SALVATORE ABATE[1] - PAOLA LANZAFAME[2] - SIGLINDA PERATHONER[1] - GABRIELE CENTI[2]
UNIVERSITÀ DI MESSINA
ERIC AISBL E CASPE/INSTM
[1]DIPARTIMENTO DI SCIENZE CHIMICHE, BIOLOGICHE, FARMACEUTICHE E AMBIENTALI
[2]DIPARTIMENTO DI SCIENZE MATEMATICHE E INFORMATICHE, SCIENZE FISICHE E SCIENZE DELLA TERRA
CENTI@UNIME.IT

DOI: HTTP://DX.MEDRA.ORG/10.17374/CI.2016.98.2.32

# THE NEW SCENARIO FOR SUSTAINABLE CHEMICAL AND ENERGY PRODUCTION: OPPORTUNITIES FOR RESEARCH AND INNOVATION

A glimpse of the possible future for chemical and energy vectors production, evidencing the change in the energy-chemistry nexus, refinery and chemical production, and priority targets, is presented. The aspects shortly discussed are the following: i) the energy-chemistry nexus, ii) moving to a new sustainable energy scenario, iii) energy storage: from smart grids to chemical storage of energy, iv) a new vision for refineries, v) $CO_2$: a key carbon source element, vi) methanol: at the crossover of new energy-chemistry nexus, vii) exploiting shale-gas, viii) biogas-based chemistry and ix) solar-driven chemistry.

The production of chemical and energy vectors in Europe and worldwide is rapidly changing to address the increasing competiveness and the societal challenges as well as the increasing endeavour for a clear and sustainable future. Traditional raw materials have to be substituted with more sustainable resources, new safer and intensified processes have to be developed, new production concepts should be implemented to couple high efficiency and flexible production, 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 [1].

To understand better this change and the opportunities for research and innovation, it is necessary to analyse some of the major aspects which may be identified to dominate the future production of chemicals and energy vectors landscape. The focus is on the role of catalysis in this future scenario for the pivotal role of catalysis to enable sustainability of chemical and energy vector production [2, 3].

## 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 [4, 5]. 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 to innovation and competiveness, combined with other driving factors (socio-environmental motivations, greenhouse gas - GHG - reduction, resource security and related motivations, creating new value chains and other aspects) that will determine the change. Enabling the transition requires inserting the new technologies/processes within the current economic and productive infrastructure, in order to reduce the investments that otherwise would be too large. In a longer term, this transition will change the current energy-chemistry nexus. *Defining a path to 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 biorefineries [6, 7]. 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, it should be realised an energy intensification to parallel the better known concept of process intensification. A larger integration of solar energy within the energy-chemistry value chain going beyond the exclusive use of photovoltaic cells is a compulsory step, requiring the development of *new advanced materials for energy*. However, extending the use to other renewable energy (RE) sources is another relevant element, whose implementation also requires often chemistry-based solutions, for example to store and transport to long distance RE through suitable chemical energy vectors.

An effective transition to a sustainable energy and chemistry future requires *extending also the use of alternative fossil fuels*, creating the new chemistry and processes for their clean utilisation [5]. The future of chemistry will be likely based on an extended use of new 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.

## Moving 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 transitory to increase the smarter use of biomass (e.g. use of biomass in more eco-efficient processes than simple combustion). In fact, on a LCA (Life Cycle Analysis) basis, electrical energy generated from coal has an estimated impact about twice (in terms of grams of $CO_2$ equivalent per kWh) than that of natural gas (but value for shale gas is higher), while RE sources (biomass, wind, solar photovoltaic - PV, hydro, etc.) have on the average an impact ten times lower than that of coal. The impact of extra-heavy crude, tar sands, shale oil is similar to coal, in some cases even worse on a LCA basis. When using RE, there is also a proportional decrease in the emissions of pollutants such as $NO_x$ and $SO_x$, and particulate matter as well. There is the need of moving 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.

The actual limit in advanced countries to the further expansion in the production and use of RE is the *transition to a smart grid system*. In fact, RE sources such as wind and solar produce electrical energy in a discontinuous and fluctuating way (over the day and the year), which matches only in part the fluctuating energy demand. This causes destabilisation of the electric grids with potential blackouts, weakening voltage and damage to industrial equipment. Today a significant fraction of the potential RE (by wind, in particular) is lost because cannot be introduced and stored in the grid. The use of biomass and non-conventional fossil fuels plays a relevant role to guarantee a smooth transition to the new energy system. However, 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 cannot be reached even with long distance smart grids, but can be realised by chemical energy storage, particularly in the form of liquid fuels. The *chemical storage of energy* (in the form of liquid fuels) will remain a technology outperforming the energy density in batteries, though the latter have a different function and role, and thus both are unavoidable components (together with other devices for energy conversion and use) of the new sustainable energy scenario [4].

