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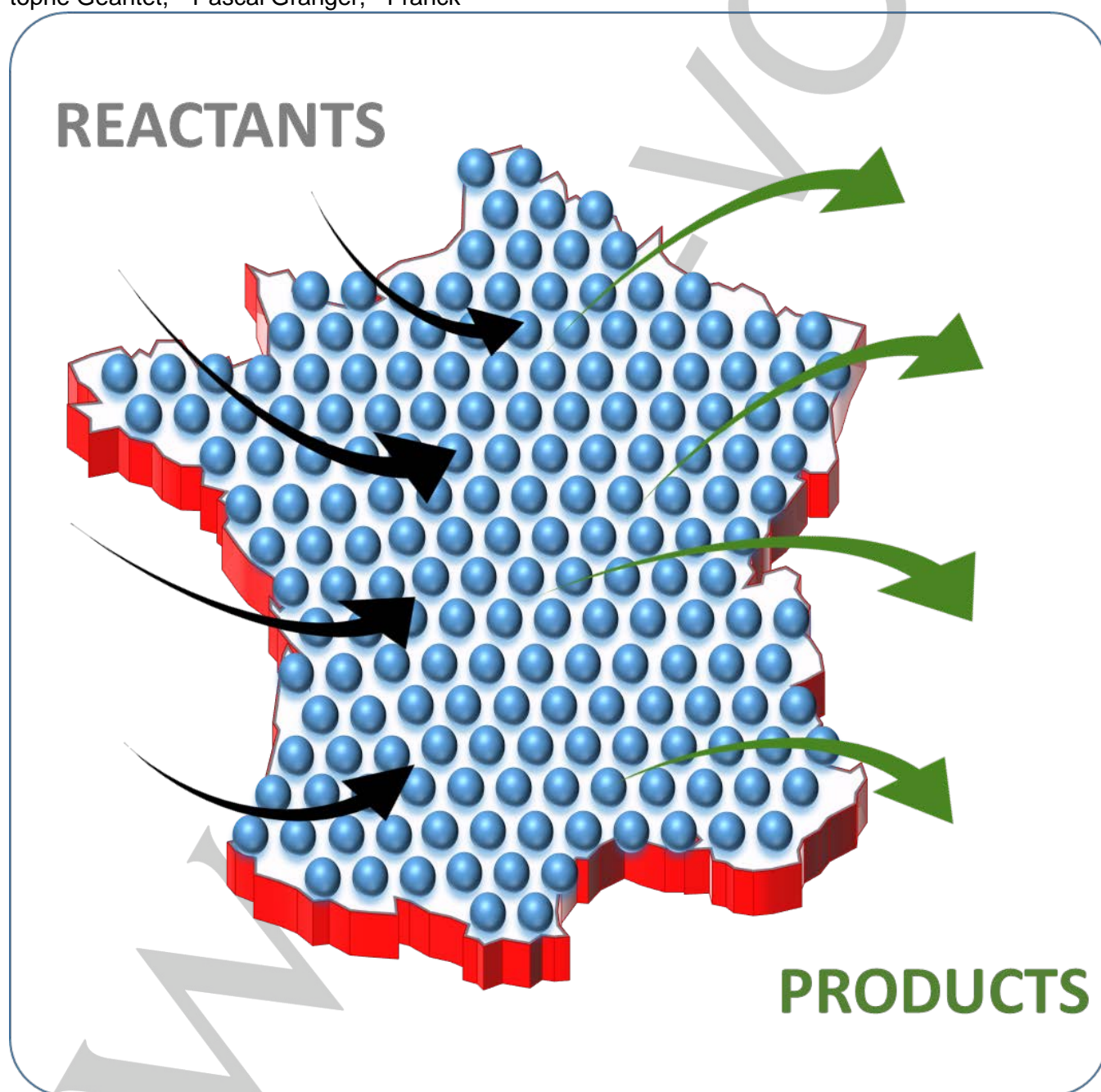
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## The pivotal role of catalysis in France: selective examples of recent advances and future prospects.

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This review is in the memory of Yves Chauvin (1930-2015), Nobel price 2010 in Chemistry for his work on metathesis. "If you want to find something new, thus look for something new".



**Abstract:** The review describes the most significant recent results achieved in France in the field of heterogeneous catalysis over the last 10 years. It focusses on the research carried out in the French academic laboratories, often in close collaboration with some industrial partners.

For the first time in 2016, Catalysis Division (DivCat) and Industrial Chemistry Division (DCI) of the French Chemical Society (SCF) together with GECAT (Groupe d'Etude en Catalyse, Group of Study in Catalysis) and GFZ (Groupe Français des Zéolites, French Group of Zeolites) joined their efforts to organize a general meeting, the French Conference on Catalysis (FCCat).

Following the heritage of P. Sabatier and Y. Chauvin,<sup>1</sup> two French Nobel Prizes in Chemistry laureates, this event was the opportunity for the French and the International Catalysis community to share most advanced results in a friendly spirit. The contributions have covered some fields of homogeneous and heterogeneous catalysis, from upstream research on catalyst mechanism understanding to catalytic process design, both from academic and industrial participants.

The exponential growth of the human population forces chemistry to urgently diversify the sourcing of raw materials and reduce the impacts on the environment by limitation or elimination of the wastes. Historically based on the exploitation of fossil carbon, chemistry is now exploring the potential of other sources such as biomass, waste, shale gas, CO<sub>2</sub> and their combination with fossil

resources as well. The gradual introduction of these diversified raw materials in chemical processes together with the need of our Society to limit its impact on the planet is currently leading to a deep revolution of catalysis which is nowadays facing important scientific challenges. The tolerance of catalysts to water and to impurities of different natures, the introduction of novel chemical functionalities, the molecular diversity and variability of raw materials (*i.e.* novel reaction mechanism pathways), the rarefaction of noble metals and the development of more energy-efficient processes are among important hurdles facing by catalysis. This revolution has led to rapid changes in the catalysis research landscape. Particularly, in France, novel research Institutes and networks were created or re-organized over the last 10 years, often in link with industry, to answer to all of these fundamental questions. Several competitiveness clusters were launched in 2005 with the objective to bring together small and large companies with academic laboratories to develop synergies and cooperative efforts on specific domains of research, including catalysis. Furthermore, Carnot institutes, funded in 2006, are research organizations, which place partnership research at the heart of their strategy.

The French community accounts more than 30 laboratories focusing on catalysis but 200 include some catalytic studies distributed on the whole territory and covering all domains of catalysis that were presented during FCCat. In this review, we describe the most recent results achieved in France in the field of heterogeneous catalysis as main topic, the homogeneous counterpart being only briefly reported despite number of recognized French groups in this domain. The first sections summarize the development of catalytic systems for specific applications (petrochemistry, biomass transformation, environmental, CO<sub>2</sub> for energy). Then, we describe significant cross-functional approaches essential to understand and to optimize catalytic processes (*in situ/operando* characterization, ab initio calculation, kinetic analysis). Finally, complementary approaches are reported. Of course, the French catalysis community is not isolated and the researchers widely participate to the development of international understanding in the different research fields involved in Catalysis. These interactions are clearly the driving forces in the efficient advances of knowledge in catalysis and are mentioned in the review. We focus on the last 5 to 10 years without being exhaustive and we position the results in France with regards to international research.

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## 1. Catalysis for Fuels and Petrochemicals: upcoming challenges for 2030

Born in the middle of 1860's in the USA, refining industry processes nowadays around 90 millions barrels per day (Mbb/d) of crude oil and this production should increase to around 100+/-20 Mbb/d in 2040 depending on the different scenarios assuming a more or less important contribution of renewable energies. Even if its contribution is expected to slightly decline in the next decades, oil will continue to be the main part of fossil energy forecasted to represent 80% of the total energy supply. Mainly focused on the transportation area, refining industry faces contradictory challenges: fulfill the needs of an ever-growing mobility demand (expected to grow by 30% in 2035) and compulsory sustainability development by limiting the GHG (Green House Gases) production. In a very competitive context, also characterized by the increasing scarcity of resources especially the light and easy to refine ones,

refining industry must operate deep mutation in order to meet the 450 ppm scenario requirements in terms of GHG concentration in the atmosphere, adapt to future regulations such as sulfur in bunker oil soon limited to 0.5wt% or be able to face the inverting balance of gasoline / diesel demand in Europe. Last but not least, current technologies have also to face the multiplication of raw resources such as tight/shale oil and gas, methane from other sources (hydrates), bio-oils, which modify the yield of petrochemicals bringing new scientific issues.

In such a stringent scenario, catalysis is clearly a key player to bring efficient solutions to improve processes performance and open the door to innovation.

Since peak oil is close to be reached (or even already reached), several uses of alternative resources such as unconventional oil or Fischer-Tropsch (FT) with methane have been developed but they drastically depend on the price of the barrel. The other alternative is the use of biofuels. In the early 2000's (between 2000 and 2007 biofuel production tripled), ethanol and biodiesel started to contribute to transportation fuels for a few % (4% of world fuel consumption in 2014). Among the advantages of biofuels is the energetic independence, the growth of a national economy and the decrease of CO<sub>2</sub> emissions. However, these technologies are often dependent on governmental subsidies and the first generation was in competition with food chain. Therefore, its use has been limited for instance to 5% in the EU in 2012. In order to maintain the objectives of 10% of biomass in transportation fuels in 2020, an alternative is offered using second generation biofuels using lignocellulosic biomass.

