

by addition of alkali metals as promoters [13]. Adding alkali(oxides) to the surface of a transition-metal induces local electrical fields. This allows one to exploit the fact that the N<sub>2</sub> dissociation transition state has a larger dipole moment than adsorbed N. Therefore, the scaling relation line in Fig. 1a is shifted downwards resulting in a circumvention of the pure-metal scaling relation and a considerably better catalyst. These industrial advancements can be contrasted to the naturally occurring systems as enzymes including nitrogenase. Despite that this biological system is known to be able to make ammonia at ambient temperatures and pressure, it is a very inefficient process. Hence, not only do we need to find inorganic catalyst but they have to be scalable and more efficient than the naturally occurring process. The challenge remains to develop a systematic approach to understanding effects like this in order to give us a toolbox of strategies to design radically better catalysts.

## CHEMISTRY

Special Topic: Catalysis—Facing the Future

## Energy-related catalysis

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Availability of energy is a vital element of our current society, but energy must be converted to usable forms, either when stemming from fossil fuel sources or from renewable (perennial) ones. Catalysis plays a central role to enable both possibilities and mitigate related impact on environment, including greenhouse gases (GHG) emissions.

Today, the energy system is largely based on fossil fuels, which need to be converted to suitable energy vectors (liquid fuels especially, for their high-energy density and easier transport/storage).

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A major current worldwide use of catalysis (especially heterogeneous catalysis) is in refinery-related processes, for example in hydrotreating, fluid catalytic cracking, etc., with a global market of about \$3.5 billion, roughly a quarter of the total catalyst industry.

Driven from both market and societal requests, the specifications of energy products have largely changed over the years. Today gasoline or diesel utilized in cars has less than 10 ppm—parts per million—of sulphur content [1]. Over the years, it was necessary to develop

specific highly active catalysts allowing to eliminate the S-compounds present in oil fractions with the amazing selectivity of converting few molecules between millions of analogous ones, but not containing sulphur. There are new demands deriving from the need to exploit non-conventional fossil fuels, for example heavy oil residues, shale gas and coal as well. New advanced catalytic processes have been developed to treat these fractions. For example, new catalytic processes of hydroconversion of heavy residues in slurry reactors have

been developed by various companies, with related nanocatalysts. An example is the newly developed Eni Slurry Technology process allowing to convert very heavy feedstock to medium distillates [2]. A nanosized MoS<sub>2</sub> catalyst has been developed for the use in these conditions.

Availability and low cost of shale gas has also largely driven research in recent years [3]. Natural gas (NG) catalytic conversion to liquid fuels or chemicals is an active research line. Pearl GTL (gas-to-liquid) (Shell, Qatar) is an example of a large plant (140 000 barrels a day) to convert methane to middle distillate, based on the use of cobalt-based catalysts for Fisher–Tropsch reaction [4]. Around one third of NG resources are defined as stranded, e.g. not usable because too far to be introduced in the NG pipeline network or because they cannot be transported by liquefaction. GTL is one possibility to convert these resources to a liquid fuel (diesel) for the market, but not spread over the specific Qatar situation, due to the need to have very large gas fields, the high costs of operation and other issues. There is the need to develop novel catalytic solutions able to produce efficiently liquid fuels in small medium size stranded gas fields. The need to produce syngas from NG is a significant part of the cost in the GTL process, around one third of the total cost. The solution is the direct conversion of methane (e.g. without passing from syngas) to produce methanol, DME (dimethylether) and aromatics. Fig. 1 summarizes the main possible alternative routes for converting methane.

A recent example is the work of Bao and coworkers [5] that have developed stable novel catalysts, based on isolated supported iron-carbide species that produce light olefins and aromatics with stable performances, although at around 1000°C. The olefins can be used for chemical market or to produce clean fuels, via catalytic oligomerization/isomerization.

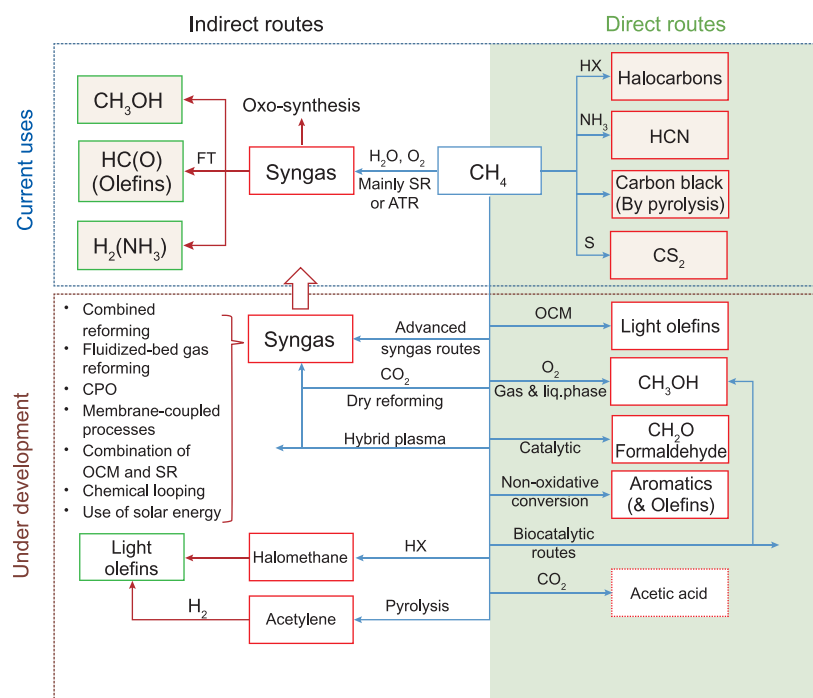
A major driver for research and development in the area of energy related catalysis is the transition from a fossil fuel-centred to a renewable-based energy system. This transition to be effective needs to minimize the large costs related to a