## 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 to create a hierarchy of storage solutions which are different in terms of energy storage capacity and time. Smart grids are a necessary step for the future energy infrastructure and will be the backbone of the future decarbonised power system.

Energy storage devices are the key element, which allow the implementation of this vision [8]. Conversion of electrical to chemical energy realises a better and more efficient transport at long distance, and the storage of energy for rather long times. In terms of smart grid, this solution enables also to import (and trade on world scale) the RE produced in remote areas. In fact, the transition to a new sustainable energy system requires to implement an energy system at least equivalent in functionality to that actually present. The world scale implementation of a sustainable energy system based on RE demands to develop RE vectors equivalent to those actually in use, e.g. with high energy density, relatively safe in use, easy to transport and store.

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 [9].

## 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 constrains related to the cost and complexity of their transformation, which likely will limit to only few platform products derived from biomass their large-scale use as biofuels. In the *energy area*, it may be suggested [10] (even if different opinions exist on this topic) that the transition to a more sustainable and low-carbon future will be driven mainly from:

i. the reduced use of energy vectors deriving from fossil fuels
ii. the use of biofuels
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 biofuels, there are still contrasting ideas, but the cost and complexity of transforming bio-feedstocks not in competition with food and their impact on environment (land use, water cycle) suggest that likely their share of total energy will not go beyond about 20% and mainly when they involve simple production processes.

The possible future integrated scheme of production of energy vectors (refinery) is schematically shown in Fig. 1 inside the crystal ball to accentuate the concept to prediction of the possible future scenario. This

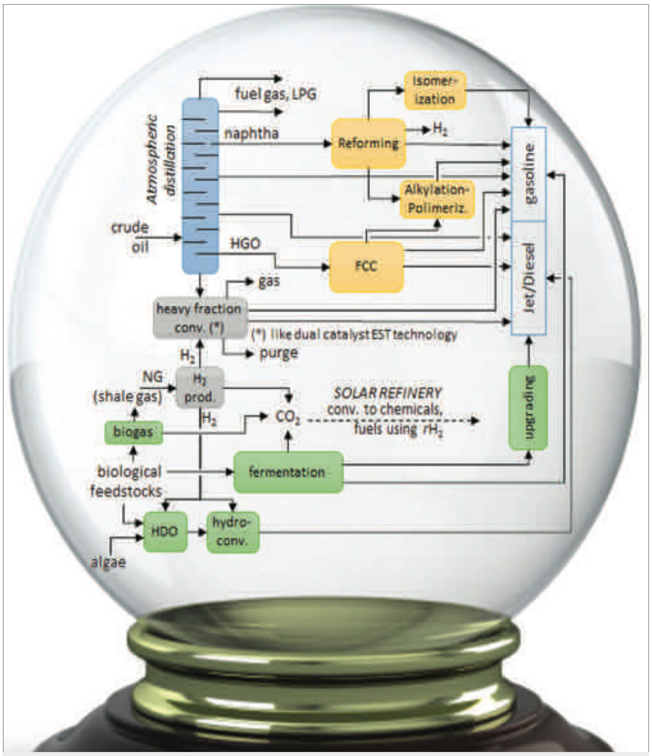

Fig. 1 - Schematic diagram of possible future integrated scheme of energy vectors production (refinery). Acronyms: FCC - Fluid catalytic cracking; LPG - Liquefied petroleum gas; HDO - hydro-deoxygenation; HGO - heavy gasoil; NG - natural gas; $rH_2$ - renewable $H_2$. Solar refinery deals with the conversion of $CO_2$ to chemicals using renewable $H_2$. Source: the scheme in the crystal ball is adapted from [11]

scheme outlines the integration with biorefinery from one side and with solar refinery from the other side. Natural (shale) gas is indicated as main source of $H_2$ production, whose use will be expanded to utilise heavy oil fractions and biomass/algae as feedstocks. This scheme outlines the substitution of vacuum distillation, and related downstream technologies, with a new technology for hydrotreatment of heavy fractions.

