRY

Bio-gas, for the possibility to utilise waste resources, is one of the key elements shaping the future of renewable energy. Actual forecasts are of a rapid extension of digestors and bio-gas production that will require the possibility to store in the form of liquid fuels some of the energy produced. **Bio-gas transformation routes** are thus one of the emerging routes. In addition to non-thermal plasma, the solar-assisted dry reforming is another valuable option, especially when solar heat is stored in the form of molten salts. These two emerging routes require a new catalyst design with respect to those actually available.

1.8 SOLAR-DRIVEN CHEMISTRY

“**Solar-driven Chemistry**” term refers to a *future scenario for chemicals production based on substitution of fossil feed-stocks as energy source and raw materials*. The concept of “**Solar-driven Chemistry**” is thus not limited to the direct use of photons, but rather refers to *direct and indirect ways by which renewable energy can be transformed into chemical energy*. Its importance relates to storage of surplus renewable energy, for which the tipping point is expected to occur in the coming decade. Therefore, electrocatalytic routes, when renewable energy comes in the form of electrons (solar panels) are part of this general concept. One can also consider plasma routes for chemicals production, when driven by using renewable energy. Catalysis is the element making the difference to extend the use of plasma from limited current uses to large-scale (energy-efficient) technologies. A new conceptual design for catalysis to work in synergy with the plasma is required. Current catalysts are not suited to work efficiently with the radical and vibra-

tionally-excited species present in plasma.

A key aspect of the “Solar-driven Chemistry” concept is the creation of a *short-term cycle of utilisation of renewable energy sources to produce chemicals and energy vectors*. This intensification in the transformation from solar to chemical energy is a key element for sustainability. A *paradigm-shift in chemical (and energy) production* involved in this aspect is the shift from “carbon-atom” selectivity with respect to the starting raw material to high energy-efficiency in storing (renewable) energy in chemical bonds. Design of new catalysts and catalytic electrodes to work with these energy sources and move from lab to industrial scale (for example, design 3D-type electrodes to intensify production) is the challenge. Also, the economy of scale issue should be addressed as renewable energy is increasingly produced at the household level, yet chemistry for storing renewable energy in chemicals (e.g., the Sabatier reaction) require large reactors to be efficient.

The production of solar fuels and chemicals, as well as the associated aspects of chemical energy storage, are among the relevant elements to move to this *new “solar-driven chemistry” scenario and, in a long-term perspective, to the possibility of a distributed energy/chemistry production in artificial leaf-type devices*. In a broader perspective, “**Solar-driven Chemistry**” is a key element of an already started *transition to a new economic cycle in chemistry/energy production*. It provides opportunities to turn the need for new concepts in catalysis into innovation and competitiveness.

The field of solar driven chemistry is a unique opportunity to Europe’s chemical industry and entrepreneurship. It may provide Europe a leading edge in an increasingly competitive world and contribute to job creation and preservation of the environment.

1.8.1 CATALYSIS FOR SUSTAINABLE ENERGY

In addition to novel concepts in the area of solar driven chemistry, developing novel materials will be key to the success. Understanding nano-architecture and its role in governing functional performances remains a major challenge for catalytic nanomaterials. An example is the development of advanced electrodes. There are several key technological areas of the energy sector, which require better electrode nanostructure to overcome current limits and/or move to new levels of their performances and these include

- photo-electrochemical solar cells,
- water photoelectrolysis,
- (photo)(electro)catalytic devices for the conversion of CO₂ to fuels,
- advanced Li-batteries,
- supercapacitors,
- fuel cells,
- third generation photovoltaic cells and
- nanostructured thermoelectric devices.

Catalysis is the key aspect in these devices to overcome current limits. Novel concepts need to be devised such as catalysis dealing with high-energy species such as photons electrons, plasma-generated fragments, etc. Many of these challenges in catalysis need to be overcome by design of novel materials.

Nanocarbons and core-shell catalysts are examples for classes of catalytic materials offering many new possibilities to develop conceptually-new catalysts, nanocarbons e.g. for advanced operations with electrons or photons

(electro- and photo-catalysts). There is also a wide range of possible hybrid materials to realise high performance systems for use in advanced devices for energy conversion and storage. In this regard, new hybrid materials with tuneable properties, such as COFs (*covalent organic framework*), where the promising stability, the combination of enhanced surface area-controlled porosity, in addition to the possibility to graft active species or support metals and metal oxides, are advantageous to open new perspectives in this area of catalysis. Core-shell particles can be tuned on the Angström, nm or micrometer scale and offer fully new properties as enhanced reactivity or selectivity, stability of exploit bifunctionalities

1.9 STRUCTURED CATALYSTS FOR PROCESS INTENSIFICATION

Process intensification (PI), which is defined as “any chemical engineering development that leads to a substantially smaller, cleaner, safer and more energy efficient technology”, is likely to be the next revolution of the chemical industry and it aims at a significant increase in resource efficiency with respect to material and energy consumption, thereby enabling more economic and sustainable processes for the future. The need for more efficient processes, including further flexible engineering designs and, at the same time, increasing the safety and environmental impact of these processes, is pushing the industry to novel research in this field. Enhancement of transport processes in chemical reactors can play a key role in process intensification, leading to more compact and more efficient equipment and allowing for a better process integration, which in turn leads to a reduced number of process steps (e.g. multifunctional reactors).

Structured catalysts and reactors provide a great opportunity for the implementa-

tion of these strategies into industrial practice. Several studies have clearly demonstrated their potential to greatly enhance both interphase (gas/solid and gas/liquid/solid) heat and mass transfer rates at the local scale, while maintaining limited pressure drops, as well as global heat transfer performances at the reactor scale. Novel opportunities for future applications of structured catalysts may arise from the combination of advanced modelling of the regular reactor geometry, able to provide an accurate description of all the relevant chemical and physical phenomena at different level of scale, with new additive manufacturing technologies, which allows for the realisation of complex and highly specialised geometries of equipment. Examples are monolithic, membrane, microchannel and hierarchical design, 3D printing. Such a combination of model optimisation with tailored manufacturing would result in process equipment with enhanced performances, which can be applied both to high-volume specialty chemical production processes and to fine chemical manufacturing process as well as to highly innovative energy and environmental technologies involving chemical transformations.

1.9.1 PROCESS INTENSIFICATION BY MOLECULAR CATALYSIS

Molecular catalysis offers unique opportunities for energy and carbon-efficient chemical transformation, but has two main current limits: i) often a limited productivity based on reactor volume and ii) limited capability to realise multi-step chemical processes. Both aspects are very relevant for process intensification, while other aspects such cost of separation and recovery have been overcome, for example by recent developments in supported molecular catalysts or by multiphase operations.

The selection of suitable solvents or multiphase systems (solvent engineering) is still a field based on expert knowledge. The transfer of this knowledge to the scientific community and into technology transfer promises additional potential for highly efficient industrial processes.

Molecular catalysis offers also unique possibilities over solid catalysts in terms of understanding the reaction mechanism, and developing better knowledge-based catalysts. The challenge is thus to address in a more systematic way the above mentioned limitations.

CONCLUSIONS

The areas outlined above provide a glimpse of possible future production methods for chemicals and energy vectors. It highlights the changing energy-chemistry nexus. Emerging trends are identified and the need to develop and improve new catalytic materials, devices and processes is highlighted.

Some of the highlighted areas entail an improvement in current catalysts, or adapting them to new feedstocks such as in the transition from oil- to bio-based feedstocks. However, some of the areas, for example in the direct methane conversion or in the production of solar fuels require new concepts in catalysis.

One example is nitrogen fixation. Ammonia production is the single most energy-intensive process, with over 2.5 EJ of energy consumption and production of 350 Mt CO₂ eq. emissions. Dramatic improvements in energy consumption for ammonia production were made prior to 1930, but further improvements were only incremental over the last five decades and nearly zero most recently. Producing NH₃ under mild conditions, for example by electro-and/or photocatalysis using renewable energy sources to drive the reaction, could completely

change the environmental impact of ammonia production and at the same time provide a new basis for competitiveness of the European chemistry industry.

There are many other examples of new catalysis directions, from i) the photo- or photo-electro catalytic production of renewable H₂, to ii) new artificial leaf-type devices to distributed production of chemicals or fuels, iii) new catalysts for methane direct conversion and iv) new synthetic catalytic strategies for chemistry, for instance photocarboxylation, or integration of chemo- or electro-catalytic steps (for example, in regeneration of cofactors in enzyme catalytic cycles).

Only a knowledge-driven approach can be successful in addressing the objectives outlined above, and thus only a balanced approach investing on research on all the components of the chain going from idea to innovation, including educational ones, can be successful in this revolutionary transition to a new economy for Europe.

Considering low reactive, or even inert molecules, such as carbon dioxide, dinitrogen or alkanes, the number of efficient catalytic process for their use as raw materials is nearly inexistent; at best, they require very harsh conditions. A closer look at the growing in the area of catalysis shows that precisely those substrates displaying a noticeable chemical inertness as CO₂, N₂ or C_nH_{2n+2} have not been extensively studied. The analysis of the number of entries in Web of Science obtained with the fields "carbon dioxide and catalysis", "dinitrogen and catalysis" and "alkane and catalysis" in the time span 1980-2014 evidences that these three areas are yet underdeveloped, while items such as "hydrogenation and catalysis" show a much larger impact in the literature, in line with the most reactive hydrogen in the presence of the appropriate catalysts. Thus, **one future direction in this area should point toward the modification of inert molecules, such as carbon dioxide, dinitrogen or alkanes that can be efficiently converted into commodity or fine chemicals.**

HIGH LEVEL GOALS

«BASED ON THE VISION AND SCENARIO ANALYSIS DISCUSSED IN THE PREVIOUS SECTION, THIS PART OF THE ROADMAP IDENTIFIES THE GRAND CHALLENGES FOR CATALYSIS, WHOSE IMPLEMENTATION IS THEN DISCUSSED IN MORE DETAIL IN THE FOLLOWING SECTIONS. THE CHALLENGES FOR CATALYSIS, TO ADDRESS SOCIETAL, ENVIRONMENTAL AND INDUSTRIAL DEMANDS, ARE LUMPED IN THREE MAIN TOPICS: CATALYSIS TO ADDRESS THE EVOLVING ENERGY AND CHEMICAL SCENARIO; CATALYSIS FOR A CLEANER AND SUSTAINABLE FUTURE; ADDRESSING CATALYSIS COMPLEXITY»

2 GRAND CHALLENGES FOR CATALYSIS

This section will present briefly the **grand challenges for catalysis** which may be identified on the basis of the scenario “analysis and vision of the sustainable future for Europe” outlined in Section 1. The roadmap for catalysis in Europe will follow this preliminary discussion on the grand challenges of catalysis, which are linked to the **EU societal challenges**, where catalysis plays a critical role:

- *Health, demographic change and well-being:* for example, in the synthesis of healthcare pharmaceuticals and bio-security.
- *Food security, sustainable agriculture and forestry, marine and maritime and inland water research:* for example, in enabling new routes of utilisation of non-food based bio-mass, water treatment, nitrogen fixation.
- *Secure, clean and efficient ener-*

gy: for example, in enabling trading and transporting renewable energy on a world scale, producing H₂ and local energy storage.

- *Smart, green and integrated transport:* for example, in reducing emissions of vehicles, H₂ and fuel cell vehicles, sustainable fuels.
- *Climate action, environment, resource efficiency and raw materials:* for example, in enabling new routes to use CO₂, to substitute fossil fuels,

and low-carbon process industry.

Two different types of grand challenges can be identified: (1) related to specific applied objectives, as energy or clean environment; (2) connected to specific methodological aspects of catalysis.

Realising the EU societal challenges requires a step forward in catalysis thinking, based on **(1) a knowledge-driven approach** in the frame of actions able to catalyse the transfer from idea to innovation; **(2) fostering the revolution-**

ary rather than evolutionary approach, with actions facilitating the use of non-conventional approaches to catalysis development.

It is necessary to **intensify the generation of new ideas rather than promoting the incremental technology development**. There is an increasing gap between the fundamental research (TRLs 1-3) and applications, which is widening by the current R&D funding mechanisms. **More directed funding to bridge this gap** constitutes the critical factor for innovation and thus constitutes **a critical element for competitiveness** of the European chemical and energy

industry.

The discipline of catalysis spans several order of magnitude in terms of space (from atomic sub-nanometric scale to reactor level - meter scale) and time domains (from picosecond level of catalytic process to year length of catalysts in industrial and other applications). All these aspects have to be accounted in design, production and use of catalysts, and entail also ex-situ and in situ/ operando characterisation of catalysts, as extensively



described in Section 5.

Catalysis is a true example of **interdisciplinarity**, involving knowledge from surface science and modelling of physico-chemical phenomena of catalytic reactions, to material science and inorganic chemistry to prepare suitable nanostructured catalysts, to organic and industrial chemistry in the use of catalysts, and to engineering of materials and processes in the application of the catalysts, their shaping for industrial use, the evaluation of reaction kinetics and modelling of catalytic processes.

The grand challenges to be described below represent this **complexity**, which outlines also the need for creating the necessary critical mass to address this complexity. The key to success is thus an **integrated approach**, with the ability and willingness to collaborate between the various disciplines and bridge the gap between fundamental- and industrial-oriented research and development. **It is necessary for Europe to pursue this objective collectively** as it is currently not well implemented at the national level in all European countries. *Fostering the industry-academy-research institutions joint collaborative research-and-development effort*, not only in technology development, but *especially* in fundamental areas is a **priority element** in the innovation of catalysis science for Europe.

In the selection of the grand challenges for catalysis, the following criteria have been used:

- The topics describe *new directions* for world-class research that will help to solve a current technological and/or societal challenge and should fit in with the strengths and expertise currently present in catalysis in Europe, although not excluding possible white spots.

- The topics should be *driven by the ambition* to create clean, efficient production processes or products that are economically viable.
- The roadmap as a whole should help to *strengthen the catalysis community* in Europe, lead to a greater integration of the heterogeneous catalysis, homogeneous catalysis and bio-catalysis communities, provide opportunities to start collaborations with other research fields (e.g. chemical engineering, biotechnology, physics) and aid the community to remain at the international forefront.
- *Strengthening collaborations through the value chain* to enhance implementation mechanisms.

It remains of **vital relevance** to continue to support research on the current production processes, since this will ensure current industrial competitiveness in Europe in key areas. Recent advances in understanding catalysis and process engineering of catalytic processes may boost performance in many processes considered mature. Some of these "conventional" areas in which there is the need to promote further R&D are the following:

- cleaner fuels in refining;
- environmental catalysis: removal of major pollutants to low levels such as NO_x, CO, hydrocarbons, SO_x and particulates;
- transformation of hydrocarbon feedstocks into commodity chemicals and materials at higher selectivity for avoiding CO₂ emissions;
- new catalytic and greener processes for fine and specialty chemicals.

2.1 CATALYSIS TO ADDRESS THE EVOLVING ENERGY AND CHEMICAL SCENARIO

The following bullet points list represents the outline of Chapters 3 to 5, and will be thoroughly addressed in the following.

- New or more efficient used raw materials (from new uses of natural gas to bio-mass and CO₂, including non-conventional hydrocarbons and hybrid bio- and fossil products);
- use of renewable energy in integration with catalysis;
- realise energy-saving processes through catalysis;
- processes efficiency: highly selective catalysis, low energy-intensive operations, complex and variable feedstocks, multi-functional "intelligent" catalysis, increasing and gradual encroachment of enzymatic catalysis/synthetic biology in areas traditionally seen as belonging to heterogeneous catalysis;
- molecular catalysis in energy processes;
- 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, H₂ production, compression and storage);
- new manufacturing methods for catalysts: atomic control of materials and properties, and the sci-

ence of scaling-up;

- cost of catalysts vs performance as key driver for improvement: many factors affect performance in real applications which are not always understood, especially in how they impact each-other from support variability through to feedstock variation;
- reduce process steps in fine chemicals/pharmaceuticals through catalysis;
- substitution or minimisation of CRMs in catalysts preparation, particularly in emerging areas (bio-mass conversion, photocatalysis, PEC water splitting, green/blue hydrogen production) and industrial processes³;
- design and set-up of robust chemo-, regio- and stereo-selective heterogeneous catalysts⁴;
- design and set-up of catalysts for graphene science⁵.

³ In synergy with current initiatives such as EU CRM Cluster, FCH-JU, KICs Raw Materials, InnoEnergy.

⁴ To replace the use of inorganic salts and stoichiometric co-reactants and reduce cumbersome separation or purification procedures, replacement of environmentally unfriendly oxidants (based on stoichiometric metal salts or active chlorine-containing species) with processes based on sustainable oxidising species (H₂O₂, ozone, oxygen, air) activated by heterogeneous catalysts.

⁵ To address relevant challenges related with graphene, in particular, 1) discovery of catalysts for the bottom-up preparation of nanostructured graphenes by solution chemistry; 2) further development of graphene chemistry; 3) use of graphene as a catalytic surface.

2.2 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;
- more robust and stable catalysts which can accommodate feed-stock of lower grade;
- catalysts in novel process design for resource and energy efficiency;
- novel catalytic processes to reduce cost and eco-impact of fine and speciality chemicals production (including asymmetric catalysis, organo-catalysis and enzymatic process, tandem process);
- catalysis for novel polymer materials, bio-polymer and intermediates;
- LCA, exergy and sustainable eco-conception of catalysts and processes, in integration with "conventional" methods such as economic and market analyses, process design, energy and product efficiency;
- new and more robust catalysts for the ultra-deep diesel oil desulfurization.

2.3 ADDRESSING CATALYSIS COMPLEXITY

2.3.1 ADVANCED DESIGN OF NOVEL CATALYSTS

- 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 nano-architectures and nanoparticles (also polymetallic and subnanoclusters) in catalysts, core-shell structures, hollow spheres, tandem catalysis;
 - * novel cost-efficient preparation methods based on safe and earth-abundant chemicals;
 - * integrating homogeneous, heterogeneous and bio-catalysis;
 - * organometallic complexes, organo-catalysis immobilised or single site molecular catalysts;
 - * controlled and environmentally sustainable heterogenisation of catalysts⁶;

⁶ In addition to supported or anchored/tethered metal complexes to ordered or non-ordered porous materials, new possibilities are offered for example by embedding catalytically active inorganic transition metal nanoparticles/clusters or carbon nanostructures into polymers. Many innovative concepts may be shown from an extended use of immobilised molecular catalysts. An example are supported heteropolyacids (HPAs) for photocatalytic reactors irradiated by LED and working at temperatures considerable lower than those generally industrially used in thermal catalysis for hydration reactions or for dehydration reaction of alcohols.

* development of new organic-inorganic hybrid catalysts⁷;

* bioinspired, biomimetic and biogenic approaches to catalyst and enzymes synthesis (e.g. genetic development of new enzymes).

2.3.2 UNDERSTANDING CATALYSTS FROM MOLECULAR TO MATERIAL SCALE

- From deductive to predictive catalysis, theory and modelling of catalysis⁸;
- new approaches in catalysts and reaction mechanism investigation, with focus on *in-situ* and *operando* methods, to address, *inter alia*, also multiscale characterisation (hierarchical approach), structure-activity relationships, dynamics of catalysts;
- development of more reliable model systems (including surface science approach and including link between surface science and real world catalysis);
- bridging molecular to reactor engineering aspects in designing new processes, including new approaches in kinetics and reaction engineering;
- improved measurement and modelling of micro-kinetics and incorporation into catalyst design processes;

⁷ An example are transition metals and bioinspired ligands, e.g. peptidomimetic ligands with well-defined secondary structure such as β -turn, helices, herpin.

⁸ Improved predictive power of computational modelling and increasing use of modelling to predict real catalysts are driver for rational catalyst design, characterisation and testing. The challenge is to integrate DFT calculations, molecular dynamics simulations and reactor modelling at different scales.

- improvements in *ex-situ* and *in situ* characterisation methodologies: better spatial/temporal resolution, implementation and combination of imaging and mapping tools;
- improved structure-activity relationships by measuring catalytic performance and structure at the same time also locally on specific catalytic entities (crystals, nanoparticles, clusters);
- enhanced use of multi-technique analytical measurements over multiple length and timescales⁹;
- science of catalyst scale-up, linking designed laboratory materials to practical catalyst manufacturing methods;
- increase sensitivity towards active site compared to spectator species.

2.3.3 EXPANDING CATALYSIS CONCEPTS

- Non-conventional energy sources in catalysts: catalysis with electrons, photons and energy sources other than heat;
- catalyst design to operate under non-conventional or extreme conditions (e.g. higher thermal stability);
- catalysis for use in non-conventional solvents;
- disruptive concepts in catalytic materials;
- new concepts in active sites;
- catalytic nanoreactors design;
- molecular traffic control in catalysis;

⁹ New capabilities becoming more mainstream such as use of XFEL and laser based characterisation techniques as well as synchrotron/neutron techniques, especially in combination with kinetic studies.

- tandem and cascade heterogeneous catalysis, with multifunctional systems prepared with a nanoscale control of the components;
- catalyst genoma;
- single atom and subnano-cluster catalysis at surfaces;
- multifunctional molecular catalysis design;
- new 1D and 2D catalytic nanomaterials;
- artificial enzymes;
- from catalytic processes to catalytic devices;
- complex and responsive, adaptive catalysts.

THE STRATEGIC RESEARCH AGENDA AND IMPLEMENTATION PLAN

«THIS SECTION ANALYSES THE STRATEGIC RESEARCH AGENDA AND RELATED IMPLEMENTATION ACTION PLAN FOR THE GRAND CHALLENGES IDENTIFIED BEFORE AND MAINTAINING THE ORGANISATION IN THREE MAIN TOPICS REPORTED IN THE PREVIOUS SECTION. FOR EACH OF THESE TOPICS, AFTER IDENTIFICATION OF THE KEY ASPECTS, AND RELATED CHALLENGES AND OPPORTUNITIES FOR CATALYSIS, THE MAIN RESEARCH AREAS AND OUTPUTS ARE DISCUSSED»

3 CATALYSIS TO ADDRESS THE EVOLVING ENERGY AND CHEMICAL SCENARIO

The scenario for **chemicals and energy vector production** discussed in Section 1 leads to gradual introduction of new raw materials, derived from biomass and CO₂, slowly replacing fossil fuels, which are expected to remain the dominant feedstock for at least the next two-three decades. Therefore, in parallel to development of new catalysts and related processes for using these novel raw materials, **fossil fuels-based production processes need to be further improved**, requiring substantial R&D efforts

to maintain a high level of innovation and to secure Europe's competitiveness. In view of the enormous volumes of converted materials, even minor improvements will have a substantial environmental and economic impact. Together with new catalysts for the activation of methane and other C1 carbon sources, including CO₂, more flexible and robust catalysts and processes for the conversion and clean-up of heavy feedstocks are needed.

In converting **bio-mass**, as one of the alternative raw materials, lies a challenge as this feedstock is of much greater complexity than traditional fossil feedstock. In addition to development of fundamental catalytic chemistry to convert bio-mass effi-



KEYWORDS advanced molecular catalysts, algae, alkane conversion, aqueous phase reforming, artificial leaf, bio- and chemo-catalysis integration, biocatalysts, biofuels and biorefineries, carbon linking reactions, carbonate, cascade processes, circular economy, CO₂ as building block, CO₂ utilisation, coal use, composite particle architecture, critical raw materials, deactivation resistance, deactivation-tolerant catalysts, electrocatalysis, electrolyzers, energy conversion, energy storage, fossil fuels, fuel cells, green H₂, green urea, renewable energy, hierarchical catalysts, hybrid bio- and fossil fuels, LCA, LOHC, low carbon economy, methane and natural gas valorisation, monomers, N₂ electrocatalytic conversion, nanostructured catalytic materials, non-thermal plasma, novel electrodes, olefins from non-fossil fuel sources, oleochemistry, ORR, PCET concerted, PEC, photocatalysis, process integration and intensification, renewable H₂, saving energy, solar fuels, solar-driven chemistry, steam and autothermal reforming, syngas from CO₂ and water, tandem catalysis and devices, valorisation heavier oil fractions, waste streams cleanup, water-tolerant solid acids

ciently to fuels and chemicals, there is a need to involve efficient process technology, agriculture, and bio-mass production chains to arrive at an economically viable and sustainable economy where bio-mass plays a substantial role. The main challenges for catalysis relate to 1) selectivity, i.e. how to convert complex bio-mass to preferably a limited number of target (platform) molecules -either drop-in or new molecules- in as few steps as possible in order to prevent separations and 2) stability, i.e. how to achieve a catalyst that can handle “poisons” present in the bio-mass and that survives the conditions needed to convert bio-mass or fossil sources of lower grade.

Thus, improved use of fossil fuels and efficient use of bio-mass require better understanding **catalyst deactivation**. Development of novel processes also offers opportunities to replace critical raw materials (CRM) such as precious group metals with base metals. This goal can be pursued in synergy with the European Cluster on Critical Raw Materials, as well as with the KICs Raw Materials Initiative.

The **conversion of carbon dioxide into solar fuels or solar chemicals** brings its own challenges, since in this case the starting molecule is simple as well as most of the target products, yet in this case efficient conversion based on various forms of renewable energy should be developed. Solar fuels/chemical production is a potential strategy to reduce the negative impact of increasing atmospheric CO₂ and also contribute to the storage of excess renewable energy. In the short term, reducing the H₂ production cost through better catalyst design in electrolyzers is a critical factor, but in long term **the direct use of RE without intermediate H₂ formation to convert CO₂ into solar fuels and chemicals should be exploited**. This requires, among other aspects, to develop new classes of electrocata-

lysts, which can also operate in synergy with photo-active materials and catalysts. Together with catalytic technology for chemicals production from CO₂, integrated in a long-term in artificial-leaf type devices, these processes will lead to the realisation of a more carbon-neutral chemical industry in the decades to come.

Advanced catalytic solutions for the production of **renewable H₂**, from water (photo-splitting, via photocatalysis or related technologies), from wastewater containing carbohydrates, alcohols and short carboxylic acids (photo-reforming) or from waste organic sources (via either photo-, bio- or heterogeneous catalytic processes) through photo-catalytic processes under direct sunlight irradiation has emerged as a valuable and intriguing solution to renewable energy and is one of the priorities to enable the conversion of carbon dioxide to solar fuels or chemicals. However, it is far from being optimised and the efficiency of these processes limits their technological application. Joint efforts of interdisciplinary expertise in the synthesis and characterisation of nanostructured and/or molecular catalysts as well as in sunlight driven photocatalytic processes can drive to the development of new competitive systems for hydrogen photo-generation for industrial applications. This especially also includes renewable hydrogen derived by bio-mass gasification.