Petrochemistry (namely petroleum and gas based chemicals) is a young industry compared to refining one. It constitutes an essential part of the chemical industry today. Petrochemicals are basically related to two major building blocks (90% of the basic petrochemical production which size around 423 MMt): olefins such as ethylene (139 MMt in 2015), propylene (demand may reach 100 MMt/Y in 2016), and C4 olefins (such as butadiene, butenes, and isobutylene) and aromatics such as benzene, toluene, and xylenes (BTX 119 MMt in 2015 of which 38 MMt for xylene). These petrochemicals are commodities and their market is cost driven and very price sensitive. These basic commodity petrochemicals are processed as raw materials in different industries such as polymers, synthetic fibres, solvents and for almost all other petrochemicals for main end-uses in major market sectors such a construction, packaging, agriculture, automotive... We owe to petrochemistry many products that contribute to making our lives easier, safer and more comfortable. The global petrochemical demand is dominated by polyolefins.

Petrochemicals represent a cyclical market of high value products. Petrochemicals market size is 10% of the whole oil market global demand and growth for petrochemicals is estimated at 4% (2015-2025) which is much faster than oil's (ICIS, Chemicals Industry News & Chemical Market Intelligence <http://www.icis.com/>). This has provided growth of opportunities in the petrochemical industry. But petrochemical industry is facing significant challenges of resources and environment. The global petrochemical feedstock slate is becoming more diverse. Access to feedstock is then an important consideration. Over the last few years, US is seeing a tremendous growth on the back of cheap and readily available shale gas feedstocks (ethane accounts for 55% of the olefin slate, propane 20%). China continues to invest in chemical production capacity, with unconventional supply routes mainly based on low value coal reserves and increase in crude oil price in 2009 (coal

to olefins CTO or methanol to olefins MTO and propane dehydrogenation PDH). But these plants may face competition from naphtha-based petrochemical production in the present context of low crude oil price. In Europe, refinery naphtha and condensates provide about 75% of the feed to the ethylene crackers. In a context of poor competitive position for Europe petrochemicals due to lack of cheap feedstocks and energy, Europe keeps on growing mainly in Eastern Europe.

The purpose of this chapter is to review the recent achievements in the field of fuels and petrochemistry in the French community of heterogeneous catalysis.

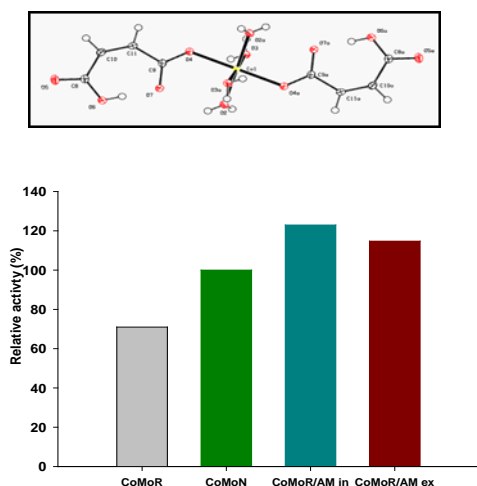
### 1.1. Trends in hydrotreatments and hydroconversion

After FCC, hydrotreatments represent the second catalyst market for refiners, half of the extracted oil being hydrotreated. Most of developed countries have adopted stringent regulations (10 ppm) for reducing sulfur content in gasoline and gas oil. This policy pushed catalysts manufactures to propose new generation of HDT catalysts. Thus, in the 2000's, all companies brought an important increase in catalytic activity by using either organic additives or new preparation methods involving heteropolyanions.<sup>2</sup> Chelating, complexing and non-complexing agents (glycol type) were found to greatly promote catalytic activity. Organic additives can be added at each stages of the preparation (support synthesis, impregnated support, by co impregnation with metallic salts or after drying or calcination stage of the catalyst). Therefore, organic additives may have many and different roles and modify the physical and chemical properties of the support and precursors or the rates of sulfidation of the metal oxides. Thus, complexing and chelating agents can interact more selectively with metallic promoters (Ni, Co) providing a better promotion during the sulfidation stage. However, the conditions of interactions, for instance pH<sup>3</sup> or pressure of sulfidation,<sup>4</sup> may generate different complexes with more or less impact. Non-complexing agents interact in a much lesser extent with these promoters but can modify support and precursors supports interactions for providing a better dispersion<sup>5</sup> as well as activation stage by delaying sulfidation.<sup>6</sup>

The use of such additives has affected the life cycle of HDT catalysts. Thus, the regeneration procedure must recover at least 90% of the initial activity of a catalyst. The regeneration process consists on an oxidative treatment at 450–550°C which remove carbon and oxidizes the active phases.

Conventional regeneration cannot recover the performances of an additivated catalyst; therefore, additives for the regeneration must be found. These additives must more selectively react with the undesired CoMoO<sub>4</sub> phase formed during oxidation stage,<sup>7</sup> maleic acid (MA) is an excellent candidate as illustrated in Figure 1.

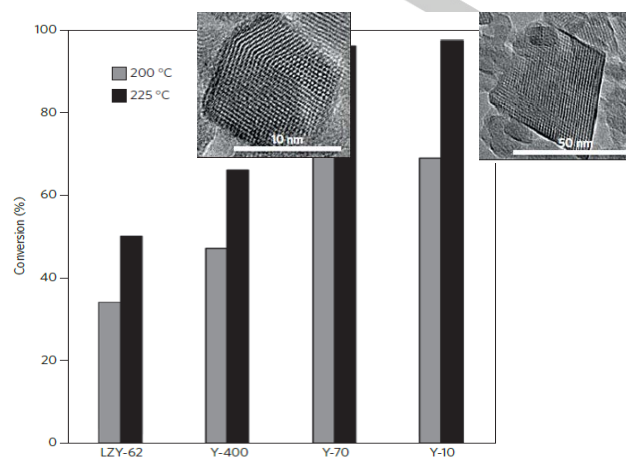
Considering the increasing use of heavier feedstock's or unconventional oils in refineries, a large extent of hydroconversion (Hydrocracking, residue hydroconversion) as well as HDN and HDN pretreatments is expected. In this respect, development of new zeolites materials, promotion of HDN performances or understanding by kinetic studies has been recently addressed in the literature.



**Figure 1.** Crystallographic structure of Cobalt(Maleic Acid) complex (Top) and impact, on SRGO conversion, of this additive on regeneration (CoMoN fresh catalyst, CoMoR regenerated catalyst and doped catalyst sulfide in (AM in) or ex (AM ex) situ).<sup>7</sup>

Solid acids and more specifically zeolites, are widely used in refining processes such as Fluid Catalytic Cracking (FCC) or Hydrocracking for the conversion of heavy feedstocks to lighter products (ie middle distillates) as well as in petrochemistry for the separation or purification processes for high purity aromatics or olefins cuts. More specifically, in catalytic processes for petrochemistry, zeolites play an important role and have a good industrial potential such as in aromatic transformation by isomerization, disproportionation/transalkylation and alkylation. Ethyl benzene (EB) hydrodimerization is an essential part of the main process of production from C8 aromatic cuts (~20% EB-80% Xylenes) of the high purity para xylene isomer (pX) used for synthesizing polyethylene terephthalate (PET) fibers, resins and films. Because of their intrinsic properties (tunable acidic sites and shape selectivity) zeolites are able to realize C-C bond  $\beta$ -scission by themselves or associated to a metal in order to combine hydro / dehydrogenation and cracking functions in a so called bi-functional catalyst, these class of solids offers the high level of versatility needed to reach the expected performances.<sup>8</sup> Among the major breakthroughs achieved in the recent years, nanocrystals engineering is likely the most promising since it addresses two important challenges: the control of the external surface reactivity for its own reactivity or selectivity effects such as pore mouths catalysis in hydro-isomerisation and the mass transfer process governed by diffusion which may be potentially improved by reducing the size of the crystals. In this context, many efforts have been devoted to design high quality nano-sized FAU Y (for catalytic applications) or X (for separation purposes) zeolitic crystals playing with (i) the extensive possibilities of inorganic or hybrid chemistry using (or not) organic or mineral templates acting as Structure Directive Agent (SDA) or (ii) alternative routes such as ionothermal (using Ionic Liquid) or microwave assisted synthesis.<sup>9</sup> In a "template free approach" a special attention was paid to the homogeneity of the mixture of the solution containing the precursors. Moreover, thanks to a precise kinetic control of the nucleation / growth steps, it has been possible to obtain ultrasmall FAU zeolites (10 nm) with narrow crystal size distribution and improved catalytic activity (Figure 2).<sup>10</sup> Always in a chemical engineering approach controlling temperature and duration time, so

called "embryonic precursors were obtained leading after hydrothermal treatment to amorphous structure of a zeolitic like material with high micropores accessibility and acidity.<sup>11</sup>

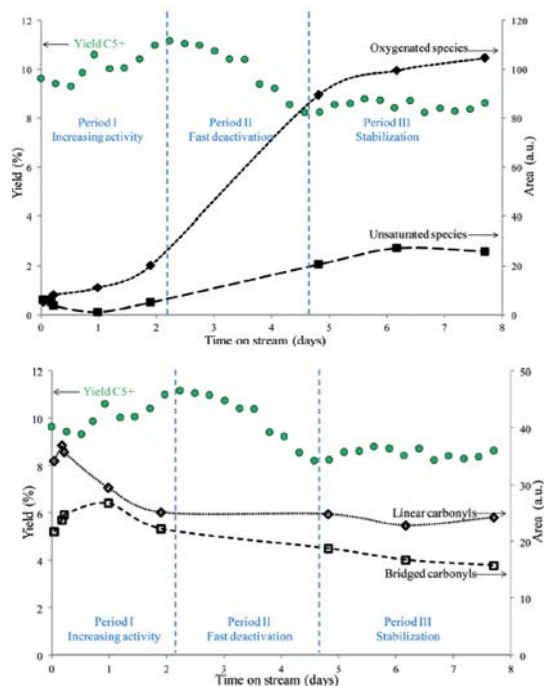


**Figure 2.** Conversion of 1,3,5-triisopropylbenzene over Y-10 (10 nm crystal size), Y-70, Y-400 and LZY-62 (reference) zeolite catalysts<sup>10</sup>

Another important highlight concerns the recent studies on hollow zeolites<sup>12</sup> containing metallic nanoparticles. This new class of materials offer fascinating perspectives since they combine mass transfer optimization, confinement effects and protection of the metallic core against poisoning or sintering phenomena.

