

## CHALLENGE 8G: CATALYSIS FOR INDUSTRIAL PRODUCTION AND OF ENERGY RESOURCES

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### Foreword

Catalysis is a key enabling technology for various challenges in the Energy Area; is also relevant for chemicals production, environment protection, selective synthesis, sensing and other key subjects. To quote a document from the European Cluster of Catalysis:<sup>1</sup>

“Catalysis and catalytic processes account directly or indirectly for about 20-30 % of world GDP.”... “Of the 50 largest volume chemicals currently produced, 30 are produced via catalytic routes... and account for more than 20 billion tons of CO<sub>2</sub> emitted yearly to the atmosphere... Technical improvements in catalyst processes could reduce energy intensity for these products by 20% to 40% by 2050.”

There are also specific issues common to many fields of general catalysis:

1-Many catalysts have complex structures, not only at molecular level, as in enzymes and homogeneous catalysts, but also in morphology (Fig. 1). Catalytic active species in solids may need to contact other phases (maybe at specific surface planes), to exist as particles

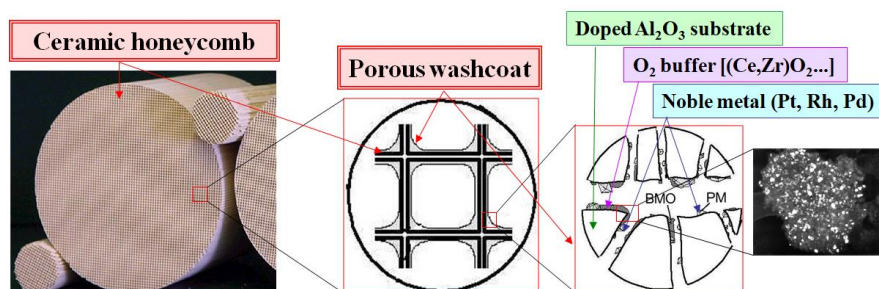


Fig. 1 Typical three-way catalyst for exhaust gas treatment in gasoline cars. Source: composed by J.C. Conesa using images from very different sources.

of narrow size range, etc. It is thus important to master catalyst synthesis methods. Besides, some catalysts require precious or rare metals, or hard to produce ligands; they should be manufacturable more easily, with less cost and/or in less steps.

2-Catalyst modelling is key to identify reaction mechanisms and catalyst active centers. Reliable predictions of catalysts behaviour need using multiscale approaches<sup>2</sup> that combine calculations of geometric and electronic structure, reaction barriers, molecular dynamics (MD) and atomic scale microkinetic modelling, to end with macroscopic transport models and classical reaction engineering. The different scales may be computed separately to higher or lower accuracy and then combined strongly or weakly.

Electronic structure calculations study bond breaking/forming steps and activation energies. MD can use atomistic potentials, semiempirical or DFT systems. Mean field or Monte Carlo methods can be used in larger scales. Powerful hardware and software tools allow realistic catalyst models at working conditions of P, T and fluids. Machine learning<sup>3</sup> and AI techniques are used today to design and prepare better catalysts (even using robotic systems) and can be combined with multiscale modeling frameworks.

Many CSIC groups use computational tools for catalysts modeling. Main ones work at ICP, ITQ, ICMM or IIQ; others working in materials modeling could adapt their tasks. Parallel supercomputers are needed, like those available in RES and PRACE networks.

3- Studying the state of a working catalyst may need *in situ* techniques. Many of them can be used: XRD, IR, Raman, UV-Vis-NIR, NMR, EPR, XPS, synchrotron radiation-based spectroscopies... Catalysis studies also require relating performance and structure. Both can be combined using the *operando* concept<sup>4</sup> (Fig. 2), where reactants and products are measured to check that the reaction takes place like in the catalytic reactor; multimodal reaction cells compatible with the probes used and working at the desired conditions (T, P, gas/liquid flows, etc.) can be designed. Catalysis may also require characterizing both catalyst and catalytic reactions with time- and space-resolution. CSIC institutes working in this line are mainly ICP and ITQ; if CSIC wants to foster research lines on catalysis it might be convenient to promote in other institutes the use of *operando* equipment.

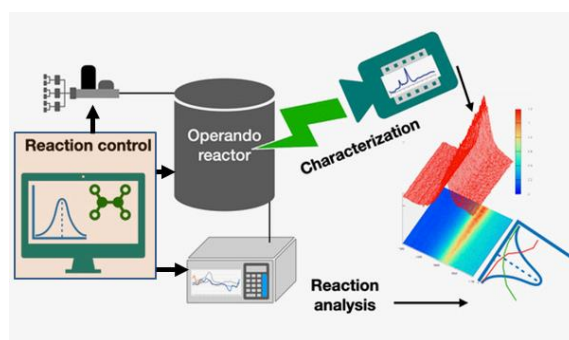


Fig. 2 The *operando* methodology. Source: made *ex novo* by Miguel A. Bañares.

4-New types of catalytic reactors need to

be engineered. Intensification implies using multiple very narrow channels in parallel;

membrane reactors allow separation of products as they are formed; photocatalysis needs clever handling of photon flow; fuel cells and electrolyzers, like photoelectrochemistry, require well-designed gas diffusion electrodes; other reactor designs may be needed to allow greener processes, etc.

Another important aspect is whether concentrated or distributed technologies should be preferred, aiming at reducing CO<sub>2</sub> emissions. This is subject of a recent review<sup>5</sup> focused on NH<sub>3</sub> synthesis, but can be applied to many processes, even to non-catalytic ones.

All these aspects are relevant for any catalytic processes, including energy-related ones.

The relevance of CSIC in Catalysis for clean energetic processes is revealed by the high impact in scientific publications, being the 1<sup>st</sup> Spanish Institution in number of articles reported between 2010-2019, including the terms “Catalysis” and “energy” or “sustainable” or “renewable” and “activity” or “selectivity” or “efficiency”. In particular, 30% of all the Spanish scientific articles in the mentioned fields are participated by CSIC (Fig. 3), which is the 2<sup>nd</sup> European Institution in number of publications, being Spain the 2<sup>nd</sup> European ranked country, with 14% of total production.

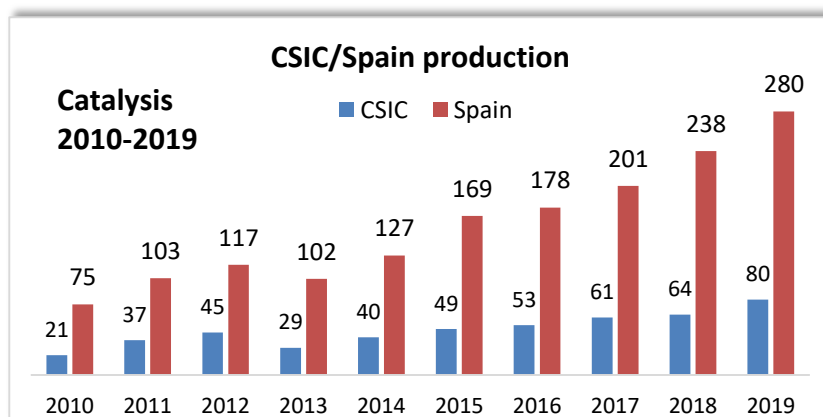


Fig. 3. Distribution of CSIC/Spain articles reported between 2010-2019. *Source: Web of Science. Clarivate Analytics. Web (May-June 2020). CSIC – URICI and BTNT (CCHS-CSIC).*

### A) Catalysis for a sustainable industrial production

#### *AI Catalysis for industrial production with lower energy demand and higher atom efficiency*

Catalysis is one key technology driving a Sustainable Chemistry; it makes possible improving energy efficiency, using renewable feedstocks and reducing waste<sup>6</sup>. Concerning

energy, catalysis enables producing clean fuels and using renewable resources (e.g. bio-ethanol), thus decreasing the overall carbon footprint. It also improves energy efficiency of chemical processes with disruptive techniques based in new catalytic routes.

Industrial chemical processes can be of two types: with high volume but low added value of the product (commodities, chemical intermediates, platform molecules) and with (very) small volume and high added value (speciality chemicals, pharma, etc.). The energy balance of a chemical reaction is fixed, but the energy input of its industrial process depends on the conditioning of its reactants (T, P) and on the need of separation and purification of products, which may cause more than 90% of the overall cost.

### **Impact in basic science panorama and potential applications. Key challenging points**

Two catalyst properties are key to improve the energy efficiency:

- a) high activity allowing process operation at milder conditions (low P and/or T) or high productivity at given reaction conditions (reducing the energy input per unit product).
- b) high selectivity to the targeted product, reducing separation/purification costs.