Solar fuels integration, besides to biorefinery integration within refineries schemes, is an important element of future scheme to lower carbon footprint at the same time reducing dependence from fossil fuels [6, 7]. 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 [4].

$CO_2$ use, in the prospective of a circular economy, is one of the critical elements of the integration of bio- and solar-refineries (within an advanced refinery scheme as outlined in Fig. 1) to move to new economy [12, 13]. Lowering the impact on greenhouse gas (GHG) emissions, in addition to other motivations (energy security, promote rural living, etc.) is a major motivation for regulations and incentives for biofuels utilisation. The possibility to further expand the use of biomass to move to a new (bio)economy is necessary to make a step forward in reducing GHG and environmental impact. Being large amounts of $CO_2$ produced in fermentation processes, one of the key elements in biofuel production, the integration of renewable (solar) energy and $CO_2$ reuse within biorefinery cycle is a necessary step forward. In fact, the transformation of $CO_2$ to fuels allows to incorporate renewable energy in the chemical energy of the fuel (or chemical), providing the more functional way to introduce renewable energy into the energy and chemical value chain.

In addition, this integration may boost overall energy efficiency and decrease carbon-footprint. There are several possible options to realise this objective, as described in the following.

### $CO_2$: a key carbon source element

One of the key elements in the new models of biorefineries is also the need to integrate $CO_2$ valorisation and renewable energy in the biorefinery value chain. It is possible to increase biomass to fuel conversion, when $CO_2$ utilisation is integrated in biorefinery. In biofactories, the scope is instead different and the target is the optimal integration of $CO_2$utilisation within the value chain. Symbiosis with near lying factories is another emerging element characterizing 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 $CO_2$, for example, in advanced microalgae processes) to enhance the energy efficiency and reduce environmental impact and $CO_2$ emissions of a productive district.

There are various interesting new models for advanced biorefineries/biofactories, two of which are emerging as a new opportunity [7, 10]:

i. bio-production of olefin and other base raw materials;

ii 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 polymerization, but with flexible type of production for a rapid switch to produce eventually fuel additives, depending on the market opportunities. Two of the elements characterizing both models are the full use of the biomass and process intensification (for efficient small-scale production).

### Methanol: at the crossover of new energy-chemistry nexus

Methanol is at the crossover of the new energy-chemistry nexus, because shows unique features of flexibility, one of the characterising 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.

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/biomass/renewable + $CO_2$). Methanol is thus one of the most important and versatile platform chemicals for 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 - methanol to olefin/MTP - methanol to propylene and related processes) or aromatics (MTA - methanol to aromatics) over zeolite catalysts, besides to be raw materials for other large-volume chemicals (acetic acid, formaldehyde and others). Olefin and aromatics deriving from refinery fractions will be progressively substituted from these alternative raw materials, and in part also from shale gas.

Fig. 2 outlines schematically a possible future integrated scheme for chemical production. The availability of alcohols at low cost from biomass fermentation processes stimulates their use as raw materials to produce other chemicals (especially ethylene deriving from ethanol). In addition, $CO_2$ emitted from biorefineries 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).

### Exploiting shale-gas

Availability and low cost of shale-gas is another of the elements which determine the future energy and chemistry scenario [14]. There are however still technical hurdles preventing the use of this resource. In fact, though it has been worldwide recognised that exploitation of natural gas, as such or as hydrogen source, for energetic purpose and also as fine chemicals precursor, replacing other fossil fuels, will contribute to lowering the global warming emissions, such statement is true if leakage of methane during drilling and extraction of natural gas from wells and its transportation in pipelines is completely avoided or drastically minimised. On this premises, heterogeneous catalysis plays an important role since all the transformation processes of methane are enhanced by the appropriate catalysts.

There is currently a big effort to develop novel catalysts and to develop novel direct routes for the selective and efficient conversion of methane. In this framework, methane valorisation to liquid fuel by efficient conversion to methanol is a strategic target, since natural gas could represent the most important fuel for the transition period towards an energy system based on renewable sources. Natural gas can be switched to methanol for energy storage, transportation fuel, and raw materials for synthetic hydrocarbons production.