## 1.2. Trends in Fischer-Tropsch synthesis

There are currently several Gas To Liquid (GTL) industrial plants in operation. For cobalt based catalysts, Shell and Sasol are the main actors. Shell operates two units one in Malaysia of 14,700 bbl/d and one in Qatar of 140,000 bbl/d, the largest capacity in the world. Sasol is associated in two units of 34,000 bbl/d each one in Qatar with Qatar Petroleum and one in Nigeria with Chevron and Nigerian National Petroleum Company. For iron based catalysts, industrial units are located in South Africa, Sasol operates units in Sasolburg with a capacity about 150,000 bbl/d and PetroSA operates the Mossel Bay unit with a capacity of 45,000 bbl/d. Fischer-Tropsch synthesis (FTS) is a key technology of XTL (X-To-Liquids, with X = Gas, Biomass or Coal) process, which converts syngas (CO+H<sub>2</sub>) into long chain paraffins converted afterwards into middle distillates mainly by hydroisomerisation. In a global context where natural gas utilization is expected to grow, FTS has received a large interest in the recent years due to its lower CO<sub>2</sub> fingerprint compared to crude oil processing technologies in addition to sulfur free products avoiding desulfurization post-treatment. Besides numerous improvements of the performances, still severe issues limiting the industrial development exist, especially in the case of the more costly but also more reactive and selective Co catalysts (compared to Fe). In particular, deactivation and selectivity items attracted a lot of attention during the last decade.



**Figure 3.** (Top) C<sub>5</sub><sup>+</sup> yield (o), IR areas of oxygenated (■) and unsaturated (◆) species adsorbed at the surface of the catalyst as a function of time on-stream (Bottom) C<sub>5</sub><sup>+</sup> yield (o) and linear (◇) and bridged (□) carbonyl IR areas, both as a function of time-on-stream during Fischer-Tropsch synthesis at 220°C, 6 bar, and H<sub>2</sub>/CO = 2.<sup>13</sup>

Among the potential solutions, intensification approaches using micro reactors or monoliths / foams<sup>14</sup> have been proposed allowing a very high C<sub>5</sub><sup>+</sup> selectivity by quite complete suppression of CH<sub>4</sub> formation compared to classical fixed bed technology.

On the kinetic analysis point of view, modeling of transient experiments (SSITKA) performed on different structured (fcc or hcp) supported nanoparticles brought important information regarding the mechanism (carbide or CO insertion) occurring on such catalysts.<sup>15</sup>

In addition to these chemical engineering oriented studies, many options exist to improve the performances of the solid including the promotion by noble metals,<sup>16</sup> or the control of the Co nanoparticle size distribution using organic additives playing the role of chelating agent (sorbitol) or nanoreactor ( $\beta$ -cyclodextrin).<sup>17</sup> Comprehensive studies and insight in terms of structure - reactivity relationship have been possible thanks to the development of *operando* characterization techniques (DRX, DRIFT, XAS) allowing to distinguish the critical phenomena among the different ones occurring during FTS real conditions (sintering, carburization of the metallic phase, reoxydation / surface reconstruction / migration of metallic nanoparticles).<sup>13</sup>

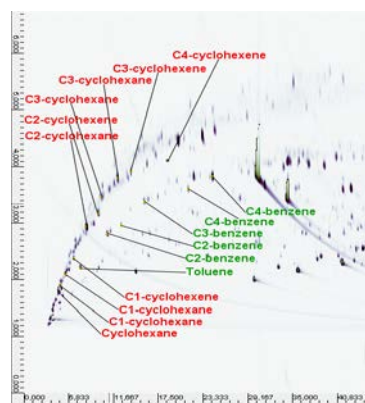
Finally, theoretical calculations based on DFT also bring their contribution to a better knowledge of the Co nanoparticle working. For instance, the role of carbonaceous deposits on model Co(111) surfaces has been investigated in function of the ASF selectivity<sup>18</sup> as well as sub-surface C and O diffusion phenomena during the reaction.<sup>19</sup>

### 1.3. Trends in thermochemical conversion of lignocellulosic compounds

Second generation biofuels are now technologically available for ethanol production from cellulose and fuels from indirect route based on FTS. In France, two large scale projects are under construction namely Futurol (ethanol via biocatalysis technology) and BioTFuel (FTS), industrial cellulosic ethanol being already industrially produced. The French community has been strongly involved in the development of the direct route through pyrolytic oils. The production of pyrolytic oil is now a well established technology<sup>20</sup> which fails to valorize the produced bio oils. Several studies assessed the sustainability of their transformation into fuels. Early works demonstrated the feasibility of specific two stages processes (stabilization and HDO) but with the enormous drawback of hydrogen consumption and high cost. In fact, the key feature of pyrolytic oil future is the cheap removal of oxygen contained in the bio-oil (either as water or in compounds) in order to reach less than 10%. Below this limit, bio-oil can be mixed for instance with hydrocarbons and involved on co-processing in HDT or FCC refinery units.<sup>21</sup> Not long ago, KiOR Company attempted to industrialize catalytic pyrolysis (Biomass FCC) but failed. An alternative of this technology, preventing troubles due to ashes, is to convert with appropriate catalysts the pyrolytic vapors before condensation. Thus, instead of an emulsified bio oil, separated phases (water and organic) can be obtained after condensation and an improved removal of oxygen content achieved.<sup>22</sup>

Due to the production of cellulosic ethanol, another lignocellulosic resource is expected to be available in a greater extent: lignin. Several conversion pathways have been investigated.<sup>23</sup> Among these pathways, hydroconversion assisted with hydrogen donor solvent is a promising route for getting phenols or aromatics (BTX) (Figure 4).<sup>24</sup>

In the framework of indirect route of biomass conversion by gasification with fluidized beds, tar removal and improvement of hydrogen production with catalysts remains a challenging task. Dedicated sorbent/catalyst (for instance CaO-Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>/olivine) presenting a good CO<sub>2</sub> sorption stability favors these reactions.<sup>25</sup>



**Figure 4.** Enhanced view of a GCxGC chromatogram of hydroconverted lignin<sup>24</sup>

### 1.4. Examples of achievements in petrochemistry

Olefins are produced primarily via Steam Cracking using feedstock such as Natural Gas Liquids NGLs (ethane, propane, butane, isobutane and pentane) or Naphta that come from oil refineries and gas processing. Ethane consumption for steam cracking has grown in North America due to the rapid development of

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shale gas and consequently ethylene is produced with the maximum efficiency.

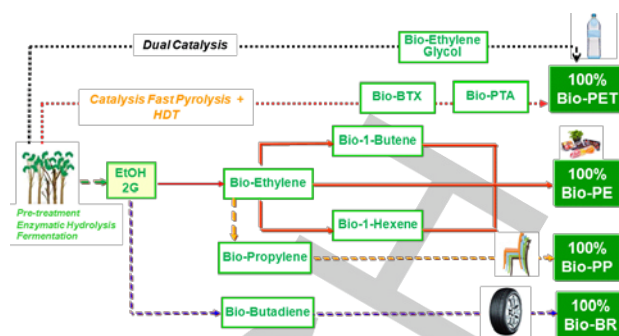
Linear Alpha Olefins (LAOs, ~5 MMt/Y in 2015, estimated 6,1 MMt/Y in 2020) are useful and versatile petrochemical intermediates for a wide range of applications like co-monomers for polyethylene (C4-C8 LAO, 60% of the total demand of LAOs, for LLDPE 49% and HDPE 11%), surfactants and detergents (C10-C18), base stock and additives for lubricants (C10-C18) or plasticizers (C6-C10). The industrial processes for producing LAOs are mainly based on ethylene oligomerization. The LAOs industry continues to rely on both “full-range” alpha-olefin technologies which result in mathematical product distribution like Schulz-Flory or Poisson, as well as highly selective “on-purpose” technologies for production of individual carbon number. These “on-purpose” technologies are mostly desirable, because of the higher demand growth for polyolefin co-monomers. These technologies rely on homogeneous transition metal catalysis. Extensive research activity from both industry and academia has been pursued. The main challenges are to selectively obtain individual alpha-olefins, with a very high level of purity, while at the same time improving the efficiency of the process and its operability and by using catalysts based on widely available metals with low toxicity. Main research approaches have been dedicated to the design of multi-dentate ligands with the aim of drawing relationship between structure of the pre-catalyst and catalytic activity.<sup>26</sup>

The availability of iron combined with its low environmental impact attracts significant interest from both academia and industry for olefin transformations. However, the lack of thermal stability and lifetime of the homogeneous iron based catalysts likely undermine their industrial developments.<sup>27</sup> Nickel has brought some interesting results for selective 1-butene production from ethylene.<sup>28</sup> Mechanism understanding is still the object of discussion.<sup>29</sup> Heterogeneous Ni based active catalysts for ethylene oligomerization have also been reported such as Ni- $\text{AlSiO}_2$  mesoporous catalyst ( $\text{Si/Al} = 6.5$ , 2.0% Ni) using mesoporous non-ordered silica as a support at 150°C.