Better energy efficiency may come also *via* process intensification, integrating chemical reaction and process physical steps, and optimizing process and reactor design. This will require developing or morphologically adapting catalysts to new environments and operational regimes: high per-pass conversion or productivity, passing from overall endothermic to exothermic systems or vice versa, etc.

Another main role of catalysis in chemistry concerns atom efficiency.<sup>7</sup> Catalysts allow substituting classical organic syntheses which require stoichiometric amounts of reagents and/or may reduce the number of steps needed. Selectivity is a key catalytic property, to keep most reactant atoms in the final product. Novel selective catalysts and improved selectivity of current ones are key research goals in this field.

Homogeneous catalysis with its high selectivity is a good example. Thus, aminations inserting NH<sub>3</sub> in simple organic molecules containing C-C double bonds, alcohol or carbonyl groups can proceed now without deactivation and high yield using recent metal complexes; this provides key compounds for the pharma industry.

The best example of these principles is given by enzymatic catalysis. It conforms most principles of green chemistry<sup>8</sup>, e.g. no. 6 stating that “Energy requirements should be recognized for their environmental and economic impacts, and should be minimized”. Most enzyme-catalyzed reactions occur in aqueous media at mild temperature (T, from now on), e.g. <60°C, lowering energy needs, though product separation may be difficult.

Enzyme-catalyzed processes can be made in batch reactors. Several enzymatic processes may operate under similar T and pressure (P, from now on) conditions, allowing integration of multiple transformations into economically attractive cascade processes. Such processes can also have very high selectivity, alleviating the need of by-product separation. Besides, many enzyme catalysts are obtained from easily available renewable resources, and are biodegradable and (except for some metalloenzymes) non-toxic. They do not need functional group activation, protection and deprotection steps, generating thus less waste than other methodologies. Biotechnology advances make now feasible to optimize and adapt enzymes to a predefined process. Protein engineering, especially directed evolution, can improve enzymes to design sustainable processes with less generation of residues. This strategy was already used successfully e.g. in industrial synthesis of pharmaceuticals.

### **CSIC advantage position and multi/inter-disciplinarity**

Groups at IQAC, IQM, ICP, ITQ, ISQCH, IIQ, IRNASE, IQOG, ICMM, ICMSe, LCH (an associated CSIC unit) work in sustainable chemistry using chemo- and biocatalysts; some of them develop energy-oriented applications.

### ***A2 Air depollution in energy-intensive industries***

The measures taken by industrialised countries after signing the 1997 Kyoto Protocol have led to reduction in emissions of greenhouse gases and toxic pollutants in transport, electricity generation and chemical industry. Spain adopted such measures (improving fuels, substituting fossil fuels by other energies) establishing end-of-pipe treatments, fixing pollutants by ad- or ab-sorption, or transforming them into harmless substances via catalytic or non-catalytic processes. This has originated a series of documents<sup>9</sup>.

### **Impact in basic science panorama and potential applications.**

Several mature technologies exist, at TRL9, to clean gases from NO<sub>x</sub> and SO<sub>2</sub> in combustion plants: low NO<sub>x</sub> burners, flue gas recirculation, selective non-catalytic (SNCR) or catalytic (SCR) reduction, etc.; the latter shows good efficiency in high dust systems working at 300-450 °C. New trends try to improve stability against K<sup>+</sup> present in ashes, especially with biomass fuels,<sup>10</sup> and to lower the catalyst working T below 200°C to use the SCR system in tail-gas, avoiding problems due to the presence of SO<sub>2</sub> and ashes

in the catalyst. Other techniques are proposed for SO<sub>2</sub> elimination: using low-sulphur fuels, injecting sorbents in the boiler and wet desulphurization using aqueous solutions to capture acid compounds. This requires improving cost reduction and reusing/recycling the products resulting from sorption. Achieving TRL7-9 needs replacing noble metals by less costly transition metal oxides in catalysts burning VOCs.

N<sub>2</sub>O emissions during fertilizers production must be avoided, as they contribute to the greenhouse effect. Several TRL6-8 options under development are being considered.

### Key challenging points

Cleaner processes, new catalysts and more efficient, durable and cheaper absorbents are needed to further reduce emissions. Activation of materials by photons or  $\mu$ w to avoid heating all the gas mass or structures like wall-flow monoliths (Fig. 4) are some options. New methods of catalyst manufacturing must be developed here, both for the synthesis of nanoparticles and for the structuring of solids, e.g. using 3D additive manufacturing.

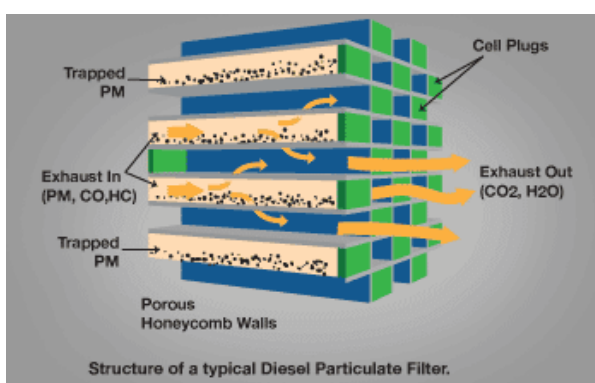


Fig. 4 Honeycomb system treating gases and soot from industrial Diesel motors. *Source: <http://urbane-missions.blogspot.com/2015/12/what-is-diesel-particle-filter-dpf.html>.*

### CSIC advantage position and multi/inter-disciplinarity

CSIC has many expert groups able to lead projects in this field. Those in ICP, ICMS and ITQ have renowned expertise both in classical technologies and new approaches such as photocatalysis. For the synthesis of nanoparticles and use of microwaves ICMM stands out; additive ceramics manufacturing is a specialty of ICV.

### ***A3 Catalytic processes directly driven by electricity and electromagnetism***

#### **Impact in basic science panorama and potential applications. Key challenging points**

Some catalytic processes (besides electrochemical ones) can be driven by electricity without transforming it to heat: *microwave (MW) activated catalysis*, *plasma-catalysis* and *use of magnetic fields* are emerging alternatives likely to spread over the next years.

*MW* is used to process materials, biomass or wastes; also for catalytic reactions,<sup>11</sup> due to high energy delivering rates, ability to provide uniform or localized activation, or reduction of process time and energy use (30-50%). *MW* can also provide better control of catalytic selectivity. Current commercial use of *MW* in catalysis, biomass processing or materials synthesis is still scarce, as the interaction between *MW* and solids/liquids or reactants/catalysts is not yet understood. Problems as measuring hot spots *T* or the need to improve reactors design also hinder the progress of this technology.

*Plasma* can be used to induce gas reactions at ambient conditions and short/zero response times. They may replace energy demanding processes, reducing their CO<sub>2</sub> footprint, e.g. in Haber-Bosch NH<sub>3</sub> synthesis (responsible for 1.7% of CO<sub>2</sub> emissions). Both *MW* and direct DC/AC activation modes can induce atmospheric plasmas for gas phase processes<sup>12</sup>. Using plasmas at high TRLs faces limitations to treat large gas volumes, have high energy costs and, in some cases, also difficulties to control selectivity.

*Magnetic fields* generated by AC currents can efficiently heat magnetic nanomaterials coupled with catalysts in microreactors and flow systems. This technology was first used in 2008 for the oxidation of alcohols, using gold-doped magnetic nanoparticles as catalysts. It has been tested recently in biocatalysis to increase and regulate the catalytic activity of linked enzymes<sup>13</sup>, and in the degradation of organic pollutants.

A challenge common to all these emerging techniques is improving efficiency at large scale; i.e. move the technology to higher TRL values. This has specific limitations:

*MW-induced catalytic processes*: i) Scaling up reactors while compensating the small penetration of *MW*; ii) Improved reactor designs (operation modes, feedback systems, automatism); iii) Catalyst design adjusting each material to its capacity to absorb *MW*.

*Plasma-catalysis*: i) Improving reaction yield (better electrode materials, alternatives for gas handling systems); ii) Increasing energy efficiency (vortex handling of gases, using gliding arcs, etc.); iii) Better selectivity via formulation of plasma-specific catalysts.

*Catalysis assisted by magnetic fields*: i) Improving the energy efficiency for large scale processes; ii) New catalyst formulations to enhance activity and reduce costs.