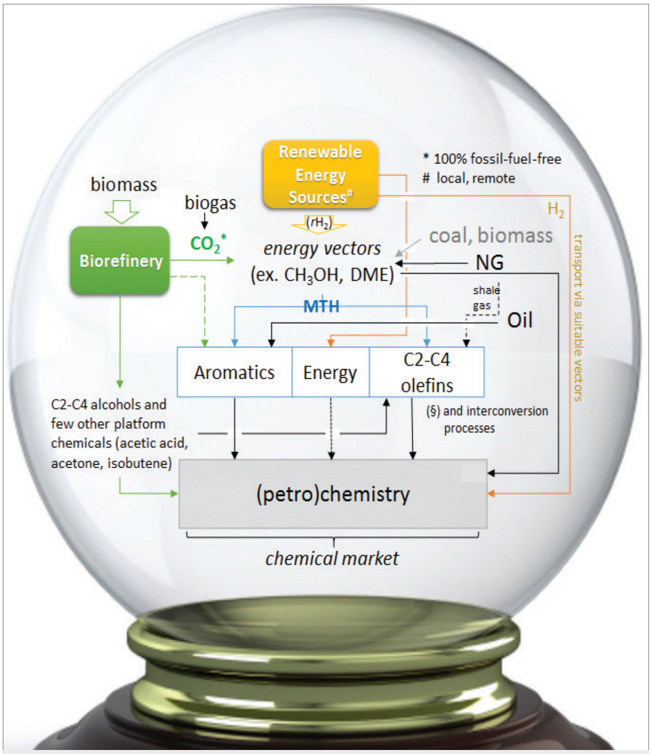

Fig. 2 - Simplified schematic diagram of a possible future integrated chemical production. Acronyms: DME - dimethyl ether; MTH - methanol to hydrocarbon processes; NG - natural gas. Source: the scheme in the crystal ball is adapted from [11]

On the other hand, the possibility to reduce energy use and costs of the production of syngas, for example by introducing new process schemes based on the integration of membranes, is a valuable option particularly for small-medium size applications. Shale gas can also be used for obtainment of light olefins. The challenges being related with the replacements of the energy intensive steam cracking. Another emerging route in this broad scenario is related to the use of *non-thermal plasma*, in the various different possible options 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 rather interesting possibilities for new gas and liquid phase transformations of methane to products such as methanol, olefins etc. Biocatalytic transformations is another promising area with interesting outlooks due to the significant progresses made in understanding the reaction mechanism. The key for exploitability of this route is to enhance productivity and reduce costs of separation, for example through the integrated use of membranes. The combination with solid (photo) catalysts to enhance the rate of reaction and/or close the cycle is one of the emerging areas.

### Biogas-based chemistry

Biogas, 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 biogas production that will require the possibility to store in the form of liquid fuels some of the energy produced. Biogas 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.

### Solar-driven chemistry

"Solar-driven Chemistry" term indicates the *possible future scenario for chemical production based on the progressive substitution of fossil fuels as energy source and raw materials*. The concept of "Solar-driven Chemistry" is thus not limited to the direct use of photons, but indicates the direct and indirect ways by which renewable energy could be transformed into chemical energy. Therefore, electrocatalytic routes, when the electrical energy is provided from renewable sources, are part of this general concept, as well as plasma routes for chemical 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 plasma is required. Current catalysts are not suited to work efficiently with the radical and vibrationally-excited species present in plasma.

A key aspect of "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 third characterising aspect of this new concept of chemical production is the paradigm-shift in chemical (and energy) production. The current focus of chemical production is on the "carbon-atom" selectivity with respect to the starting raw material (typically hydrocarbon). In a future sustainable production, providing selectively (renewable) energy for chemical transformations will be an additional key aspect, i.e. an energy-economy rather than only atom-economy. 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 [8].

The production of solar fuels and chemicals, and associated aspects of chemical energy storage, are between 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. However, it may be limitative to consider only these aspects, and not the more in depth impact on the entire chemical/energy production, which may derive from a proper consideration of the "solar-driven chemistry" scenario and its influence on the way we actually produce chemicals and energy, starting from scale-economy. The transition to a new economic cycle in chemistry/energy production is started, and "Solar-driven Chemistry" will be a key element of this future (sustainable) scenario. It is necessary to accelerate the development of new catalysis concepts, technologies and materials to turn this challenge into innovation and competiveness. It is necessary to change the catalyst chemistry from what it is today (dark operations) to some which operates with the sun, like artificial leaves (PEC approach) [15, 16].

Solar driven chemistry is a unique opportunity for chemical (and energy) production in Europe. It could create the knowledge-driven driver for competitiveness of Europe's industrial production, while preserving job and environment, for example by creating the sustainable chemistry/energy of the future. But only with a large integrated effort it is possible to meet these ambitious objectives.