Propylene demand is continuously growing, primarily because of increases in polypropylene, propylene oxide, and acrylonitrile consumption and also because steam cracking used to obtain propylene have difficulties in adjusting their production capacities. Cross-metathesis of 2-butene and ethylene is one of the “on-purpose” route to supply propylene. Heterogeneous  $\text{WO}_3/\text{SiO}_2$  catalyst is mostly used in industry for this purpose. Alternative methods have been developed to produce propylene from ethylene by coupling ethylene dimerization Ni- $\text{AlSiO}_2$  catalyst with metathesis  $\text{MoO}_x/(\text{Al})\text{SiO}_2$  or  $\text{MoO}_x/(\text{Al})\text{SBA-15}$  catalysts<sup>30</sup> or with tungsten on alumina based systems.<sup>31</sup>

Fluctuating steam cracking traditional ethylene prices as well as consumer orientation toward renewable materials, initiated the search for new resources able to bridge the gap between bio-based and traditional petrochemicals.<sup>32</sup> In that context, bio-ethanol is an interesting platform molecule that can bridge the gap between biomass fuel production and traditional petrochemical engineering (Figure 5). Different materials have been developed for dehydration of ethanol.<sup>33</sup>

New technologies for bio degradable plastics, renewable PVC, rubber etc. will also play a major role in the petrochemical industry in the future.



**Figure 5.** From fossil to renewable resources for the production of bio-plastics and elastomers.<sup>33</sup>

The proven reserves of natural gas are huge (over 150 proven and 200 trillion  $\text{m}^3$  as potential reserves). The oxidative coupling of methane (OCM) to ethane and ethylene comes back as an interesting alternative route to produce valuable hydrocarbons without going through reforming or requiring syngas as feedstock. Large European project with the collaboration of French community has been undertaken on this matter.<sup>34</sup>

To conclude, catalysis for refining remains the main actor of transportation fuels production and improving their quality needs a constant effort. Thus, research for more active and selective catalysts are continuously performed either in academic or industrial laboratories. Whatever the domain, the introduction of organic additives brought new types of interaction and improved activities. Progresses have been achieved through the appearance of new generations of catalysts (HDT, zeolites) with new preparation methods and better understanding of deactivation and selectivity improvements. Rarefaction of metals and use of less toxic active phases (REACH regulation) is also pushing for alternative formulations. Progress in catalytic science is intimately linked to the improvement of kinetic modeling and *in situ* characterization methods. As a consequence, process improvement with these new catalysts will be supported by intensification and multi scale approaches. Biofuels are well established in the energetic mix and second generation is now starting to be industrialized in the case of ethanol production. The direct or indirect thermochemical routes assisted by heterogeneous catalysts are now under deep investigation with still strong economical and scientific issues. Third generation involving algae as well as alternative fuels (solar fuel, electrocatalytic fuels...) are extensively investigated. Transition-based homogeneous catalysis for alpha-olefin co-monomer production from ethylene have seen some recent breakthrough related to the design of ligands and use of less toxic metals such as iron. The conversion of available, low cost but particularly inert feedstocks such as methane, ethane, propane to higher valuable chemicals is still a main scientific challenge which motivates creative research combining catalyst and engineering developments.

## 2. Catalytic processing of concentrated feed of biomass

### 2.1. The French networks

The development and implementation of biorefinery processes is of the utmost importance to meet the vision towards a sustainable

economy based on bio-resources, namely, the so-called 'bioeconomy'. The French landscape around biorefineries is encountering a strong defragmentation effort, with, e.g., the European Biorefinery institute comprised of an integrated biorefinery and an innovation platform,<sup>35</sup> the Federative Research Structure "Condorcet - Agro-Science, Environment and Sustainable Development",<sup>36</sup> which pools together skills and expertise present in the research laboratories (public and private) working in the field of agro-science; the E<sub>2</sub>P<sub>2</sub>L "Eco-Efficient Products and Processes Laboratory"<sup>37</sup> an associate laboratory between Solvay and CNRS-France, as a unique International Research & Innovation Hub in China at the interface between industry & academia dedicated to Eco-Innovation for Sustainable Chemistry; and IN-CREASE "International Consortium on Eco-conception and renewable resources", a network between public laboratories, R&D centres and industrial companies involved in green chemistry. More especially in the field of biotech, we can also mention remarkable initiatives such as TWB (Toulouse White Biotechnology)<sup>38</sup> to develop products and processes with biobased raw materials, from laboratory level to pre-industrial pilot level, and the Carnot Institute 3BCAR, an organized research network of research units working in the field of transformation of biomass into bioenergies, biobased materials and molecules.<sup>39</sup> Three French clusters are especially at the forefront of this sector: IAR, Axelera and Matikem.<sup>40</sup>

Contrary to petro-resources of which the nature and composition variations are 'relatively' limited, under the term 'bio-resource' or 'biomass', at the base of biorefineries, are gathered compounds of very different natures, namely cellulose, hemicellulose, oils, lignin, etc. Thus, a complete set of specific technologies must be developed in order to convert each fraction as smart as possible. This implies, among others, the elaboration of a lot of (bio-) chemical and thermochemical transformations, which constitute core technologies that have to be developed and implemented in a global sustainable framework along the whole valued chain.<sup>41</sup> In this context, France was awarded the coordination of two FP7 European projects among the three laureates of the Large Scale Collaborative Project FP7-ENERGY.2009.3.3.1 integrated call. The EuroBioRefproject and the Biocore project, together with their UK SupraBio sister project, encompassed the whole value chain of a biorefinery (2010-2014).<sup>42</sup> In EuroBioref, catalytic technologies were at the core of the project and hereafter are cited some examples of developments: catalysts were developed to synthesize nitriles from fatty acids or esters;<sup>43</sup> and to convert fatty unsaturated compounds notably through variations of metathesis reactions;<sup>44</sup> tandem isomerization/hydroformylation was used for the production of polyamide-12 precursor from bio-sourced 10-undecenitrile;<sup>45</sup> acetals synthesis was further envisioned through a conventional approach<sup>46</sup> and through reactive distillation<sup>47</sup> or simulated moving bed membrane reactor (SMBR) to overcome chemical equilibria;<sup>48</sup> glycerol was valorised to various compounds including acrylonitrile,<sup>49</sup> or hydroxymethyl-2-oxazolidinones;<sup>50</sup> glycerol-derived products were hydroformylated;<sup>51</sup> Guerbet reaction was used to yield various alcohols<sup>52</sup> with uses as aviation fuel;<sup>53</sup> 1-butanol direct conversion to maleic anhydride<sup>54</sup> was developed to be implemented in an original phthalic anhydride (ex *o*-xylene) co-production configuration; syngas conversion technologies were improved to yield alcohols,<sup>55</sup> as well as methyl-mercaptan,<sup>56</sup> taking advantage the presence of H<sub>2</sub>S in black liquor-derived syngas. In Biocore, chemocatalysis was notably used to convert C6 cellulose pulp into isosorbide<sup>57</sup>. Further,

in parallel, the Star Colibri project, a 2-year Coordination and Support Action, was also funded by FP7 (2009-2011) and produced a Joint European Biorefinery Vision for 2030<sup>58</sup> and European Biorefinery Joint Strategic Research Roadmap for 2020, also showing the importance of catalytic developments in the field.<sup>59</sup>

In the meantime, the French government launched a very large scale investments for the future ("PIA") initiative, under the umbrella of which biorefinery-oriented Institutes of Energetic Transition ("ITEs"), P.I.V.E.R.T.<sup>60</sup> and IFMAS<sup>61</sup> were selected. The ITE P.I.V.E.R.T. (Picardie Plant Innovations Teaching and Technological Research) aims at developing a competitive plant-based chemistry using a renewable and promising, raw material: the oilseed biomass. One of the four main axes of this institute is the research axis (GENESYS program), in which catalytic approaches, including new chemo- and bio-catalytic systems are developed, including their one-pot combination under the new concept of hybrid catalysis.<sup>62</sup> Since the GENESYS program launch year (2012), many results were obtained, some of which being now disclosed after a patenting process, with a consequent portfolio of efficiently developed reactions such as: conversion of glycerol to value added products such as glycolic or glyceric acid including raw glycerol reactivity,<sup>63</sup> as well as to divinylglycol;<sup>64</sup> direct conversion of alcohols to carboxylic acids<sup>65</sup> as well as to cerides/symmetrical esters;<sup>66</sup> hydroformylation of triglycerides<sup>67</sup> in a self-emulsifying medium;<sup>68</sup> synthesis of conjugated dienyl derivatives by green bisallylic substitution;<sup>69</sup> decarbonylation of fatty acids.<sup>70</sup> Similarly, in the ITE IFMAS "French institute of agro-based materials", new green synthons are catalytically synthesized, notably through selective polyol anhydration. As another PIA project laureate in the field of catalysts development for bio-sourced application, the EQUIPEX ("excellence equipment") REALCAT<sup>71</sup> "Advanced high throughput technologies platform for biorefineries catalysts design" consists of a high-throughput platform, unique in the world, devoted to innovation in heterogeneous, homogeneous catalysis, bio-catalysis, and hybrid catalysis. Fully operational since early 2015, the platform contributed to the discovery of efficient catalysts and optimal reaction conditions for, e.g., selective oxidation of allyl alcohol to acrylic acid,<sup>72</sup> glucose selective oxidation to glucuronic acid,<sup>73</sup> glycerol dehydration to acrolein.<sup>74</sup>

Although chemical processes are nowadays rather selective from renewable feedstocks, the production cost of bio-based chemicals still exceeds in many cases that of chemicals from a fossil origin.<sup>75</sup> This tendency is mostly due to the low productivity of bio-based routes caused by (i) the deactivation or low activity of current catalysts and (ii) high dilution. CNRS, ADEME and the Research National Agency (ANR) have recently launched several calls in France related to the search of innovative catalytic processes capable of converting concentrated feed of biomass to fine chemicals such as polyols, aromatics and furanic derivatives.