New promising research lines can thus arise using renewable electricity. *MW* may find use in pyrolysis or reactions valorizing biobased chemicals, polymers and waste in medium/large scales. *Plasma-catalysis* may expand to treat small gas volumes, e.g. for *in situ* H<sub>2</sub> production from organics or NH<sub>3</sub> or in on-board reactors for cars or ships. *Magnetic field* activation can be used in niche applications: biocatalysis or sanitization.

### **CSIC advantage position and multi/inter-disciplinarity**

ICP uses MW for efficient gas treatment and catalysis; CSIC groups in many institutes use it for food or material processing, and may try it also for catalysis. Plasma-catalysis for gas treatments is an emerging topic, developed in CSIC only in ICMS. In both cases TRL values of the technology are low: 4-5 for MW, 2-3 for plasmas. ICMM and ICMA use magnetic fields for efficient activation of reactivity, also at a low TRL (2-3). Much can be learned from  $\mu$ w material processing, already implemented at industrial scale with relevant Spanish actors. CSIC research may catalyze here national initiatives fostering the interaction with sectors using already  $\mu$ w at higher TRLs; implementation of these new techniques will require a tight collaboration with electricity suppliers.

### **B) Catalysis for the use of biomass**

#### **Impact in basic science panorama and potential applications.**

In last years industrialised countries have turned to biomass as a renewable carbon source for producing food, fuels, materials and chemicals in the so-called biorefineries (Fig. 5), fully aligning with the European *Bioeconomy* and *Circular Economy* Strategies and the longer-term *Objective of Going Carbon Neutral by 2050* announced by EU.



The second-generation biofuels sector (those not competing with food) is well established in Europe. However, the bio-based chemicals sector, even being already a reality in EU with annual turnover of 9.17 M€, still represents only 3 % of EU chemical industry according to a report issued by the European Joint Research Centre (JRC)<sup>14</sup>. Some sectors (coatings, paints, inks, etc.) are mature; others (platform chemicals, plastics, adhesives, lubricants, etc.) have high growing potential.

Processes to transform biomass to products can be fermentative, enzymatic or chemical. The first one is out of the scope of this text as it cannot conduct many needed reactions feasible only with chemo- and biocatalysts. Chemocatalysis is robust, productive and suited for lower cost chemicals; enzymes, with better selectivity, operate in milder conditions<sup>15</sup>. Combination of both types of catalysts (combocatalysis) in a single cascade process is a promising option which is currently at early stages of research.

### Key challenging points

#### *Catalysis in production of biofuels and renewable chemicals from biomass*

The main research challenge in chemo- and biocatalysis is to produce cost-effective bio-based products. Processes must be efficient, robust (coping with impurities or water, leaching, thermal changes, etc.), durable, flexible to adapt to different biomass types and to meet the green chemistry rules; separation/purification steps must be integrally considered. Research should include also techno-economic and life cycle analyses.

Using mild conditions and non-toxic solvents is challenging. Chemocatalysis, producing now many petrochemical commodities, is used to apolar and unreactive feedstocks, con-

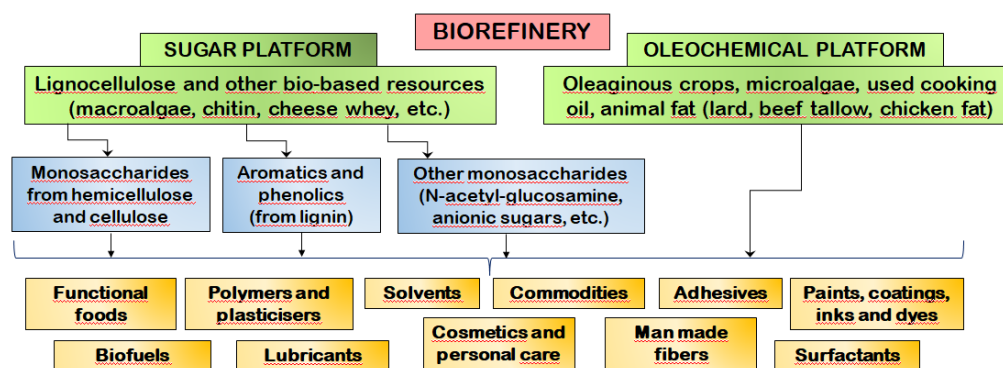


Fig. 5 The biorefinery concept. Source: made ex novo by F. Plou, with additions and rearrangements by M.A. Centeno and M. López Granados.

ducting reactions in gas phase at high T and P; biomass implies instead oxygenated, reactive polar molecules with water ubiquitously present in feedstocks. Enzymes are in better position here, while chemo-catalysts are more robust against thermodegradation.

Producing low-volume/high-value bio-based products, in contrast to high-volume/low-value ones frequently relying on cheap non-precious metal catalysts, is a key issue also for commodity markets, as it may allow sustaining an integrated bio-refinery model. Here homogeneous catalysis, even if using costly precious metals (Ru, Ir, etc.) but with well-established synthetic methods, can come into play.

Intensification of processes to increase efficiency, lower the production costs and improve viability and energy and environmental efficiencies is also challenging. Implementing continuous processes in conventional flow reactors increases the productivity, but using micro- or structured reactors is a challenging step forward.

Another possibility is synthesizing bioproducts in electrolytic cells. O<sub>2</sub> and H<sub>2</sub> can be made in-situ from water using renewable electricity (photovoltaic or wind); using non-precious metal electrocatalysts in neutral pH and concentrated solutions to improve efficiency and developing cost-effective purification procedures are the challenges here.

#### *Catalysis producing renewable building blocks from biomass.*

Bio-based industry might replicate oil-refineries, as the chemicals that our society needs are now made directly from oil. Bio-commodities produced via chemical catalysis (e.g. furfural, sorbitol, xylitol) are now in the market, from which other chemicals can be made; other compounds (levulinic acid, propylene glycol, etc.) are not yet cost-competitive<sup>16</sup>. Bioethanol or lactic and succinic acids, made via fermentation, are also in the market and could become platforms for other renewable chemicals; cheap glycerol from the biodiesel industry may also allow accessing multiple products at affordable prices. Developing efficient catalysts to achieve transforming all these platforms to valuable products is a vast and challenging field of investigation for the future.

#### *Accessing cheap and widely distributed feedstocks.*

A widely-spread biomass feedstock is lignocellulose, a recalcitrant composite present in plant cell walls. It is built-up basically by lignin, a refractory aromatic polymer packing two polysaccharides: cellulose and hemicellulose (made up of different pentoses and hexoses). Cheap lignocellulose is widely available, but developing a cost-effective lignocellulose fractionation process to access this source of sugars and aromatics still remains a

challenge. Bioethanol industry solved the problem, and has access to sugars breaking the lignin seal; but lignin, still recalcitrant, is used only for energy purposes.

Combining solvents and catalysts can fractionate lignocellulose, giving access to its sugar and aromatic content. Two chemocatalysis examples are the Triversa Process<sup>TM</sup> and the H<sub>2</sub>-assisted Reductive Catalytic Fractionation; other possibilities are available<sup>17</sup>. Lignocellulose degradation is catalysed by enzyme cocktails; oxidoreductases may depolymerise it. Protein engineering techniques can improve the activity and specificity of enzymes; advances are still needed to tailor these processes for the targeted products.

Other agro-food industry by-products can be also feedstocks, like chitin, a biopolymer present in crustaceans, mollusk shells and fungi cell walls; lactose-rich byproducts like cheese whey permeate; or marine seaweeds, also a good carbohydrate source. The challenge is to develop efficient and robust chemo- and bio-catalytic technologies converting these residues in added-value renewable chemicals.

#### *Deploying the 2<sup>nd</sup> and 3<sup>rd</sup> generation biofuels.*

Lignocellulosic bioethanol and used cooking oil (UCO) biodiesel account for most 2<sup>nd</sup> generation biofuels consumed in Europe. Fuels from synthesis gas (or syngas; from now on, SG), a mixture of mostly CO and H<sub>2</sub> which can be derived also from biomass, are close to be cost-competitive (see Challenge 8E for details); also the interest in biofuels for air and marine transport (Fischer-Tropsch fuels, Hydrogenated Vegetable Oil kerosenes) is growing. The latter process needs noble metal catalysts to transform/crack the oil molecule; non-precious metal catalysts are needed here.

Concerning 3<sup>rd</sup> generation biofuels (obtained from microalgae), the real problem is the growing and harvesting of dry biomass at affordable cost; heterogeneous catalysts must also cope with interferences by phosphor- and sphyngo-lipids present in microalgae oil.