New catalysts also need to be developed for the stabilisation/upgrading of the *flash pyrolysis oils* that are more resistant to various forms of deactivation. This research on co-FCC process should be extended to all the main processes in a conventional refinery. Other sources of bio-liquids as produced under hydrothermal conditions should be explored as well.

In the transition to new fuels, a realistic alternative to the first generation bio-fuels is to produce **hybrid bio- and fossil fuels** by co-refining bio-mass pyrolysis oil in a conventional mineral oil refinery, in order to

meet the international renewable energy targets by 2020. Co-processing makes sense as a compliance solution controlled by the refiner, allowing to produce renewable gasoline & diesel hybrid stocks at the refinery. As such, co-processing, or re-purposing specific refinery units, aim at utilising existing refinery infrastructure to produce pipeline-compatible bio-fuels. Different refinery processes apply for this approach, the most obvious ones being FCC, hydrotreating, and hydrocracking, the two last processes involving high hydrogen pressure¹⁰. On the other hand, given that European refining faces long term over-capacity, some refiners are looking to re-purpose specific units to 100% bio feed rather than co-process.

Saving energy in chemical processes through **i)** the use of **less-severe reaction conditions** and the development of alternative process options, **ii)** process intensification to improve energy and resource efficiency, and bypass thermodynamic limitations (for example, by integration of membranes in chemical processes e.g. removing water which is a by-product), and **iii)** realisation in a **single unit multi-step processes** are between the targets to improve current processes, and requiring the development of improved catalysts. Catalyst and related process improvements could reduce energy intensity in the manufacture of the main chemical products by 20% to 40% as a whole by 2050. This will correspond to an improvement in process economics critical to maintain competitiveness of chemical production in Europe. Achieving deeper energy and emissions cuts (to comply for example with the political targets in the reduction of CO₂ eq. emissions) will require development and deployment of emerging or disruptive catalytic technologies.

Enabling the novel and sustainable energy scenario, and secure energy sup-

plies, requires investing in **R&D on devices for energy conversion, storage and use**. Fuel cell technology offers significantly higher efficiency than conventional energy conversion processes, although the degrees of efficiency achieved in practice are still largely below the theoretical efficiencies, when the heat of reaction cannot be exploited. Improvements in catalysis for fuel cells, and in other energy conversion devices, would require a better understanding of the process occurring at the surface of the electrocatalyst. This understanding will also boost the **extension of the use of electrocatalysis** to a wider area, but it would require developing also **novel electrode concepts**, such as 3D-like electrodes to intensify the process and reduce the costs. Electro-organic synthesis processes have not been able to establish themselves on a larger scale, except in few cases (adiponitrile synthesis, in particular), but has a large potential of application when new catalytic materials and electrodes will be developed.

3.1 CHALLENGES AND OPPORTUNITIES FOR CATALYSIS

3.1.1 FOSSIL RAW MATERIALS

As already mentioned, widespread use of fossil raw materials will remain the reality for the next decades, but it is necessary to increase security of the supplies and reduce environmental impact. For this rea-

¹⁰ Initial results for co-FCC in lab-scale units and pilot plant testing are promising. They indicate similar gasoline fractions but reduced hydrogen production and increased coke formation when co-processing upgraded or stabilised bio-oil produced by fast pyrolysis compared to crude oil distillate (VGO) processing alone. The most stable oxygenated compounds found in the gasoline fraction are alkyl-phenols. These can be separated from the gasoline and used as a green resource for petrochemicals, but to improve the overall hybrid fuel yield, modified new FCC catalysts need to be developed that convert alkyl-phenols and at the same time produce less coke.

son, there will be pressure to expand the fossil raw materials portfolio by using

- **stranded NG** (natural gas) resources as well as shale-gas¹¹ in areas where these cannot be distributed by pipelines; the economic conversion of methane by direct and indirect routes (via syngas, but using advanced energy-saving solutions, see Fig. 6) to liquid fuels/chemicals is still a challenge, and there may be new investment opportunities for valorisation of the light alkanes associated to these fields. The exploitation of high-CO₂ natural gas fields will require finding solutions for use of CO₂ other than re-introduction in the field.
- **coal and solid fuels**, with the improvement of current technologies especially in terms of energy efficiency of the processes, reduction of CO₂ emissions¹² and environmental impact; improved catalytic processes like hydrogenation, sulphur resistant gasification, and methods for the selective conversion of aromatics from coal tar are relevant.
- valorisation of **oil heavier fractions**, with the introduction of improved process schemes and technologies (for example, the substitution of bottom barrel refinery processes with new one); the necessary larger use of H₂ requires to develop advanced energy-saving solutions to produce hydrogen.

There are various challenges associated to these objectives. Better understanding of the initial C-H activation and carbon-carbon coupling reactions governing the above chemistry is needed. Novel catalysts to realise these reactions under mild conditions

are required, as well as better understanding of the **deactivation phenomena**. **Controlling radical chemistry** present in some processes (some routes of methane conversion, like **Oxidative Coupling of Methane** or **non-thermal plasma processes**) is another challenge, requiring developing radically -new catalytic concepts. Many processes for transforming non-conventional hydrocarbon feedstocks (for example, oil sands) or heavy-oil fractions are based on thermal radical processes. The development of novel catalysts able to operate with these fractions will open new perspectives in this field.

The shift in raw materials is influencing the value chain, opening new needs. For example, the use of shale-gas instead of naphtha for olefin production by steam cracking leads to shortage in availability of C4-C6 building blocks (especially high purity butadiene). This provides opportunities for development of improved oligomerisation catalysts and processes starting from e.g. ethylene or even ethane. At the same time, there will be increased need for alternative routes to produce olefins, via CO₂ or bio-mass (eventually via methanol as intermediate, see Fig. 5), and for olefins interconversion (via methathesis, for example). Improved approaches for light alkane dehydrogenation for on-purpose olefin synthesis are also necessary.

Process integration and large-scale plants to improve energy efficiency and economics should be paralleled by the development of **integrated processes** (energy efficient on small-medium scale, through the use of microreactor and process intensification concepts) to respond to changing feedstock availability, and exploit bet-

¹¹ Coalbed methane and gas hydrates are other vast potential resources.

¹² In principle, it is preferable to avoid use of coal and solid fuels instead that minimise their GHG impact through the use of CO₂ (or its sequestration), but the use of these fossils fuels may be motivated from cost and geopolitical reasons, and thus technologies for their cleaner use should be developed.

ter small-size natural gas fields. Among these **challenges** there is the development of flexible processes for converting smaller molecules to larger ones, the dehydrogenation or functionalisation of alkanes, or an improved process for catalytic steam cracking with added product flexibility have to be mentioned. New (Cr-free) catalysts are necessary for cope with these challenges.

In conventional processes, separation is often the critical factor for both investment and running costs. The challenge is to **avoid separation steps**, either by designing catalysts and reactors that can handle complex mixtures of raw materials or by coupling catalytic solutions with separation technology. It would also be interesting to look at ways of introducing energy only at the catalytic site, i.e. without heating up the whole medium.

The shift in the worldwide requirements of fuel products is introducing **new challenges**. Currently, Europe is exporting gasoline and importing diesel fuels, but predicted trends in fuel use indicate that this cannot be maintained in the future, which is creating an imbalance in refinery outputs. This in turn generates the need for new processes displaying a higher selectivity to diesel at the cost of gasoline, such as diesel-selective FCC¹³, although hydrocracking (whose capacity is currently expanding) is a diesel producer. In order to cover the increasing demand for paraffin hydrocarbons with a low degree of branching, methods need to be developed for hydrogenation and subsequent selective cracking of condensed aromatic compounds.

The ever more stringent product specifications and the increased variability in the quality of the crude oil are major hurdles for new catalytic methods to overcome. The key to the continued supply of raw materials from crude oil is

a tailor-made control of the molecular weight along with the introduction of hydrogen into heavier crude oils. At the same time, improved catalytic technologies for the production of – in particular – olefins and aromatic compounds or their direct secondary products from natural gas are required. Important research goals which can only be achieved with the aid of **heterogeneous catalysis** include among other:

1. carbon linking reactions (aromatic compounds and olefins from methane, synthesis gas based methods e.g. methanol to hydrocarbons, Fischer Tropsch synthesis),
2. alkane activation reactions (dehydrogenation processes) and
3. alkane oxidation processes (partial oxidation, e.g. methanol from methane).

The **refinement of coal** for the production of fuels and bulk chemicals requires further investment in catalysis research. New, innovative catalytic processes will enable even more efficient conversion of the coal via hydrogenation, gasification or degasification. Between the need for catalysis research and development work in the field of coal refinement, the following priority topics may be indicated:

1. **coal hydrogenation**: i) replacement of current single-use catalysts with resistant, efficient and recyclable catalysts for liquid phase hydrogenation), ii) optimisation of the catalysts for hydrotreating for further processing of the coal oil, and iii) development of integrated process engineering concepts;
2. **coal gasification**: i) development of

¹³ It should be evidenced, however, that this is the case today, but not necessarily in the near future. Gasoline/hybrid/electric will replace diesel in light-duty engines (passenger cars) due to emission problems in cities.

sulphur resistant catalysts ("sour gas shift catalysts") for use at optimum temperatures for the shift reaction, ii) new catalysts and methods for using synthesis gas;

3. *coal degasification*: development of catalytic methods for selective conversion of aromatics from the coal tar;
4. *CO₂ emissions minimisation*: development of catalytic methods to minimise CO₂ emissions.

There are several opportunities for catalysis to address above challenges. In view of the increasing effort required for the *conversion of heavier* and more disadvantageous crudes, improved catalysts for heavy-oil conversion, including novel type as combination of MoS₂ and zeolite 1D-type catalyst, are needed. Improving the traditional refinery processes towards both clean traditional fuels (low S, N, PAH) and premium bio-derived products (premium diesel, oxygenated bio-products), pursue more effective catalysts for hydroconversion also starting from low-quality heavy feedstock and engineering catalyst and performance evaluation with new potential bio-feedstocks (2° & 3° generation) are related open challenges.

In more conventional catalysts, materials with *hierarchical structure and resistant to poisoning and deactivation* are necessary. Control of low levels of impurities such as antimony, arsenic and mercury, is becoming of increasing relevance. In addition, fundamental research on catalyst fouling, deactivation, feedstock variability, mechanical deactivation, breakthrough curves, roles of contaminants in catalyst stability, etc., is required. This also implies a challenge in analytical research, where new (micro-) spectroscopic techniques can be used to increase our understanding of catalysts (and their deactivation) on all

length scales. These techniques can also increase the fundamental understanding of the effect of promoters, as extensively highlighted in Section 5 focused on "Addressing catalysis complexity",

Apart from feedstock cleanup, the *cleanup of waste streams*, i.e. environmental catalysis, is a still increasingly important field. Catalysts and processes for the *in situ* (pre-) treatment of crudes will improve transportability and recoverability. Flexible systems and processes would allow for a rapid response to the changing availability of feedstock, for instance in catalytic steam cracking. Current large-scale processes target steady state operation, and transients lead to considerable off-spec production. More flexible systems and understanding of the transient states is necessary.

Steam cracking is one of the most energy-intensive processes in current petrochemical complexes. Developing a more energy-efficient process with an improved selectivity to the desired products like ethylene would be a great opportunity for catalysis. The scale of operations and multipliers in refinery and petrochemistry are so large that even relatively small improvements will have a large impact, also on CO₂ emission.

3.1.2 BIO-MASS AND RENEWABLE RESOURCES

Challenges for bio-mass use have been changed in recent years, and should be considered in light of the changing scenario for energy vectors and chemicals production discussed in section 2. The use of bio-mass as a resource brings up some specific topics in relation to the production of chemicals higher up in the value chain, i.e. chemicals and materials. *Bio-mass can be a source of olefins*. In addition to the already commercially practiced production of ethylene from bio-ethanol, attractive is the synthesis of C₄+, due to the change in olefin production related to a

shift from naphtha to shale-gas as feedstock for steam cracking. This is likely an area which will grow in relevance, even if the bio-based production of *light* olefins is still in infancy, and actually economic in few limited cases. Better catalysts to convert bio-derived intermediates to C₂-C₄ olefins via dehydration, deoxy dehydration, hydrodeoxygenation, metathesis, aldol condensation etc. should be derived.

Bio-mass shows also potential advantages in the *production of functional chemicals*, particularly monomers for polymerisation¹⁴. In the production of advanced materials, a main driver for the use of renewable resources is the customer-based demand for sustainable production (and products) at competitive costs. A series of barriers still limit this possibility of using bio-mass, for its complexity. The challenge is thus to develop catalytic approaches which:

- operate on mixture rather than pure platform molecules derived from bio-mass,
- minimise as much as possible costs of separation,
- operate on concentrated solutions rather than on diluted ones,
- minimise energy costs (in solution rather than in gas phase).

Chemo-catalytic approaches, with respect to bio-catalytic ones, should be focused on *process intensification, tandem catalysis and reduction of separation costs*, as well as *long-term stability*, between the main barriers of current bio-technology processes. Optimal integration between chemo- and bio-catalysis is a requirement to be met. Degradation of bio-mass to bio-crude or gasification products should be evaluated in consideration of the costs for further purification and upgrading of these fractions.

Extending the type of non-food competitive bio-mass sources is a necessary direction. *Micro- and macro-algae sources* are one opportunity, when their cost of processing can be addressed by new advanced solutions, for example by using ionic liquids, and when full-use of the algae can be realised. New technology solutions are needed, which open further requirements for catalysts.

New catalytic routes for *lipid upgrading* are needed to make the use of lipids competitive. Proteins and their building blocks, the aminoacids (only the nonessential ones should be used for chemicals), are potentially suitable for bulk chemicals. However, cost-effective isolation and selective conversion are still in their inception phase.

An *integrative thinking* with respect to bio-mass production is essential. To determine which bio-mass is available and how we can modify that bio-mass in such a way that feed, food, chemicals and fuels can all be prepared in an economical way, input from the agricultural side is needed. In addition, since bio-mass suffers from seasonal variation, the issues of transport and storage also need to be addressed.

For catalysis, when dealing with the catalytic conversion of bio-mass as a renewable resource, three main challenges stand out:

- developing chemically and hydrothermally stable, possible multifunctional catalysts, able to withstand aqueous and aggressive environment,
- going towards more selective reactions, and

¹⁴ For instance, pentoses or hexoses derived from carbohydrate feedstock are processed to obtain potentially important C₅-C₆ bio-derived platform molecules such as LA and FFR, while the hydrolysis of cellulose gives LA and/or esters. Hence, one of the major subject areas in biomass conversion is aimed at designing, developing new catalytic systems for selective transformation of LA and FFR into specialty monomers and fuels/fuel additives.

- integrate catalysis with separation, with the development of new advanced solutions (catalytic membranes, catalytic distillation, etc.)¹⁵.

Development of *water-stable catalysts/carrier materials* is necessary, because most of the catalytic processes for the conversion of biogenous raw materials occur in the aqueous phase. For instance, hydrodeoxygenation reactions are very often encountered during the processing of vegetable raw materials and in general many reactions involve acidic catalysts and production of water such as esterification. Therefore, the *identification of water resistant solid acid catalysts* is a priority as well as the combination of metal and acidic sites in a single catalyst. Stability of the catalysts and/or the catalyst carriers is an issue as well.

Acid catalysts are the most used in industrial processes. Solid acids have to be developed to substitute liquid acids used in homogeneous catalytic reactions that cause problems of corrosion of the reactors and safety for the operators and environment. Beside the conventional heterogeneous acids used for reactions of oil transformation (zeolites, mixed oxides, clay, etc.), *new acid catalysts* have to be developed for reactions of bio-mass valorisation that run in water, aqueous vapour, or in general in polar-protic solvents. Bio-mass, in particular that obtained from processing waste agricultural forestry, is the most attractive alternative feedstock with wide available carbon source. Among the main catalytic routes to transform bio-mass into fuels and value added chemicals, the hydrolysis is the most complicated as it requires the use of specific water-tolerant acid solid cata-

¹⁵ Although some of these solutions (for example, catalytic distillation) are known, still their industrial use is limited.

lysts. Several families of *water-tolerant solid acids* have been identified and they are being studied in several reactions like polysaccharide (cellulose, inulin) hydrolysis, C5/C6 dehydration, and others.

The use of *bio-based resources* introduces further requirements for the catalysts used. As for chemical catalysts, *stability* is a major issue, as they should work in a liquid (slurry), often an aqueous or acidic environment, and they should be resistant to the relatively high ash content (in bio-mass), which can poison the catalyst. Moreover, coke formation resulting in catalyst fouling should be prevented. Thus studies of catalytic behaviour under both model and real conditions are essential. Concerning *biocatalysts*, with the use of whole cells (in which the enzyme/biocatalyst is incorporated) is desirable to use them in a (one-pot) biotechnological environment or in a modular set-up operating in tandem or cascade mode. The transport of the reactant and/or products into and out of the cell is still a challenge and offers opportunities for catalyst development. In the downstream processes the applied catalysts have to tolerate the side products of the upstream processes when one wants to omit (expensive) intermediate product separation.

Going towards higher reactant selectivity presents a specific challenge for bio-based conversions, as crude bio-based feedstocks are generally heterogeneous in nature or at least multifunctional, e.g. purified carbohydrates. Their composition will vary depending on location, time of the year and production methods. Moreover, the advantage of a bio-mass feedstock, i.e. a feedstock containing complex and over-functionalised molecules, can only be used to its full potential if we can convert these molecules selectively. Developing *redox neutral reactions* is beneficial since the use of (expensive) hydrogen can then be prevented. *Cascading multiple conversion* reactions and separation steps could be

an option to find economically viable process routes. The *integration of chemocatalysis within industrial biotechnology processes* is a promising option in the design of a reaction cascade, as it discloses the possibility to combine various types of resources, i.e. not only bio-mass, but also fossil and CO₂. Specifically, for bio-renewables, the integration of length scales of the process and corresponding logistics is a challenge, e.g. in the development of local, small-scale production processes.

When stable and *poison tolerant catalysts/catalytic process* are developed, the range of available feedstocks for making products (chemicals, fuels) desired by society becomes significantly wider. For example, wastewater which still contains organic matter can be used as feedstock. A typical example is the use of wastewater containing volatile fatty acids (VFAs). These VFAs can be converted by micro-organisms to polyhydroxyalkanoates (PHAs). PHAs as such can be used as polymers, though their properties have to be improved. Alternatively, they can be used as feedstock for the production of bulk chemicals by chemocatalytic processes. Use of waste streams from biotechnology processes to produce H₂ by aqueous phase reforming is another option, when the waste products cannot be used directly.

Other valuable products, which can be recovered from bio-mass, are *oil and fats or terpenes*. Oleochemistry is already an important economic factor. Different products such as soaps, detergents, paints/varnishes, hydraulic fluids/lubricants, bio-fuels, printing inks etc. can be produced. *Catalytic innovations in oleochemistry* offer the basis for further use of these raw materials. Both the acid groups and in particular the double bonds in the fatty acid molecules offer wide potential for modifica-

tion and material changes to raw materials from plant-based and animal-based fats and oils. Terpenes can be converted by selective oxidation processes and C-C linking reactions as well as be used in polymerisation and copolymerisation processes.

In this peculiar framework, there is an emergent need of *combined chemical and biocatalysis*. At the moment, approaches have been devised only on an academic level, whereas transfer to the industry is not yet well developed. Both disciplines could benefit from a better interaction. The challenges that need to be addressed, concerning bio-refinery concepts and more environmental-friendly production routes, require thinking outside the box. Especially the combination of heterogeneous catalysts with immobilised enzymes will massively contribute to sustainable solutions of bio-mass conversion. By combining both approaches, completely novel, very efficient synthetic process routes can be established which show superior energy and atom efficiency compared to separated chemical or bio-chemical processes.

Between the research and development areas which need to be intensified are:

1. the decomposition and depolymerisation of cellulose; new chemical catalytic and bio-catalytic processes, including those involving innovative solvent concepts can open up new approaches;
2. the decomposition and depolymerisation of lignin, in particular the production of defined chemicals;
3. de/refunctionalisation of the biogenous raw materials; more selective catalytic route for the defunctionalisation, and insertion of specific functionalities in already highly functionalised (and reactive) biogenous substrates should be developed;
4. hydrogen production from bio-mass,

more extensively described in the next section.

3.1.2.1 HYDROGEN PRODUCTION FROM BIO-MASS

A topic which could become more relevant is the [hydrogen production from bio-mass](#)-derived products. Hydrogen is considered one of the key energy carriers, as fuel for transportation and as intermediate in the conversion of renewable energy sources because a majority of evolving drop-in bio-fuel technologies require hydrogen (H₂) inputs or other chemical reduction processes to upgrade oxygen-rich carbohydrate, lignin or lipid feedstocks to hydrogen-rich hydrocarbons that are functionally equivalent to petroleum-derived liquid fuels. Hydrogen is produced mainly in large industrial units by steam reforming of natural gas (85%) or heavier hydrocarbons. In the near future, research should focus on the transition of the hydrogen production from renewable resources. A bio-mass strategy of hydrogen generation can be the intermediate step between the current fossil fuel technology and the dream of efficient water splitting with sun light. A wide range of bio-mass materials (sugars, cellulose slurries, ethanol or bio-oils) can be reformed to hydrogen. Ethanol, pyrolysis and sugars are the most likely candidates for hydrogen production. For bio-derived liquids, three main reforming technologies are used: steam reforming, gasification, partial oxidation/autothermal reforming and aqueous phase reforming.

[Steam reforming \(SR\)](#) is typically the preferred process for hydrogen production in industry because their high efficiency. Steam reforming of ethanol and bio-oils has been studied over different oxide, metal-based (Ni, Co, Ni/Cu,) and noble metal-based catalysts (Pt, Pd, Rh). So far, the development of catalyst for bio-derived liquids is basically a

trial-and-error approach. Although an important body of work exists, three challenges in the catalysts development need to be solved: activity, [carbon formation and sintering](#). New catalyst development will require a better understanding of the relation between catalyst properties and reactivity and coking mechanisms. [Tailoring of activity, selectivity and deactivation](#) should include the [perfect control of the shape, size and electronic structure](#) of active metal surfaces.

[Autothermal reforming \(ATR\)](#) of ethanol, glycerol and pyrolysis oil has been investigated, with less intensity than in the case of the steam reforming, using noble metal based catalysts supported onto various high surface area oxide substrates. Autothermal reforming of bio-mass derived liquids follows a very complex pathway, including homogeneous reaction paths and several reaction intermediates. The high reaction temperatures associated with ATR requires the use of catalysts with extreme thermal stability. This requirement puts strenuous demands on the catalyst materials in their agglomeration and vaporisation resistances and structural/morphological stabilities. Additionally, the carbon formation and deactivation by sulphur are also key challenges for ATR catalysts. To develop new ATR catalysts is important to understand the overall mechanism by which the ATR catalyst works and the specific sites responsible for selective-activity. New ATR catalyst development should improve the design of catalysts that allows the tailoring of the structure and size of active metal surfaces to use a very low precious metal content and develop of new precious metal-free catalysts.

[Aqueous phase reforming \(APR\)](#) of oxygenates is another interesting route for the production of hydrogen. This technology is not as well developed as its gas phase reforming counterpart but offers the potential advantage of low temperature (<300°C) processing. APR has been primarily proposed for reforming of bio-mass or the aqueous

phase of the pyrolysis oil. However, the process is very slow and large volume H₂ production is not economical at present. Substantial catalyst and process improvements will be necessary before it can be put to commercial use. Therefore, catalyst development is a primary need for APR. Foreseen developments in the next 20 years in this specific field are:

- understanding the parameters governing the activity, selectivity and deactivation mechanism operating on steam reforming, ATR or APR processes either via theoretical or experimental tools.
- Design of new catalysts based on theoretical ideas from fundamental atomic-scale and nanoscale understanding of SR, ATR and APR processes.
- Development of new catalyst formulations with increased activity, selectivity and durability based on nanoscale control of catalyst site architecture from new preparation routes (core-shell structures, pre-synthesis of metal particles with desired metal crystal planes preferentially exposed, 3D nano-architecture) that allows to design desired active sites and materials with desired properties.

In this field, topics and activities to be supported are:

- design of new catalysts based on theoretical ideas and models,
- development of new catalyst formulations based on nanoscale control of catalyst sites with higher stability.

3.1.3 CO₂ CONVERSION AND SOLAR ENERGY STORAGE

To avoid irreversible and/or undesirable climate change the concentration of greenhouse gases in atmosphere has to be stabilised and preferably reduced. The EU has indicated, as long-term goal (2050), the reduction of 80% of current emissions of CO₂. Alternative to energy and cost-expensive carbon capture/subsequent sequestration (CCS) the utilisation of CO₂ appears a cheaper and equally effective large-scale solution¹⁶.

The production of chemicals from CO₂ can be interesting because CO₂ is cheap and nontoxic (and it can sometime be used instead of toxic chemicals), and capable of yielding totally new materials. New sustainable catalytic processes for the production of high value added molecules can be optimised starting from readily available carbon oxides as building blocks, also employing microwave techniques as an energetically less consuming alternative to conventional heating, in combination with more ecofriendly unconventional solvents, such as Deep Eutectic Solvents (DES), Ionic Liquids (ILs), polyethylene glycols (PEGs), and supercritical carbon dioxide (sc-CO₂). Fuels derive their value by their energy content and the easiness of their storage and transportation; strategic is the reduction of CO₂ to methanol, methane, carbon monoxide, dimethyl ether. The use of renewable energy, characterised by intermittent characteristic, to recycle CO₂ to high value fuels and chemicals, could be a sustainable process with neutral or even neg-

¹⁶ See for example, L. Barbato et al., *Energy Technology* 2014, 2, 453-461. The effective impact of CO₂ use in terms of reduction of CO₂ eq. emissions should be analyzed in terms of [circular economy](#), in which CO₂ conversion is used to impart RE sources otherwise not used. By accounting this aspect, typically not considered, the impact in terms of LCA and a timescale of 20 years, is 10-20 times higher with respect to CCS, with a cost lower than CCS (up to half) and even biofuels on equivalent reduction CO₂ eq. emissions.

ative carbon balance (on LCA bases, by considering the introduction of RE in the production cycle as alternative to the use of fossil fuels). Conversion of CO₂ to transportable liquid fuels will allow to trade renewable energy (used in the conversion process) on a world-scale.