## 2.2. Catalytic transformation of platform molecules

Glycerol is the smallest polyol substrate issued from biomass. Since it is the co-product of the biodiesel production and since Diesel is largely used in France, the catalytic transformation of this molecule has been significantly studied (Figure 6).

The main challenges to be addressed for the catalytic transformation of glycerol (as well as other polyols) concern the selectivity of the reaction in order to avoid expensive separation steps<sup>76</sup> and the development of catalysts efficient with low purity glycerine.



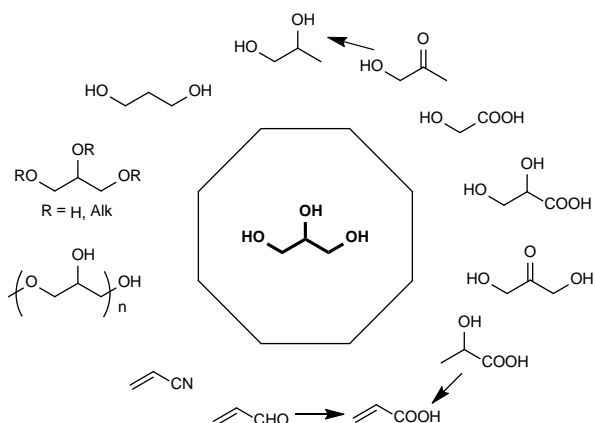


Figure 6. Glycerol as a platform molecule

Even if deactivation is observed when crude or partially purified glycerol is used, oxidation in the presence of Pt-based catalysts is possible.<sup>63b, 63c</sup> The assessment of reaction mechanisms<sup>77</sup> and the design of long-term stability of the catalysts play also substantial role in the design of an efficient process. This later is of particular importance when highly reactive products are formed such as acrylic acid, acrolein or acrylonitrile.<sup>78</sup> Tungstated zirconia prepared by W impregnation of crystalline ZrO<sub>2</sub> has been shown to be stable for acrolein synthesis when small mesopores were avoided.<sup>78d</sup> Some ZrNb mixed oxides<sup>78e</sup> were also stable in the same reaction. Combined experimental and theoretical approaches allowed to understand better the role of the catalyst.<sup>79</sup> Catalytic transformation of higher alcohols mainly issued from hydrogenation of saccharides is even more challenging since a large number of reactions occurs simultaneously: C-C or C-O hydrogenolysis, deshydration, isomerization, retroaldol reaction, Cannizzaro reaction...<sup>80</sup> Optimisation of the catalytic system (mainly bifunctional catalysts) as well as the reaction conditions allowed optimization of the selectivity to a desired product.

Aqueous media is largely used to solubilize biobased platform molecules since they are highly oxygenated and they are often produced from transformations carried out in water (chemical hydrolysis or enzymatic transformation). The characterization of the acid-base properties of designed solid catalysts allows the identification of the best catalysts efficient in the dehydration of glycerol to acetol or of monosaccharides (glucose or fructose) to hydroxymethylfurfural (HMF) or levulinic acid.<sup>81</sup> The platform molecules issued from biomass can be further transformed to desired products.<sup>75</sup> So, bimetallic catalysts are efficient in the hydrogenation of bio-based acids to the corresponding diols (levulinic or succinic acid).<sup>82</sup> Mono and bimetallic catalytic systems based on platinum metalloid allow selective oxidation of bio-based alcohols (HMF to FDCA (furan dicarboxylic acid), glucose to gluconic or glucaric acid...<sup>83</sup>

Direct transformation of biopolymers is still challenging using both homogeneous and heterogeneous catalytic systems. A series of acid catalysts are efficient in the depolymerization of cellulose, homopolymer of glucose. Depending on the nature of the catalysts (Bronsted/Lewis acid) and the nature of the atmosphere, the main product changes from lactic acid, HMF, hexanedione or propylene glycol.<sup>84</sup> In addition, the non-catalyzed hydrothermal liquefaction of cellulose has been studied.<sup>85</sup> This allows to dissociate the chemophysical phenomenon from the catalytic one. Proper

design of the catalysts avoids the formation of undesired humins. Alternative media are also studied for this transformation (*vide infra*). The depolymerization of lignin is even more difficult since the structure of the biopolymer is more heterogeneous (series of several aromatic moieties) but is a promising route to the production of bio-based aromatic moiety.<sup>23, 24, 86</sup>

### 2.3. Non-thermal technologies: an access to catalytically processable sugars

Non-thermal technologies are one of the options explored in France to facilitate the conversion of concentrated feed of biomass.<sup>87</sup> A public/private consortium hosted by the CNRS (project INCREASE) has been created to evaluate the potential of breakthrough of these non-thermal technologies in the field of biomass. Among the most popular non-thermal technologies, one can cite atmospheric plasma, ultrasound, milling, electrochemistry, microwaves or supercritical fluids. These works have opened breakthrough routes to convert biomass, sometimes without any catalyst or solvent, to novel high value materials that can be further functionalized/processed through conventional catalytic ways. It is for instance the case of atmospheric plasma which is capable of deeply reorganizing the macromolecular structure of cellulose without any solvent or catalyst through radical depolymerization/repolymerization reactions (Figure 7).<sup>88</sup>

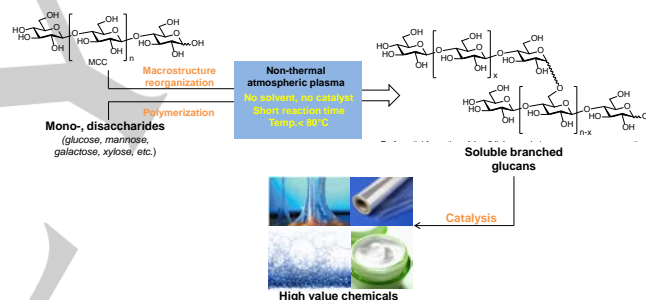


Figure 7. Synthesis of catalytic processable glucans by non thermal atmospheric plasma.

This transformation selectively occurred within few minutes only at a temperature below 70°C and led to a large library of soluble branched glucans with controlled degree of polymerization. Mono- and disaccharides were also quasi instantaneously polymerized by atmospheric plasma thus widening the library of poly- or oligosaccharides which can be synthesized with this technology.<sup>89</sup>

Other technologies are also the topic of intense researches in France such as high frequency ultrasound, milling and electrochemistry. One may cite for example the electrocatalytic dehydrogenation of polyols,<sup>90</sup> the glycosylation of carbohydrates assisted by ball-milling<sup>91</sup> or the catalyst free oxidation of carbohydrates by high frequency ultrasound.<sup>92</sup> Although promising results were claimed, the energy consumption of these technologies is nowadays the main cost driver. At the moment, most of researches in this field are thus focused on the synthesis of high value chemicals such as glucans or derived chemicals. These technologies are not mature yet for the production of low value chemicals such as glucose, furanic derivatives, etc. To widen the business capability these technologies may support, much effort is now paying

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on the elucidation of reaction mechanisms but also on reactor engineering. Particularly, clarifying the nature of exited species generated by these non-thermal technologies and how do these species interact with biomass are essential questions that are currently the subject of national projects.

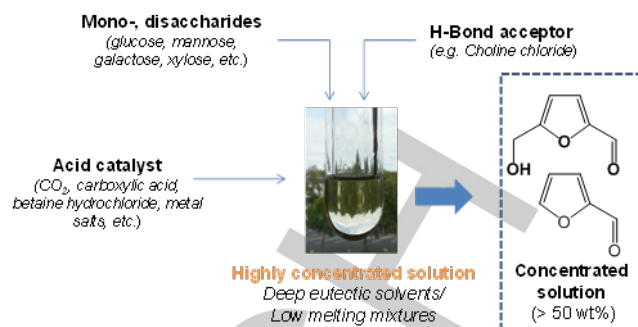
Getting more insight on reaction mechanisms is not an easy task. The characterization of active species formed by these technologies is indeed complex due to (i) their short life time and (ii) the formation of a cocktail of active species whose composition is strongly affected by the nature of biomass. Real time *in-situ* FT-IR characterization has allowed a better understanding on how active species react with the surface of a material exposed to a non-thermal technology<sup>93</sup>. However, this method only gives information on reactions taking place on the surface of materials while monitoring reactions taking place in the bulk remains difficult.