#### **CSIC advantage position and multi/inter-disciplinarity**

Well-reputed groups in several CSIC institutes (CIB, ICMS, ICP, IQAC, IRNASE, ITQ, ISQCH, IATA, and others) conduct front-line investigations in biorefinery processes. Their TRL is 3-4; some may reach TRL 5, and/or participate in EU projects pursuing or accomplishing higher TRLs. Based on their expertise, CSIC has a strong position for leading an ambitious research program in order to confront, in a 10-year horizon, the challenges described above up to higher TRL levels (7 and even 8).

## C) Catalysis for the production of clean fuels from renewable sources

### *C1 Catalytic production of SG from renewable sources*

The new energy scenario requires replacing fossil carbon resources by carbon-neutral renewables. Options involving production and then conversion of SG to fuels and chemicals stand out as most attractive. Producing SG from non-food biomass, or from captured CO<sub>2</sub> (which can be a source of CO via the Reverse Water Gas Shift reaction, RWGS) and H<sub>2</sub> (made by water electrolysis) appears as an attractive option.

### **Impact in basic science panorama and potential applications. Key challenging points**

SG from biomass gasification or pyrolysis usually contains impurities (N<sub>2</sub>, CO<sub>2</sub>, hydrocarbons, tars, etc.) and potential catalyst poisons (containing S, Cl, etc.) requiring costly cleaning pre-treatments. Adjusting the H<sub>2</sub>/CO ratio in biomass-derived SG using e.g. downstream RWGS reactors, membrane separators or pressure swing adsorption may be necessary prior conversion to fuels or chemicals. Producing clean SG with the proper H<sub>2</sub>/CO ratio requires optimizing process parameters and catalysts, adjusting them to all ranges of biomass feedstocks; using modular and scalable microreactors is a promising approach. For production of synthetic fuels, efficiently integrating the stack producing SG with the SG-to-fuels conversion reactor is another challenge to be addressed.

SG production from CO<sub>2</sub> and H<sub>2</sub>O using C-neutral electricity is challenging (see sections C2 and D1 below). Cutting electrochemical cell fabrication costs, increasing cell efficiency and durability and developing new electrodes with better mass transport and over-voltage can allow a real, large-scale, one-stage SG production technology.

SG might also be produced by thermolysis of CO<sub>2</sub> and H<sub>2</sub>O at high Ts using solar or nuclear reactor heat, but the O<sub>2</sub> produced needs to be removed from CO+H<sub>2</sub>. Thermochemical cycles using oxides allow higher energetic efficiency, easier SG/O<sub>2</sub> separation and better process security. Redox pairs stable at high T (ferrites, CeO<sub>2</sub>...) or showing phase transitions during reduction (e.g. Zn/ZnO) are promising. New materials should work efficiently at lower T, minimizing volatilisation and/or melting. Increasing the solar-to-fuel energy efficiency is a main challenge here. Photon-driven schemes can also convert CO<sub>2</sub> and H<sub>2</sub>O into clean fuels; see section D2.

## ***C2 Catalysis converting CO<sub>2</sub> to useful products***

Efficient routes converting CO<sub>2</sub> to fuels and chemicals are needed to reduce emissions of CO<sub>2</sub>.<sup>18</sup> A description follows of relevant catalytic routes for CO<sub>2</sub> transformation.

### **Impact in basic science panorama and potential applications.**

#### *Conventional catalytic routes for CO<sub>2</sub> reduction*

The mature Sabatier process hydrogenates CO<sub>2</sub> to CH<sub>4</sub> at mild Ts (150-500 °C) and pressures from 1 to 100 bar. One challenge here is improving catalyst resistance to coke and sulphur. New routes, still at early stages (TRL 3-4), use photothermal catalysts, e.g. Ni/g-C<sub>3</sub>N<sub>4</sub> (operating at mild Ts) or In<sub>2</sub>O<sub>3-x</sub>(OH)<sub>y</sub>.

Methanol production is interesting as it can be transformed to a variety of chemicals and fuels and has high energy density. The typical catalyst for methanol synthesis from SG, Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, works at 10-50 bar and mild T (200-280 °C); it can be modified to work with CO<sub>2</sub>/H<sub>2</sub> blends by replacing Al<sub>2</sub>O<sub>3</sub> with other oxides. Catalysts using reducible oxides are also good for CO<sub>2</sub> hydrogenation to methanol at high T (~400 °C). Other chemicals like formic acid (allowing H<sub>2</sub> storage) and dimethyl ether (DME) can also be made by CO<sub>2</sub> catalytic hydrogenation. This mature process still needs better resistance to coking and the water by-product.

Fischer-Tropsch synthesis (FTS) can be fed with CO<sub>2</sub> and H<sub>2</sub>; combining its catalysts with acidic ones like ZSM-5 can lead to liquid fuels with narrow hydrocarbon distribution. Reducing directly CO<sub>2</sub> to aromatics and olefins (key building blocks in petrochemistry) is possible but challenging. Dry reforming of CH<sub>4</sub> with CO<sub>2</sub> (DRM), operating at Ts around 750 °C over Ni-based catalysts, can also produce SG. A chemical looping scheme for DRM, still under development, has resulted in better resistance to coking.

#### *Catalytic processes for the conversion of CO<sub>2</sub> and H<sub>2</sub>O mixtures.*

Electrocatalysts using renewable electricity can convert directly CO<sub>2</sub>, but they still operate at high overpotentials, have low current densities and may deactivate easily; see sections C2 and D1 below. Solid state electrochemistry may convert CO<sub>2</sub> at high T to several products (CH<sub>4</sub>, SG, larger molecules) with better kinetics and lower overpotential; electrodes based on complex perovskites show here good performance.

Photoreduction of CO<sub>2</sub> with water, named also artificial photosynthesis (AP), is a very challenging but appealing way for obtaining fuels. It is addressed, with or without help of electricity, in part D2 below; such technology remains still at lab scale (TRL 3-4). As for electrocatalysis selectivity, stability or high overpotentials remain still issues.

### *Processes incorporating CO<sub>2</sub> into chemicals and polymers*

One niche for the industrial use of CO<sub>2</sub> is the synthesis of organic carbonates. This avoids using toxic phosgene to make dimethyl carbonate from methanol. The direct reaction is equilibrium-limited, but cyclic carbonates can be made reacting CO<sub>2</sub> with an epoxide using ammonium halide catalysts. Ethylene oxide can be converted to diethyl carbonate with MgO catalyst and by transesterification into a polymer, as in commercial synthesis of Bisphenol A-based polycarbonate. Making poly(ether carbonate) polyols from propylene oxide and CO<sub>2</sub> is also feasible using Zn based catalysts.

Also homogeneous catalysts can insert CO<sub>2</sub> in organics. Examples are N-formylation and N-methylation of amines; reductive formylations or methylations using hydrosilane reductants can be made with transition metal-based and metal-free catalysts. H<sub>2</sub> can be used as reductant, but the use of non-noble metal-based catalysts remains a challenge. Urea derivatives (e.g. carbamates) can be made from CO<sub>2</sub> also with organocatalysts.

### *Utilization of CO<sub>2</sub> as mild oxidant.*

Hydrocarbon dehydrogenation (DH) allows getting olefins and aromatics. This needs high Ts (600-700°C), causing rapid catalyst deactivation by coking. Use of CO<sub>2</sub> as a milder oxidant for ODH (CO<sub>2</sub>-ODH) avoids flammability and overoxidation and reduces coking, reducing also the reaction endothermicity. Two main catalyst types studied are those based on classical DH ones (Cr<sub>2</sub>O<sub>3</sub> or Ga<sub>2</sub>O<sub>3</sub>) and on CeO<sub>2</sub> oxides.

### **Key challenging points**

#### *Developing a new generation of catalysts for CO<sub>2</sub> conversion.*

Most catalysts used in CO<sub>2</sub> hydrogenation are already efficient, but work to improve durability and selectivity and reduce costs is needed. Synergy with processes like production of renewable H<sub>2</sub>, improving energy efficiency or bringing technologies to high TRL(8-9) by cooperating with international companies will also be needed. The impact of different CO<sub>2</sub>+H<sub>2</sub> routes will depend on the availability of renewable H<sub>2</sub> and electricity.