## Conclusions

The areas shortly outlined above provide a glimpse of the possible future for chemical and energy vectors production, evidencing the change in the energy-chemistry nexus, refinery and chemical production, and priority targets. It is not fully exhaustive of the possibilities and perspectives in this broad field, but evidences some emerging area and the need to develop and improve new catalytic materials, devices and processes.

Some of the highlighted areas entail an improvement in current catalysts, or adapting their characteristics, for instance the transition from oil- to bio-based chemicals or process intensification. However, some of the areas, for example in the chemical use of shale-gas, require new disruptive catalysts. As a matter of fact, many obsolete processes need to be revised through the use of disruptive (game changer) catalysis approaches. Disruptive approaches may be divided in two boundary scenarios:

1) radically new and large scale workflows which integrate different feedstocks and energy sources which can be addressed only by the construction of novel catalytic and separation units,
2) radically new drop-in catalysts which can be in reactor used today and which can accommodate different (bio) feedstock or different raw material grades

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 $CO_2$ eq. emissions. Dramatic improvements in energy consumption for ammonia production were made prior to 1930, but further improvements were incremental over the last five decades and nearly zero recently. Producing $NH_3$ under mild conditions, for example by electro-catalysis using renewable energy sources to drive the reaction, could completely change the environmental impact and at the same time providing new bases for competiveness of European chemistry industry.

There are many other examples of disruptive catalytic technologies, from i) the photo- or photo-electro catalytic production of renewable $H_2$, 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 photo-carboxylation, 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.*

## REFERENCES

[1] S. Abate *et al., J. Energy Chem.*, 2015, **24**, 535.
[2] S. Perathoner, G. Centi, *J. Chinese Chem. Soc.*, 2014, **61**, 719.
[3] F. Cavani *et al.*, Sustainable Industrial Chemistry: Principles, Tools and Industrial Examples, Wiley-VCH, Weinheim, Germany, 2009.
[4] S. Abate, G. Centi, S. Perathoner, *Green,* 2015, **5**, 43.
[5] S. Abate, G. Centi, S. Perathoner, *Nat. Science Review*, 2015, **2**, 143.
[6] S. Abate *et al., ChemSusChem*, 2015, **8**, 2854.
[7] P. Lanzafame, G. Centi, S. Perathoner, *Chem. Soc. Rev.*, 2014, **43**, 7562.
[8] D.S. Su, G. Centi, *J. Energy Chem.,* 2013, **22**, 151.
[9] L. Barbato *et al., Energy Techn.*, 2014, **2**, 453.
[10] P. Lanzafame, G. Centi, S. Perathoner, *Catal. Today*, 2014, **234**, 2.
[11] S. Abate *et al., Catal. Science & Techn.*, 2016, Adv. Article, DOI: 10.1039/C5CY02184G.
[12] C. Ampelli, S. Perathoner, G. Centi, *Phil. Trans. Royal Soc. London A: Math. Phys. and Eng. Sciences*, 2015, **373**, 20140177.
[13] S. Perathoner, G. Centi, *ChemSusChem*, 2014, **7**, 1274.
[14] G. Centi, *ChemSusChem*, 2015, **8**, 212.
[15] C. Ampelli *et al., Catal.Today*, 2015, **259**, 246.
[16] S. Perathoner, G. Centi, D.S. Su, *ChemSusChem*, 2015, Adv. Article, DOI: 10.1002/cssc.201501059.

### Il nuovo scenario per la produzione chimica sostenibile e di energia: opportunità per la ricerca e l'innovazione

Viene presentata una visione del possibile futuro per la produzione chimica e di vettori energetici, evidenziando il cambiamento del nesso tra energia e chimica, tra raffineria e produzione chimica. Gli aspetti discussi in breve sono i seguenti: i) il nesso tra energia e chimica, ii) l'evoluzione ad un nuovo scenario energetico sostenibile, iii) l'evoluzione nello stoccaggio di energia: da reti intelligenti allo stoccaggio chimico di energia, iv) una nuova visione per le raffinerie, v) $CO_2$: un elemento chiave come fonte di carbonio, vi) metanolo: il punto di incontro del nuovo nesso tra energia e chimica, vii) la valorizzazione del shale gas, viii) una nuova chimica da biogas e ix) chimica basata sull'uso di energia solare.