In most cases, these processes involve radical reactions rendering the control of the reaction selectivity difficult. The synergy of these technologies with catalysis is a promising option to tune the reached selectivity and few projects have been recently launched on this aspect in France. In this context, catalysis in supercritical fluids (SC) is probably the most mature technology for solid biomass processing. Besides Sub- and SC water applied for a long time to break down or liquefy solid biomass, various SC organic solvents such as alcohols (*i.e.* methanol, ethanol, propanol, olefins..) have also been envisaged due to their milder critical coordinates and much better solvency for biomass derivatives.<sup>94</sup> Compared to SC water, reports on the processing of lignocellulosic materials in SC organic fluids are scarcer but this topic is gaining a growing attention in France. If the majority of the works deals with the liquefaction of lignocellulosic biomass,<sup>95</sup> other aspects were recently addressed such as the selective fractionation of lignocellulosic biomass<sup>96</sup> or the possible modification of the bulk chemical structure of wood.<sup>97</sup> A way of high potential relies on the use of heterogeneous catalysts in SC organic solvents. For instance, the presence of a catalyst in a SC media is capable of driving the liquefaction of biomass into bio-oils with a higher energy value<sup>98</sup> or to the selective formation of chemicals of interest.<sup>99</sup>

### 2.3. Alternative media for catalytic biomass processing

The search of alternative non-aqueous media capable of dissolving large amount of biomass is another strategy explored by different French groups to improve the productivity of bio-based processes. Initially, ionic liquids were investigated for the dissolution and the catalytic conversion of carbohydrates (including lignocellulosic biomass) but these catalytic processes were cost-prohibitive for industrial deployment. More recently, an impulsion was given to deep eutectic solvents (or low melting mixtures) that are considered as a second generation of fluids for biomass processing (Figure 8).<sup>100</sup>

The concept relies on the ability of carbohydrates to interact with hydrogen bond acceptor such as choline chloride for instance. These H-bonding interactions result in a deep depression of the freezing point of the mixture. Using this concept, concentrated solutions of carbohydrates (up to 70%) were obtained and these solutions were sometimes even liquid at a temperature close to room temperature. Addition of a homogeneous or heterogeneous acid catalyst to these media has opened straightforward routes to produce concentrated solutions of 5-hydroxymethylfurfural (HMF) and furfural from hexoses and pentoses, respectively.<sup>101</sup>



**Figure 8.** Catalytic dehydration of concentrated feed of carbohydrates in deep eutectic solvents.

As compared to more conventional solvents such as water, ionic liquids or dimethylsulfoxide, the selectivity to the corresponding furanic derivatives remained close to 70% up to a concentration of carbohydrate as high as 60 wt% (vs 5–10 wt% in conventional solvents).

Despite not clear at the moment, it was suspected that HMF and furfural were strongly stabilized in such mixtures which contributed to decrease their degradation rate. Thermodynamic modelizations are the topic of current investigations to rationalize this particular behavior. Because of their chemical stabilization, extraction of HMF and furfural from these media is obviously difficult and even not desirable. Current projects now consist in converting *in situ* furanic derivatives to more easily extractable chemicals such as dimethylfuran,  $\gamma$ -valerolactone, etc. Influence of water and impurities present in raw biomass on the physico-chemical properties of these solvents is also carefully investigated.

### 2.4. Biphasic catalysis: towards biosurfactants

Regarding industrial applications of biomass, intense efforts have been made in France to the production of biosurfactants. In this field, many calls were launched by the CNRS, ADEME and also by private companies such as SOLVAY, ARD, SEPPIC, among many others. Biosurfactant is a growing market with enormous opportunities of product development and employment which explains the high scientific activity in this field. To date, few strategies were explored and patented or published. Among them, one can cite the catalytic esterification or etherification of polyols (glucose, glycerol, polyglycerol, sorbitan, sorbitol, polysaccharides, etc.) with fatty chains, the reductive amination and reductive alkylation of polyols, the telomerization of polyols with diene or the glycosylation of carbohydrates with fatty alcohols. To reach high process productivity, reactions are conducted without any solvent and polyols are used in their liquid form or in suspension. Scientifically, the large difference of polarity between polyols and fatty chains remains an important hurdle. Particularly, the biphasic nature of reaction media induces mass transfer problems but it also lowers the catalyst activity and process productivity and even sometimes raised selectivity issues. To overcome this problem, catalysis under surfactant-free emulsion conditions have been extensively investigated. For instance, cyclodextrins were proposed to carry hydrophobic substrates in catalytic polar phases.<sup>102</sup> This concept was particularly applied to catalytic hydroformylation and Tsuji-Trost reactions. More recently, the concept of Pickering-interfacial catalysis (PIC) has been revisited and adapted by French groups (Figure 9).<sup>103</sup> The design of heterogeneous catalysts with

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amphiphilic properties such as Aquivion PFSA or sulfonated hybrid organic-inorganic materials have been proven as an efficient strategy to produce surfactant-free emulsion from polyols, thus resulting in a selective coupling of polyols with fatty chains. Furthermore, as compared to more conventional methods involving surfactants, the heterogeneous nature of PIC systems allowed their convenient recovery at the end of the reaction by decantation. These PIC systems were found particularly efficient for the solvent free acetalization of glycerol with fatty aldehydes and the glycosylation of carbohydrates with fatty alcohols. Owing to their amphiphilic properties, PIC systems even led to a higher productivity than  $\text{H}_2\text{SO}_4$  (the current reference in industrial processes in the field), thus opening promising perspectives with respect to industrial deployment.



Figure 9. Concept of Pickering-interfacial catalysis.<sup>103</sup>

### 3. Environmental catalysis

#### 3.1. General context

Different topics dealing with environmental catalysis were tackled during the French Catalysis Conference reflecting the growing demand of more efficient technologies to clean up air and water. Most of them became in the past ten years more and more sophisticated, particularly in the case of post-combustion catalysis where more compact technologies are foreseen especially for light duty vehicles powered by Diesel engines.<sup>104</sup> By way of illustration, the sequential abatement of unburnt hydrocarbons, CO, soot particles and  $\text{NO}_x$  requires the implementation of an oxidation catalyst (DOC), Lean- $\text{NO}_x$ -Trap (LNT) or Urea-Selective Catalytic Reduction (SCR) system and ionically conducting ceramic filter<sup>105</sup> for the sequential removal of  $\text{NO}_x$ , and particulates. The DOC usually plays a crucial role in such a technology generating the formation of  $\text{NO}_2$  as key intermediate for LNT, fast-SCR and soot combustion. Within such a scenario, academia faces significant technological obstacles for combining high efficiency and durability, especially for lean burn applications, or more generally for converting selectively trace amounts of air and water contaminants into non-toxic products. In this context, extensive researches for developing PGM-free systems arose in the past two decades, with a renewed interest of perovskites thanks to the development of their textural properties through innovative synthesis methods.<sup>106</sup>

The introduction of photocatalysis for air and water treatment or of non-thermal plasma for the abatement of pollutants and wastes<sup>107</sup> at low temperature can be an outstanding issue able to

protect heterogeneous catalysts from thermal deactivation phenomena. However, major drawbacks still exist due to the low activity of known systems reachable by solar light, which imposes to develop innovative catalytic processes and novel methodologies for solid synthesis.<sup>108</sup> Rational approaches were suggested during this meeting especially through the development of *in situ* and *operando* spectroscopic investigations, with relevant illustrations<sup>109</sup> looking for ultimate goal in rational catalyst design instead of trial and error approaches. Such type of methodology which consists in combining different techniques able to probe simultaneously the interacting surface and adsorbates, can provide useful information on the composition, architecture, and behavior of the active sites. Future needs in the development of efficient catalytic end-of-pipe technologies should also take into account a better integration of new generations of heterogeneous catalysts.<sup>110</sup> An important issue that was stressed out is the need to develop simple and green methods for the preparation of catalysts<sup>111</sup> with the ultimate goal to reduce the use of critical materials i.e. Platinum Group Metals (PGM) and of rare earth. Electrochemically-assisted end-of-pipe technologies provided significant improvements maximizing the catalytic efficiency of PGM. Based on this, a lowering of PGM loading can be reasonably envisioned.<sup>112</sup>

#### 3.2. Recent achievement for reducing $\text{NO}_x$ to nitrogen in lean conditions from Diesel engine

Among different catalytic after-treatment processes already commercialized to treat exhaust gas from Diesel engines,  $\text{NO}_x$  Storage Reduction (NSR) and urea-Selective Catalytic Reduction (SCR) are still competing. Both technologies have significant kinetic and thermodynamic limitations but offer significant efficiency to convert  $\text{NO}_x$  to nitrogen in lean conditions (large excess of oxygen). Regarding the urea-SCR, urea is first thermally decomposed releasing ammonia and isocyanic acid (HNCO) and then a second molecule of ammonia forms through the hydrolysis of isocyanic acid (HNCO). HNCO is generally slowly hydrolyzed into ammonia which represents a significant drawback with side reactions leading to the undesirable formation of polymeric compounds which can alter durably the catalyst efficiency through pore blocking. However, recent findings also found that the kinetics of urea-SCR can be also affected by the presence of NCO species which can also exhibit a high specific reactivity towards  $\text{NO}_x$  suggesting an alternative “HNCO-SCR” route. A new reaction sequence has been recently proposed involving the intermediate formation of HONO in the ultimate production of nitrogen as target products.<sup>113</sup>

Important issues are also related to the development of innovative catalytic SCR catalysts for replacing unstable  $\text{V}_2\text{O}_5/\text{WO}_3(\text{MoO}_3)/\text{TiO}_2$ .<sup>114</sup> Supported Vanadium-based catalysts can be considered as a benchmark for the ammonia and urea-SCR but could be inapplicable for after-treatment of exhaust from mobile sources with extreme temperature conditions reaching  $650^\circ\text{C}$  leading to the sublimation of  $\text{V}_2\text{O}_5$  aggregates. Aggregation process of mono- and polyvanate species to larger  $\text{V}_2\text{O}_5$  crystallites has also a detrimental effect on the selectivity<sup>115</sup> with a more extensive production of  $\text{N}_2\text{O}$  characterized by a global warming potential  $\sim 300$  times higher than that of  $\text{CO}_2$ . In this context, the FCCAT1 conference gave the opportunity to suggest new varieties of more thermally stable catalytic materials corresponding to a greater stabilization of vanadium entities in the zircon-type

structure of  $\text{CeVO}_4$ .<sup>114</sup> Some controversies arose regarding the origin of unprecedented high Turn-Over-Frequencies calculated on those materials because SCR usually proceeds more slowly on unreducible metal oxide sites, with a substantial moderation of the valency of V(+V) species. Further increase in TOF values after running in typical lean burn exhaust has been ascribed to the restoration of  $\text{V}^{5+}/\text{V}^{4+}$  redox cycle through partial diffusion of oxidic vanadium species from the bulk to the surface generating Brønsted acid sites correlatively to surface vanadium enrichment. A. Brückner as invited speaker during the FCCAT1 demonstrated the relevance in analyzing supported  $\text{V}_2\text{O}_5/\text{Ce}_x\text{M}_{1-x}\text{O}_2$  (with  $\text{M} = \text{Zr}, \text{Ti}$ ) oxide catalysts during the ammonia-SCR of NO by a multi-technique *in-situ/operando* approach<sup>116</sup> especially to elucidate structural features responsible for high catalytic performance at low temperature on the basis of results reported elsewhere.<sup>117</sup> Interestingly, it was found that the most active samples at low temperature with  $x = 0.3\text{--}0.5$  corresponded to the highest atomic V/Ce+M ratio with vanadium coordinated to the support likely within  $-\text{O}-\text{Ce}-\text{O}-(\text{V}=\text{O})-\text{O}-\text{M}-\text{O}$  moieties. As a conclusion both a  $\text{Ce}^{4+}/\text{Ce}^{3+}$  and a  $\text{V}^{5+}/\text{V}^{4+}$  redox cycle would originate the exceptional low temperature activity of such system which seems consistent with the conclusion drawn on  $\text{CeVO}_4$ <sup>114</sup> with catalytic performances also associated to both redox cycles. Several French laboratories develop such *in situ* and *operando* approaches in the particular case of environmental catalysis in order to identify reaction intermediates among all adsorbates characterized and acting in most cases as spectators, as well as to extract quantitative kinetic and thermodynamic data relative to adsorption of intermediates (see § 5.2).