Green hydrogen (rH₂) can be used to reduce CO₂ the obtained products being driven by the process conditions and catalysts. CO₂ is a highly stable molecule and require a substantial input of energy; the process can be carried out with photocatalysis, electrocatalysis, solar-thermal/catalysis, thermochemical/catalysis. Optimised reaction conditions and active catalysts are necessary for any chemical conversion of CO₂. Among the critical issues in several CO₂ conversion processes is the development of high-performance, robust, and inexpensive catalysts operating at low temperatures. The availability and cost of green hydrogen is another point that can be fronted by the use of renewable energy sources and through optimised processes and catalysts: as an example it can derive from wastes. CO₂ can derive initially from bio-based processes (fermentation, bio-gas) as well as some highly concentrated CO₂ industrial streams. The actual amount available is enough for a CO₂ circular economy, where CO₂-based energy vectors are re-captured after specific use (for example, in gas turbines) and thus act as storage/transport medium for RE. From this perspective, the need to capture CO₂ from fuel gases to produce CO₂-based solar fuels is minimal. However, techniques for advanced (energy-efficient) **capture of CO₂** should be explored, as well as techniques for direct use of CO₂, as "tri-reforming" that couples dry-reforming, steam reforming of methane, partial and complete oxidation of methane. Due to concerns whether this approach is really saving

CO₂, studies in this area should be coupled with **in-depth LCA evaluations**. Other critical aspects regard process/catalyst optimisation and control of deactivation. Promising techniques to improve gas-solid efficiency in this reaction regard the use of external magnetic field, although scaling of the technology could be difficult.

The conversion of CO₂ into fuels or chemicals involves its reduction, which requires energy that should be provided by renewable sources of energy. Catalyst development will be the key to lower the activation energies and kinetic barriers for industrially relevant applications. While there have been technological successes with the reaction of CO₂ with high energy substances such as epoxides, advancement in this area needs to focus more on less energetic reagents, such as alcohols and amines. Better understanding of the **catalytic reaction mechanisms** is needed. Faster catalysts for CO₂ conversion reactions with limited equilibrium yields will also permit a better synergy with membranes to remove co-products. Development of electrocatalysts holds promise for better control of the initial reduction and enhancement of product yields. Development should be directed both toward energy vectors such as methanol and formic acid, as well as toward the commodity and fine chemical industry, for example the production of aliphatic and aromatic carboxylic acids.

In virtually all of these approaches, **catalysis plays an important role with significant challenges for electrocatalysis, photocatalysis, and heterogeneous and homogeneous catalysis**. Intermittent operation of catalytic processes under a daily cycle is becoming important, along with classic issues such as catalyst activity, selectivity and stability, also in the presence of dynamic processes.

In a circular economy, CO₂ is increasingly viewed by the chemical industry as a **building block**, rather than a waste product. In some cases, the use of CO₂ for the pro-

duction of chemicals is already at the commercial level. Efforts are underway to react CO₂ with olefins, dienes and alkynes to form carboxylates, carbonates and carbamates. Many of these processes are catalytic ones. Some processes are endergonic and thus more difficult to implement. Currently, many chemical processes rely on synthesis gas (CO + H₂), e.g. Fischer-Tropsch synthesis, hydroformylation and carbonylation. Opportunities should be explored to develop chemistry based on CO₂ + H₂ instead of CO + H₂ as a way to functionalise hydrocarbons while skipping WGS reaction (otherwise it is obvious as the RWGS process enable that and is a mature technology).

The formation of **carbonates and polycarbonates** from CO₂ offers direct access to extensive markets in the chemicals and plastics sectors¹⁷. Recently, significant progress has been made in this area of catalysis. **Catalytic carboxylation** offers new routes to produce carboxylic acids. **Electrocatalytic conversion of CO₂** represents another very elegant form of use for carbon dioxide. Recent advances have shown the possibility not only to reduce CO₂, but also to form C-C bonds during the conversion, opening new routes for the synthesis, of acetic acid for example. However, significant improvements are necessary before technical efficiency levels are reached which can be commercially exploited.

There are a number of reactions of high interest, but still largely at a **dream stage**, even though new interesting approaches and catalysts have been proposed. Examples of reactions include the conversion of methane and CO₂ into acetic acid, benzene and CO₂ to benzoic acid, ethylene and CO₂ to acrylic acid, butadiene and CO₂ to adipic acid. Even for well-established routes, such as the **synthesis of DMC** from methanol and CO₂, new solutions (for

example, the use of organic recyclable dehydrating agent¹⁸ to shift the reaction equilibrium, may significantly improve the performances. DMC can act as a nontoxic methylating and carbonylating agent or as an intermediate in the production of higher carbonates, polyurethanes, isocyanates, and polycarbonates.

Biotechnological conversion of CO₂ involves the use of (modified) organisms to convert CO₂ into useful products under optimised conditions, e.g. the cultivation of bio-mass in greenhouses under increased CO₂ concentration, the growing of aquatic bio-mass by dissolving CO₂ in water, and the targeted synthesis of chemicals. Modifying the organisms by for instance genetic engineering is one of the possibilities to arrive at the right chemicals.

In a **short-to-medium-term** perspective, CO₂ utilisation will continue its progression especially in areas that are technologically more advanced (e.g. CO₂-containing polymers, CO₂ hydrogenation). CO₂ conversion will also have an increasing role to exploit unused renewable energy or to mitigate instabilities on the grid (related to the discontinuous production of energy by renewable sources; thus, chemical conversion as a way to store and distributed energy). These driving elements will open a larger use of CO₂.

In the long term, **CO₂ utilisation will become a key element of sustainable low-carbon economy in chemical and energy companies**. CO₂ will be a **strategic molecule** for the progressive introduction of renewable energy resources into the

¹⁷ Bayer/Covestro, for example, has already launched its dream production of polyols (partially) based on carbonate chemistry showing thus the potential of carbonates in an industrial environment. In order to improve the EU position, innovative solutions for the polymer industry increases the competitiveness with regards to Asian (cf., SK in Korea) and US (cf., Novomer) activities in the area of polycarbonates, a market with a prospect to grow significantly.

¹⁸ Bansode and Urakawa, *ACS Catal.* 2014, 4, 3877–3880.

chemical and energy chain and be part of the portfolio of critical technologies for curbing CO₂ emissions (with an estimated potential impact of gigatons equivalent CO₂ emissions, similar or even superior to the impact of CCS and bio-fuels, but with lower cost for society - see footnote¹⁶).

The **innovation potential** for use of CO₂ as a material thus lies predominantly in the following areas:

- *Photocatalytic or electrocatalytic activation.* Development of electrocatalysts and/or photo(electro) catalysts for production of solar fuels (hydrogen, alcohols, hydrocarbons) from water and carbon dioxide.
- *Synthesis of products with high added value,* in which CO₂ remains in the product as a C1 building block.
- *Hydrogenation of CO₂ with hydrogen from regenerative sources,* to form large-volume chemicals such as methanol and light olefins.
- *Novel routes to green urea,* with ammonia produced using renewable H₂ sources or via novel electrocatalytic approaches.
- *Use CO₂ conversion products* (produced using renewable energy) *to store and transport on a large world scale renewable energy.*

The technology for **solar fuels** production should be robust, scalable and efficient. It should have an operating life of longer than ten years and be based on abundant elements, and the overall system efficiency should be sufficient for it to be able to compete with non-sustainable energy generation. The intermittency of sustainable electrons will pose challenges to the future catalytic processes that store electricity. Direct

electrochemical CO₂ reduction will require **breakthroughs in the field of electro-catalysis** and is considered a medium/long-term target. The most likely scenario, therefore, involves water electrolysis by renewable electrons generated by photovoltaics technology or direct photocatalytic water splitting to produce the H₂ needed for the reduction of CO₂.

The large-scale implementation of **electrolysers** for renewable H₂ production is hampered by the low abundance of active and stable electrocatalysts and their inability to deal with fluctuating conditions. Noble metals are most active for the difficult oxygen-evolution reaction. RuO₂ is the most active material, but it degrades. Usually, titania-stabilised IrO_x is used for oxygen evolution, while Pt is used for hydrogen evolution in an acidic electrolyte. Alkaline electrolytes allow the use of more abundant materials (such as nickel, for both anode and cathode) but still suffer from an order-of-magnitude lower current. Nevertheless, alkaline electrolyzers form a very active field of research. In addition, electrocatalytic reduction of CO₂ to formic acid, methanol, and hydrocarbon is a challenging field.

Integrated photocatalytic devices are increasingly being considered as an attractive alternative. There are many opportunities for improved materials for light absorption, better catalysts for water oxidation with low overpotential, the use of non-noble metal catalysts and their integration into devices in which aspects as light management also need to be considered. With regard to light absorption, the currently available semiconductors are either robust but not very efficient (e.g. TiO₂, Fe₂O₃) or efficient but unstable (e.g. CdS, CdSe). Tandem devices are needed to reach efficiencies that can compete with PV technology. Specific challenges to catalysis are the development of better catalysts to reduce the overpotential of water splitting, especially the water oxidation reaction, and to

build smart interfaces between photo-absorbing and catalytic layers.

The production of **synthesis gas from CO₂** required H₂ under pressure and thus to avoid compression cost, it should be preferably produced at high pressure using solar or other renewable energy sources. From synthesis gas, a wide range of products (methane, methanol, liquid hydrocarbon fuels) can be manufactured with established catalytic technology. Nevertheless, issues remain to be solved with respect to **scaling** such operations to the optimum in terms of local/centralised H₂ generation and allowing for the variable process conditions associated with the possibly **intermittent** availability of H₂. Another aspect of photocatalytic reduction processes of water or carbon dioxide is that pure **oxygen** can be obtained as a by-product. This by-product stream has economic value, because the alternative route, via air separation, is very expensive.

Catalytic CO₂ conversion to chemicals is rapidly developing and new developments are dominated by homogeneous systems, which can selectively reduce CO₂ or build CO₂ in other molecules. The challenge here is to **widen the scope of reactions and products** and to develop more active and selective catalysts. The use of **heterogeneous systems** for this purpose is underdeveloped, except in already existing industrial processes, such as methanol synthesis.

CO₂ is not the only option for storing excess energy in the form of chemical energy. Another opportunity is to use **nitrogen** as the feedstock. It shares with CO₂ conversion the opportunity to use abundant stable chemicals as feedstock to fuels and chemicals.

The results of these researches are expected to develop and optimise a low

cost, highly sustainable technology for turning CO₂ into fuels or chemicals. In general, demonstration of the effectiveness of this process through the implementation of advanced materials and operating strategies can promote the practical application of policies aiming at CO₂ reduction that also support high penetration of renewables. The conversion of CO₂ will positively impact on the global carbon balance while providing a source of renewable fuels. The researches will also promote the deployment of catalysts, tailored for specific applications, and ceramic materials. These researches should be society-driven since are strongly beneficial for environment and health. The objective of the efforts will be addressing mid to long term applications with relevant social and economic advantages. Exploiting CO₂ emissions for producing fuels and organic substrates will address society needs by contributing to implement energy and environment solutions.

3.1.4 ENERGY STORAGE AND CONVERSION

Chemical energy storage is an essential component of the future sustainable energy infrastructure. There are three main options for chemical energy storage¹⁹:

- *producing H₂ from water molecule either using sunlight through water photoelectrolysis/splitting, or using electrical energy (water electrolysis) produced from renewable energy sources;*
- *using reversible reactions (for example, dehydrogenation/ hydrogenation of some organic molecules (LOHC). An alternative could be the synthesis/decomposition of ammonia or of formic acid;*
- *using the H₂-equivalent (H⁺/e⁻) pro-*

¹⁹ Chemical energy storage indicates the storage of renewable energy in the form of highly-energetic chemical molecule.

duced as in the first path to convert low-energy molecules (particularly CO₂) to higher-energy molecules (fuels or chemicals). This approach, although more challenging, will **avoid overpotential and energy losses** in the production or use of H₂, and it is thus intrinsically more efficient. It is part of the development of **photoelectrocatalytic (PECa)** approaches to develop artificial-leaf type (or artificial photosynthetic) devices.

The **solar driven chemistry** offers many different approaches to this issue, even though challenges span from (catalytic) materials to engineering of the devices in order to improve the efficiency. Key issues to master are among others effective catalysts, electron/hole separation and stabilisation and the rate of process. Hence, integrated or decoupled processes to convert solar energy into chemical energy have both to be investigated. To put efficient energy storage into use, superior catalysts are essential. **Molecular catalysts** play an important role in this respect. Between the relevant concepts to explore is the **coupled transfer of multiple electrons and proton (PCET)s**. The concerted PCET of a metal hydride is potentially an energy-efficient pathway.

At the moment it is **necessary to pursue the transition between fundamental research and technological applications**. That includes the integration of new materials, molecular chemistry and biosciences. The implementation of hybrid systems and adding nanoscience to model the interface molecules of materials are between the elements to highlight. It is also very important to integrate all these different subthemes including biochemistry into chemistry.

Catalysis by **nanostructured materials** and **advanced molecular catalysts** are

fast growing research areas all over the world, due to the increasing concerns regarding future energy security and environmental sustainability. Currently, **EU holds a dominant position in terms of investment levels in catalysis research**. The recent advances in the **control of nanoscale materials with atomic-scale precision and in tailored molecular catalysts**, as well as in the characterisation and in situ probing of catalytic processes at the atomic, active site scale envision new scenario for nanoscience-inspired design, synthesis, and formulation of industrially important catalytic materials. Such a control can, in principle, enable a broad development and usage of catalysts for increasingly efficient and selective conversion of hydrocarbons into higher-value fuels and chemical products, thus reducing dependence on oil, providing more effective pollution abatement, and efficiently using solar power²⁰.

A step change in the ability to deliver molecules quickly and efficiently and with 100% efficient synthesis are searched for²¹. Related to this, research into how **assembly processes occur at the molecular and supramolecular levels** with catalysis being a key factor is also a challenging research topic²².

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²⁰ For example, the synthesis of small metal and metal oxide nanoparticles, together with controlled size, shape, and specific surface orientations, points toward a future in catalyst preparation enabling a rational design and synthesis of catalysts with the specifications required for highly specific, structure-sensitive catalytic reactions.

²¹ See, for instance, the UK project called "Dial-a-Molecule".

²² See, for instance, the UK Directed Assembly project. The Directed Assembly project promotes research into how assembly processes occur at the molecular and supramolecular levels with catalysis being a key factor in a number of the project themes. The CO₂Chem project also considers the utilisation of carbon dioxide as a single carbon chemical feedstock for the production of value added products with catalysis as an overarching theme.

²³ For heavy duty vehicles, marine vessels where range is important, FC are regarded as having higher potential than batteries.

molecular levels with catalysis being a key factor is also a challenging research topic²². In addition, complementary, integrated means of carrying out **high-throughput synthesis** and screening of nanostructured catalysts are amenable to allow faster convergence to optimal structures and compositions. Also, realisation and control of **composite particle architecture** over multiple length scales are fundamental for catalyst scale-up and large-scale manufacturing as well as for their exploitation in specific chemical processes (design and realisation of advanced reactors based on properly fabricated reusable and recoverable catalysts).

Characterisation of catalysts by means of *in situ* electron, paramagnetic, Raman, absorption spectroscopic tools, atomic-resolution electron microscopy, at high temperature and pressure or with sophisticated aberration correction tools, along with X-ray diffraction techniques with synchrotron radiation source, or anyway high brilliance sources, need to be developed to further **revolutionised the understanding of catalyst structures** at the nanoscale.

Fuel cell technology is another key technology for converting energy which could greatly benefit from a more integrated use of catalysis. Between the expected benefits: i) the reduction and virtual elimination of energy losses due to overpotential in H₂ activation and O₂ reduction, ii) the elimination, or great reduction, in the use of noble metals as active elements in the electrodes, iii) the extension of the electrocatalyst life-time, especially for operations at full load, high pressure or under frequent shut off/on, and iv) the reduced sensitivity to poisons such as CO. The hydrogen PEM fuel cell (H₂ PEMFC) is the technology which is foreseen to have larger impact, though the interest on Solid oxide fuel cells (SOFC),

particularly for stationary applications, is growing. Nevertheless, PEM fuel cells need further improvements to become a cost competitive and long term stable technology for use in electric vehicles. In this framework, nanostructuring of platinum based electrocatalysts to achieve **a)** highest platinum efficiency (activity per platinum content) and **b)** stabilisation of the catalyst by surface nanostructuring are pursued. The overall goal is to reduce PGM costs and to enhance the stability of catalyst under the challenging operation conditions in fuel cell cars. Among the critical aspects of SOFC, there are the development of anode catalysts with long-term stability and significantly reduced tendency towards carbon formation for conversion of higher hydrocarbons, and the realisation improved performances.

The power densities currently achieved with the direct alcohol fuel cell (DMFC in the case of methanol) are around 10 times below those achieved with H₂ PEM fuel cells. The main difficulties here are – on the material side – the anode activity, which is far too low, and the too high crossover of methanol to the cathode where it causes losses in voltage potential; as a result, it is necessary to work with lower water/methanol ratios in practice. Another task which is of general importance is the miniaturisation of the fuel cell and its peripheral components for use in portable devices. For this, special structures need to be developed which allow passive operation, i.e. without the support of auxiliary units. Current devices for portable applications are delivering power in the range of 100 mW. Systems for charging stations and energy supply systems for on-board electronics in caravans and on yachts are currently delivering in the region of 50-100 W.

In the field of SOFC, developments have to pursue in intermediate temperature SOFC (IT-SOFC), in particular innovative perovskite-based IT-SOFC high-conducting and high-surface area cath-

odes, where the B-site activity is promoted by noble metal doping.

In general, among the further need for research on **electrocatalysis**, the following may be indicated:

- Improved electrocatalysts which will **lower the necessary cell voltage** even further and thus lead to lower energy consumption.
- Improved and **more stable electrocatalysts** (and cell materials) for operations in non-conventional electrochemical cells, such as operating at high temperature and pressure, in tandem cells.
- Extension of the use of the technologies to a **broader range of processes**, which require to develop **innovative and highly productive electrodes** (for example 3D-type) able to **intensify** the processes and reduce the costs.
- Development of **thermal and non-thermal catalysts** (electro- and photocatalysts) for selective conversion of low-value feedstock (e.g. bio-mass, glycerol, etc.) to high-value chemicals.
- Design and development of **oxygen reduction electrocatalysts** for fuel cells applications.
- Development of **bifunctional** (oxidation/reduction) **electrocatalysts** for energy conversion and storage applications (e.g., metal-air batteries).
- Substitute or significantly reduce dependency on CRM such as PGM.

3.2 RESEARCH NEEDS & EXPECTED OUTPUTS

Based on the above discussion, a series of priority areas of catalysis for the **grand-challenge of catalysis** to address the evolving energy and chemical scenario could be identified. Although the previous discussion on the challenges has been divided in four sub-topics, it will be discussed in a unified approach, because in part some of the priority areas may be common to different topics.

In topic of **fossil raw materials**, some main priority areas can be identified. At one end of the spectrum, the increasing exploitation of shale-gas resources is creating new investment opportunities for petrochemical investments based on low cost light alkanes. There are therefore opportunities to add value through improved catalytic transformations such as dehydrogenation and oxydehydrogenation to C2-C4 olefins, the direct functionalisation of light alkanes, C-C-coupling and C1 chemistry bypassing CO/H₂ formation (direct CH₄ conversion) or CH₃OH, as main raw material for chemistry. The integration of catalyst and process design will be instrumental in creating the desired process improvements and flexibility. At the other end of the spectrum, there is the design of robust catalysts and systems for heavy oil conversion (and other heavy hydrocarbons feedstocks such as sand oil, or even coal and solid fossil fuels) that can bridge the widening gap between increasingly variable (heavier and dirtier) feedstocks and the (cleaner) products required. The effects of catalyst-structural parameters and chemistry (including promoters) on the stability and deactivation of catalysts, and the effects of poisons are crucial in this respect.

Even often part of these are considered mature technologies (for example, in the treatment of heavy fractions in refinery), there is still significant space to develop

more **energy-efficient and selective** catalytic processes, for example the modification of steam cracking to lower CO₂ production, would be a great challenge for catalysis. This requires **combining an advanced process design with new catalysts formulations**. Reduction of the overall CO₂ emissions in refinery, for example through the use of catalytic technologies for CO₂ use, is another challenge.

In particular for the area of bio-refineries, there is the need to change the model of production, from large-scale plants focused mainly to bio-fuel production, to small-medium size plants (at regional level), but highly integrated in combined energy vectors and chemical production. Integrated flexible processes (see footnote²⁴) and catalysts for efficient carbon coupling, allowing rapid response to changes both in raw material and energy input, as well as type of product formation, should be developed. The forecast of R&D outputs in above area in the **next one-two decades** will be the following:

- Integrated flexible processes and catalysts enabling rapid response to changes both in raw material and energy input, as well as type/volume of production (see footnote²⁵). This will allow for the design of easily adaptable refinery complexes that can handle a greater variety of feedstocks and follow more closely market demands.
- Improved catalytic processes for the direct use of natural gas and light alkanes to produce chemicals or transportable fuels.
- More robust, stable and efficient catalysts and processes for conversion of heavier and dirtier feedstocks (including coal and solid fossil fuels), thereby increasing tolerance to variable feed-

stocks, as well as catalysts and processes for *in situ* (or at least pre-transport) improvement of crude quality;

- Catalytic systems to allow European refiners to process bio-mass-derived feedstocks in existing or modified refinery infrastructure, alongside conventional petroleum fractions (production of hybrid bio- and fossil fuels);
- Optimised catalysts based on non-precious metals that can replace noble metals and heavy transition metals that are linked to health or environmental concerns.

In **bio-mass utilisation area**, sixth areas of research are defined to address the three catalytic challenges in the development of a mature bio-based economy - stability, selectivity, and integration:

- understand and control the reaction mechanisms and the catalyst functions such as hydrogenation, and acid/base-functions, for operation in water. This will aid the development of stable and selective catalysts;
- understand and control the catalyst selectivity, both chemoselectivity as well as regioselectivity for overfunctionalised feedstock, as this will lead

²⁴ Flexibility in this context indicates the possibility of adapting plant to variable outputs in terms of volume and type of products - see, for example, the F3 Factory EU project.

²⁵ Even if it is often argued that the size of the market is very different between refinery and chemicals, and thus the two productions should be disjointed, the case of biodiesel, with chemical utilisation of the by-product glycerol evidences that this is not correct. Bio-fuels, especially in EU with scarce local bio-mass resources to be used for energy, should be oriented to the production of higher added value bio-fuel additives, whose production can be more comparable in size to chemical production. Bio-refineries at a regional level (to minimise impact of bio-mass transport) should be flexible in terms of type of feeds and products.

to fewer by-products and thus a more efficient process in general;

- understand and control the catalyst reliability and stability under industrial-like conditions, (e.g. in continuous-flow reactors), to overcome typical issues with destruction, fouling (e.g. in true bio-mass-derived feedstocks), or poisoning of the catalyst, all hurdles still hindering the industrial implementation for instance of metal NPs-based catalysts, and to develop an effective process;
- activate bio-mass, i.e. make the solid bio-mass suitable for further conversion. By proper activation of the bio-mass downstream processing becomes more facile i.e. more selective process can be developed. Input from e.g. plant sciences is essential;
- integrate the catalysis with separation technology in order to mitigate the challenges presented by high dilution, feed contaminants/heterogeneity or abundant by-products;
- integrate different forms of catalysis (hetero, homo-, bio-enzymatic-, electro- photo-) to arrive at more efficient product formation (in terms of atom and energy economy).

Research in all these directions will benefit from an **inclusive approach** in which bio-catalysis, homogeneous catalysis and heterogeneous catalysis are considered along with other scientific disciplines (in particular, engineering aspects of process development) and, if beneficial, integrated for the development of efficient, low-cost conversions. Moreover, the options for the integration of fossil and renewable feedstock for an optimised product mix should be considered, i.e. one with the

highest added value. This means establishing which resource (or mix of resources) can be best used in a specific production chain.

Issues with catalysis in general – such as the replacement of scarce and expensive metals in catalysts and the development of dedicated computational tools for modelling experimental results and for data handling – apply to renewables resources just the same for all the other catalysis areas.

The ambition is that **Europe becomes the world-leading in sustainable chemistry**, and more specifically to realise within two decades the **full use** of industrial and agricultural **waste streams** as a resource in the production of chemicals and fuels. The **forecast of R&D outputs** in above area in the next one-two decades will be the following:

- new catalysts with improved reactant selectivity, i.e. the catalyst converts only the desired molecules in a complex mixture.
- understanding factors that determine the stability of catalysts under relevant bio-mass conversion conditions, i.e. stability in water, with respect to poisons and coke formation;
- integrated systems, i.e. integrating the unit operations (bio-mass activation, conversion separations) which make the overall process robust and cost effective;
- integrated scientific knowledge by combining different areas e.g., plant sciences and catalysis

In **CO₂ utilisation area**, there is a great need for a solution regarding the storage of energy from excess renewable electricity in chemical energy. At this point, the most viable solution seems to be to use electrolyzers since it is proven technology, although it can only be scaled up if more

abundant electrode materials are developed. Renewable hydrogen can then be used to convert point-source CO₂ to fuels. Catalysts for both these processes need to be optimised to deal with contaminants present in flue gases (although there are abundant sources of nearly-pure CO₂, from bio-gas and fermentation processes and also from chemical processes, which postpone the issue of CO₂ purity to a second phase) and with the intermittency of renewable energy sources (although also this problem could be solved either using in a first stage untapped continuous sources - hydropower, in particular - and suitable storage systems). The scale at which such operations can be done remains an important issue.