Concerning solar fuels (obtained via AP), designing better photo-(electro)catalysts boosting energy conversion yields is key to bring technologies from current TRL 3-4 to TRL 6-7 so as to reach commercial level. Using CO<sub>2</sub> via direct solar activation of catalysts will continue to be a hot topic, but many of its basic aspects are still badly understood; real

breakthroughs are needed to replace technologies using H<sub>2</sub>. Other catalytic processes converting CO<sub>2</sub> can gain industrial relevance in niche applications (e.g. polycarbonates, making olefins). Finally, developing new multifunctional catalysts or smart process couplings can reduce for all technologies the number of steps for transforming CO<sub>2</sub> into fuels and chemicals.

### ***C3 Catalysts for obtaining clean hydrocarbon fuels and oxygenates from SG***

Catalytic SG conversion is one pillar in the chemical industry for producing clean fuels and value-added chemicals. SG is obtained now from fossil resources (>95%); its production from biomass and CO<sub>2</sub> (see previous sections) and the increasing use of renewable H<sub>2</sub> will give new chances for developing flexible and viable small scale processes with lower carbon footprint. Designing catalysts with better activity, selectivity and stability will be a key factor to improve the existing processes. Fig. 6 below summarizes the renewables-to-SG-to-products main routes.

### **Impact in basic science panorama and potential applications. Key challenging points**

Converting SG (from fossil sources) to liquid fuels via Fischer-Tropsch synthesis (FTS) is a mature technology (TRL 9); FTS processes using SG from renewable CO<sub>2</sub> have a lower degree of maturity (TRL 5-9); a deeper knowledge of active sites and reaction mechanisms, with advanced *operando* techniques and theoretical methods, is still needed here. Due to polymerization kinetics FTS products usually follow the so-called ASF distribution, limiting the attainable selectivity to a specific liquid fuel. FTS processes operate at conditions that generate mainly waxes; these can be subsequently upgraded in a downstream hydrocracker. The expensive hydrocracking step can be avoided with catalysts including a FTS catalyst and a zeolite to transform, via acid-catalyzed cracking and isomerization, FT-derived waxes. This approach has not yet achieved commercialization due to fast zeolite deactivation; further developments in this area are anticipated.

SG conversion can also make light olefins and aromatics, key building blocks for the petrochemical industry. Lower olefins can be made from SG in a single reactor via a high-T FT-to-olefins (FTO) process using iron catalysts. Improving the selectivity to C<sub>2</sub>-C<sub>4</sub> olefins while lowering CO<sub>2</sub> formation, as well as enhancing the lifetime and integrity of Fe-based catalysts in these harsh conditions are major challenges in this process. Another route exists via oxygenated intermediates. It needs bifunctional catalysts coupling a methanol synthesis (MS) catalyst and a methanol-to-olefins (MTO) zeolite catalyst. Non-Cu-based catalysts (e.g. ZnO-ZrO<sub>2</sub>) are better than Cu-based systems, being active at higher Ts as is required for MTO; deactivation of MTO catalysts is however a key issue. Converting SG to aromatics is feasible using dual-function catalysts, the choice of catalysts depending on the pathway intermediates: oxygenates or light olefins. Catalysts for the olefins route mix a Fe-based FTO catalyst with a Ga<sub>2</sub>O<sub>3</sub>- or ZnO-modified zeolite ZSM-5 catalyzing the aromatization of the formed olefins. For the oxygenates route bifunctional systems mixing a methanol/DME catalyst like ZnO-ZrO<sub>2</sub> and ZSM-5 zeolite are promising. Further studies to improve the aromatics productivity and the selectivity to the demanded *para*-xylene isomer will be needed.

The SG to methanol route is a mature technology using Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts. However, devising new catalysts with better activity at lower T and pressure, selectivity, stability and resistance to poisons, and gaining understanding on the reaction mechanism, nature of active sites and promoter effects are still scientific and technical challenges. DME is, besides methanol, a key intermediate in chemical industry, usually obtained by a two-stage process: i) methanol synthesis from SG and ii) methanol dehydration. The growing interest in using DME as a clean fuel replacing oil-derived LPG and diesel has

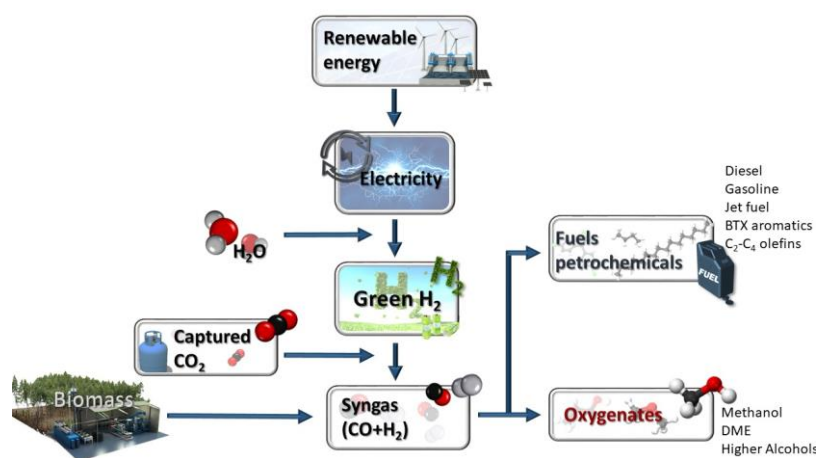


Fig 6 Possible routes for renewables-to-SG-to-products processes. *Source: freely elaborated and adapted by M.A. Centeno with a student of his, starting from Z. Jiang, T. Xiao, V. L. Kuznetsov, P. P. Edwards: Phil. Trans. R. Soc. A (2010) 368, 3343; and G. Leonzio: Waste and Biomass Valorization, doi: 10.1007/s12649-019-00914-4. With due permissions.*



promoted developing a one-step process (STD: SG-to-DME), a relatively mature technology. This process is more competitive and thermodynamically favorable, enabling higher per-pass CO conversions. STD catalysts are bifunctional, comprising a Cu-based methanol synthesis catalyst and alumina or, preferably, zeolites. Fine tuning of zeolite acidity and porosity to suppress coking and a good integration with the Cu catalyst are needed to improve DME selectivity and catalyst lifetime.

Higher alcohols are valuable compounds with uses in the chemical, pharmaceutical and energy industry. Their direct synthesis from SG can give a more environmentally friendly, versatile and economic alternative to their current production by fermentation of sugar or hydration of oil-derived olefins. Catalysts developed for this process can be classified in four categories: i) Rh-based, ii) Mo-based, iii) modified FTS, and iv) modified methanol synthesis catalysts<sup>19</sup>. Mo-based systems (mostly alkali-promoted MoS<sub>2</sub>) appear most promising in cost/performance terms; further improvements in catalyst design are expected to shift alcohol distribution from methanol to the desired higher alcohols. Future studies here should focus on a better understanding of the nature of active sites and mechanisms, to guide the design of better catalysts. Better reactor and separation technologies will also be needed for a real industrial implementation.

### **CSIC advantage position and multi/inter-disciplinarity**

Several groups at CSIC institutes are active in this topic of clean fuel production; their activities cover generally TRL 3-4. INCAR and ICB lead studies producing SG from biomass gasification and pyrolysis, with a higher TRL of 5. Main CSIC institutes converting SG (produced from renewables) to clean fuels are ICP, ITQ, and ICMS. Among them ICP and ITQ currently participate in highly competitive H2020 projects developing technologies at TRL 5, producing in one case DME and in another one diesel biofuel using biomass resources via gasification and subsequent SG conversion.

For CO<sub>2</sub> hydrogenation ITQ, ICP, ICB and ICMS, as well as ISQCH and IIQ using homogeneous catalysis (among others), work at TRL 4-6 and are well positioned to lead national or European initiatives. ITQ is at international level in photocatalytic or electrochemical CO<sub>2</sub> conversion; other CO<sub>2</sub> converting processes are led by ITQ or ICP.

## **D) Electro/photo/catalysis for energy conversion**

### ***D1 Catalysts for fuel cells and electrolyzers***

The performance and cost of fuel cells (FC) and electrolytic cells (EC) depend on the performance and cost of their electrocatalysts. These devices can be classified in three classes: low T (<200°C), including proton membrane exchange (PEM) and alkaline cells; intermediate T (400-800 °C), mostly using proton conducting or solid oxide electrolytes; and high T (>800°) solid oxide (SO) cells. See Fig. 7 below for PEMFC and EC schemes. Reviews are available for PEM and SOFC<sup>20,21</sup>.