major change in the energy infrastructure and solves main drawbacks of current renewable energy sources (solar photovoltaic, wind, etc.): intermittency, difficulty to store and transport to long distance of electrical energy. Catalysis plays a role in the development of the electrodes for the devices used in electrical energy storage and conversion, but the challenge for catalysis is to develop new and cost-effective catalytic technologies to produce solar fuels, e.g. 100% fossil-fuel-free fuels preferably integrating within the actual energy infrastructure, produced indirectly via biomass or in a longer term using directly solar energy [6].

Many different routes and related catalysts have been developed to produce biofuels from biomass, requiring in general different classes of catalysts with respect to those currently used in refinery [7]. However, the biorefineries scenario is rapidly evolving and as a consequence the type of catalysts needed [8]. Two new directions are emerging: (i) olefin biorefineries and (ii) biorefineries for sustainable chemical production. There is a shift from a focus on biofuel production to

a focus on bioproducts, e.g. from biorefineries to biofactories. GHG emissions should be reduced, with new catalytic routes for using the CO<sub>2</sub> produced in bio-based processes. The energy for the conversion of CO<sub>2</sub> should derive from renewable sources (integrated solar biorefinery approach [8]). Catalysis for CO<sub>2</sub> conversion is highly linked to the future of energy and a preferable route to introduce renewable energy in the energy and chemical production value chain [9].

Currently, most of the activities in catalysis for solar fuels are limited to H<sub>2</sub> production, an important area for catalysis, but an intermediate step. The challenge is to combine photocatalysts to produce H<sup>+</sup>/e<sup>-</sup> from water (the equivalent of H<sub>2</sub>) to catalysts able to utilize them to convert (electro)catalytically CO<sub>2</sub> to fuels and chemicals. Distinct zones of reaction are necessary to avoid separation costs and for safety reasons. New design for these photoelectrochemical (PEC) cells and more productive, robust and stable photo- and electrocatalysts are required [10,11] to move to artificial leaf-type solar cells and to the future of sustainable and clean energy production.



**Figure 1.** Scheme of the current and under development catalytic routes for indirect and direct conversion of methane.

Electrocatalysis is a key component in these PEC cells, but also an essential element in the energy storage (batteries, supercapacitors) and conversion devices (fuel cells and electrolyzers). There is the need to develop more active and stable catalysts, not containing rare elements, for both direct alcohol fuel cells and SOFCs (solid oxide fuel cells). Solving these and other challenging for catalysis requires passing from a fit for use to a true design of catalyst in energy-related aspects. Today, advances in development and manipulation of structures at the nanoscale [12] and theoretical design are impressive [13]. There is the need to develop also conceptually new catalysts based on earth abundant and cheap metals [14] or nanocarbons [15], for example.

Energy-related catalysis plays thus an enabling role to find new solutions to societal challenges and to create a sustainable future. A knowledge-driven development bridging the many aspect

necessary to develop novel advanced catalysts, spanning over an incredible  $10^{10}$  scale dimension (from molecular nanoscale level to the multimeter size of the catalytic reactors) is necessary.

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## CHEMISTRY

Special Topic: Catalysis—Facing the Future

# Photocatalysis in solar fuel production

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With the increasing concerns on energy and environmental problems caused by the combustion of fossil fuels, solar energy becomes vitally important because it is the only viable renewable energy source that can replace the fossil fuels in vast volume. The research on photocatalysis for solar fuel production, especially  $H_2$  production by photocatalytic splitting of water and conversion of  $CO_2$  to chemical fuels such as  $CO$ ,  $CH_3OH$ ,  $CH_4$ , etc., is regarded as the most ideal way for solar energy conversion, storage and utilization. In view of the current research status and the near future practical

applications, particulate semiconductor photocatalyst (PSP), photoelectrochemical cell (PEC) cell and photoelectrochemical cell coupled with photovoltaics (PEC-PV) system are the three most promising solutions for solar fuel production.

The best PSP reported so far for water splitting under UV light irradiation is La doped  $NaTaO_3$  loaded with Ni/ $NiO_x$  cocatalyst, reaching quantum efficiency (QE) of 56% [1]. Because UV light takes only less than 5% of the solar spectrum, solar energy conversion by UV-active photocatalyst is rather limited. Since

visible light occupies more than 40% in the solar spectrum, development of visible light active photocatalyst is necessary. The best visible light photocatalyst for water splitting is  $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$  semiconductor photocatalyst loaded with  $Rh_{2-y}Cr_yO_3$  cocatalyst, which can reach QE of 5.6% under visible light irradiation ( $\lambda > 420$  nm) [2]. Visible light QE of 6.3% has also been reported for a  $ZrO_2/TaON$  and  $PtO_x/WO_3$  coupled system with  $I^-/IO_3^-$  as the shuttle redox mediator. Though it is still far from the practical application requirement of at least 10% solar energy conversion