The development of **integrated photocatalytic/photoelectrochemical devices** to produce H₂ is another important area of research for the coming decades. The challenge is to develop both cheap materials for photo absorption and new catalysts and then to integrate those in a device with an overall solar-to-hydrogen efficiency of at least 20% in order to compete with photovoltaic/electrolyser technology. This will require improved characterisation methods for studying photochemical processes in relation to photocatalysis as well as new computational chemistry to deal with specific issues of photocatalyst systems. Another type of integrated device would have to be developed **for storage of renewable energy in the form of chemical energy**. The development of integrated devices will require a systems-catalysis approach that includes such engineering aspects as small-scale and intermittent operation.

In the **long term**, the focus will be on highly integrated solutions enabling the carbon-neutral production of energy in all areas, including mobility and chemicals. To arrive at this desired situation, technology capable of capturing CO₂

from the atmosphere will need to be developed. This may involve **artificial leaf** approaches, in which CO₂ from the air is photocatalytically converted into useful products or intermediates, or approaches in which CO₂ capture is followed by conversion, either electrochemically or by renewable H₂. Biomimetics as well as genetically modified organisms may also be an option. In such a scenario, where humanity no longer depends on fossil resources for energy, these resources (including biomass) could become the starting chemicals for the production of consumer products. CO₂ would no longer be a waste product but would be considered a primary building block. New catalytic processes have to be developed that will allow for an efficient use of CO₂ as a monomeric unit in the production of fuels and chemicals.

The forecast of **R&D outputs** in above area in the **next one-two decades** will be the following:

- scalable electrolyser technology based on cheap and abundant catalytic metals to convert renewable electricity into hydrogen;
- a device with a solar-to-hydrogen generation efficiency ≈ 20%, beating the efficiency of PV technology;
- catalytic technologies to store renewable electricity and/or renewable hydrogen in liquid fuels;
- the integration of solar energy and CO₂ use in chemicals and fuels production;
- emergence of a world-scale system to trade solar fuels and chemicals, and thus the associated renewable energy, as currently made using fossil raw materials.



4 CATALYSIS FOR A CLEANER AND SUSTAINABLE FUTURE

Catalysis is a **key enabling technology for a cleaner and sustainable future**, and it is thus necessary to intensify research in these areas. Two main directions can be identified

- *Catalysis for eco-technologies*, from air to water and waste, to address stationary to mobile; this area includes the aspects of photocatalysis related to depollution, while other related to energy are included in the previous section.

This area includes, *for instance*:

- * Environmental heterogeneous catalysis: catalytic combustion/oxidation of VOC and CI-VOC, removal of organochlorinated compounds and abatement of combustion emissions.
- * Development of novel (photo) catalysts and (photo)catalytic technologies for water and air depollution, and for sterilisation in health and hygiene applications
- *Catalysis to improve sustainability of chemical processes*, in terms of atom economy (the aspects related to energy economy are included in the previous section) and improved pro-

cesses to produce the main intermediates and chemical prod-

KEYWORDS alkanes direct use, asymmetric catalysis, bio-based polyesters, biocatalysis, bio-mimicking systems, cascade reactions, catalyst design, catalytic combustion, C-C coupling, CH₄ emissions, chemocatalysis, chiral catalysts, circular economy, compartmentalization of catalysts, copolymerisation of nonpolar olefins, curing and vulcanization, depolymerisation, dialkyl and diaryl carbonates, DMC, eco-technologies, enantiomerically pure active ingredients, enzymatic catalysis, exhaust gases from internal combustion engines, fuel efficient engine operation, functional polymeric materials, greenhouse gases, hybrid materials, hydrodehalogenation, hygiene and bio-security, industrial gases treatment, integration of multiple catalytic cycles, low temperature catalysis, metagenome, metallocene, micellar catalysis, monomers, nanocatalysis, nanoreactors new synthetic reaction types, NO decomposition, NO_x, olefins, organocatalysis, photocatalysts, polycondensation catalysis, polymers, polyolefin catalysis, post-polymerisation surface modification, renewable raw materials, single-electron transfer living radical polymerization, smart catalysts, smart synthetic routes, soot removal, sustainable catalytic processes, sustainable chemical processes, very small particulates, vinyl monomer copolymerization, VOC, water treatment, wastewater purification, zeolites

ucts/monomers; this area includes:

- * the effort to move towards 100% selectivity;
- * catalysts in novel process design for resource and energy efficiency;
- * novel catalytic processes to reduce eco-impact or risk of fine and specialty chemicals production (including asymmetric catalysis, organocatalysis and enzymatic process, tandem process);
- * catalysis for novel polymer materials and intermediates; one of the examples is the synthesis of industrial relevant polycyclic carbonates, for which effective catalysts are still lacking.

Realise these objectives require an **integrated effort** between catalyst and process design/engineering, the two aspects being intertwined and not sequential. For this reason, a challenge is also to proceed towards a new eco-conception (based on an integrated LCA and sustainability catalysts and processes evaluation.

4.1 CHALLENGES AND OPPORTUNITIES FOR CATALYSIS

4.1.1 CATALYSIS FOR ECO-TECHNOLOGIES

Although several of these technologies are already in practice, new areas, in particular for catalytic water and wastewater purification, and the increasing demand of lower emissions levels, require continuing R&D effort in this section.

Catalytic water and wastewater purification

Catalytic water and wastewater purification is an **emerging area**, even if some of the technologies, for example for wet catalytic oxidation or nitrate catalytic removal as well as photocatalytic depollution, are known from years. Due to the increase in global population and improved standards of living, demands for clean water are set to rise dramatically in the future, and this will ultimately result in a massive shortage. Consequently, the **protection of water** as a vital resource is of fundamental importance for society. Today, the fraction of contaminated surface waters and groundwater reservoirs by chemicals such as pesticides and their metabolites, halogenated or halogen-free hydrocarbons like methyl tert-butyl ether (MTBE), nitrate as well as pharmacologically or endocrine-active substances is dramatically increasing. In addition to intensive farming, these problems are also caused by communal and industrial wastewater treatment processes which are not effective enough.

Current water and wastewater treatment technology must be improved in order to meet the increasing demands of the future, also from the point of view of catalysts. Photocatalysis is a potential great clean technology, but

there are different limitations, in particular the low activity by solar light. Therefore, the development of real industrial applications must be addressed by developing new catalysts with high activity in the visible region of the spectrum, no waste or toxicity production and easy recyclability.

Consequently, there is a demand for **new, innovative technologies for water and wastewater purification**. Different technologies should be used for industrial or domestic water treatment (and recycle), point discharge and diffuse contamination. This includes the treatment of biological as well as chemical hazards and contaminants. Catalytic pre-treatment may be also used to augment the efficiency of current processes and the best integration within technology trains should be explored.

The expansion of bio-based processes is also increasing the need for efficient technologies for water purification, because the **impact of biotechnologies** on water system is much larger to that related to production/use of fossil raw materials.

Catalysis for hygiene and bio-security

Catalysis and photocatalysis may have a role in controlling biological hazards; for example, in hospitals or commercial premises through technologies for sterilisation of surfaces or air conditioning systems. With an increasing abundance of drug resistant bacteria, creating hygienic environments in medical facilities, commercial or municipal premises, or in public transport may become increasingly important. Catalytically activated surfaces or surface treatments, or sterilisation of water and air flows may provide solutions in some areas.

Treatment of industrial gases

Treatment of industrial gases is another major challenging area in catalysis for eco-technologies. With the aid of catalysts for air purification, a wide range of different emissions has been controlled for many

years – particularly in the fields of transport and traffic (catalytic converters in car exhaust systems), emissions from power stations (flue gas desulphurisation and denitrification), but also from a range of industrial and commercial applications. Today, the aim in most cases is to achieve or surpass legal limits on the emission of organic solvents, nitrogen oxides, SO₂, dioxins or carbon monoxide.

Addressing **greenhouse gases** emissions in another challenge. The contribution of catalysis to decrease CO₂ emissions has been addressed in the previous challenge, but other greenhouse gases contribute significantly to global effect. Methane and nitrous oxide (N₂O), even if emitted in relatively low concentrations, have a greenhouse effect per molecule several times higher than that of carbon dioxide. Modern catalyst developments offer a significant potential here for a sustainable reduction of these greenhouse gas emissions as well. One successful example is the use of catalysts to reduce nitrous oxide from nitric acid plants, an application which today already accounts for savings of around 10 million tons of CO₂ equivalents per year.

After-treatment of exhaust gases from internal combustion engines

Pollution of the atmosphere is one of the prominent challenges of the developing as well as industrialised societies. About 50% of the atmospheric pollution originates from mobile sources (i.e. transportation vehicles) via combustion of fossil fuels. Thus, environmental pollution generated by human activity is strictly regulated by governmental agencies in order to improve the air quality particularly in the urban settings (see EURO VI emission control standards active from 2014 in the European Union (EU) countries).

After-treatment of exhaust gases from internal combustion engines currently is the largest technical application of catalysis and will most likely remain so in the foreseeable future. In recent years, working in tandem with catalyst and fuel producers, the European automotive industry has managed to significantly reduce both fuel consumption and emissions, at least as long as measurements are performed during the predefined test-cycles. For gasoline engines, the continuous improvement of the performance has led to meet the continuously more severe thresholds imposed by the European standards. For diesel cars, more powerful oxidation catalytic converters and improved soot filters have also been able to reduce the carbon monoxide/hydrocarbon emissions and the soot particulate emissions. The current public discussion about high NO_x emissions in urban areas and the shortcomings of the current test cycles clearly show the need for new technological solutions to meet the requirements for **real driving emissions**.

Furthermore, it is clear that the more stringent legislation limitations (EURO VI) require the addition of De-NO_x catalysts to oxidation catalysts (DOC) and catalytic soot filters (CSF, or DPF). Although several investigations on the soot combustion catalysts have been conducted and catalysts for NO_x storage and simultaneous NO_x-soot removal have been developed and studied, some problems still remain. Among them, the too high temperature of soot combustion and the relatively low NO_x storage capacity (NSC) are the main aspects. So how to simultaneously remove soot and NO_x in the low and same temperature region, such as 200–400°C, is still a challenging task. In addition, with the more efficient motors either more efficient catalysts at lower temperatures are required or, alternatively, catalysts are operated at pre-turbo conditions at elevated pressure. An important aspect is also the decrease of the complexity of the catalytic systems in future.

The **marine sector** has seen much less development, due to lack of regulations. In addition, the fuel quality is lower and more diverse. New regulations are however coming and will be enforced in coast near areas and harbours where emissions are a severe problem. The MARPOL convention of the International Maritime Organisation (IMO) regulates NO_x and SO_x emissions to air from ships. Supply of efficient, reliable emission abatement technologies will therefore be required in future marine propulsion.

Although **automotive catalysis today can be viewed as one of the great success stories of applied catalysis**, severe challenges are ahead, driven by both, the ambitions of the European Union with respect to air quality and CO₂ reduction, as well as by the specific technical requirements (transient operation, harsh ageing conditions).

The main challenges can be identified as follows:

- **Real driving emissions:** new legislation is required that guarantees functional exhaust treatment during real life driving, not only in specified test cycles. This legislation will substantially increase the cost (in terms of money but also raw material consumption and fuel economy) of the exhaust treatment, especially for Diesel engines. This increased cost impairs the competitiveness of the CO₂ efficient Diesel engine. Since the use of Diesel engines is essential for Europe's strategy to meet its CO₂ targets, new breakthrough technologies are required that significantly reduce the cost of Diesel exhaust treatment.
- **Low temperature catalysis:** increased fuel efficiency of future

engines naturally will lead to lower exhaust temperatures. For Diesel exhaust treatment, catalysts will be required that show near 100% conversion at temperatures below 100° C. Today, this target could only be reached with excessive precious metal concentrations. Therefore, there is a need for new concepts that allow obtaining **low temperature activity with low amounts of precious metals**.

- **Enabling more fuel efficient engine operation:** in many cases, there is a trade-off between fuel efficiency and engine-out raw emissions. A prominent example is the heavy duty truck Diesel engine, where NO_x raw emissions strongly increase if the engine is operated in the most fuel efficient mode (i.e. without exhaust gas recirculation). Therefore, more efficient and robust catalysts are required, that show large enough conversion, so that engines can be run in the most efficient way.
- **Abatement of CH₄ emissions (especially in lean exhaust):** one way to reduce CO₂ emissions is the increased use of CH₄ as a transportation fuel. The main challenge for the introduction of CH₄ propelled engines is the CH₄ abatement. For this reason, new technologies for the **catalytic activation of CH₄ at low temperatures** under exhaust conditions are required. The most fuel efficient mode of operation would be lean combustion of CH₄. However, activation of CH₄ under lean conditions is even more challenging than under stoichiometric conditions, so that new ideas are required to overcome this challenge.
- **Reduction of very small particulates:** efficiency of current automotive catalytic filters with small particulate (PM 2.5) should be improved.

- Pre-turbo applications
- Operation of the catalysts at elevated pressure and harsher conditions.

As for all other application fields discussed in this Roadmap, also in automotive catalysis, **a knowledge based approach will be the key to find solutions** for the above-mentioned problems. It needs to be kept in mind though, that in automotive catalysis the situation is complicated by the **specific operating conditions of the catalyst**, namely harsh ageing conditions and a highly transient operation. A **mechanistic understanding** of exhaust catalysis is complicated by the highly transient operation conditions and by the fact that the state of catalyst continuously adjusts to these changes. A full understanding can therefore only be pursued if transient changes in the catalyst state are incorporated into the analysis, which will require a very close synergy of **in situ and time-resolved experimental methods, transient experiments and computer modelling**. The catalysts need to be designed, characterised and modelled at the molecular and the global scale (hierarchical design, characterisation, modelling)

A number of **possible solutions** are outlined below:

- **New redox active materials** that show low temperature activity with low or no precious metal content (for example perovskites as recently demonstrated by some companies).
- **New Zeolites with optimised pore structure** to increase thermal stability and to be active in a large temperature window, for example chabasites.
- **Multifunctional catalyst devices.** The reduction of system complexity

- **New Zeolites with optimised pore structure** to increase thermal stability and to be active in a large temperature window, for example chabasites.

- **Multifunctional catalyst devices.** The reduction of system complexity and cost by integrating several functionalities into a single device. For example, layered/zoned designs and the integration of SCR washcoat into particulate filter or three-way catalyst into the gasoline particulate filter.

- **Design of catalysts and exhaust systems based on multiscale modelling** that relies on a mechanistic understanding of the surface chemistry. Application of modelling for the development of integrated operating strategies for engine and exhaust system.

- **NO decomposition in lean exhaust.** Decomposition of NO in oxygen excess remains the grand challenge of exhaust catalysis.

- **Improved catalyst performance by better control of meso- and microporosity.** New synthesis strategies for meso- and microporous nanomaterials with increased thermal stability.

- **Photocatalytic abatement** of VOC, NO_x, particulate.

- **Smart catalysts that allow reactivation by composite formation or core-shell particles**

Catalytic combustion

Catalytic combustion is another well-known area, but which still need some developments. Catalytic combustion processes not only deliver a rationalised and low-emission mean of converting energy in burners, gas turbines, reformers and fuel

cells, but can also be used for after-treatment of exhaust gases in stationary and mobile systems. Catalytic combustion offers important advantages over flame combustion in relation to reduced levels of pollutants and a higher degree of efficiency.

One of the still open issues is the need to substitute noble-metal based catalysts. The search for cheaper alternative catalyst materials has shown that relatively good catalytic activities can also be achieved with oxides and mixed oxides, but improvements are still necessary. One of the challenges here is to keep the high specific surface areas stable even under the high temperatures (gas turbine) which sometimes occur during the energy conversion process – even in long-term operation. Current challenges in the development of catalytic burners include improvements in terms of performance capability, improved long-term stability and the reduction of costs. One of the areas of activities is the catalytic combustion under localised low-air conditions (rich-catalytic lean-burn combustion, RCL) in order to provide hydrogen and synthesis gas (CO, H₂) for gas turbines and for auxiliary power units (APUs) in vehicles. Here, variations in the chemical composition of the fuels, unsteady operating conditions (load changes, variation in the air/fuel ratio) and exhaust gas recirculation place special demands on the catalysts.

Significant applications for catalytic combustion include the purification of low-polluting industrial exhaust gases and the after-treatment of exhaust gases from internal combustion engines. However, the operating conditions in relation to fuel, concentration and temperature are very different here than they are in pure energy conversion systems. Particularly the use or admixture of natural gas and/or fuels produced from bio-mass results in exhaust gas

compositions and temperatures for which no adequate catalyst systems are yet available.

4.1.2 CATALYSIS TO IMPROVE SUSTAINABILITY OF CHEMICAL PROCESSES

This topic includes several areas of interest, from the sustainable synthesis of monomers (for polymer sector), to new "green" processes to produce active ingredients in the fields of pharmaceuticals and agriculture, to approaches aimed at replacing organic solvents with water, and in general to afford greener production. A further stringent issue is the efforts devoted to development of catalytic procedures to implement *energy and atom efficient processes* promoted by *eco-friendly catalysts*. In order to address these two main objectives possible solutions could be i) to produce benign by-products (such as H₂O and N₂) with low molecular weights, ii) to use earth-abundant first row metal catalysts (such as Fe, Co, Mn) which reduces the environmental impact of processes and reduces the costs of the processes and iii) to employ a low loading of bio-inspired catalysts to improve the ecological aspect of catalytic procedures and reduce waste to achieve a low E-factor (defined as the mass ratio of waste to desired product and the atom efficiency).

Also, and not less relevant, a precise conceptual distinction of different scientific-technical approaches in catalysis according to the *EU Waste Hierarchy* will facilitate both, revealing the full potential catalysis offers and translating scientific findings into industrial benefits. Also referred as "The 3R's" this principle should be incorporated in catalysis²⁶:

- Reduce

²⁶ A first attempt has been published online in Speciality Chemicals Magazine (2015): <http://www.specchemonline.com/articles/view/the-3-rs-in-homogeneous-catalysis#.VTfUCZPDsoQ>.

- Reuse
- Recycle

Albeit partially incorporated in catalysis, the impact of Green Chemistry approaches (e.g. water-based catalysis, low E-factor) cannot be overestimated. Hence, this field in catalysis should be broadened as well as deepened. Since the industrial implementation of Green Chemistry approaches is often linked to socio-economic barriers, the role of start-ups should be intensified.

Catalysis for novel monomers and polymer processes

Polymer materials are indispensable in almost all industrial sectors, with a wide range of applications as functional materials and body materials which is constantly expanding and constantly being redefined. For many sectors of industry, commercial and technological progress depends to a large extent on technological advances in the field of polymer materials. This is defined in turn by the progress made in terms of catalytic processes and the availability of the necessary monomers.

Polymer industry faces the following fundamental challenges:

- For simple monomers, the challenge is to find more sustainable routes which can *bypass the previous dependency on oil*, as well as to improve the energy efficiency of established methods. Preferably, monomers produced by these alternative raw materials should be drop-in products, otherwise should lead to polymers having superior performances. One example is the production of bio-based PEF (polyethylene furanate) in substitution of PET (polyethylene-terephthalate).
- For environmental and commercial reasons, process engineering faces the task of *replacing catalytic liquid phase processes* with solvent-free gas phase processes, which will require the development of innovative catalyst systems. For composite-polymers, the challenge is to use the additive both as catalyst (for polymerisation) and reinforcing agent to allow an optimal dispersion within the polymer matrix and reduce process costs.
- The improvement of *techniques and catalysts for the production of monomer building blocks* on the basis of low cost raw materials (e.g. methane → synthesis gas → methanol → olefins). Here, top priority goes to the improvement of MTO catalysts (methanol-to-olefins). Alongside methanol as a C1 source, it is desired to develop more efficient synthesis routes to higher alcohols (propanol, butanol), so that these products can then be converted into olefins via catalytic dehydration. The primary objectives of catalyst development are: improvement of the mechanical stability of powdery and formed catalyst types, optimisation of resistance to catalyst coking and poisons, and better control of product distribution and hence more efficient and sustainable utilisation and recycling of raw materials.
- Processes and bio-catalytic systems for the *saccharification of lignocellulose and conversion* into bio-ethanol as a raw material for ethylene.
- Single-step processes for the *conversion of ethylene*, preferably regenerative ethylene, into propene, e.g. via catalytic "one-pot" combination of ethylene dimerisation/isomerisation/metathesis into C3 monomer.

- New methods and catalysts for heterogeneously catalysed fixed bed synthesis of **dimethyl carbonate** for the polyurethane industry, starting from natural gas as an inexpensive and environmentally friendly raw material variant.
- New processes and catalysts for **less energy-intensive capture** of nitrogen in natural gas based hydrocarbons (acrylonitrile, caprolactam, amines, imines, aniline).
- Improved processes for **dialkyl and diaryl carbonates** starting from carbon dioxide.
- Design and catalytic synthesis of materials (plastics and coatings) with targeted properties. This involves both control of the bulk as well as the surface properties of the material. Underlying catalytic technologies address polymerisation and cross-linking, monomer design and synthesis, and (post-polymerisation) surface modification.
- Production of materials based on renewable feedstocks, in particular carbohydrates and fatty acids. The approach may target at replacement of petrochemical routes for known drop-in monomers, or at new bio-based monomers for materials with improved properties, such as poorly hydrophilic materials derived from fatty acid based monomers.
- Catalytic technologies that contribute to the set-up of a circular economy by enabling recycling of plastic waste. Catalysis may contribute to the development of depolymerisation technology. It may also address specific plastic recycling steps that are crucial to regenerate a material that meets

the requirements to re-enter the product manufacture chain.

In addition, work that aims at **improving existing processes** by increasing fundamental knowledge should be also encouraged. For example, polycondensation is of very high industrial importance, yet it is plagued by a lack of control of undesired transesterification or transamidation, molecular weight/distribution, and chemoselectivity. As another example, a better understanding of widely applied but toxic catalysts for polycondensation (tin) or curing (cobalt) is highly desirable to enable the development of alternative catalysts with properties that are more in line with current legal and SHE requirements.

Due to the enormous diversity of their material properties and their advantages, from a quantitative point of view, polymers are the biggest organic end products in the chemical industry. The selective development of **new polymer structures** will require the application of catalytic processes. Today, it is already possible to manufacture polyolefins with a desired microstructure with the aid of Ziegler-Natta catalysts and metallocene catalysts or other "single-site" catalysts. Alongside the molecular structure of the active centres, suitable carrier structures are significant for industrial polymerisation techniques and for controlling the morphology of the product. Here, one of the challenges for the future is to develop improved catalysts which are also more temperature-stable and more cost-effective.

Another important challenge is the development of technically usable polymerisation catalysts which enable the conversion of polar substrates and reactions in polar media. New routes to polymers which exploit the **molecular structure of renewable raw materials** will require a degree of tolerance to the functional groups containing oxygen which are present in fats, oils and carbohydrates. This will also open up access to materials and functional materials with

innovative microstructures which to date have not been technically accessible. Suitable catalysts are also the key to the utilisation of **carbon dioxide** as an ecologically and commercially advantageous **building block for polymers**.

Although catalytic methods allow many polymers to be made, to measure and hence offer many different ways to improve material properties, processes for the **copolymerisation of nonpolar olefins** with polar vinyl monomers like acrylates, vinyl esters, acrylonitrile or amides are in the domain of traditional radical processes. Even though encouraging process has been made in this field recently, the development of catalysts which can be used on an industrial scale is a major long-term challenge. Aqueous emulsion polymerisations are applied on a large scale for the production of environmentally friendly water-based paints and coatings. Compared to these traditional radical methods, catalytic emulsion polymerisation will enable the fine-tuning of microstructures and open up access to new emulsion polymerizates.

For industrial realisation of e.g. paints which are more resistant to light and hydrolysis, improved, water-stable catalysts are once again the key. Catalysts which are insensitive to polar groups are also desirable for the direct production of macroscopic components with a controlled pore structure which can serve as carrier materials e.g. for chemical analysis. To date realise a strictly defined sequence of **two or more building blocks** is still an issue. Nature shows us the exceptional opportunities that this would open up, for example in the case of polypeptides, which are made up of just 20 amino acids. As more than 100 monomers are available for these techniques, a corresponding ability to selectively combine these building blocks could result in polymers with un-

known properties and potential applications we cannot even dream of yet. Undoubtedly, this type of copolymerisation process will only be achievable in the long term with the aid of innovative catalysts.

New materials with an **improved combination of mechanical properties**, in particular modulus and impact strength, as well as innovative properties like conductivity, can be manufactured by incorporating nanofibers and nanoparticles in the polymer matrix. One possible technique would be to add functional groups to such nanoparticles and to polymerise them or provide for the uptake of soluble catalysts onto the surface of the particles and thus polymerise olefins and vinyl monomers. This would produce nanocomposites in which the nanoparticles would be dispersed in the matrix in non-aggregated form. Even under high levels of energy input, it is often not possible to achieve such a high degree of dispersity through retrospective incorporation of nanoparticles.

A major inroad into innovation for polymeric materials will be the **design and catalytic synthesis of functional polymeric materials** displaying targeted properties. This involves both the bulk as well as the surface of the material. Catalysis with tailored properties plays an important role in polymerisation, cross-linking, degradation and (post-polymerisation) surface modification. It is applied to influence the chemical nature of the material as well as the temporal and topological aspects of its function. The increased introduction of catalytic concepts within materials-surface science may lead to important breakthroughs in the manufacturing of functional polymeric and hybrid materials.

Polyolefins are the largest scale polymer class, but other important polymers are polyesters, polyurethanes and polycarbonates. By strengthening the potential of "catalysis" to serve all these markets by appropriate innovative approaches it will

appropriate innovative approaches it will create a higher degree of competitiveness by European industry and preserve/strengthen employment in this relevant area. In 2011, the global production of polyolefin-based plastics has surpassed 110 million metric tons per year. Nevertheless, polyolefins suffer of scarce surface properties such as adhesion, dyeability, printability and compatibility. Despite its huge industrial importance, [polyolefin catalysis](#) still deserve R&D. Increasing our level of understanding of this type of catalysts is highly desirable as that would allow better fine-tuning and control of the polymer properties. In general, the challenge in catalytic technologies for polyolefins synthesis is the [control of the product micro-structure by a suitable catalyst](#). This includes the use of block copolymerisation, the control of bimodality, and the inclusion of a polar functionality in the product material, which for example could render the material oil-resistant or lead to improved adhesion. This latter is one of the main unsolved problems in the field of polymer chemistry is represented by the synthesis of functionalised polyolefins.