### **Impact in basic science panorama and potential applications.**

Most FCs use pure H<sub>2</sub> or H<sub>2</sub>-rich gases as fuel (including CO, although CO is a poison for Pt catalysts used in PEMFCs); some devices use other fuels, bioethanol being the most interesting one for low T FCs. Most EC developments produce H<sub>2</sub> from renewable electricity (and this H<sub>2</sub> can be catalytically converted to liquid carriers, and then back, for its easier transportation), and some prototypes produce SG by co-electrolysis of water and CO<sub>2</sub>; other catalysts like Cu, Zn or Sn can give other products of CO<sub>2</sub> reduction, from formic acid to CH<sub>4</sub> or C<sub>2+</sub> hydrocarbons. For cases where weight and size are limited, unitized regenerative fuel cells (URFC) combine fuel cells and electrolysis in one device. For portable applications micro-FCs are being developed, some of them without membrane for use in disposable devices.

Carbon-supported Pt is a standard catalyst for both electrodes of PEMFC; PEMEC anodes require Ir supported on non-carbon materials (like Ti-based structures) due to corrosion by O<sub>2</sub>. Alkaline EC, the most mature electrolysis technology, uses Ni-based electro-catalysts. Alkaline membrane technology for FC and EC is still in progress, due to the low conductivity and stability of such membranes, but the higher kinetics in the oxygen electrode holds promise for application of lower cost catalysts. High T SOFC and SOEC electrodes use similar electrocatalysts, e.g. a cermet of Ni metal and the electrolyte (yttrium stabilized zirconia, YSZ) for the H<sub>2</sub> electrode; a La-Sr-Mn perovskite oxide for the O<sub>2</sub> electrode. URFCs are mainly PEM-type, combining FC and EC materials (Pt-Ir supported in Ti compounds) for the O<sub>2</sub> electrode. Finally, direct-ethanol fuel cells (of PEM-type) require a bimetallic catalyst (Pt-Ru or Pt-Sn) in the anode.

EC and FC electrodes have several common features: high electronic conductivity; high ionic conductivity, for an effective connection with the electrolyte; and tailored porosity, for the mobility of reactants and products to and from the catalytic active site. The electrode conformation should include the active catalysts with these characteristics.

The electrochemical synthesis of  $\text{NH}_3$  from  $\text{N}_2$  and  $\text{H}_2\text{O}$  at ambient  $T^{22}$  deserves now much attention. The technology is still starting, but has high interest if it can compete with the Haber-Bosch process needing high Ts and pressures.

### Key challenging points

Alkaline EC is well established; although improvements are possible in the electrodes conformation. PEMEC have much higher efficiency and allow better integration with renewable energies due to a greater operation range. The high cost and scarcity of catalysts and the electrode durability are the main barriers for the competitiveness of PEMFC and EC. PEM is the most advanced FC technology, but only motor vehicle companies provide commercial products reliable enough. Using non-precious metal catalysts, especially for alkaline membrane FC and EC, and increasing the intrinsic activity using multicomponent nanostructured catalysts are two of the main objectives.

High T SOFC and SOEC electrodes have problems of compatibility with the electrolyte, due to different thermal expansion coefficients. Besides, high T migration of La and Sr from the SOFC cathode to the electrolyte interface degrades the cell. The low ionic conductivity of the catalytic layer is also a handicap. Also, manufacturing of high T electrodes increases the final cost of the devices. Finally, there is much interest in lowering the T operation range of SOFC, to allow using cheaper construction materials and increasing the stability with time at lower Ts.

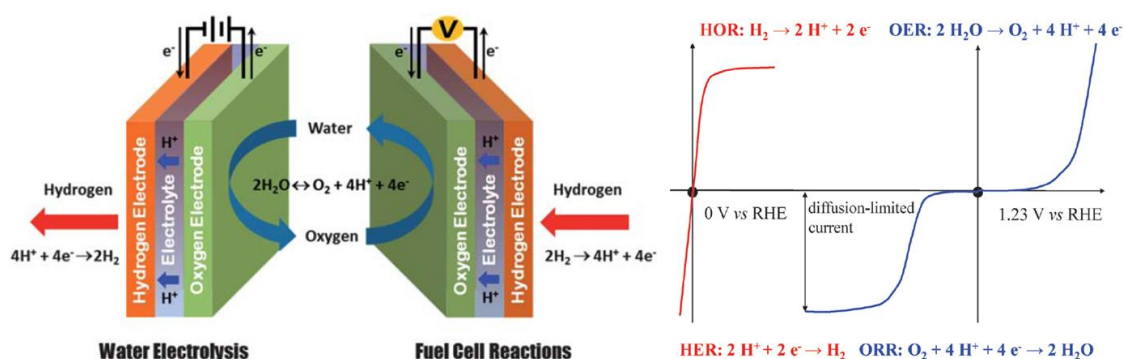


Fig. 7 Scheme of PEMFC and PEMEC, and polarization curves of the main electrode reactions. Sources: S. Park, Y. Shao, J. Liu, Y. Wang, *Energy Environ. Sci.* (2012) 5, 9331; Y. Jiao, Y. Zheng, M. Jaroniec, S.Z. Qiao, *Chem. Soc. Rev.* (2015) 44, 2060. With due permissions.

The practical use of the rest of the FC and EC are further away. Direct ethanol FC catalysts have very low activity and selectivity to total electrooxidation, so that these FC are unpractical as energy equipment; URFC need specific bifunctional catalysts (anodic-cathodic) for the O<sub>2</sub> electrode; and there is scarce information about the appropriate electrocatalysts to be used in the intermediate T fuel cells.

Scale-up of electrode manufacturing is of key importance for final commercialization. Current procedures rely on wet chemical, liquid printing, ceramic, sol-gel or related chemical methods, but some of them are costly for large scale production. Others based on physical surface treatments (e.g. magnetron sputtering) might be also considered.

Finally, although there is a great knowledge of the electrochemical behaviour of model surfaces, the whole understanding of the electrochemical processes in real catalysts working in real cells is far away to be reached.

### **CSIC advantage position and multi/inter-disciplinarity**

Groups in ICB, ICMA, ICMM, ICMS, ICP, ICV, ITQ and ICN2 work actively in FC. Some of them work as well in EC; here ISQCH develops homogeneous catalysts oxidizing water, coupling them to electrodes in collaboration with INCAR. For acid and alkaline PEM FC and EC they use catalysts without precious metals, e.g. heteroatom-doped carbon, for neutral media inorganic or bio-catalysts (enzymes). Electrochemical NH<sub>3</sub> synthesis is also studied. For URFC they use nitrides, carbides and carbon-based catalysts. Modified Pd and Pt are used for direct bioethanol FC. Cathodes for SOFC and EC use perovskite oxides, and even membrane-based assemblies are being built. Vacuum techniques like magnetron sputtering can produce with good control porous electrodes. Microtubular cells and SOFC stacks for portable applications and CO<sub>2</sub> electrolysis are studied also. Most institutes work at TRL2-3; portable systems reach TRL5.

Active and durable catalysts and electrodes have been developed, but final tests in TRL6-7 prototypes is mandatory for any practical application. Collaboration between the different institutes involved is necessary. The recent start of the “Mobility 2030” PTI and integration in it of groups working in catalysis could lead in the next years to advances in two key lines: low T FC/EC prototypes using durable non-precious metals, and high T SOFC/EC devices using stable catalysts. Collaboration of this PTI with other institutions as the National Hydrogen and Fuel Cell Technology Testing Centre (CNH2) will be needed for reaching the indicated TRL.

## ***D2 Photon-induced water splitting and CO<sub>2</sub> reduction***

Photocatalysis is used for environment protection, selective synthesis or energy-related aims; in the latter case, it allows fixing photon energy in chemical form. Such “artificial photosynthesis” (AP) can follow two ways: H<sub>2</sub> production (by H<sub>2</sub>O splitting or photo-reforming) or CO<sub>2</sub> reduction, both providing "solar" fuels and chemicals.

### **Impact in basic science panorama and potential applications.**

A *purely photocatalytic process* fixing energy has high potential due to scalability and high efficiency, but does not compete yet with other routes. Also separating oxidation and reduction products can be difficult, except in photo-reforming of organics where value-added chemicals besides H<sub>2</sub> can result. This process works at milder T than thermal reforming, saving thus energy especially if using sunlight. A special case is that of homogeneous photocatalysis using elaborate metal complexes (which may try to mimic enzymes) combined with a molecular photon absorber, as e.g. for H<sub>2</sub> production or synthesis of NH<sub>3</sub> using protons plus electrons provided by the absorber. Photocatalysis can be however combined advantageously with other technologies (e.g. thermo-, electro-) into photo-thermal and photoelectrochemical catalysis.