New insight into the development of more stable vanadium based catalysts could be of practical interest especially for coupling SCR with Diesel Particulate Filters (DPF). Clearly, obtaining more compact technologies can be a cost efficient approach but in this particular configuration structural and textural properties of the SCR function grafted on the DPF must resist to strong exotherms especially during the regeneration of the particulate filter. An alternative can be the development of new vanadium free systems such as  $\text{WO}_3/\text{Ce}-\text{Zr}$  which exhibit promising catalytic performances with improved redox properties limiting undesired side-reactions due to oxidation of ammonia into NO. A complete oxidation of ammonia to  $\text{N}_2$  is promoted at high temperature with 80% of ammonia oxidized exclusively into nitrogen at 500°C.<sup>113b</sup> However, the prevalence of strong acidic properties is crucial to ensure a complete ammonia conversion and prevent ammonia slip. For this reason, the coupling of Pt-Ba/Al model NSR with  $\text{WO}_3/\text{Ce}-\text{Zr}$  SCR system did not led to successful practical achievements because of low acidity and part of stored ammonia oxidized fortunately to nitrogen. Such an option previously envisioned consisting first to regenerate the LNT with reformate and then to valorize the ammonia produced through ammonia-SCR by coupling LNT with SCR catalysts insure a higher overall efficiency.<sup>118</sup> However, the environmental benefit did not completely balance the cost investments provided by the implementation of such technology. As a matter of fact, the cost efficiency could be more debatable if at constant  $\text{NO}_x$  conversion, a reduction of PGM loading in LNT system can be envisioned. Such an opportunity would be possible according to combined technology earlier developed by Ford's catalyst suppliers including: – desulfation of LNT at lower temperature – advanced SCR catalysts close to those encountered in commercial zeolite-based SCR applications

– synergetic coupling of the LNT and SCR catalyst performance preserving high efficiency even on aged systems.<sup>119</sup>

An important issue for LNT is related to the production of  $\text{N}_2\text{O}$  during the purge. If  $\text{N}_2\text{O}$  emissions are not strictly limited, they represent a significant environment issue for car manufacturers. In fact,  $\text{N}_2\text{O}$  primarily forms after switching in rich conditions when PGM are not fully reduced. A secondary detection is also observed when LNT switches from rich to lean condition ascribed to the reaction between  $\text{NO}_x$  and reductive species. Castoldi et al. concluded that the presence of high O-coverage prevents the dissociation of NO and  $\text{N}_2\text{O}$  is no longer formed when the reductant scavenges O-adatoms on a reduced surface.<sup>120</sup> Let us note that particular attention was paid by French researchers on the behavior of such materials during the storage phase among numerous investigation published with original viewpoint related to the inhibiting effect of sulphur as well as the beneficial effect of potassium on Pt/K/Mn/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> ascribed to the formation of a particular phase characterized by *operando* FTIR spectroscopy and TEM measurements.<sup>121</sup>

Now, it is obvious that among the wide panel of solids already investigated in the urea- and ammonia SCR, the superiority of doped-zeolite materials is demonstrated. However, the stability of the doping agents under working conditions is still a matter of discussion and debates. The structure of different type of zeolite i.e. Y, ZSM-5, SSZ-13 allows the stabilization of isolated or dimer copper species stabilized in different structural environments.<sup>122</sup> Isolated  $\text{Cu}^{2+}$  species predominantly stabilized for SSZ-13 in planar 6-membered ring environments enhance the SCR whereas Cu-oxo species would more favors the decomposition. Clustering effects taking place in the supercages of the zeolite Y has significant detrimental on the catalytic properties. This is an important issue especially for coupling DPF with SCR catalyst which requires a stable SCR function up to 850°C. A recent investigation pointed out that Cu-SAPO-34 containing only 1.2 wt. Si exhibits a high stability under hydrothermal conditions at such a temperature.<sup>123</sup>

### 3.3. Challenges in the simultaneous removal of $\text{NO}_x$ to nitrogen and particulates from Diesel exhaust.

The removal of soot particles is an important target for Diesel powered engines with more stringent regulations which will also concern spark ignition engines producing finer particles. An important challenge resides in the simultaneous removal of  $\text{NO}_x$  and particulates globally in a large excess of oxygen which imposes sophisticated technologies as aforementioned. DPF exhibits a high filtering efficiency and periodic regeneration are needed to avoid backpressure due to soot accumulation. Generally, soot combustion occurs at high temperature which can be reached through an active regeneration thanks to fuel post-injection. Obeid et al.<sup>124</sup> investigated an alternative which consists in a continuous regeneration DPF avoiding fuel penalties based on the utilization of ionically conducting ceramics. They found that soot oxidation can be activated on a non-reducible yttria-stabilized zirconia oxide obeying a fuel-cell type electrical mechanism at the nanoscale. The soot oxidation represents the anodic reaction taking place at the soot/YSZ contact surface whereas cathodic reactions would occur at the triple phase boundary between soot particles, gas phase, and YSZ. Soot particles act both as a reactive and a current collector.

### 3.4. Volatile Organic Component abatement processes: stationary and diffuse sources

A challenge faced nowadays in the domain of VOCs remediation is to find solutions for the treatment of very low concentrations of gaseous pollutants (from ppm down to ppb levels) in very large volumes of indoor or outdoor atmospheres. Even if they remain relevant, methods based on adsorption, traditionally used for instance for toluene removal from air, still suffer from the drawback of competitive adsorption especially in presence of humidity. Moreover, adsorption is a non-destructive pathway and complementary steps are required for pollutants degradation and adsorbents regeneration.<sup>125</sup> This can be done through cycling processes involving thermal or plasma-assisted regeneration or by combining adsorption with photocatalytic oxidation as was efficiently tested for the abatement of formaldehyde, a common air pollutant with high toxicity even at very low concentrations.<sup>126</sup>

Non-thermal plasma technologies are amongst the most promising routes for VOCs abatement at room temperature. However, they generate ozone and NO<sub>x</sub>, which elimination necessitates as well a post treatment by filtration and/or catalytic decomposition of the exhausts.<sup>127</sup> For good efficiency, such system should be placed downstream of the plasma discharge (Post-Plasma Catalytic or PPC system) as illustrated in the case of trichloroethylene abatement on Pd/LaMnO<sub>3</sub><sup>128</sup> or of methanol oxidation on Mn, Ce and Cu oxides supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>129</sup> The synergetic association of the plasma technology with a photocatalytic pathway is also of particular interest, as proposed in recent studies on ethanol abatement in air on MnO<sub>x</sub>/TiO<sub>2</sub> catalysts<sup>130</sup> or on the elimination, on a TiO<sub>2</sub> supported on glass fiber material, of isovaleraldehyde, a molecule present in the exhaust gases from animal quartering centers.<sup>131</sup>

Besides, total thermal catalytic oxidation at low temperatures remains a route widely considered. An issue in the domain is however to replace noble metal based catalysts, commonly recognized as the most efficient,<sup>132</sup> by cheaper transition metal oxides or by mixed oxides catalysts,<sup>126,133</sup> which activity and stability levels are however not yet satisfying enough for industrial development, improvements being therefore still needed. This was discussed in a recent review focussed on the catalytic oxidation of formaldehyde on manganese oxides or on mixed manganese oxides (nanoparticles combining MnO<sub>x</sub> with other oxides) identified as very promising catalysts, allowing formaldehyde abatement at temperatures below 120°C.<sup>126</sup> Also, new preparation routes involving microwave irradiations were tested, and a positive effect in the synthesis of Co<sub>6</sub>Al<sub>2</sub>HT hydrotalcite-like compounds used as precursors of cobalt alumina mixed oxides was found, resulting in an increased activity for toluene catalytic oxidation.<sup>133</sup> For low pollutant concentrations in the atmosphere, the association in a same hybrid system of VOCs adsorption and catalytic oxidation capabilities was moreover proposed, allowing to perform an energy saving cycling process with a first step during which the VOC is concentrated, followed by a second step of oxidative catalytic decomposition carried out once the concentration is high enough. Such approach was successfully tested for toluene removal using copper exchanged NaX zeolites, well known for their adsorbant and catalytic properties.<sup>125</sup>