Among the different typologies of [functionalised polyolefins](#), two classes are highly desirable: **(a)** branched polyolefins having randomly distributed functional groups; **(b)** linear polyolefins having the polar monomer into the main polymer chain. Currently, the two technologies applied for the industrial production of functionalised polyolefins are *i)* radical polymerisation and *ii)* post-polymerisation functionalisation. Both technologies are based on radical reactions that require high temperature and pressure, thus implying high energy consumption, low cost efficiency and poor control over the macromolecule structure. To overcome these limits, the most straightforward approach consists in the development of [highly efficient ho-](#)

[homogeneous catalysts for the direct, controlled apolar/polar vinyl monomer copolymerisation](#). Up to now, two major catalytic systems have been reported in the literature for the ethylene/vinyl polar monomer copolymerisation. Both of them are based on palladium complexes and differ in the nature of the ancillary ligand present in the metal coordination sphere. Both catalytic systems lead to real copolymers and not to a mixture of the two homopolymers. Nevertheless, all the catalytic systems reported show productivity values which are far below for any industrial exploitation of the reaction, therefore there is a strong requirement [for novel catalysts that lead to an enhancement of catalyst efficiency](#) of two or three orders of magnitude and that at the same time incorporate at least 20 % of the polar monomer.

To that end, polymerisation catalysts are needed, including those that allow block copolymerisation and those that accept monomers functionalised with heteroatoms. Such monomers may go beyond olefinic monomers.

[Polycondensation catalysis](#) for polyesters, polyamides, and polysiloxanes is still a largely unexplored territory for the catalysis community. Actually there are approaches reported in the recent literature that show nicely that micro-control over the synthesis of such polymers is indeed possible. This creates therefore added potential towards tailor-made materials/plastics, some of which incorporate renewable building blocks. This will surely serve the European polymer industry upon development of new catalytic and innovative polymerisation processes.

The [catalytic reactions form a complex kinetic network with poorly understood multiple equilibria](#). So far, little control over undesired transesterification or amidation is present as well as over molecular weight/distribution or chemoselectivity (e.g. the distinction between aryl and alkyl monomers). There is

also a need for methods that will allow selective end-group functionalisation without breaking the polymer chain. Gaining control of these aspects would mean getting closer to true precision (tailored) synthesis. Another challenge concerns the development of [lower-temperature technology](#), which is desirable for reasons of LCA impact, atom efficiency, selectivity control, and the extra opportunities for the use of thermolabile monomers. HSE regulation might prompt us to look for low-toxicity substitutes for the current tin catalysts, as well as for catalytic technologies to recycle these materials. The development of "restriction catalysts" that would cut the bond between specific monomers analogous to enzymatic degradation is an interesting option here.

There are also various challenges arising from (autoxidative) [curing and vulcanisation](#) as application areas. Here, too, HSE regulations put pressure on the development of substitutes for the widely applied cobalt catalysts for autoxidative curing of alkyd resins. The development of efficient reversible rubber-vulcanisation technologies presents another challenge that addresses the increasing need for efficient recycling technologies. Catalysis is generally expected to contribute the set-up of a **circular economy** by enabling recycling of plastic waste and to the [development of polymers that can reversibly be depolymerised](#) and trigger (bio)degradation, addressing environmental problems (e.g. "plastic soup"). It may also address specific plastic recycling steps that are crucial to regenerate a material that meets the requirements to re-enter the product manufacture chain.

Another challenging area concerns the research and development of [latent catalysts that become active in curing or self-healing on demand](#) and can be included within the product. Related to these topics,

catalytic technologies that enable innovations for advanced, renewable, and recyclable materials in the field of polymers are sought:

- design and catalytic synthesis of materials (plastics and coatings) with targeted properties. This involves both control of the bulk as well as the surface properties of the material. Underlying catalytic technologies address polymerisation and cross-linking, monomer design and synthesis, and (post-polymerisation) surface modification.
- materials based on renewable feedstocks, in particular carbohydrates and fatty acids.

The approach may target at replacement of petrochemical routes for known drop-in monomers, or at new bio-based monomers for materials with improved properties, such as poorly hydrophilic materials derived from fatty acid based monomers. Finally, there are also various challenges arising from the limitations of the technologies that are currently employed in the [post-polymerisation surface modification](#) of materials. The most widely used method, i.e. plasma treatment, requires specialised, dedicated equipment, is very aggressive and unselective, and suffers from a lack of topological control. A key requirement is that the bulk properties of the polymeric material not be significantly altered, e.g. by undesired chain-breaking reactions. Evidently, especially the surface modification of polyolefins presents a very challenging task, given the very unreactive nature of the aliphatic methylene groups.

Opportunities for catalysis in this area are relevant. Bio-catalysis for material-science applications is an active and fast-growing field of research. Significant progress has been achieved in this area, not only with respect to enzymatic polymerisation catalysis, but also with respect to enzymatic surface modification.

For catalytic surface modification, research on chemocatalytic approaches strongly lags behind enzyme catalysis. There are clear opportunities for both bio- and chemo-catalysis in this area, with strong synergism arising from exchanging reactivity concepts. Recent approaches in homogenous catalysis such as ligand-assisted catalysis or outer-sphere catalysis should be explored as leads for **new concepts in catalyst design**. Clear opportunities also arise from the need to achieve improved control of material properties by a better understanding of the various types of commercially relevant heterogeneous polymerisation catalysts, such as Ziegler-Natta and siloxane polycondensation catalysts. An interesting approach with many opportunities towards improved materials is the development of **hybrid materials** made of polyolefins and engineering plastics.

The development of a **heterogeneous block-copolymerisation catalyst** is also of great interest in order to achieve better control of material properties. Block copolymerisation in general offers many opportunities to improve the current situation. **Organo-catalytic** approaches appear to be of particular interest, given the increasing pressure imposed by HSE regulations to avoid toxic metals. **Supplemental Activator and Reducing Agent Atom Transfer Radical Polymerization (SARA-ATRP)**²⁷ is one of the more interesting new developments with potential to meet industrial demands given the sub-ppm level catalyst loadings.

The transition towards bio-based monomer production (e.g. from fermentation) offers an opportunity to rethink the traditional process routes. If, as in the

case of **polycondensates**, monomers need to be activated before polymerisation, they could be activated directly through an appropriate catalytic process. This would require the **integration of multiple catalytic cycles**. Integration of bio- and chemo-catalytic cycles may require development of enzymes that operate efficiently in media that allow sufficient solubility of the polymeric material.

The polymer industry is under the urge of mitigating the environmental cost of petrol-based plastics. Biotechnologies contribute to the gradual replacement of petrol-based chemistry and the development of new platforms of renewable products leading to the closure of carbon circle. An array of bio-based building blocks is already available at industrial scale and is boosting the development of new generations of sustainable and functionally competitive polymers. Polylactide already represents a successful case.

Innovations in the field of **bio-based polyesters** can be regarded as a paradigm of the **increasingly intimate integration between biotechnologies and sustainable chemistry**. Homogeneous molecular systems have shown great potential amplifying the role of catalysis as a KET in the development of bio-based polymers. Bio-catalysts are able to add higher value to bio-based polymers by catalysing their selective modification but also their *in vitro* synthesis under mild and controlled conditions. The ultimate aim is the introduction of chemical functionalities on polymers surface while retaining their bulk properties, thus enlarging the spectrum of advanced applications. Although industrial projections indicate that by 2025 sustainable biotechnologies will contribute to the production of one quarter of chemicals and polymers, their success will depend not only on technological factors. This target looks quite ambitious, but even lower levels of market penetration can be relevant. Availability of renewable feedstock not competing with

²⁷ On this new theory, see for instance "SARA ATRP or SET-LRP. End of controversy?" in *Polym. Chem.*, 2014, 5, 4396 and further papers *Macromolecules* 2015, 48, 5517–5525 and *Macromolecules* 2014, 47, 560–570.

food is one of the issues, together with the capacity of new products to penetrate the market. Great expectations are rising from bio-conversion of CO₂, but strong efforts are still required in this field. Algal technologies and other non-conventional sustainable sources of bio-mass (e.g. insects) may also contribute to relieve the pressure on soil exploitation.

Research must be directed not only towards the replacement of existing petrol-based polymers but also for conferring higher value and competitive functions to bio-based polymers. A stronger integration between biotechnologies and chemistry is necessary for the success of the new generation of bio-based polymers, which must compete with well-established products, optimised through decades of innovation practices. Efforts are still needed for **enlarging the portfolio of enzymes and catalysts** but also for the optimisation of bio-catalysed processes, moving away from conventional chemical-engineering paradigms.

Novel sustainable catalytic processes to active ingredients and fine chemicals

The development of new active ingredients in the fields of pharmaceuticals and agriculture plays a significant role in terms of feeding and providing healthcare for an ever growing world population. Due to the stereoselective nature of interactions between active ingredients and the target, there is an increasing demand for enantiomerically pure compounds. This increase in demand for enantiomerically pure compounds is accompanied by huge academic advances in the field of asymmetric synthesis and catalysis, although in many cases these cannot yet be translated into industrial practice.

In detail, the development of **highly selective and active chiral catalysts**

which would enable cost-effective production of highly valuable enantiomerically pure compounds [e.g. chiral catalysts for: **a)** C-C bond formation to yield either acyclic or (poly)cyclic molecules, **b)** C-Heteroatom bond formation, **c)** C-H bond activation / functionalisation processes, and **d)** dynamic asymmetric resolutions] is foreseen. In fact, in the last decades there has been a constant increase in the demand for enantiomerically pure compounds by many industrial sectors, such as pharma, agrochemical, nutrition and cosmetics, among others. This increase has been accompanied by huge academic advances in the field of asymmetric synthesis and catalysis but with very poor translation to industry.

Indeed, although **asymmetric catalysis** is often the most advantageous process in terms of its ecological impact, the **chiral resolution process**, which results in the loss of 50 % of the material, is still the most commonly applied method for the production of **enantiopure active ingredients**. New developments and uses of **chiral catalysts** will have a positive effect on a cleaner and sustainable production of enantiopure active molecules and privileged structural motifs, as well as on the process of finding new active molecules. The challenge is to develop techniques for dynamic chiral resolution, in which the enantiomer which is not used is re-racemised. This is usually done through a combination of different catalytic steps.

While in the academic research, asymmetric homogeneous methods and biocatalytic methods currently dominate, only few of these methods are applied in the industry, e.g. asymmetric catalytic hydrogenation processes and biocatalytic kinetic chiral resolution processes, as the majority of the known asymmetric catalysis reactions are not up to the required industrial and hence commercial standards. In this framework, applications of some free or immobilised bio-catalysts, such as lipases, phospholipases, enoate reductas-

es, etc., in kinetic resolutions, in enantio- or regio-selective synthesis of some industrial interesting compounds is being developed. Further important issues requiring improvement include the reliability of these processes and the frequent need for complex (catalyst) optimisation, as swift realisation is hugely important for commercial success. The **development of robust and predictably successful catalyst systems** on the basis of a quantitative understanding of the processes taking place would thus represent an important breakthrough. At least to some extent this has already been realised in the area of bio-catalysis, where metabolic pathways of bacteria are being altered accordingly on the basis of material flow analyses.

Catalytic reactions used in the fields of bulk and fine chemicals are applied to modify known pharmaceuticals lead structures of active ingredients. **Organometallic catalysed C-C coupling and selective oxidation** reactions should be mentioned here in particular. It is anticipated that the increased use of catalysts will, on the one hand, have a positive effect on the production of active ingredients, while on the other hand it will also help with the process of finding new active ingredients.

In this regard, it should be pointed out as transition metal catalysed C-C bond forming reactions have been traditionally developed using pre-made organometallic reagents. These procedures are inherently limited to the availability and reactivity profiles of the reagent itself. In addition, the use of these pre-functionalised reagents entails the formation of a stoichiometric amount of inorganic salt as a reaction by-product. Thus, the development of **C-C bond forming reactions** using simple and abundant reagents, such as alkanes, is highly warranted in terms of sustainability and atom-efficiency.

Alkanes (or hydrocarbons) are very abundant in our planet. The most important sources of alkanes are natural gas and oil. This natural abundance makes their use as chemical feedstocks very attractive. However, their inertness in terms of bond dissociation energy, ionisation potential and pK_a has rendered the use of alkanes extremely difficult for purposes beyond aerobic combustion and the production of syngas. Thus, the **activation and functionalisation of alkanes represents** a major challenge.

The **direct use of alkanes in organic transformations** could lead to clean and highly atom-efficient processes as the formation of inorganic waste, usually generated when organometallic reagents are used, would be eliminated in these cases. Thus, development of new technologies based on metal catalysts which enable the conversion of simple alkanes into more complex organic molecules will lead to cleaner and more sustainable synthetic avenues for the production of highly valuable chemicals.

Bio-catalysis and chemo-catalysis play thus an important role for **enantiomerically pure active ingredients**. In order to widen the scope of potential applications, better mechanistic understanding followed by the development of predictable catalyst systems are required.

New bioactive compounds with applications spanning from food and feed to health industries are also required. It is of key importance to be able to develop new catalytic tools to make the organic synthesis of bioactive molecules more efficient. These tools will reduce the related costs and make synthetic routes more sustainable. This means that new and improved, environmentally benign catalysts need to be developed, taking full advantage of the exciting new tools and methods being developed in both bio-catalysis and chemo-catalysis. These new systems will enable **cost-efficient one-pot cas-**

cade reactions and are expected to give access to a variety of new, selective synthetic reaction types, allowing the efficient synthesis of a wide variety of bioactive molecules.

Catalysis will enable synthesis routes with **fewer** (but preferably no) **protection groups** and discloses new transformations towards the desired products that provide synthetic shortcuts, for example through the activation of bonds. Catalytic synthesis is expected to create new reactions for making cyclic compounds, both heterocyclic and purely carbocyclic. In **biocatalysis**, combining bio-informatics (analysis of the metagenome) with enzyme development should lead to the discovery and development of new enzyme activities. Using non-toxic first-row transition metals as catalysts or metal-free catalysis will contribute to reducing chemistry's dependence on scarce elements. Finally, catalysis will lead to higher chemo-, regio-, diastereo- and enantioselectivity in chemical transformations, preferably with a broad substrate scope.

Another important target is the **transformation of stoichiometric reactions into catalytic ones**. Mechanistic research will enable the development of active and robust catalysts with high TOF and TON, leading to economically viable processes. Merging homo/heterogeneous catalysis will enable to develop new catalyst formulations with the best of both worlds (high TON, high(er) stability, good/excellent selectivity, recyclability).

Improving on the current situation for one-pot cascade processes is expected to yield more efficient synthesis requiring less high-energy reagents. Lastly, using **immobilised catalysts and enzymes as well as bio-mimicking systems (artificial enzymes)** will enable the development of

continuous reactions rather than batch reactions.

Concerning **enzymatic catalysis**, it has many attractive features in the context of sustainable catalytic approaches: first of all, **mild reaction conditions** in terms of pH and temperature, environmentally **compatible catalysts and solvents**. In addition, bio-catalysts offer **high activities** and **chemo-, regio-, and stereoselectivities** in multifunctional molecules. This affords processes which are shorter, generate less waste, and are, consequently, both environmentally and economically more attractive than conventional routes. In order to reduce their environmental impact, these processes are based on the use of alternative solvents (supercritical fluids, pressurised gases, ionic liquids, and micellar systems) and energies (microwaves and ultrasound), recycle of bio-catalysts, waste minimisation. For an optimal use of the potential of enzyme-driven synthesis, the development of suitable **immobilisation techniques** is critically required. All these techniques can be applied to develop innovative configurations of enzymatic reactors (including microreactors), to ensure a full retention of the bio-catalyst properties under the conditions required for the commercial application of green bio-transformations.

Catalytic methods in complex organic synthesis involve either homogeneous or bio-catalysis. The combined use of (chemo and/or bio) catalysts allows one-pot cascade-type reactions preventing elaborate (waste-generating) work-up procedures and/or the strict need to protect groups. Important goals in this field are to develop **smart, efficient, short-cut synthetic routes**, using cheap and nontoxic catalysts based on first-row transition metals (or even metal-free) catalysts and to develop innovative ways to make such catalysts and bio-catalysts mutually compatible.

Interesting **new methods** to steer us towards

these goals include the following: smart ligand design; screening for [new enzymes in the metagenome](#); making many variants of one type of enzyme available; modifying enzymes through site-selective mutagenesis through directed evolution or rational design or a combination thereof, i.e. smart libraries and synthetic biology (modifying natural enzymes with chemical components); compartmentalisation; open-shell (radical-type) organometallic catalysis; and supramolecular approaches in catalysis. All of this should contribute to more efficient synthetic routes that will generate less waste, be less time consuming and generally lead to a cheaper and easier production of bioactive compounds.

A key problem in the chemical synthesis of bioactive compounds is inefficiency. The main product obtained is often waste, rather than the desired compound. To solve these issues, three strategies can have been envisioned.

To enable [cost reductions](#), it is of crucial importance to develop improved, environmentally benign catalysts based on [abundant metals or enzymes](#). They should be cheap and safe, allow for catalyst recycling and lead to high TONs and TOFs. Furthermore, they should also enable new selective catalytic synthetic reactions that do not rely on protection-group chemistry. In chemo-catalysis the development of environmentally benign catalysts will be made possible by utilising a variety of bio-inspired tools based on both "cooperative" and "redox-active" ligands. A transition from the use of rare and noble metals to abundant and cheap, first-row transition metal catalysts is typically associated with a switch to entirely different (radical-type) reaction mechanisms. Selective radical-type processes are certainly possible in the coordination sphere of transition metals, as a variety

of highly selective enzymatic radical-type processes have been demonstrated. Equally, selective radical-type processes will be developed with synthetic chemo-catalysts. Mechanistic research is crucial to arrive at the desired catalyst improvements and cost reductions. Understanding the behaviour and reactivity of metallo-radicals and metal-bound "substrate radicals" during catalytic turnover is crucial. This applies both to the development of [catalysis with abundant metals](#) and to uncover new, [selective \(one-pot, cascade-type\) radical-type reactions](#) such as C-H bond functionalisation and catalytic radical-type ring-closure reactions without the need for using protection-group strategies. Besides catalyst activation, also catalyst deactivation pathways should be studied, as deactivation is frequently an important reason for low total TONs and decreasing TOFs over time. Bio-catalysis is the alternative. In [bio-catalysis](#), major steps forward will be made, extending the currently limited spectrum of enzymes by tapping into the vast number of the bio-synthetic enzymes that nature utilises for the synthesis of very complex structures. By way of metagenomics and sequencing, this toolbox is now coming into reach. Progress towards this goal further assisted by the fast robotic synthesis of DNA, making all enzymes essentially commercially available, scalable and thus affordable.

Cost-efficient one-pot cascade-type reactions will be developed based on sustainable starting materials replacing step-by-step syntheses with many purification sequences. To enable this, catalyst immobilisation, [compartmentalisation of catalysts](#) (e.g. in MOFs or supramolecular capsules) and flow systems for cascades will be studied. In this regard, tandem reactions in flow – cascade reactions coupling multiple steps into a single process using bifunctional catalysts in flow reactors could be useful in bio-chemo transformations.

The results will be [drastically shortened synthesis](#)

[routes](#). When several enzymes that do not belong to one natural route are combined and co-expressed in one organism, the cascade can be realised and immobilised inside cells. Combining enzyme catalysis with chemo-catalysis offers further exciting prospects. This also holds for the combination of chemo- and bio-catalysis with [fermentation](#). In particular, the synthesis of non-natural antibiotics in combined approaches is very valuable and to some extent already a reality.

The above mentioned new and improved catalysts should enable a variety of [new, selective synthetic reaction types](#) that are catalytic and do not require protection-group chemistry. Challenging new C-C bond formation strategies, (radical-type) ring-closing reactions and C-H bond functionalisation strategies will be developed. Additionally, the replacement of C=O by carbene precursors, isonitriles and other building blocks will be investigated, aiming for the development of new, generally applicable synthetic methodologies. The currently very polluting amide synthesis as well as heterocyclic chemistry will be converted into catalytic chemistry based on bio-catalysts and homogeneous catalysts. In particular, nitrogen containing heterocycles and complex (hetero)cyclic compounds demand new catalytic approaches that can be of an equally revolutionary power as cross-coupling reactions. New homogeneous catalysts will be developed and bio-catalysis will be expanded from degrading enzymes to synthetic enzymes. This approach has been developed in part for peptide synthesis, but the scope needs to be broadened to a variety of other amides.

Among alternative methods to afford easier dispersion of catalysts and environmentally affordable processes, **micellar catalysis** should be mentioned. It is based on the use of surfactants as

assembling molecules to arrange a dispersed nano-phase made of small "nanoreactors" (micelles) where catalysts, reactants and products can easily dissolve, is nowadays an emerging technology to eliminate organic solvents and use water as the reaction medium for a variety of catalytic reactions.

Surfactants are a wide class of generally cheap commercially available chemical ingredients. Furthermore, surfactants specifically designed for catalytic applications (the so-called designer surfactants) have been recently introduced thus greatly widening the choice of suitable [micellar nano-environments](#) available for all kind of chemical transformations. However, micelles are not merely a greener medium to perform catalytic reactions, as they can impart extra properties that can have important economic outcome, namely:

- they can improve catalyst activity because the concentration of catalyst and reactants inside the micelle is at least one order of magnitude higher than in a bulk solution.
- they can improve catalyst selectivity at all levels (chemo-, regio-, stereo-, enantio-) because of their internal polarity anisotropy that can favor certain transition states with respect to others.
- they can induce substrate selectivity, a property unknown to ordinary catalysts, because of their ability to wrap around the catalyst thereby influencing the approach of different substrates to the catalytic site.
- they allow easy catalyst separation and recycling because the reaction products can be extracted with suitable water immiscible solvents, leaving the catalyst in the micellar aqueous phase and allowing separation by simple decantation.

Many of the above properties have al-

ready proven their economic potential in terms of improved process performance with respect to traditional methods, as has been recently demonstrated by researchers at Novartis in a multistep process for the synthesis of active pharmaceutical ingredients. Cuts of about 50% in both process costs and cycle time were calculated for the process carried out in micellar media vs. organic solvents.

With the aim of replacing hazardous and not easily handled liquids or solvents, solid acids have to be developed to substitute liquid acids used in homogeneous catalytic reactions that cause problems of corrosion of the reactors and safety for the operators and environment.

Beside the conventional heterogeneous acids used for reactions of oil transformation (zeolites, mixed oxides, clay, etc.), new acid catalysts have to be developed for reactions of bio-mass valorisation that run in water, aqueous vapour, or in general in polar-protic solvents. Bio-mass, in particular that obtained from processing waste agricultural forestry, is the most attractive alternative feedstock with wide available carbon source. Among the main catalytic routes to transform bio-mass into fuels and value added chemicals, the hydrolysis is the most complicated as it requires the use of specific water-tolerant acid solid catalysts.

4.2 RESEARCH NEEDS & EXPECTED OUTPUTS

4.2.1 CATALYSIS FOR ECO-TECHNOLOGIES

Catalytic water and wastewater purification

Concrete challenges with a strategic importance are faced in the following areas:

- Increasing the selectivity and long-term stability of catalysts in order to reduce nitrates in groundwater and wastewater.
- Optimising catalysts for the hydro-dechlorination of chlorinated hydrocarbons.
- Development of catalysts for oxidation of ammonia or ammonium to nitrogen under mild reaction conditions.
- Expansion of the range of iron-based oxidation catalysts, e.g. by incorporation in zeolites.
- Screening of redox-active catalysts, such as metalloporphines, immobilised on suitable, coordinating, insoluble supports, for remediation of industrial wastewaters. Also water-insoluble catalysts should be tested, provided that they could be made compatible with aqueous media by means of immobilisation on highly hydrophilic supports. Different oxidants could be used, ranging from hydrogen peroxide to oxone, chlorites, and hypochlorites.
- Screening of heterogenised biomimetic preparations, based on redox-active elements such as metalloporphines, for their action towards selected drugs, to investigate their *in vitro* degradation compared to (putative) hepatic catabolic pathways mediated by cytochrome P450 family.

- Development of colloidal reagents and catalysts which are suitable for *in situ* applications in contaminated groundwater aquifers – nanocatalysis, as well as of nanocomposites
- Development of catalysts for breaking down pharmaceuticals in hospital wastewaters.
- Combination of adsorptive enrichment of trace pollutants and their catalytic conversion.
- Catalytic and photo-catalytic systems for sterilisation of wastewater
- Protection of catalysts against being overgrown by bio-films and hence deactivated in long-term operation.

Catalysis in contaminated waters only has a chance if the catalyst systems offer sufficient long-term stability against a large number of possible catalyst poisons, particularly natural organic water components.

Catalysis for hygiene and bio-security

Catalytically and photo-catalytically activated agents for sterilisation of surfaces and water, including conditioned air flows.

Treatment of industrial gases

Future strategic development lines in the field of exhaust gas after-treatment include:

- Widening of the catalytic reduction of greenhouse gases (e.g. methane, N₂O) to new fields of application (combustion of sewage sludge, fluidised bed process, gas motors, cement and glass industry).

- Development of effective adsorption methods for volatile hydrocarbons from e.g. paint shops, printing plants (enrichment with subsequent catalytic oxidation and possible recovery of solvents or thermal energy).
- Development of adsorption and oxidation processes for trace gases from the semiconductor industry.

There is potential for the development of new catalysts particularly in the areas of low-temperature reduction of NO and N₂O and low-temperature oxidation of difficult-to-oxidise hydrocarbons, especially methane.

After-treatment of exhaust gases from internal combustion engines

Further developments are necessary especially in the following areas:

- Reduction of the precious metal content of the catalysts through improved understanding of sintering behaviour.
- Lowering of the light-off temperature of oxidation catalysts.
- NO decomposition in lean exhaust
- Extend the understanding of novel Cu-CHA catalysts to allow efficient operations in a wide temperature range.
- Increased temperature stability of the catalyst carriers
- **Multifunctional catalyst devices.** The reduction of system complexity and cost by integrating several functionalities into a single device.
- Develop catalytic particulate filters which are so active during normal operation that soot is continuously burned off the filter.