*Photothermal* CO<sub>2</sub> reduction is a recent double route using both light and heat activation. Heat can be obtained directly from an external source (e.g. a solar concentrator) or by light absorption (e.g. by surface plasmon resonance). Coupling to a semiconductor with ability for photo e<sup>-</sup>/h<sup>+</sup> pair generation and charge transfer gives good activities, e.g. in methane production via Sabatier reaction ( $\text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O}$ ) on oxide-supported metal catalysts at mild Ts under UV-visible light.

*Photoelectrochemistry* (PEC) is used for water splitting or CO<sub>2</sub> reduction. One electrode containing a light absorber (or two in tandem systems) is illuminated driving chemical changes. PEC electrodes reducing H<sup>+</sup> to H<sub>2</sub> or CO<sub>2</sub> to a fuel require conduction band potentials more negative than the relevant redox pair; valence bands of those doing oxidation must be more positive than the O<sub>2</sub> couple. Co-catalysts are needed, like in electrolysis, to lower reaction barriers. MoS<sub>x</sub> or metal alloys work for H<sub>2</sub> evolution; Zn, Ag, Cu or Sn (depending on the sought products) for CO<sub>2</sub> reduction; Ni, Co or Fe oxides for O<sub>2</sub> evolution. Enzymes (formate dehydrogenases, laccases, hydrogenases...) can also serve as co-catalysts. All this may result in complex multilayered electrodes.

### **Key challenging points**

For these technologies light absorbers with somewhat lower bandgaps, more efficient co-catalysts and better carrier separation efficiency are required. For all photodriven processes better band edge (or redox levels of complexes) positions versus redox pairs are needed, as well as smart, more compact photoelectrode designs in PEC. In photothermal CO<sub>2</sub> reduction it is also necessary to lower the T window.

### **CSIC advantage position and multi/inter-disciplinarity**

Groups in ICP, ITQ, ICMS<sub>e</sub>, ICN<sub>2</sub>, ICB work in photodriven systems within TRL2-3 range projects. They are expert in catalyst characterization, *in situ* and *operando* studies of reaction mechanisms and use of model catalysts. For PEC water splitting they develop photocatalysts using hematite nanowires, metalloenzymes linked to semiconductors, MOFs having electron-rich linkers with hole transport ability, solvothermally prepared CdS and other sulphides and model catalysts like gold platelets on multilayer graphene. Two groups work in alcohol photoreforming using Cu-Ni particles on TiO<sub>2</sub> and P-doped graphene, or photothermocatalysis using Ru on TiO<sub>2</sub>.

In these groups the technical development of photo(electro)catalysis for water splitting is low; new formulations are needed to reach higher TRL. TRL4-5 could be obtained by optimizing catalysts or combining photons and electrical energy, and collaborating with other CSIC research groups with experience in reactors scale-up. The “Mobility 2030” PTI mentioned in section D1 above might provide a suitable framework for this aim.

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		NEAR TERM (<5 YEARS)	MID TERM (5-10 YEARS)	LONG TERM (10-20 YEARS)	
<i>A Catalysis for a sustainable industrial production</i>	<i>A1. Catalysis for industrial production with lower energy demand and higher atom efficiency</i>	*Obtaining better selectivity to the desired products using improved homogeneous and heterogeneous catalysts	*Improving enzymes through directed evolution; better stabilization of them on specific solid carriers, allowing cascade processes.	*Improving largely atom efficiency, so that separation and purification steps can be reduced	
		*Allow operation at milder P and T conditions	*Process intensification, integrating chemical and physical steps to achieve better energy efficiency		
	<i>A2 Air depollution in energy-intensive industries</i>	*Replacing noble metals by less costly transition metal oxides in catalysts burning VOCs.	*Activation of catalytic materials by photons or microwaves to avoid heating all the gas mass		
		*Development of new catalysts to avoid N2O emissions during fertilizers production.			
		*NOx: Development of new low-temperature SCR catalysts for use in tail gas systems.			
		<i>CROSSCUTTING ACTIVITIES:</i>			
		*Design and manufacture of improved catalysts through simulation and controlled synthesis of nanoparticles by new methods.	*New techniques for structuring solids by means of 3D additive manufacturing.		
		*Use of real-time spectroscopy and chemometric analyses and <i>operando</i> methods at lab scale and pilot plants for developing catalysts and process control in their industrial manufacture and use.			
	<i>A3 Processes directly driven by electricity and electromagnetism</i>	*Improving the knowledge about the interaction between MW/plasma/magnetic fields and reactants/catalysts.	*New reactor designs able to treat large volumes of reactants. Improving the control of applicators and process command.	*Useful engineering solutions for an efficient connection to the electricity grid.	
		*Improving basic parameters of the reaction such as energy efficiency and selectivity.	*Developing new catalysts specific for electricity-driven catalysis. * <i>MW-specific</i> : Implementation in complex processes and development of automatic control	* <i>MW-specific</i> : Study of new reactions not achievable today; use of phase mixtures (gas, liquid, solid, plasma); microreactors operated by batteries.	
<i>B Catalysis for the use of biomass</i>	<i>Production of biofuels and chemicals from biomass</i>	*Developing technologies to produce bio-based products either from previous building blocks or directly from biomass (up to TRL 4). * Techno-economic and LCA analysis of the above-mentioned technologies to assess on their economic and environmental viability and to identify the bottle-necks for further improvements	*Improvement of the most promising technologies to tackle down the bottle-necks identified by the techno-economic and LCA analyses (up to TRL 6).	*Scaling-up and intensification of the technologies up to TRL 7-8.	

<b>C Catalysis for the production of clean fuels from renewable sources</b>	<b>Renewable building blocks from biomass.</b>	*Developing environmentally friendly technologies to produce bio-based building-blocks (up to TRL 4). *Techno-economic and LCA analysis of the above-mentioned technologies to assess on their economic and environmental viability and to identify the bottle-necks for further improvements.	*Improvement of the most promising technologies to tackle down the bottle-necks identified by the techno-economic and LCA analyses (up to TRL 6).	*Scaling-up and intensification of the technologies up to TRL 7-8.
	<b>Accessing cheap feedstocks</b>	*Developing at least two environmentally friendly catalytic (chemo- or enzymatic) technologies efficiently fractionating cheap lignocellulose feedstocks into carbohydrate and lignin (up to TRL 4). *Developing at least two environmentally friendly technologies to process cheap non-lignocellulosic feedstocks (chitin, cheese whey permeate or marine seaweeds) into valuable chemicals (up to TRL 4). *Techno-economic and LCA analysis of the technologies to identify the two most viable technologies and the environmental and economic the bottle-necks for further improvements	*Improvement of the two most promising technologies to tackle down with the bottle-necks identified by the techno-economic and LCA analyses (up to TRL 6).	*Scaling-up and intensification of the technologies up to TRL 7-8.
	<b>2<sup>nd</sup> and 3<sup>rd</sup> generation biofuels</b>	*Developing environmental-friendly catalytic or enzymatic technologies to produce biodiesel from UCO and HVO kerosene from (preferably) microalgae (up to TRL 4). Catalysts for the latter process must be based .on non-precious metals. *Techno-economic and LCA analysis of the above-mentioned technologies to assess on their economic and environmental viability and to identify the bottle-necks for further improvements.	*Improvement of the most promising technologies to tackle down the bottle-necks identified by the techno-economic and LCA analyses (up to TRL 6).	*Scaling-up and intensification of the technologies up to TRL 7-8.
	<b>C1 Production of syngas from renewable sources</b>	*Development of optimized catalysts, reactors and processes for SG production from residual biomass and/or CO <sub>2</sub> + H <sub>2</sub> O.	*Achieving an efficient SG production from CO <sub>2</sub> and H <sub>2</sub> O using C-neutral electricity.	*Reaching the threshold yield for commercial exploitation of SG production from photo(electro)catalytic processes and other promising advanced technologies from CO <sub>2</sub> + H <sub>2</sub> O. * On-demand production of SG with the appropriate characteristics for its final use, from localized and specific residual biomass. * Emergence of new catalytic processes for economical SG production with zero carbon footprint.