- Improved control of meso- and microporosity
- Increased use of modelling in order to reduce development times through better understanding of the physical and chemical interplay.
- Increase the long term stability of automotive catalysts with high catalyst activity, especially in contact with poisoning substances. This issues requires to focus on the basic understanding of catalyst degradation in operation with and without contact to poisoning substances. These investigations should be supported by development and application of the respective modelling techniques.
- Replacement of Platinum Group Metals (PGM) for methane conversion. The number of natural gas fuelled engines (especially marine vessels and heavier vehicles) is increasing worldwide and in Europe. Due to the relative inertness of the methane molecule, current exhaust gas after-treatment catalysts for natural gas driven cars need a surplus of PGM for the conversion of the greenhouse gas methane. PGMs are identified as critical raw materials by the EU and the technology based on their use is not sustainable.

Catalytic combustion

Important fields of development with a strategic importance for catalytic combustion include:

- The development of precious metal-free catalysts and/or catalysts which require only very low precious metal content on account of the use of suitable carriers and additives.

ers and additives.

- Stabilisation of the dispersion of active centres and/or suppression of agglomeration and sintering processes.
- The development of catalysts and/or carrier materials which offer high specific surface areas at application temperatures in excess of 1100°C for long periods of time.
- The development of robust catalysts for the combustion of methane at low temperatures, among other things for the after-treatment of exhaust gases on vehicles powered with natural gas.
- The development of robust catalysts for the combustion of methane at low temperatures, among other things for the after-treatment of exhaust gases on vehicles powered with natural gas.
- Catalysts for use in ignition boilers for petrol and diesel reformation, which are very robust and insusceptible to catalyst poisons and coking.
- The development of compact burners and micro-burners for energy conversion, including in MEMSs (micro electromechanical systems).

4.2.2 CATALYSIS TO IMPROVE SUSTAINABILITY OF CHEMICAL PROCESSES

There are some common challenges:

- develop novel approaches to move towards 100% selectivity, thus improving use of resources and reducing environmental impact,
- use of novel raw materials, alternative to fossil ones, and more sustainable on LCA bases,
- use an advanced design of catalysts, which allow to reduce the number of separate steps and reac-

tor units; for fine chemicals there is also the need to pass from batch-type to continuous reactors to decrease waste formation,

- develop integrated processes combining different type of catalysts (including asymmetric catalysis, organo-catalysis and enzymatic process) to optimises the overall performances; use tandem process, when possible, to reduce the use of reactants.

Catalysis for novel monomers and polymer processes

Important lines of development in the field of tailor-made polymer materials and functional materials include:

- Catalysts for the production of innovative polymer materials and functional materials from renewable resources.
- Catalysts which are tolerant towards polar groups and reaction media for copolymerisation and homopolymerisation of polar monomers.
- The improvement of catalysts which enable the production of materials with a defined microstructure and morphology.
- Catalysts for sequentially accurate configuration of polymer chains.
- Catalytic integration of nanoparticles into the polymer matrix for the production of nanocomposites.
- Use of catalytic fillers or reinforcing agents for composites able to catalyse the polymerisation itself to obtain a better and more efficient dispersion
- The development of biodegradable

ble polymer materials.

Also in this field, the development of innovative catalysts which are more temperature-stable, more resistant to aging and more cost effective will enable the production of materials with a defined microstructure and morphology.

The use of renewable raw materials as the basis for innovative polymer materials and functional materials requires the development of catalysts with a degree of tolerance towards polar media.

Two main priority areas of research may be identified. Firstly, a better understanding and control of the properties of polymers resulting from either PO or polycondensation catalysis is necessary, to obtain a more precise control of the molecular weight (distribution), the chemoselective polymerisation, the selective end-group functionalisation, and the incorporation of polar monomers and block copolymerisation. Research into new or modified catalysts for these reactions is necessary. A specific area of catalyst development is formed by the latent, "on-demand" polymerisation catalysts for curing or self-healing. Finally, post-polymerisation surface modification through bio- or chemo-catalysis, as a less conventional way to engineer polymer properties, should be highlighted.

Secondly, alternative polymerisation technologies should be explored. These would include controlled radical polymerisation technologies (e.g. RAFT and SARA-ATRP/ SET-LRP) with low-cost, universal applicability and excellent functional group tolerance without toxicity, odour and/or colour issues. Also new (advanced) polymerisation technologies based on new monomers, including non-olefinic monomers such as carbene precursors, epoxides and aziridines, should be mentioned here.

A particular alternative technology is formed by the integration of multiple catalytic cycles that enable formation of hybrid ma-

terials made of polyolefins and engineering plastics. The increasingly strict LCA and HSE requirements drive the need towards low-temperature PO or polycondensation technologies. Also more attention for the recyclability of polymers (e.g. via reversible rubber-vulcanisation technologies), materials and polymerisation technologies based on renewable monomers, and catalysts based on earth-abundant, non-toxic metals, bio-catalysts, or organo-catalysts.

The forecast of R&D outputs in above area in the next one-two decades will be the following:

- a tuneable, heterogeneous polymerisation or block copolymerisation catalyst for both simple and polar olefins;
- an integrated catalytic system based on multiple cycles for the formation of hybrid materials made of polyolefins and engineering plastics;
- polycondensation catalysts that meet HSE requirements and are selective with respect to the control of molecular weight (distribution) and distinct monomer reactivity;
- curing catalysts that meet HSE requirements;
- catalytic technology for post-polymerisation control of material properties: selective end-group functionalisation without chain breaking, surface modification of polymers as a substitute for plasma treatment;
- controlled (radical) polymerisation technologies for polymerisation and block copolymerisation, also of highly functionalised monomers;

- Low-carbon-footprint technologies: low-temperature polycondensations, recycling via easily depolymerisable polymers (e.g. via reversible rubber vulcanisation), materials based on renewable monomers;
- latent, "on-demand" polymerisation catalysts for curing or self-healing;
- polymerisation technologies for (advanced) new and drop-in materials based on non-conventional monomers, e.g. epoxides, aziridines, etc.

Last, but not least, new generation catalysts should in general comply with stringent normative such as REACH, FDA (see Appendix A "Regulations and standardisation").

Novel sustainable catalytic processes to active ingredients and fine chemicals

The following development lines are particularly important in the field of chiral active ingredients:

- development of highly selective and active catalysts which enable cost-effective production of enantiomerically pure compounds.
- Development of innovative biomimetic catalysts for asymmetric catalysis.
- Development of generally applicable chiral (bio-)catalysts for asymmetric oxidation and carbonylation reactions.
- Development of catalysts for enantioselective reductive amination processes.
- Development of catalysts based on different metals exerting an important synergistic effect showing peculiar activity and selectivity
- Development of new methods for

dynamic racemic resolution.

- Mechanistic investigation and subsequent development of robust and predictably successful asymmetric catalyst systems.

In addition to the pharmaceutical active ingredients, which belong more in the field of medicine, there are also numerous compounds which play an important role in e.g. the cosmetics industry or other branches of industry due to their specific properties.

The following **core research areas** deserve special mention in the area of fine chemical synthesis:

- new approaches for direct regioselective and (in part) diastereoselective or enantioselective functionalisation of aromatic compounds (hydroxy, amino, carbonyl and carboxyl groups).
- Avoidance of (or at least reduction of) by-products in conventional reactions which are used in many applications (e.g. Friedel-Crafts reactions).
- Development of catalysts – homogeneous and heterogeneous transition metal catalysts, biocatalysts, organo-catalysts – in order to realise transformations which cannot succeed without a catalyst.
- Development of synthesis methods in which biocatalytic stages are combined advantageously with conventionally performed catalytic stages.
- Increased application of techniques such as high throughput screening (refer to section 7.2.) which enable faster production and market launch ("time-to market").

- Introduction of new reactor technologies, such as microstructured reactors, which can offer higher efficiency and the possibility of reduced costs.
- Reduction of the synthesis stages through the use of multifunctional catalysts.
- Use of renewable raw materials.

The forecast of R&D outputs in above area in the next one-two decades will be the following:

- Development of improved or environmentally benign catalysts:
 - * catalysts based on readily available metals and ligands;
 - * mutually compatible chemo- and bio-catalysts;
 - * mechanistic insights that enable the desired catalyst improvements (cheap and safe metals, catalyst recycling and increasing TONs and TOFs) and, hence, cost reductions;
 - * reduction, recycling and replacement of key building blocks for catalysis (e.g. P-ligands);
 - * bio-catalysis readily available as a standard tool.
- Cost-efficient one-pot, cascade-type reactions:
 - * efficient synthetic catalytic shortcuts;
 - * of-the-shelf ordering of tailor-made and designed enzymes;
 - * application of new catalytic methods in commercial processes;
 - * better catalyst recovery methods (late transition metal catalysts, also modified with water-soluble ligands (e.g. biogenically prepared metal-

polysaccharide catalysts), these latter allowing an easy recovery of the catalyst and the use of an environmentally friendly solvent such as water);

* continuous reactions for enzymes and homogeneous catalysts.

- New, selective synthetic reaction types:

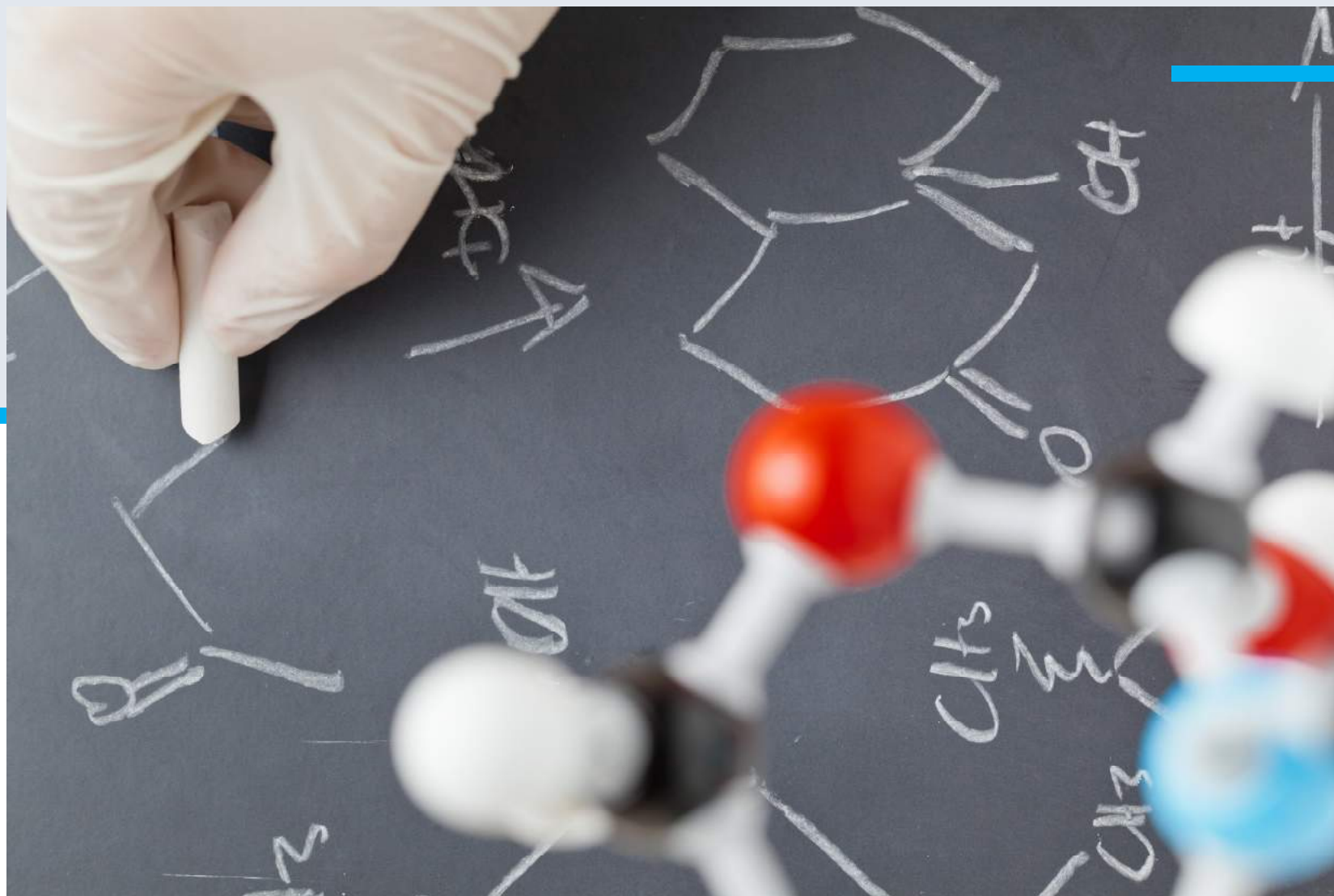
* transition from stoichiometric chemistry to catalytic chemistry;

* new methods to run cascades from low-energy starting materials;

* new catalytic processes with new (bio)catalysts running with low catalyst loading and achieving high TOF and TON values;

* new reactions towards polycyclic and heterocyclic compounds;

* development of entirely new catalytic reactions to facilitate (chemo-, region-, diastereo- and enantioselective) organic synthesis.



5 ADDRESSING CATALYSIS COMPLEXITY

Innovation in catalysis impact and in addressing the societal challenges discussed before requires a **knowledge-based approach** and **fostering capabilities** in four main areas:

- Advanced design of novel catalysts.
- Understanding catalysts from molecular to material scale.
- Expanding process concepts including catalysis.

- A scientific approach to link advanced design to catalyst scale-up and manufacturing.

The future development of new and improved catalytic material and processes will require a methodological shift towards **rational design based on fundamental knowledge**. The integration of new spectroscopic and microscopic tools along with predictive modelling strategies will allow designing and synthesizing novel catalysts for targeted reactivity of new molecules and materials. A scientific approach to **scaling-up and practical manufacturing** of these catalysts is the further step to more cost-effective and sustainable catalytic processes. Improved fundamental knowledge of catalysts, including their functioning and manufacturing pro-

cesses, will enable, among other advances, the replacement of noble,

processes, will enable, among other advances, the replacement of noble, scarce, and toxic elements by more abundant and environmentally safe metals for catalysis.

Important contributions to the resolution of the complexity of catalysts, that are often developed by empirical methods, will be provided by studies at model catalysts like thin films of the catalytically active material. Such model catalysts allow for the application of a variety of **surface science methods** that have no access to real catalysts present as particles. By this approach, single functionalities can be separated and studied individually. In addition, they are essential for the validation of **theoretical methods** before predictive contribution become possible. The identification of catalyst descriptors and structure-reactivity relations with model catalyst studies will foster fundamental understanding as well as advanced design concepts.

Addressing **catalysis complexity** also pushes forward the need to reach a next level in the development of **syn-**

thetic multi-catalyst (multi-reactor) systems. Two complementary approaches can be

KEYWORDS 1D and 2D catalytic nanomaterials, artificial enzymes, assembling nano-catalysts, atomic-scale precision, bioinspired ligands, catalysis complexity, catalyst functionality at the atomistic level, catalyst genoma, catalytic membranes, concerted cooperation between theory and experiments, confined systems, cooperative catalysis, coupling of a catalytic reaction with selective excitation, design of novel catalysts, electrocatalysis, engineering of the interface, expanding process concepts, from catalytic processes to catalytic devices, high-throughput-experimentation, hybrid materials, ionic liquids, layered materials, LEGO approach, microstructured reactors, molecular traffic control, multi-catalyst (multi-reactor) systems, multifunctional molecular-type catalysts, multifunctional reactor, multifunctionality, multi-level pore network, nano-manipulation, nanoreactor design, nanostructured catalysts, new class of catalysts, new reaction media, new ways to use catalysis, operando characterization, predictive modelling, responsive and adaptive catalysts, scale-up catalysts, self-repairing catalysts, single atom catalysis, single-site catalysts, structured catalysts, subnanoclusters, supercritical fluids, supported ionic liquid phase, time-resolved spectroscopy, understanding catalysts, understanding realistic complex systems

identified: The first aims at improving the efficiency with which chemicals are produced by integrating modular catalytic systems in a plug-and-play fashion within a flow system (also known as the “LEGO” approach). The second approach aims at the integration of multiple catalysts in a single environment in which catalytic processes influence each other through multiple feedback loops, with the ultimate aim of synthesising life de-novo and producing a synthetic cell.

Both approaches touch on the concept of molecular complexity, in which control over different length scales and timescales is crucial. Modularity can be also pursued through the use of **structured catalysts**, allowing generation of modular reactors and providing similar conditions as packed beds with the advantage of low pressure drop. The most common method to produce structured catalysts is extrusion but casting and additive manufacturing can be also used. Additive manufacturing is an advanced technique that has the potentiality to tailor the catalysts to simultaneously optimise mass, heat and momentum transfer for each specific reaction.

5.1 CHALLENGES AND OPPORTUNITIES FOR CATALYSIS

The main challenges that need to be addressed in order to make more complex catalytic systems a reality are **catalyst and process compatibility**. A single synthetic catalyst is usually only effective under its own set of special experimental conditions and usually has limited tolerance for other chemical species in the system. Yet, building more complex systems or devices requires compatibility – ideally between different catalysts, but at least between conditions and/or process parameters. Chemo-selectivity needs

more attention. Now that we are contemplating complex feedstocks, reaction cascades, one pot syntheses, CO₂-activation and systems catalysis, the rational design of targeted catalytic functionalities that do not interfere with other functionalities will be important. Catalysts would be desirable that can selectively convert a single functionality in complex, multifunctionalised molecules.

5.1.1 ADVANCED DESIGN OF NOVEL CATALYSTS

A first element to remark in the design of novel catalysts is that the **traditional separation between homogeneous, heterogeneous and biocatalysis has to be overcome**. It is necessary to develop “catalytic solutions” where each catalyst type can be considered as an element, whose use depends on the desired reactivity. An innovative design derives from merging these approaches to provide long-term use, cost-reductions and higher selectivities.

Solid catalytic materials still offer advances in terms of separation, productivity, multifunctionality and extended range of operations, especially when atomic-scale precision is achieved. Molecular catalysts, on the other hand, offer unique possibilities of controlling active site reactivity. Biocatalysis offers unique characteristics of low temperature performances and selectivity. Integrating all these characteristics in a single catalytic solution is a great challenge. A first step to proceed in this direction is to develop new methods to **assemble in tailored manner different building blocks**, and develop a specific structure with control of the characteristics from the molecular and nanosize level, to the macroscopic one necessary for industrial operations.

One of the tasks of modern catalysis research is to explore their synthesis (structuring over multiple orders of magnitude in scale using chemical methods) and verification (chemical analysis of structure-forming processes under in situ

conditions). There are currently various examples of nanostructuring in the synthesis of carrier materials, e.g. of microporous and mesoporous systems, also functionalised with transition metal ions (Co, Ti), zeolites (e.g. new hierarchically organised zeolites (HOZ) or zeotype materials such as aluminophosphates (AIPOs) and silicoaluminophosphates (SAPOs)) and coordination polymers (MOFs). Novel catalysts based on **layered materials** containing metal ions (i.e. V, Nb, V, Fe) in framework position and nanostructured oxides (TiO₂, ZnO, Al₂O₃) for selective oxidation reactions and selective on-field decontamination of chemical warfare agents (CWA) analogues and toxic compounds are also worth to be considered. In this latter case, samples with controlled textural properties (in terms of platelets dimensions and specific surface area) and surface features (i.e. distribution and strength of acid sites) should be produced controlling the synthesis conditions.

A further development would be the design and development of materials with a **multi-level pore network** to increase the catalytic performances and to overcome the diffusion drawbacks of microporous catalysts and/or of ordered porous materials containing metal species (Pt, Pd, Cu, Co) or functionalised with organic species for the production of catalysts for environmentally friendly processes (CO₂ transformation, NO_x conversion).

So that this can be widened to the nanostructuring of catalysts (e.g. metal/carrier, mixed oxides), there is the need of a much **better understanding** of the options afforded by target-oriented product controlling during catalyst synthesis. In the process, it is to be expected that the checking of the building blocks which control the (nano) structure in the carrier matrix will also contribute to the development of **de-**

finied single-site catalysts.

The last decade has seen an unparalleled progress in the fundamental description of catalytic processes, which has allowed for a rigorous interpretation and understanding of the catalytic cycles under different operating conditions by means of first-principles calculations. Nevertheless, the rigorous understanding of the *catalyst functionality* at the atomistic level is still prevented by the strong approximations in the description of the active site. In particular, the enormous complexity associated with the atomically correct description of the active site precludes a direct inclusion of all the possible effects and details. There is no doubt that the **concerted cooperation between theory and experiments** will be essential. On one side, *in situ* experiments will allow theory to fill the gap to complexity and practical performances by giving essential details for setting up atomistic models of the catalyst. On the other side, the fundamental theoretical description will enable correlations to be derived between experimental observations and mechanistic insights. It will be of relevant importance to increase the interaction between the theoretical description of the active sites and characterisation techniques (e.g., operando X-ray photoelectron spectroscopy, XPS) coupled simultaneously with the measurement of activity and selectivity to directly extract kinetic information. This requires **synchrotron radiation sources and beamlines** that allow focusing on the specific problem (as easy available tools) and those that allow novel photon-in/photon-out, microscopic and time-resolved studies. Moreover, the inclusion of the accurate description of the active site within the first-principles multiscale framework will permit the determination of the relevant local conditions of pressure, temperature and composition at given operating conditions, thus allowing a **coherent** interaction between experimental information and theory under **operando** conditions.

Other promising approaches for chemo-catalysis are aimed at the development of **nanstructured catalysts from defined molecular**, in particular organometallic, catalyst precursor compounds, the use of preformed metal (hydr)oxide colloid/carrier systems (e.g. PVP-stabilised, supported PdO_xH_y particles), nanostructured carbon-based materials and conductive polymers (e.g. polyaniline).

Selective design of the catalyst surface/morphology with a large number of atoms with coordinatively unsaturated sites delivers highly active catalysts and can open up new reaction paths. **High-throughput-experimentation** helps in reaching this objective, because a close integration of synthesis, testing and data evaluation in a workflow forms is the key to success. There are trends towards larger high-throughput experimentation systems which can be flexibly used to obtain kinetic data which can be directly correlated with data from the pilot plant.

For the **"LEGO" approach** there is a need for **plug-and-play catalytic modules**, whether as units that can be combined within the same homogeneous environment or separated by compartmentalisation or immobilised in (micro) flow reactors. Systems may require structured reactors, in which reactors and catalysts are ideally optimised simultaneously, requiring close collaboration between chemists and engineers. It will also be important to develop and incorporate **inline analytical technologies** (ultrasound tomography, temperature tomography, NMR, etc.) into the reactors to be able to study (in the development phase) and monitor (in the production phase) the processes. A cascade flow processing needs also to ensure that solvents, concentrations, ingredients, etc. are compatible with each other in what is referred to as **"flow orthogonality"**.

Another major challenge results from differences in the rates at which catalysts lose their activity, usually through poisoning or leaching. A workable integrated multi-catalyst system will therefore have to offer the opportunity of independent catalyst-activity management.

When combining chemical processes side-by-side (as in the "LEGO" approach) or within a single system (as in the bio-inspired approach), catalysis is essential as it allows independent control over the rates at which the various reactions occur. Such control is crucial if the various reactions are to be efficiently integrated. Without catalysis, such control is largely absent and one would be dependent on the rate constants of the various reactions. That, in turn, would severely restrict the ability to engineer well-integrated complex chemical systems. For example, a cell would not be able to function in the absence of ways to independently regulate – through catalytic processes – the rate at which the various chemical reactions inside it occur. Thus, by developing **integrated catalytic systems**, we will be opening up new opportunities, ranging from a more cost-efficient production of chemicals that require multiple reaction steps to functional complex chemical systems leading to life de-novo and cells that are completely synthetic.

A series of more specific topics can be identified:

- 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 nano-to micro architectures in catalysts (e.g. egg-shell, core-shell,

- * hybrid and/or composite catalysts, as well as novel preparation methods,

- * integrating homo-, hetero- and bio-catalysis,

- * novel and sintering stable nanoparticles and subnano-clusters,

- * organometallic complexes, organocatalysts,

- * biomimetic catalysts and enzymes,

- * catalysis with immobilised or single site complexes.

5.1.2 UNDERSTANDING CATALYSTS FROM MOLECULAR TO MATERIAL SCALE

An improved **fundamental understanding of catalysts and catalytic reactions** will **unlock** many new opportunities for the application of catalysis and lead to new catalytic routes to new molecules. These advances are key to – and will go hand-in-hand with – the necessary shift towards a more sustainable and economically valuable catalysis, from academic research to industrial application levels.

A prerequisite for tackling the challenges defined above is the further development of **sophisticated characterisation tools**, capable of mapping activity and chemistry at the surface. This includes the integration of spatially and temporally resolved spectroscopy with microscopy methods, as well as real-time spectroscopy. Key technologies are all the lab based techniques like IR, Raman, UV-vis etc. That would be allowed by operando studies as well as by excellence centres like those focussing on electron microscopy or synchrotron radiation²⁸. By using at the synchrotron radiation sources existing well-established and important problem-

solving beamlines the basis and backbone of the operando studies by X-rays is formed. Plans on the upgrade of sources like PETRA III/IV, SLS, MAX-IV will allow highest brilliance and elevated time-resolution probably culminating with XFELs. **Time-resolved spectroscopy**, in particular, is a key to be able to fully describe catalytic events such as photocatalytic processes. In other cases, completely new tools for probing molecular catalysts and catalyst surfaces will be required. Examples of these new tools are free-energy lasers (FEL) and THz excitation, which can be used to probe femtosecond dynamics in single bond-breaking events. Synchrotron sources present the opportunity to characterise structural and electronic changes down to the lifetime of reactive intermediates in the pico- and nanosecond regime. It is fundamental for the development and improvement of (homogeneous) catalysis to determine the reaction mechanisms via reaction kinetics and diverse spectroscopic studies in order to identify reaction intermediates. In situ **electron and X-ray microscopy** will complement each other in future.

An important aspect to consider in the context of the theory and modelling of realistic catalytic systems is whether physical insight is possible from **studying realistic systems** or **model systems under realistic conditions**. The catalytic truth at atomic scale may be hidden under various "onion rings" of effects that govern the process at larger length scales or higher temperatures, like mass transport and diffusion effects. In biocatalysts, small changes remote from the active site can induce significant improvements. With the newly developed tools, these distant interactions will help to improve all types of catalysis. At the same time, experimental validation should be done in realistic systems, bridging the temperature and pressure gaps.

²⁸ See, in this regard, for instance, the document ESRF EBS: EXTREMELY BRILLIANT SOURCE/ Call for Expressions of interest on <http://www.catalysiscluster.eu/shared-resources/>.

Understanding realistic complex systems will tremendously speed-up progress in all fields of catalysis. As an example: recent developments in bio-informatics provide the opportunity to extract and predict the reactivity and structure of complex enzymes, combining data from gene, protein and x-ray databases. Translation of concepts like these to homogeneous and heterogeneous catalysis will unlock completely new possibilities.

In order to develop catalysts based on abundant first-row metals, we need to understand the reactivity of these catalyst complexes in detail, including their radical-type behaviour. After all, these complexes can be based on **non-innocent and innocent ligands**, resulting in complementary reactivity. These ligands have more of a general applicability and can thus minimise the metal costs through lower catalyst loadings. We should find a way to reduce the time for ligand development via a **modular approach** and in particular using computation, which should become the main tool for ligand design instead of the present broad screening approach. In addition, the development of metal-free catalysts should be further explored by developing new catalyst systems and concepts.

By using **bio-inspired ligands** for transition metals, the use of these catalysts for the study of challenging chemical reactions and development of the studied catalytic cycles into a valuable industrial process can be addressed. To reach these goals, several different points will be addressed:

- molecular modelling design of peptidomimetic ligands with well-defined secondary structure: b-turn, helices, herpin;
- synthesis and characterisation of non-natural aminoacids;

- peptide and peptidomimetic synthesis;
- synthesis and characterisation (both in solution and in solid state) of the metal complexes.

The **engineering of the interface** between different components of heterogeneous catalysts at nanometer level can radically alter their performances and the control of the contact points on the surface over various lengths and time scale will allow the design of new complex materials. In this regard, the **fundamental understanding of effect of crystal shape and face**, the development of new synthetic approaches and novel characterisation tools capable of mapping chemistry at the surface are needed to unlock several unexpected properties and functionalities.

In these particular systems, traditional spectroscopic techniques (IR, NMR) are less conclusive, and require less established and often more difficult to interpret characterisation tools, such as EPR and Mössbauer spectroscopy, as well as X-ray absorption and emission techniques as a complement to the development of new synthetic procedures. The sensitivity of spectroscopic techniques can be enhanced by modulation experiments and by using data processing tools such as phase separation and multivariate curve resolution (chemometrics).

The increased understanding from characterisation and theory gives a unique opportunity to combine our insights and to gain improved control over the synthesis of new catalysts, both heterogeneous and homogeneous and their design from the atomic scale upward. For heterogeneous catalysts, **atomic-scale precision** should be combined with the 3D meso- and macroscale location of components to create realistic, strong and stable new catalysts. This must be linked to practical catalyst manufacturing through a scientific, well instrumented and characterised ap-

proach in order to realise the commercial potential. Improved resolution on 3D printing, hand in hand with atomic modelling tools opens the capacity to build well-defined systems via **nano-manipulation** and the possibility of performing catalysis on a single nanoparticle are identified as long-term development opportunities. The controlled synthesis of **hybrid materials**, which combine homogeneous building blocks with heterogeneous surfaces, will give a powerful impulse especially to the fields of cascade reactions and solar fuels.

A series of more specific topics can be identified:

- from deductive to predictive catalysis, theory and modelling of catalysis,
- new approaches in catalysts and reaction mechanism, with focus on in-situ and operando methods
- model systems (including surface science approach),
- bridging molecular to reactor engineering aspects in designing new processes, including new approaches in kinetics and reaction engineering,
- scale-up and manufacture of 'designed' catalysts through scientific understanding of large scale synthesis methods.

5.1.3 EXPANDING CATALYSIS CONCEPTS

Addressing the changing scenario requires not only to continue to improve current catalysts, particularly through a better understanding of the reaction mechanism and a more precise control of catalyst architecture (evolutionary catalysis), but also an effort towards **developing new class of catalysts as well as new ways to use catalysis**.

Between the area relevant to expand catalysis concepts, may be cited the following:

- catalytic nanoreactors design,
- catalyst genoma,
- molecular traffic control in catalysis,
- single atom and subnanocatalysis at surfaces,
- multifunctional molecular catalysis design,
- new 1D and 2D catalytic nanomaterials,
- artificial enzymes,
- from catalytic processes to catalytic devices,
- complex and responsive, adaptive catalysts.

Nanoreactor design indicates the realisation of nano-sized reactors to obtain nano-sized products or control of the reactions. It is linked to the control of the reactivity in **confined systems**, and often at the interface between nanotechnology and nanobiotechnology. It is also considered a key step towards artificial cell-like devices. Even if research on nanoreactors is ongoing from about a decade, and today computational advances also allow ab initio studies on nanoreactor²⁹, a significant step forward is necessary to implement these concepts to intensify catalytic processes, or even the synthesis of novel industrial catalysts.

Catalyst genoma indicates the equivalent of Human Genoma Project, but dedicated to the possibility to map the elements (equivalent to genes) responsible for cat-

²⁹ See, A highly accelerated first-principles molecular dynamics simulation of chemical reactions that discovers new molecules and mechanisms without preordained reaction coordinates or elementary steps - see *Nature Chem.* 2014, 6, 1044-1048.

alytic functionality and build the techniques to assemble them in the form to realise the aimed catalytic behaviour, avoiding side reactions.

Molecular traffic control in catalysis indicates the possibility to realise specific mechanisms to control the mass, charge and heat flow in catalysts along specific directions, in order to avoid side reactions or to force a specific sequence of transformations on sequential active sites (vectorial cascade reaction).

Single atom catalysis and subnanocatalysis at surfaces indicates the catalytic behavior of single atoms (typically transition metals, but not limited to them) located in specific sites at the surface and where the solid support acts as equivalent to ligands in molecular catalysts. Advanced characterisation techniques, like aberration-corrected high-resolution transmission microscopy have evidenced the presence of these single metallic atoms and their possible catalytic role. By doping the support (for example, by doping graphene or other nanocarbons materials with N or B) it is possible to stabilise single metal atoms having performances equivalent to those of the same metal complexes, but advantages in terms of use, stability and possibilities of further modification. In conductive support, the application of a potential may offer further possibilities to tune reactivity. These catalysts offer thus a bridge between molecular and heterogeneous catalysis, and the possibility to realise **multifunctional molecular-type catalysts**, as well as **new 1D and 2D catalytic nanomaterials**. The field of electro- and photo-catalysts may have a greatly benefit from advances in this field.

Artificial enzymes indicate synthetic, organic, inorganic or hybrid assemblies prepared to recreate the active site of an enzyme, but with improved stability

(performances, stability, solvents of use. Although research is active from over a decade in this field, exploitation of the results requires still large effort.

From catalytic processes to catalytic devices indicates the effort to reduce strongly the size of processes and realise miniaturised production devices which can be fast parallelised to increase productivity. Improvements in microelectronics and sensor technology make it possible to control smaller plants and devices. It is now possible to construct devices to a precision of a few micrometers. This opens up all sorts of new opportunities to downscale chemical processes and to produce materials with a nanometer precision. So far, this approach has only been applied in laboratory equipment. The next breakthrough will be to use it in chemical production – to create a factory on the scale of a chip. New types of catalysts are required for operations in these catalytic devices.

Complex and responsive, adaptive catalysts indicates the possibility to develop new catalysts which combine the catalytic function to a sensor function, and may be able to adapt the performances in response to change in the environment, feedstock, etc. This behaviour mimics that present in life, where, in addition **self-repairing** functions are often present. Although some attempts have been made in these directions, still no practical application of these concepts exists. By mastering some of the processes that underlie life, it will be possible to make materials much more efficiently and sustainably. Many chemists are inspired by the complexity of nature and the evolution of life. It offers them the possibilities to extend the reach of their efforts to adapt chemistry to the needs of mankind.

There are thus many possibilities of innovation offered by **expanding catalysis concepts**. Those shown above are example, but not covering the whole range of possibilities. It is necessary to stimulate R&D effort in this

direction through the introduction of specific support mechanisms. Other more general topics can be identified in the area of expanding catalysis concepts:

- catalysis with electrons, photons and energy sources other than heat,
- catalyst design to operate under non-conventional or extreme conditions,
- catalysis for use in non-conventional solvents,
- disruptive concepts in catalytic materials.

To intensify this effort in expanding catalysis concepts, it is necessary to move to a next level in integration and synergy between understanding, including theoretical modelling, and precise testing. Parallel development in new multifunctional reactors/hybrid processes offer many possibilities in this direction. The term '**multifunctional reactor**' is used to describe e.g. the combination of a reaction stage with selective material separation in a device. Other concepts use the **coupling of a catalytic reaction with selective excitation** through plasma, light or microwaves. In all the areas outlined below, one of the key elements of success is the design of novel catalysts tailored for the specific multifunctional reactor. In parallel, exploration of catalysis under **non-classical conditions** (e.g. plasma, ultrasounds, ionic liquids, supercritical conditions, etc.) represents also an open challenge.

Membrane reactors and catalytic membranes

The development of new **membrane materials** has highly energised this field in recent years in order to establish new processes or develop more eco-sustainable approaches in chemical

production processes. Examples with major technological and commercial potential include the following: (1) energy-saving production of synthesis gas or hydrogen in new process schemes with membrane integration, (2) enhanced productivity in mild conditions in equilibrium-limited reactions, (3) increased performance of multi-phase reactions in a catalytic membrane contactor.

The development of **membrane reactors** is very attractive since i) an efficient contact between reactants and catalytic site can be achieved (e.g. catalytic membrane reactors); ii) safe control of the contact on the catalyst between very reactive species can be carried out (e.g. membrane reactor with a reactant distribution control); iii) simultaneous removal of a reaction product from the catalytic reaction zone allows for higher conversions than predicted by equilibrium in traditional reactors; iv) mass transfer control allows for a better selectivity to desired products. Membrane reactors which exploit presence of a heterogeneous catalyst may play a key role in the development of several processes in the next future as for example:

- Hydrogen production from renewable sources (e.g. steam reforming bio- oil, glycerol, bio-ethanol, etc...).
- Hydrogen from water thermolysis.
- Synthesis of intermediates through either partial oxidation or hydrogenation routes.

New membrane materials and preparation procedure are under development (e.g. MIEC membranes) which will push the development of new catalytic systems for the new operating conditions required by the membrane reactors. The catalyst itself by controlling the rate of surface processes will provide the key function to the membrane in order to achieve better performances when at high separation selectivities the diffusion will be not anymore a

limiting factor.

Reactive distillation and adsorptive reactors

The simultaneous performance of reaction and material separation is particularly advantageous in equilibrium controlled reactions. The simultaneous separation of the reaction products from the reaction space allows almost complete conversion to take place. Compared to conventional methods, reactive rectification allows investment and operating costs to be lowered whilst the reaction turnover, selectivity and mass transfer are all improved.

Instead of distillation, adsorption processes can also be exploited in order to separate materials; in conjunction with heterogeneous catalysis this leads to the adsorptive reactor.

Coupling of reactor and heat exchanger (wall reactor)

By coupling exothermal and endothermic reactions in a heat exchanger reactor, it is possible to realise autothermal reaction controls, as a result of which energy losses can be reduced. Here, e.g. the tubes of a tube bundle heat exchanger are coated with a catalyst and alternatingly charged with reactants. Rigorous further development of this reactor concept leads to microstructured reactors.

To exploit the potential of microreactor technology, the catalysts need to be adapted to the system. Great potential is associated particularly with heavily endothermic reactions, heavily exothermal and mixture-sensitive reactions and/or reactions which are problematic in terms of safety, as well as with multi-phase reactions. Investigations have progressed furthest in the case of heterogeneously catalyzed gas phase reactions. Here, the catalyst is used as a

as a wall catalyst or in the form of a micro fixed bed.

Catalysis reactors with selective excitation

In principle, it is possible to positively influence the course of catalytic reactions through selective excitation in the form of plasmas, laser radiation, light or micro-waves in suitably constructed reactors.

New reaction media

The choice of solvent plays a vital role for the chemical reaction and its technical implementation in a catalytic process. Organic solvents are often used here, but there are significant objections to the use of these solvents for reasons relating to the environment, toxicological concerns and technical safety issues. The complete separation of the solvents from the products and their recycling (via a material cycle) or disposal represents also major factors in terms of process costs. The solvent can intervene in the catalysis cycle at a molecular level and thus influence activity and selectivity. In general, very little is known about this from a mechanistic point of view. As a result, in the development of sustainable catalytic processes special importance is placed on the search for new solvent concepts.

Among the systems of particular interest from a scientific and process engineering point of view as innovative solvent concepts for catalysis, may be indicated:

- Ionic liquids, which open up new possibilities for the catalytic conversion of biogenous raw materials, in electrocatalysis, and in modifying the properties itself of heterogeneous catalysts (the so-called 'supported ionic liquid phase' - SILP).
- supercritical fluids, offering new possibilities to design novel processes and CO₂- expanded fluids.

5.2 RESEARCH NEEDS & EXPECTED OUTPUTS

Some general areas of research for this grand-challenge (addressing catalysis complexity) may be identified. They provide the fundamentals and methodology to address the grand-challenges discussed before.

5.2.1 OPTIMAL CONTROL OVER CHEMICAL SYSTEMS AND REACTIONS

A detailed understanding of chemical kinetics and reactivity, focused particularly on structure- activity relationships, will be the basis for the rationalisation of reaction mechanisms, leading to an improved design of catalysts and catalytic processes: higher efficiency, stability and selectivity. Simultaneously, the ability to *design, prepare, manufacture and characterise new materials with 3D control at atomic or molecular resolution and at various length scales* must be developed. New concepts in ligand design must be explored to allow for catalysis with more *abundant, first-row transition metals*. Examples may include those based on Fe, Al, Zn, Co etc. The use of new systems based on these metals and able to guide specific chemical transformations will lead to a decreased dependence on expensive, less abundant raw metal materials and strengthen the economic position of the EU chemical community.

The molecular chemistry of these catalysts and metal complexes needs further development. The availability of characterisation tools for a diamagnetic system like Pd has led to a good understanding of this system, but the organometallic chemistry of for instance Fe is hardly explored. Apart from activity, stability of this type of catalyst needs to be examined.

In order to improve the catalytic trans-

transformations in particular in homogeneous catalysis novel synthetic methods for *ligand preparation* as well as predictive modelling for achieving sophistication in ligand engineering in order to develop ligands with desired chemo-, stereo- and regioselectivity and high values of TOF and TON are required. Another important aspect would be a development of *heterobimetallic catalysis* in order to provide *cooperative catalysis* coming from two different metals. Only a few examples are known, mainly due to the lack of corresponding ligands to bind to different (soft and hard) metals.

5.2.2 PREDICTIVE MODELLING

Theory, multiscale modelling, and computational chemistry together form *one of the pillars* of the strategy proposed in this Roadmap for Catalysis, also in coordination with the manifold activities of the recently established European Materials Modelling Council (EMMC, <https://emmc.info/>). The development of descriptive and predictive methodologies based on input from new spectroscopic tools will provide a much more detailed insight into the parameters that play a role in catalysis. Research in this area will benefit from development in the adjacent fields of complexity and big data research. Rather than simply understanding such parameters, the focus will now be on predicting which set of conditions will be most suitable for a given catalytic process. This modelling activity should be implemented to real models. For instance, in the area of automotive catalysts, model based development approach combines understanding on molecular scale, mesoscale, device scale and plant scale involves also coupling to traffic models. The current exhaust development process is heavily based on drive cycle testing and this is one main reason why catalysts do not optimally work under real driving conditions. Coupling of traffic/vehicle models with chemically based multiscale catalyst

models allows for a targeted development of exhaust systems that work under real driving conditions. Hybrid systems of EV and internal combustion will give less transient operation.

5.2.3 UNDERSTANDING COMPLEX AND REAL SYSTEMS

Enhanced spectroscopy and microscopy on realistic systems, incorporating 3D atomic resolution characterisation techniques, *in situ* and *ex situ* methodologies, broad time resolution, and data processing and analysis tools (e.g. dephasing, multivariate procedures) will allow the identification of the **key descriptors** that can serve as the basis for design rules for new catalysts and molecules. This field is strong for heterogeneous catalysis, but needs development for homogeneous systems, especially with respect to homogeneous catalysis with first-row transition metals.

In this perspective, the use of computational tools to better understand spectroscopic measurements which are otherwise difficult to interpret (e.g. EPR, Mössbauer, XAS/XES spectroscopy) in catalysis research is also important. This should again be concerted with the development of theoretical methods that incorporate more realistic, more complex systems, moving away from small molecular models, model surfaces, clusters and single molecules.

5.2.3.1 OPERANDO METHODOLOGIES

It is necessary to strengthen industry through **game changing** technology and development at key stages. This is particularly valid for catalytic materials, which lower production costs, energy consumption and environmental impact for the majority of industrial sectors; the competitiveness of these industries therefore relies directly on the

development of better catalytic solutions by European catalyst manufacturers. Insights into mechanistic and structural changes during operation are of unambiguous importance for improving existing catalysts and the development of novel ones. Applied chemical reaction kinetics can be significantly improved by the input from catalyst characterisation on working catalysts at realistic conditions. However, industrial interest is mainly focussed on best practice in the extraction of intrinsic reaction kinetics in catalytic reactions. The capability of *in situ* and *operando* techniques for providing such information therefore needs to be improved and made more readily available to European industry.

It is necessary to develop innovative solutions to **improve *in situ* and *operando* catalyst characterisation techniques**. These might include: **(i)** chemical mapping of bulk or single spot detection; **(ii)** increased lateral and time resolution; **(iii)** increased experimental time scales to make it possible to study preforming and deactivation phenomena. To increase applicability to European industry the techniques shall further: **(iv)** show increased throughput and/or **(v)** bring developments to bench scale size and reasonable price.

In order to ensure the industrial relevance and impact of the research efforts an exemplary catalyst optimisation shall be carried out in parallel to the method development and be accompanied by a cost analysis of the benefit obtained and cost for the *in situ* and *operando* studies.

The result of these developments will be

- an enhancement of information depth for *in situ* and *in operando* characterisation of catalysts to be able to deduce critical data for materials optimisation in thermal, photo- or electrocatalysis for processes.
- Lowering costs and/or throughput of catalyst characterisation techniques

and/or making techniques for industrial conditions available.

- Supporting the penetration of advanced characterisation techniques for catalytic materials by a catalyst optimisation case study.
- Exploiting high brilliance synchrotrons for microscopy and time resolved studies.
- Combine kinetic and characterization studies in the laboratory and at well-accessible synchrotron radiation sources with appropriate infrastructure (catalysis lab at the synchrotron).

5.2.4 INTEGRATED MULTI-CATALYST/MULTI-REACTOR SYSTEMS

For **multifunctional reactors/hybrid processes** the following development targets are expected:

- the development of selective membranes with high permeability which can be used e.g. in a membrane reformer even under high temperatures.
- New, cost-effective preparation techniques for multifunctional catalytic active membranes.
- The development of selective catalysts which enable the advantages of the membrane separation which is integrated in the reactor to be fully exploited.
- The development of catalytic systems with long-term stability which are permanently coupled to the membrane.

For **microstructured reactors** the following development targets are expected:

- For heterogeneously catalysed

gas phase processes, catalysts with significantly increased activity and same or higher selectivity compared to conventional catalysts are required in order to fully exploit the potential of microreaction technology.

- For catalysed liquid phase reactions (heterogeneous catalysis, molecular catalysis and bio-catalysis), experimental and theoretical investigations are needed in order to be able to technically assess the potential of these systems.
- Methods and correlations for the design of catalysed processes in microstructured reactors both in terms of reaction technology and technical safety.

For **new reaction media** the following development targets are expected:

- the synthesis of specific catalysts which are adapted to the properties of the new reaction media.
- New process engineering concepts for recycling catalysts.
- Understanding of the interaction between catalyst and solvent system at molecular level.

For **plug-and-play ("LEGO") approach** the following development targets are expected:

- a toolbox of plug-and-play catalytic modules in which catalysts are integrated into tailored reactors;
- several industrial (flow) processes in which multiple catalysts are integrated which enabled a more cost-effective production of (fine) chemicals.

5.2.5 FUNDAMENTALS AND METHODOLOGY

The forecast of R&D outputs in the general fundamentals and methodology area in the *next one-two decades* will be the following:

- computational methods that account for the complexity of chemical/catalytic processes on various timescales and length scales;
- a transient view of catalysis that accounts for out-of-equilibrium processes, instead of the current steady-state view;
- precise control of morphology, composition and defect structure, leading to influence optical, electronic and catalytic properties on multiple scales;
- a toolbox to translate chemical descriptors of catalysis and catalysts into predictors and design rules for new molecules and synthetic methods;
- the science-based development of highly stable catalytic molecules and materials with self-repair and self-assembling properties;
- mechanistic insight by combining spectroscopy with computational spectroscopy;
- control and efficient generation of highly reactive (hypovalent) catalytic intermediates;
- the precise control of selectivity in synthesis and catalysis, including regulation mechanisms to accommodate changes in reaction conditions (e.g. as observed in natural photosynthesis);
- the targeted activation of specific catalytic sites and the control of reaction speeds and mechanisms, allowing for a cost-effective utilisation of catalyst materials and an efficient replacement of noble metals by cheaper and more abundant materials;
- novel synthetic methods for ligand preparation as well as predictive modelling for achieving sophistication in ligand engineering in order to develop ligands with desired chemo-, stereo- and regioselectivity and high values of TOF and TON;
- new homogenous (organo)catalysts for photoredox catalysis, molecular redox catalysis and challenging group-transfer reactions;
- chemoselective catalysts that can selectively convert a single functionality in complex, multifunctionalised molecules.

APPENDIX A - STANDARDIZATION, REGULATION, SAFETY ISSUES

This report has been prepared within the Cluster on Catalysis sub-Working Group WG3d: Standardisation, regulation, safety issues. The aim of this sub-WG is to address specific aspects of standardization, regulation and safety issues in the scientific and technological fields related to catalysis.

To promote growth of the catalysis on European basis several cross-cutting issues that need to be addressed. They include the regulatory framework for catalysis coupled to the important issue of standardization to promote good practice and to facilitate communication; the innovation/value chain for environmental health and safety and innovation and means to foster the effectiveness in the value chain; the development of infrastructures for safety to promote research, education, and innovation; and international collaboration and global dialogue, with a view towards a global research area in catalysis, along with communication and dissemination of research to key stakeholders beyond the research community, including industry, regulatory bodies, and others.

In particular, standardization issues play a pivotal role as the design and development of novel catalytic materials as well as the effective application of the existing catalysts needs accurate and prompt information about their catalytic properties and performances. A comprehensive overview is required to cover several aspects of catalysis, including catalytic materials preparation, their chemical analysis, characterization of catalytic, physical-chemical and physical-mechanical properties, process parameters, risk assessment.

In this perspective, this sub-WG is intended to provide an outline of the ex-

isting organizations in the different countries devoted to standardization tasks, to the documentations and databases available on standard test methods for catalytic materials and processes, regulation on emerging risks in novel catalytic materials, with particular attention on nanomaterials, that an increasing role play in the field of the heterogeneous catalysis.

Coordination with main parties acting in Europe in the field of standardization, regulation, safety is also planned.

Standardization and regulation

There is a plethora of regulation and standard concerning the preparation, the test the use of catalysis, as well as many other aspects of their life cycle, extremely detailed is for instance the Guideline on the specification limits for residues of metal catalysts or metal reagents, aiming at recommend maximum acceptable concentration limits for the residues of metal catalysts or metal reagents that may be present in pharmaceutical substances or in drug products (http://www.ema.europa.eu/docs/en_GB/document_library/Scientific_guideline/2009/09/WC500003586.pdf). Similarly, very accurate standards are available on emission control in automotive or heating systems (for instance new EPA rule will affect spent catalyst management (<http://www.ogj.com/articles/print/volume-96/issue-41/in-this-issue/general-interest/new-epa-rule-will-affect-spent-catalyst-management.html>)).

Industries involved in catalysis and using catalytic materials and processes, like the majority of the chemical industry, catalyst manufacturers must comply with the REACH regulation (see for instance by the European Catalyst Manufacturers Association - European Catalyst Manufacturers Association - position paper on REACH and catalysts: <http://www.cefic.org/Documents/Industry%20sectors/ECMA/ECMA-position-paper-on-REACH-and->

[catalysts-2012%2005.pdf](#)).

Most catalysts are considered to be mixtures of substances, and these individual substances must be registered separately under REACH by the catalyst manufacturer/importer or only representative. In many cases, there are consortia/SIEFs that cover the substances present in catalysts, but also categories like ECMA work to ensure that the special nature of catalysts, and the needs of the catalyst sector, are taken into account to enable compliance with REACH and to ensure the sustainability of the catalyst industry.

In the frame of catalysis within ASTM, the international standards organization, the Committee 32 is specifically devoted to the development of test methods, classifications, practices, and terminology pertaining to catalysts, zeolites and related materials used in their manufacture, and the stimulation of research related thereto. The work of this Committee is coordinated with other ASTM Committees and other organizations having mutual interests, and is composed of subcommittees that address specific segments within the general subject area covered by the technical committee, such as Physical-Chemical Properties (D32.01), Physical-Mechanical Properties (D32.02), Chemical Composition (D32.03), Catalytic Properties (D32.04), Zeolites (D32.05), Nomenclature and Definitions (D32.92).

ISO Standard catalogues also cover issues of interest in catalysis and in particular relevant is the set of standard concerning nanomaterials and nanotechnology (http://www.iso.org/iso/home/store/catalogue_tc/catalogue_tc_browse.htm?commid=381983&published=on&includesc=true, http://www.iso.org/iso/home/store/catalogue_tc/catalogue_tc_browse.htm?commid=381983&includesc=true&development=on).

In Europe, there is a list of national standardisation bodies pursuant to Article 27 of Regulation (EU) No 1025/2012 of the European Parliament and of the Council on European standardization (2013/C 279/08) and most of them are involved in standardization tasks somehow concerning catalytic materials, process and applications.