	<i>C2 Converting CO<sub>2</sub> to useful products</i>	<ul style="list-style-type: none"> <li>*Broad deployment of optimized catalytic processes for Power-To-Gas and Power-To-Liquids technologies.</li> <li>* Design of more efficient catalyst for CO<sub>2</sub> utilization in chemical production.</li> </ul>	<ul style="list-style-type: none"> <li>*Improvement of catalysts and scaling up of transformation routes, particularly those for implying direct solar CO<sub>2</sub> activation.</li> <li>* Development of hybrid CO<sub>2</sub> conversion routes by synergic coupling of processes.</li> </ul>	<ul style="list-style-type: none"> <li>*Reaching the threshold yield for commercial exploitation of photo(electro)catalytic processes and other technologies for CO<sub>2</sub> + H<sub>2</sub>O conversion.</li> <li>* Emergence of novel catalytic schemes for CO<sub>2</sub> conversion.</li> </ul>
	<i>C3 Obtaining clean fuels and oxygenates from syngas</i>	<ul style="list-style-type: none"> <li>*Gaining in-depth understanding of catalyst structure-performance relationships.</li> <li>* Developing efficient multifunctional catalysts for direct (one-step) SG conversion with high selectivity to target products (process intensification).</li> </ul>	<ul style="list-style-type: none"> <li>*Demonstration plants for direct conversion of SG to liquid fuels and chemicals.</li> <li>* Deployment of new SG conversion technologies using renewables.</li> </ul>	<ul style="list-style-type: none"> <li>*Scaling-up of cost-effective sustainable SG conversion technologies based on renewables with low or neutral carbon footprint.</li> </ul>
<i>D Electro/photo/ catalysis for energy conversion</i>	<i>D1 Catalysts for fuel cells and electrolysers</i>	<ul style="list-style-type: none"> <li>*Optimum electrode conformation for alkaline electrolysers.</li> <li>* Electrodes for PEMFC with low Pt content (under 0.15 g/kW).</li> <li>* Durable electrodes for solid oxide fuel cells and electrolysers (higher than 40.000 h).</li> </ul>	<ul style="list-style-type: none"> <li>*Active and durable electrodes, based in non-precious metal catalysts, for low temperature fuel cells and electrolysers.</li> <li>* Low cost methods for manufacturing components for high temperature fuel cells and electrolysers (e.g., based on physical surface treatments).</li> <li>* Deciding whether there is promise in schemes for production of NH<sub>3</sub> via electrolysis</li> </ul>	<ul style="list-style-type: none"> <li>*Development of practical electrocatalysts for direct ethanol fuel cells.working in real cells.</li> <li>* Development of low cost bifunctional electrocatalysts for URFC.</li> <li>* Whole understanding of the electrochemical processes in real catalysts.</li> </ul>
	<i>D2 Photon-induced water splitting and CO<sub>2</sub> reduction</i>	<ul style="list-style-type: none"> <li>*Developing light absorbers with lower bandgaps and providing better carrier separation efficiency; and more efficient co-catalysts.</li> </ul>	<ul style="list-style-type: none"> <li>*Developing smart, more compact photoelectrode designs in photoelectrochemical reactors.</li> <li>* Reducing the working temperature for the photothermal CO<sub>2</sub> reduction.</li> </ul>	<ul style="list-style-type: none"> <li>*Developing photo(electro)catalysts with high efficiency for water splitting, using materials with an optimized life cycle.</li> <li>* Suppressing the use of sacrificial compounds for O<sub>2</sub> evolution in water splitting photoreactors.</li> </ul>

## ONE SLIDE SUMMARY FOR EXPERTS.

### CHALLENGE

This challenge deals with catalysis (heterogeneous, homogeneous and enzymatic) as applied to energy purposes: clean fuel synthesis from renewables, carbon dioxide transformation to obtain fuels and chemicals, use of electricity in conventional (e.g. electrolysis) and less common (e.g. microwaves, plasmas) ways, use of biomass, solar energy driven processes, atom- and energy- conserving economy... The specific challenges are very different, as are these applications, relating mainly to the need of developing catalysts behaving more efficiently, with high selectivity, working in milder conditions, being more durable and using (if possible) earth-abundant elements.

### APPROACH

One first general approach involves designing advanced catalyst synthesis methods (microemulsions, fibers, single-atom species, control of interaction with carriers...), characterizing catalysts with a high variety of structural and spectroscopic techniques (including *operando*), multiscale modelling of reactions (maybe with machine learning and AI), design of advanced reactor types (with multiple narrow channels, for photocatalysis, gas diffusion electrodes for fuel cells, etc.). Then each energy-oriented application has specific needs: biomass use requires cheap but selective processes; electrolyzers and fuel cells require low overpotentials; plasmas must be able to use large gas amounts; clean fuel synthesis needs different selectivity for different fuels...

### SOCIAL AND ECONOMIC IMPACT

- Catalysis may help to decrease pollution, both by greenhouse gases (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) and toxic substances (NO<sub>x</sub>, CO, dioxins, herbicides, ...), improving people's well-being
- Catalysts may lead, first of all, to processes which are cheaper and consume less energy and material resources. This will already have large economic consequences
- The changes coming to chemical industry will lead to suppression and creation of jobs
- The social awareness of the importance of technology must increase; this is especially true for the climate change issue, which will lead to changes in energy, migrations, etc. Education plays a key role here
- Electricity generation (by windmills, PV fields, etc.) is already changing the landscape, as has happened already with its hydraulic generation. This should not be overlooked. Catalysts may also change gradually in composition; new mines may have then to be established while others may need being cancelled, impacting both landscape and jobs

### INVOLVED TEAMS

Many groups in CSIC work on catalysis of different types. The main ones are located at ITQ and ICP, this latter institute being particularly active in enzymatic catalysis (besides the heterogeneous one); other important groups working significantly on heterogeneous catalysis and related systems exist in ICB, ICMSE, INCAR, IRNASE, ICN2, ICMM and ICMAB, while homogeneous catalysis is pursued mainly in ISQCH and IIQ. There are also other research centres working actively in catalysis; not only in universities, but also in other institutions like ICIQ and IREC in Catalonia, the IMDEAs in Madrid Community or the different technology centres in the Basque Country.

## ONE SLIDE SUMMARY FOR THE GENERAL PUBLIC.

### CHALLENGE

Catalysis was defined in the XIX century as the way to change the course of a chemical reaction by adding a substance that is not consumed in the process. This challenge deals with catalysis of different types as applied to energy purposes: clean fuel synthesis, fuel cells, use of biomass, carbon dioxide transformations, sunlight-driven processes to fight climate change... Its importance is glimpsed from phrases in a recent report by the European Cluster of Catalysis: “Of the 50 largest volume chemicals now produced, 30 are produced via catalytic routes... and account for more than 20 billion tons of CO<sub>2</sub> emitted yearly to the atmosphere... Technical improvements in catalyst processes could reduce energy intensity for these products by 20% to 40% by 2050.”

### APPROACH

The many possible uses of catalysis imply also many approaches to solve the different challenges. Some are common to all catalysis types: designing better catalyst synthesis methods, studying catalysts with structural and spectroscopic techniques, modelling catalytic reactions, performing studies of the reaction rates, designing new reactor types for catalysis... Then each energy-oriented application has specific needs: fuel cells need more durable catalysts and low (or none) amounts of precious metals, clean fuels synthesis requires directing the result to each fuel desired, biomass processes normally need a sequence of chemical reactions to end with the specific product sought, photocatalytic processes need high solar efficiencies; and so on.

### SOCIAL AND ECONOMIC IMPACT

- Catalysis may help to decrease pollution, both by greenhouse gases (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) and toxic substances (NO<sub>x</sub>, CO, dioxins, herbicides, ...).
- Catalysts may allow processes which are cheaper and consume less energy and material resources.
- The changes produced to the chemical industry will lead to suppression and creation of jobs; it is expected that the latter will be in higher numbers and more specialized.
- The social awareness of the importance of a better technology must increase; education plays here a key role. The climate change issue, leading to changes in energy use, society transport models, migrations, etc. is particularly relevant here.
- Electricity production (by windmills, solar panels) is changing landscape, as happened already with hydraulics. The debate on concentrated vs. distributed energy generation, and changes in mining needed for producing new catalysts, will have also impact here.

### INVOLVED TEAMS

Many groups in CSIC work on catalysis of different types. The main ones are located at ITQ and ICP, this latter institute being particularly active in enzymatic catalysis (besides the heterogeneous one); other important groups working significantly on heterogeneous catalysis and related systems exist in ICB, ICMSE, INCAR, IRNASE, ICN2, ICMM and ICMAB, while homogeneous catalysis is pursued mainly in ISQCH and IIQ. There are also other research centres working actively in catalysis; not only in universities, but also in other institutions like ICIQ and IREC in Catalonia, the IMDEAs in Madrid Community or the different technology centres in the Basque Country.