European Commission addressed a mandate to CEN, CENELEC and ETSI, asking these bodies for the elaboration of a report identifying with respect to nanotechnologies and nanomaterials: the programme of standardisation items, the status of foreseen standardisation deliverables, an assessment of the feasibility of having standardisation work carried out at the international level, and a draft roadmap of the progress of standardisation activities considered necessary. In this respect catalytic nanomaterials with catalytic properties are definitely included (Mandate addressed to CEN, CENELEC and ETSI for standardization activities regarding nanotechnologies 2010)

Moreover, there are some specific fields in catalysis that are receiving a specific attention from the standardization point of view, such as photocatalysis. Several ISO tests involve semiconductor photocatalysis are considered, covering different areas, including air purification, water purification, self-cleaning surfaces, photosterilisation and UV light sources for semiconductor photocatalytic ISO work. (Overview of the Current ISO tests for Photocatalytic Materials A. Mills Journal of Photochemistry and Photobiology A Chemistry, 07/1997; 108(1):1-35).

In addition, "Photocatalytic materials standardization" is within the scope of CEN/TC 386 by European Committee for Standardization, that is intended to provide a standards, mainly concern test and analysis methods. for different photocatalysis applications in the following sectors: - Air purification - Water purification - Self cleaning application (surfaces: glass, metals, concretes, cements, plastics, ceram-

ics, textiles, paints and varnishes, etc.) - Medical application - Light sources (UV A, UVB, UVC, visible,..) with the objective to introduce performance standards for photocatalytic effects (including photo induced effects).

Specifically looking specifically at materials at nanoscale, and their relevant catalytic properties, CEN/TC 352 is devoted to standardization in the field of nanotechnologies that includes either or both of the following: i) understanding and control of matter and processes at the nanoscale, typically, but not exclusively below 100 nanometres in one or more dimensions, where the onset of size dependent phenomena usually enables novel applications; ii) utilising the properties of nanoscale materials that differ from the properties of individual atoms, molecules or bulk matter, to create improved materials, devices and systems that exploit these new properties.

Finally, it has been also generally recognized the need of establish and maintain standards and certifications for the research procedure, including, in principle, general standardization procedures for performing and assessing research, according to quality management practices (see for instance ISO/IEC 17025:2005, or the even more general ISO 9000:2008 and ISO 9001:2015).

Safety

Catalysis represent one of the most relevant sectors where nanotechnology clearly plays the role of enabling technology that has the potential to bring benefits to multiple areas of application benefitting society in many.

Among catalytic materials increasing emphasis are receiving nanomaterials, due to their size dependent properties that make them ideal candidates for a wide range of catalytic processes in

chemistry, environmental remediation technology, energy capture and storage technology (e.g., solar cells, batteries, fuel cells, fuels)

In this perspective safety concerns arising from nanomaterials closely apply to catalysts, as they are seen as the fields that are mostly impacted by novel nanomaterials design and developments, thanks to novel surface and size dependent chemistry, such as enantioselective catalysis at surface.

Therefore, the current safety assessment approach for nanomaterials needs to be closely followed by catalytic nanomaterials, their processing, their life cycles.

Such an approach starts from a precautionary perspective and refine the strategy once sufficient knowledge is available to understand hazards, exposure potential and the means to protect workers, consumers and the environment from unwanted levels of contact. This is analogous to the European Chemicals Legislation (REACH) process.

The challenge is to accomplish this assessment when the number and extent of industrial applications is growing rapidly, and to ensure that benefit-risk is judged rather than risk alone. If nanotechnology is to realise its potential, it is vital to empower the research and regulatory community to apply the precautionary principle in a focused and cost-effective manner. (Impact of Engineered Nanomaterials on Health: Joint EASAC JCR Report 2011). Risk assessment and management requires intelligent and case-specific consideration guided by potential exposure scenarios. It is also relevant to note that new knowledge will help to engineer safer nanomaterials.

Of great relevance, in view of the growing importance of nanomaterials and nanotechnologies in catalysis is the work performed by the Scientific Committee on Emerging and Newly Identified Health

Risks (SCENIHR), to provide a scientific opinion on the appropriateness of existing methodologies to assess the potential risks of nanotechnologies. SCENIHR concludes that current risk assessment methodologies require some modification in order to deal with the hazards associated with nanotechnology and, in particular, that existing toxicological and ecotoxicological methods may not be sufficient to address all of the issues arising with nanoparticles.

The EU NanoSafety Cluster, that is a DG RTD NMP initiative, is devoted to maximise the synergies between the existing FP6 and FP7 projects addressing all aspects of nanosafety including toxicology, ecotoxicology, exposure assessment, mechanisms of interaction, risk assessment and standardisation.

Conclusions

Finally, this sub-WG intends, covering the described fields of standardization, regulation and safety, to provide specific tools for the development of standards for classification, terminology and nomenclature; metrology and instrumentation, including specifications for reference materials; test methodologies; modelling and simulation; science-based health, safety and environmental practices; and nanotechnology products and processes. Standards in each of these areas could be specific to a product, process or industry.

A comprehensive requirement survey and classification, ultimately aims at provide effective instruments to tackle the fundamental issues coming from the need for the establishment of simplified and common sets of regulatory requirements, for the identification and assessment of tests and certification methods for catalytic materials and processes, suited to the specific operational environment in different sectors.

An effort to overcome, with such com-

mon regulatory and standardization requirements, local and regional, European and international differenced in approaches and labelling systems, or, at least link them in a more harmonized and homogenized way, is definitely essential.

Also it is evident the need for the development of new standards, specific to the distinct technology and application areas, and consistently referring to existing standards in specific areas, such as ASTM, ISO, IE standards.

The introduction of new materials and technologies for catalysis highlights also the need of new standard and regulations, not yet envisaged in the existing systems.

General and established characterization tools for evaluation of performance and safety are critical to define test and certification methods specific for the different operational environment, in the diverse sectors and especially for the most public safety critical application areas, and, finally to demonstrate the compliance of the new materials and processes to the standards and the regulations. As far as safety, an efficient synergy the different actors playing in the area, with their own peculiar roles, including the European Commission initiatives, is amenable to design and plan common, sensible and agreed nanosafety assessment toolbox.

APPENDIX B - INTERNATIONAL COOPERATION

This report has been prepared within the Cluster on Catalysis sub-Working Group WG2b: International Cooperation.

The aim of this sub-WG is to specifically address the issues related to international cooperation aspects in the field of catalysis. Indeed, several benefits can be recognized in research, as well as in aspects related to governance, regulation and safety issues of catalysis. Indeed it is evident as an international collaboration dimension is amenable for many topics within catalysis, like green industry, energy and environmental remediation, which are strongly multidisciplinary and cross-sectorial in nature, therefore including scientific and technological activities that require a synergistic combination of complementary expertise and visions of scientists, located both in Europe and in non-European Countries.

The globalization of research is proceeding rapidly and this is having significant implications for the European catalysis research and innovation landscape. The setting of the production of new scientific knowledge are shifting from European to worldwide arenas and comparisons of certain indicators across countries point to a positive relationship between measures of research collaboration and overall scientific and technological impact.

International partnerships can create unique opportunities for enhancing scientific excellence, intellectual research environments and innovative training of young scientists, and, at the same time, increase the technological development, the economic potential and the societal impact.

Particularly relevant are those issues

that bring mutual benefit at a global level, with the aim of building on the strong research capacity, which already exists not only in Europe but also in different areas of the world, a coordinated interdisciplinary joint action goal on crucial themes, including materials supply, environmental protection and depollution and clean energy supply and usage.

Many of such catalysis related topics could strongly benefit from a joint transnational approach, with possible impact on the global needs the needs of EU as well as third countries and effectively contribute to their solution, with the ultimate idea is to develop a genuine synergy between the different regions in the world can be beneficial in a situation of mutual interest.

This sub WG intends to provide an overview of existing initiatives on catalysis based research and innovation in the world and to establish network of interest around such a topic in view of the scientific, technological, economic and social impact.

APPENDIX C - TRAINING & EDUCATION, DISSEMINATION, POPULARISATION IN THE FIELD OF CATALYSIS

This report has been prepared within the Cluster on Catalysis sub-Working Group WG3bd: Training & Education, Dissemination, Popularisation in the field of catalysis. This sub-WG was aimed to identify the possible actions deriving from synergy between projects to promote training and education on one side and dissemination and popularization on the other side.

As mentioned in the Introduction, catalysis is the **single most important and pervasive interdisciplinary technology in the chemical industry**, and perhaps one of the disciplines having the largest societal impact, although often hidden or underestimated.

Its role is even ignored by the broad public, and therefore investment and public funding are often neglecting this important field.

A Work Group in the European Cluster on Catalysis, has been dedicated to the development of ideas and suggestions to enhance the public awareness and acknowledgment on the paramount role of catalysis in addressing most of the societal challenges outlined by Horizon 2020.

Though catalysis is as important as biomedical sciences or engineering in improving the quality of our lives and of our environment, its role is often underestimated by the public and by policy makers. In this regard, manifold activities have been suggested, which can be performed either in the framework of research projects (e.g. NMBP), or in dedicated calls, as concisely described in the following.

Education and training:

1. organisation of PhD schools on selected topics in catalysis (in the framework of research projects on catalysis, e.g. NMBP, SPIRE etc.).
2. Organisation of tutorials and thematic sessions at international conferences (e.g. EMRS) .
3. Creation of dedicated and interdisciplinary European training networks devoted to topics in catalysis (e.g. ITN Marie- Curie Training Networks).
4. Creation of an attitude among catalysis researches to participate science communication and organisation of the necessary training events (see also below).

Dissemination and popularisation (to be specifically addressed in devoted calls such as CSA or "Science with and for Society" calls):

1. Increasing the public awareness on the important role of catalysis through dedicated popularisation events (e.g. Science festivals, science fairs and "open door" events).
2. Organisation of one-day workshops for policy makers.
3. Organisation of experimental activities and workshops for kids (8-18 years) on catalysis.
4. Organisation of dedicated modules (both experimental as well as theoretical) on catalysis to be offered to high schools (age 14-18 years) integrating their didactic activity.
5. Development, realisation and release of media products explaining to a broad audience what is catalysis and which are its outputs (e.g. video, web site, interactive games etc.).

6. Increase presence of catalysis-related topics in TV programs and reports.

KEYWORDS



2D MATERIALS **9; 94**

3D CONTROL AT ATOMIC OR MOLECULAR RESOLUTION **98**

ABUNDANT, FIRST-ROW TRANSITION METALS **73, 78, 98**

ACID CATALYSTS **47; 79**

ACTIVE INGREDIENTS AND FINE CHEMICALS, ROLE OF CATALYSIS **83**

ALKANE ACTIVATION **44**

ALKANE OXIDATION **44**

ALKANES IN ORGANIC TRANSFORMATIONS **75**

AQUEOUS PHASE REFORMING **48**

ARTIFICIAL ENZYMES **76; 94**

ARTIFICIAL LEAF **27; 30; 41**

ASSEMBLY AT THE MOLECULAR AND SUPRAMOLECULAR LEVELS **55**

ASYMMETRIC CATALYSIS **35; 62; 74**

ATOMIC-SCALE PRECISION **93**

AUTOTHERMAL REFORMING **49**

BIO-BASED POLYESTERS **73**

BIO-BASED RESOURCES **47**

BIO-CATALYSIS **33; 46; 75-84**

BIO-CATALYSTS **74-92**

BIO-CATALYSED PROCESSES **74**

BIODEGRADABLE POLYMER MATERIALS **82**

BIO-FACTORIES **19-21**

BIO-FUELS **16-20; 41; 47-49; 58**

BIO-GAS **27**

BIO-INSPIRED LIGANDS **93; 95**

BIO-MASS SOURCE OF OLEFINS **45**

BIO-MASS AND RENEWABLE RESOURCES **45**

BIO-MASS/BIO-MASS UTILISATION **16-20; 39-46**

BIOMIMETICS **60**
 BIO-REFINERIES **17-20**
 BIO-REFINERY FUTURE **17-20**
 NEW MODELS **22**
 BIOTECHNOLOGICAL CONVERSION OF CO₂ **52**
 BUILDING BLOCKS ASSEMBLING IN CATALYSIS **90**
 CAPTURE CO₂ **51**
 CARBON DIOXIDE INTO SOLAR FUELS OR CHEMICALS **41**
 CARBON LINKING REACTIONS **44**
 CARBONATES AND POLYCARBONATES FROM CO₂ **52**
 CATALYSIS FOR A CLEANER AND SUSTAINABLE FUTURE **61**
 CATALYSIS FOR A SUSTAINABLE ENERGY **39**
 CATALYSIS COMPLEXITY **87**
 CATALYSIS CONCEPTS ,EXPANDING **94**
 CATALYSIS REACTORS WITH SELECTIVE EXCITATION **99**
 CATALYSIS WITH ABUNDANT METALS **81**
 CATALYST DESIGN **13; 14; 30; 38; 39; 40; 44; 76**
 CATALYST GENOMA **96**
 CATALYSTS ADVANCED DESIGN **37**
 FROM MOLECULAR TO MATERIAL SCALE **39; 94**
 CATALYST STABILITY **48**
 CATALYTIC CARBOXYLATION **55**

CATALYTIC COMBUSTION **65; 70**
 CATALYTIC FILLERS **86**
 C-C COUPLING **78**
 CH₄ EMISSIONS ABATEMENT **69**
 CHEMICAL AND BIO-CATALYSIS COMBINED **52**
 CHEMICAL AND ENERGY VECTOR PRODUCTION **43**
 CHEMICAL ENERGY STORAGE **20; 21; 58**
 CHEMICAL ENERGY VECTORS **19**
 CHEMO-CATALYTIC APPROACHES **49**
 CHEMOMETRICS **95**
 CHIRAL CATALYSTS **78**
 CIRCULAR ECONOMY **22; 55; 72; 75**
 CLEANER AND SUSTAINABLE FUTURE ROLE OF CATALYSIS **33**
 CLEANUP OF WASTE STREAMS **39; 44**
 CO₂ A KEY CARBON SOURCE **26**
 CO₂ CONVERSION FOR RENEWABLE ENERGY **56**
 CO₂ CONVERSION AND SOLAR ENERGY STORAGE **53**
 CO₂ EMISSIONS/MINIMISATION/MITIGATION **17; 19; 48**
 CO₂ USE/UTILISATION **20-27; 50-63**
 COAL HYDROGENATION **48**
 COAL DEGASIFICATION **48**
 COAL GASIFICATION **48**

COAL AND SOLID FUELS **46**

COMPARTMENTALISATION OF CATALYSTS **81**

COMPLEX AND REAL SYSTEMS **101**

COMPLEX AND RESPONSIVE, ADAPTIVE CATALYSTS **97**

COMPLEXITY OF CATALYSIS **35**

COMPOSITE PARTICLE ARCHITECTURE **59**

CONCERTED COOPERATION BETWEEN THEORY AND EXPERIMENTS **92**

CONFIGURATION OF POLYMER CHAINS ROLE OF CATALYSIS **85**

CONFINED SYSTEMS **96**

CONVERSION OF ETHYLENE **72**

COOPERATIVE CATALYSIS **100**

COPOLYMERISATION OF NONPOLAR OLEFINS **73**

COPOLYMERISATION AND HOMOPOLYMERISATION OF POLAR MONOMERS **85**

CORE-SHELL **32**

COUPLED TRANSFER OF MULTIPLE ELECTRONS AND PROTON **58**

COUPLING OF A CATALYTIC REACTION WITH SELECTIVE EXCITATION **97**

COUPLING OF REACTOR AND HEAT EXCHANGER **97**

CRITICAL ROW MATERIALS **34; 41**

CURING AND VULCANISATION **72**

CURING CATALYSTS **83**

DEACTIVATION (CATALYST) **41-45; 49-51**

DEPOLYMERISATION **48; 69**

DIALKYL AND DIARYL CARBONATES **69**

DIMETHYL CARBONATE **69**

DIMETHYL ETHER **23**

DIRECT FUNCTIONALISATION OF LIGHT ALKANES **57**

DIRECT REGIOSELECTIVE **84**

DIRECT USE OF NATURAL GAS AND LIGHT ALKANES **58**

DISRUPTIVE CATALYSTS **42; 96**

DMC SYNTHESIS **52**

DMFC **56**

ECONOMIC CYCLE, NEW **27**

ECO-TECHNOLOGIES **35; 68; 79**

ELECTRICAL TO CHEMICAL ENERGY **17**

ELECTROCATALYSIS **27; 42; 511-55**

ELECTROCATALYTIC CONVERSION OF CO₂ **52**

ELECTRODE CONCEPTS, NOVEL **28; 42**

ELECTROLYSERS **41; 53**

ENANTIOMERICALLY PURE ACTIVE INGREDIENTS **74; 83**

ENERGY AND CHEMICAL SCENARIO ROLE OF CATALYSIS **34**

ENERGY INTENSIFICATION **16; 19**

ENERGY SCENARIO **16**

ENERGY STORAGE AND CONVERSION **16; 54**

ENERGY-CHEMISTRY NEXUS **15; 23**

ENERGY-EFFICIENT AND SELECTIVE CATALYTIC PROCESSES **57**

ENGINEERING OF THE INTERFACE **93**

ENZYMATIC CATALYSIS **34; 76**

EU SOCIETAL CHALLENGES, ROLE OF CATALYSIS IN **31**

EXHAUST GASES AFTER TREATMENT **64; 67; 80**

EXPANDING CATALYSIS CONCEPTS **36 ; 94**

FINE CHEMICALS **34; 74; 83**

FISCHER TROPSCH **25**

FLOW ORTHOGONALITY **91**

FOSSIL FUELS **11-21; 39-41**

FOSSIL RAW MATERIALS **42; 58**

FUEL CELL TECHNOLOGY **42; 56**

FUNCTIONAL CHEMICALS **46**

FUNCTIONAL POLYMERIC MATERIALS **74**

FUNDAMENTAL UNDERSTANDING OF CATALYSTS AND CATALYTIC REACTIONS **92**

GRAND-CHALLENGES FOR CATALYSIS **31**

GREEN HYDROGEN **51**

GREEN UREA **53**

GREENHOUSE GASES **64**

H₂ PEMFC **56**

HALOMETHANE **24**

HETEROBIMETALIC CATALYSIS **98**

HIERARCHICAL STRUCTURE **45**

HIGH-THROUGHPUT SYNTHESIS **56**

HIGH-THROUGHPUT-EXPERIMENTATION **91**

HOMOGENEOUS CATALYSTS, FOR COPOLYMERISATION **70-72**

HYBRID BIO- AND FOSSIL FUELS **41; 58**

HYBRID MATERIALS **28; 70; 82; 94**

HYDRODEOXYGENATION **46; 47**

HYDROGEN PRODUCTION FROM BIO-MASS **49**

HYDROGENATION OF CO₂ **53**

HYGIENE AND BIO-SECURITY ROLE OF CATALYSIS **63; 80**

IMMOBILISATION TECHNIQUES **76**

IN SITU/OPERANDO **12; 13; 14; 96; 101; 102**

INCLUSIVE APPROACH **63**

INDUSTRIAL GASES TREATMENT **84**

INNOVATION POTENTIAL FOR USE OF CO₂ **56**

INTEGRATED EFFORT **66**

INTEGRATED FLEXIBLE PROCESSES AND CATALYSTS **62**

INTEGRATED MULTI-CATALYST/MULTI-REACTOR SYSTEMS **102**

INTEGRATED PHOTOCATALYTIC/PHOTOELECTROCHEMICAL DEVICES **64**

INTEGRATION OF CHEMO-CATALYSIS WITHIN INDUSTRIAL BIOTECHNOLOGY **51**

INTEGRATIVE THINKING **49**

INTERDISCIPLINARITY IN CATALYSIS **36**

KEY-ENABLING TECHNOLOGY **17; 18; 77**

KNOWLEDGE-DRIVEN APPROACH **33**

LAYERED MATERIALS **92**

LCA EVALUATIONS **13; 38; 54; 66; 75; 75; 86**

LEGO APPROACH **93; 103**

LIGAND PREPARATION **100**

LIPID UPGRADING **50**

LOW TEMPERATURE CATALYSIS **69**

LOW-CARBON ECONOMY **56**

LOW-CARBON FUTURE **20**

LOW-CARBON-FOOTPRINT TECHNOLOGIES **87**

LOWER-TEMPERATURE TECHNOLOGY **75**

MEMBRANE REACTORS AND CATALYTIC MEMBRANES **98**

METALLOCENE **73**

METALLOPORPHINES **79**

METHANE NOVEL ROUTES OF CONVERSION **30; 31; 84; 86**

MICELLAR CATALYSIS **82**

MICRO- AND MACRO-ALGAE SOURCES **49**

MICROSTRUCTURED REACTORS **88; 99; 102**

MOLECULAR CATALYSTS ADVANCED **59**

MOLECULAR TRAFFIC CONTROL **97**

MOLECULAR WEIGHT CONTROL ROLE OF CATALYSIS **86**

MONOMERS AND POLYMER PROCESSES ROLE OF CATALYSIS **71; 85**

MULTI LEVEL PORE NETWORK **92**

MULTIFUNCTIONAL REACTOR **98**

MULTIPLE CATALYTIC CYCLES INTEGRATION OF **86**

MULTI-STEP PROCESSES **41**

NANOCARBONS **28; 93**

NANOCATALYSIS **79; 93**

NANOCOMPOSITES **70; 79; 81**

NANOFIBERS **70**

NANO-MANIPULATION **92**

NANOREACTOR DESIGN **96**

NANOSCIENCE INSPIRED DESIGN **59**

NANOSTRUCTURED MATERIALS **59**

NEW ENZYMES IN THE METAGENOME **80**

NH₃ NEW SYNTHESSES **32**

NITROGEN AS THE FEEDSTOCK **53**

NON-INNOCENT AND INNOCENT LIGANDS **95**

NON-PRECIOUS METALS **62**

NON-THERMAL PLASMA **30**

PROCESSES **44**

NOVEL CATALYSTS ADVANCED DESIGN **91**

OIL HEAVIER FRACTIONS **46**

VALORISATION **46**

OLEOCHEMISTRY **51**

ONE-POT CASCADE REACTIONS **79**

OPERANDO **90-94; 99**

OPERANDO METHODOLOGIES **99**

ORGANO-CATALYSIS **35; 62; 82**

ORGANO-CATALYTIC **73**

OXIDATIVE COUPLING OF METHANE **24; 26; 43**

OXYDEHYDROGENATION **57**

OXYMETHYLENE ETHERS **23**

PGM, REDUCTION OR REPLACEMENT **56; 57; 81**

PHOTOCATALYSIS AND PHOTOCATALYTIC TECHNOLOGIES **34-35; 41; 51-54; 60; 63**
66; 92; App. A

PHOTOCATALYTIC OR ELECTROCATALYTIC ACTIVATION OF CO₂ **53**

PHOTOELECTROCATALYTIC APPROACHES **55**

POISON TOLERANT CATALYSTS **48**

POLYCONDENSATION **69**

POLYCONDENSATION CATALYSIS **71-73; 83**

POLYMER MATERIALS AND FUNCTIONAL MATERIALS FROM RENEWABLE RESOURCES **82**

POLYMERISATION TECHNOLOGIES **69; 82**

POLYOLEFIN CATALYSIS **71**

POLYOLEFINS **69; 72**

POST-POLYMERISATION SURFACE MODIFICATION **72; 82**

PRACTICAL MANUFACTURING OF CATALYSTS **87**

PREDICTIVE MODELLING **87; 98; 101**

PRIORITY ELEMENT IN THE INNOVATION OF CATALYSIS SCIENCE **33**

PROCESS INTEGRATION **43**

PROCESS INTENSIFICATION **16; 20; 29; 29; 34; 42**

PYROLYSIS OIL **41**

RADICAL POLYMERISATION CONTROLLED **73; 82**

RATIONAL DESIGN **87**

REACTION MEDIA, NEW **97; 100**

REACTIVE DISTILLATION AND ADSORPTIVE REACTORS **97**

REAL DRIVING EMISSIONS **65; 98**

RECYCLING, OF PLASTIC WASTE **69; 72**

RENEWABLE FEEDSTOCKS **59; 69; 71**

RENEWABLE H₂ **19; 30; 41; 53**

RENEWABLE ENERGY **16-23; 27; 34; 41-43; 50-54; 60**

REVOLUTIONARY RATHER THAN RATHER THEN EVOLUTIONARY STUDIES **32**

SACCHARIFICATION OF LIGNOCELLULOSE **68**

SCALING-UP **87**

SCENARIO ANALYSIS **13**

SELECTIVE OXIDATION **9; 48**

SEPARATION STEPS, AVOID **44; 46**

SHALE-GAS **24; 43; 57**

SHORT-CUT SYNTHETIC ROUTES **76**

SINGLE ATOM CATALYSIS AT SURFACES **37; 95**

SINGLE-SITE CATALYSTS **90**

SMALL PARTICULATES REDUCTION **65**

SMART GRIDS **16**

SOFc **56**

SOLAR (BIO)-REFINERY **17-19**

SOLAR-DRIVEN CHEMISTRY **27**

SOLAR FUELS **17; 19; 29; 41; 51-53; 59**

SOLID ACIDS, WATER TOLLERANT **47**

STEAM CRACKING **43-46; 57**

STEAM REFORMING **549-51 ; 96**

STRANDED NG **43**

STRUCTURED CATALYSTS **28; 33; 56; 89; 91**

SUBSTITUTION OF FOSSIL FUEL **17; 23; 27**

SUSTAINABILITY OF CHEMICAL PROCESSES **67; 81**

SYMBIOSIS **20; 22**

SYNTHESIS GAS , FROM CO₂ **54**

SYNTHETIC MULTI-CATALYST (MULTI-REACTOR) SYSTEMS **88; 91**

TANDEM CATALYSIS **9; 35; 46**

TANDEM DEVICE **53**

TANDEM PROCESSES **35; 61; 81**

TEMPERATURE AND PRESSURE GAPS **92**

TIME-RESOLVED SPECTROSCOPY **66; 90**

UNDERSTANDING OF CATALYST **36; 99**

UNDERSTANDING REALISTIC COMPLEX SYSTEMS **99**

VISION FOR REFINERIES **19**

WATER-STABLE CATALYST **47; 70**

WATER AND WASTEWATER PURIFICATION ROLE OF CATALYSIS **63; 79; 103**