Additional efforts that deserve to be cited are the recent ones that addressed, beyond the conventional question of the efficiency of the degradation process, that of the non-toxicological character of

the emitted products. An innovative approach thus recently combined, in a same study, the assessment of the catalytic performances in toluene abatement of Pd on alumina catalysts and an on line evaluation of the toxicological character of the exhaust gases using an air-liquid interface exposure system.<sup>134</sup> Similarly, even if being slightly outside of the VOCs domain, it is worth mentioning the attempts recently dedicated to the photo-degradation of pollens on nano-functionalized photocatalytic materials upon UV-Visible exposure at room temperature and in presence of humidity.<sup>135</sup>

### 3.5. Waste water treatment

The contamination of water is becoming of great importance because of increasing industrialization and population. This includes extensive use of agricultural fertilizers, septic, tank systems and animal waste disposal, rejected pollutants (nitrates, pesticides, medicines...). Particular attention has been paid to inorganic and organic N-containing compounds with the aim to produce selectively nitrogen and CO<sub>2</sub> from mineralization. To fulfill such requirements biological and physicochemical treatments are conventionally implemented but some illustrations emphasize the relevance of catalytic processes which could be cost-efficient in case of high efficiency. In some cases, the catalytic wet air oxidation can be more advantageous to treat high concentration of *p*-nitrophenol instead of biological treatments<sup>136</sup> and the combination of both processes can enhance the biodegradability of phenolic effluents with conversion reaching 90%. The use of precious metal is usually privileged in association with doping elements deposited on functionalized materials having oxygen storage properties.<sup>137</sup> A major concern is certainly the reduction PGM loadings with likely a better controlled of the pore structures since pore size and confinement effects are well known to strongly affect diffusion and catalytic properties as well as the involvement of significant deactivation phenomena.

However, previous attempts also demonstrated that catalytic processes could not be the optimal solution because of significant deactivation phenomena as reported elsewhere.<sup>137g</sup> Indeed, parallel to a poor selectivity toward the conversion of N,N-dimethylformamide with essential production of amines and ammonium instead of nitrogen, a dramatic leaching of Pt, Pd and Ru deposited on TiO<sub>2</sub> and ZrO<sub>2</sub> occurred through their complexation with the unpaired electrons on the N-atom in amines. It causes the question if the development of catalytic processes for the purification of drinking water can be envisioned especially for the removal of nitrates into nitrogen. A two-step process is usually involved with the intermediate production of nitrites. Bimetallic catalysts with platinum or palladium in association with copper were found efficient combining the redox properties of copper to reduce nitrates to nitrites and the subsequent reduction of nitrites to nitrogen promoted hydrogen activated on PGM.<sup>137b</sup> The close proximity of copper and platinum was found to play a crucial role preserving the metallic state of copper than the reductive behavior of chemisorbed H atoms on Pt sites. However, those authors also mentioned the negative effect of copper on the selectivity with significant production of ammonia. All these examples emphasize the relevance for developing catalytic processes but also pointed out the main issue in a better control of the selectivity and the durability.

#### 4. CO<sub>2</sub> as carbon source for energy: Power-To-Gas

To follow the 2°C Scenario (2DS) of International Energy Agency which reduces CO<sub>2</sub> emissions (including emissions from fuel combustion and process and feedstock emissions in industry) by almost 60% by 2050 (compared with 2013), with carbon emissions being projected to decline after 2050 until carbon neutrality is reached, a deep modification of our energy sources is requested. The world electricity production is expected to increase by 100% in 2050 and being mainly produced from renewable decarbonised processes.<sup>138</sup> For the specific case of France the Law on Energy Transition for Green Growth (17/08/2015)<sup>139</sup> aims to « bring the share of renewables up to 32% of the energy mix by 2030 ». This implies that our production of electricity from renewables has roughly to double by 2030. The strong penetration of intermittent electricity into the grid will generate strong modifications in the electric grid management and large electric surpluses are predicted, up to 14 TWh in France in 2030<sup>140</sup>. The best solution to store and transport over large periods of time and large distances these electric overproductions is their initial conversion into hydrogen through water electrolysis (around 100 Wh per mol of H<sub>2</sub>) and further chemical transformation with captured CO<sub>2</sub> either for chemistry (low volumes) or more intelligently for energy (larger volumes, in line with the electricity excesses to be valorized). Processes involving CO<sub>2</sub> hydrogenation into methane (Synthetic Natural Gas, SNG), Power-To-Gas and more specifically Power-To-SNG, are under development, which allow the interconnection between electric and gas grids, thus facilitating the development of renewables in the energy mix. The CO<sub>2</sub> conversion into energy by such hydrogenation processes through electrolysis is not driven by the CO<sub>2</sub> reuse: around 0.3 % of CO<sub>2</sub> emitted in France could be converted in SNG with 14 TWh of electricity. The effect on CO<sub>2</sub> emissions is mainly an indirect effect, through the easier implementation of decarbonised energy sources.

The catalytic hydrogenation of CO<sub>x</sub> has been extensively studied in the context of solid carbon-based materials (coal, biomass) gasification followed by methanation reactors<sup>141</sup>. These processes are based on CO methanation and generally involve a Ni/alumina catalyst, alumina being a dispersing and stabilizing support for Ni(0) as active phase.

With the objective of developing catalytic materials more specific for CO<sub>2</sub> hydrogenation for Power-To-SNG, Ni/ceria-based catalysts have been studied by Ocampo et al.<sup>142</sup> They studied a series of Ni-Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts prepared by a pseudo sol-gel method. All catalysts gave impressive CO<sub>2</sub> conversion and extremely high selectivity to methane (superior to 98%). Ni<sup>2+</sup> incorporation into the CZ structure was proved to enhance catalysts specific activity. The global performance depended not only on the surface of available metallic nickel but also on the composition of the support and on its modification by Ni<sup>2+</sup> doping. These catalysts presented much better performances than other Ni-based reported materials, and competed with highly active Ru-based systems<sup>143</sup>. Noble metal addition led to higher Ni dispersion, resulting in a raise of both activity and catalyst life-time. It did not modify the support intrinsic activity. The deactivation was shown not to be due to carbon deposits, as it is generally the case for CO hydrogenation, but rather to nickel particles sintering. The influence on the support in the reaction of CO<sub>2</sub> methanation was further studied with other Ni/ceria-based catalysts prepared by simple impregnation<sup>144</sup>.

Mesoporous ceria-zirconia was demonstrated to promote stability by reducing Ni sintering.

The mechanism of CO<sub>2</sub> methanation has been studied by *operando* IR spectroscopy on this type of catalysts<sup>145</sup>. Interactions between Ni and the ceria-zirconia support seem to be a key parameter for the methanation reaction. The use of IR *operando* spectroscopy revealed that the main mechanism for CO<sub>2</sub> methanation does not require CO as reaction intermediate but goes through formate species. The enhanced activity observed can be explained by the importance of weak basic sites of the oxide support in the adsorption of CO<sub>2</sub>. Metallic Ni sites are involved in the H<sub>2</sub> adsorption and dissociation steps. The close metal support interaction is thus crucial for the reactivity of such catalytic systems. This mechanism has been later confirmed on ceria-doped Ni/USY zeolite, by FTIR *in situ/operando* study too<sup>146</sup>. The positive effect of oxide support basicity has been recently reported for other types of supports. Ni/Mg/La/Al mixed oxides derived from Ni-La-hydroxalcite precursors have been studied by various techniques<sup>147</sup>. The catalytic activity of such materials was shown to be directly connected with basicity of medium strength that is brought by the presence of La.

In parallel to the studies on catalyst formulations, some groups recently published their works on different activation technologies. Nizio et al.<sup>148</sup> studied Ni/ceria-zirconia catalysts activated by a cold dielectric barrier discharge (DBD) plasma. They demonstrated that NiO can be efficiently reduced under plasma<sup>149</sup>. High methane yields, around 80 % at GHSV of 20,000 h<sup>-1</sup> (STP), were measured under hybrid plasma-catalytic conditions at temperature as low as 90 °C. In the absence of plasma, similar catalytic performance was only achieved at 300 °C under similar conditions with the same catalyst. Azzolina-Jury et al.<sup>150</sup> have studied nickel-zeolites and demonstrated that plasma-assisted CO<sub>2</sub> hydrogenation under partial vacuum can be performed under milder conditions, lower temperature and residence time compared to conventional methods with higher CO<sub>2</sub> conversion and CH<sub>4</sub> yields. They also studied the plasma-assisted CO<sub>2</sub> hydrogenation mechanism using high resolution (μs) time-resolved FTIR Spectroscopy in an original home-made IR *operando* plasma cell. They reported that the real intermediates of the CO<sub>2</sub> methanation under plasma irradiation are the adsorbed CO molecules which are mainly generated by electron impact CO<sub>2</sub> dissociation in the gas phase and further adsorbed on Ni-USY zeolite as carbonyls. Novel type of catalysts based on Ni deposited on Fe<sub>2.2</sub>C nanoparticles of extremely high specific absorption rates (SARs) were developed by Bordet<sup>151</sup>. Their exceptional heating properties were exploited for the CO<sub>2</sub> methanation, the catalyst being activated through magnetic induction. The SARs of synthesized iron carbide nanoparticles were high enough to obtain promising results in a continuous flow reactor. For the first time the concept of magnetically induced catalysis has been successfully applied to the CO<sub>2</sub> methanation reaction.

In view of developing reactor configuration able to face the major difficulty of methanation unit, which is the management of the exothermal reaction heat flow release, CO<sub>2</sub> methanation catalysts have been deposited on different structured supports and tested at medium catalytic bed size. Danaci et al.<sup>152</sup> deposited a conventional Ni/alumina catalyst on a stainless steel support of around 25 cm<sup>3</sup> prepared by 3-Dimensional Fibre Deposition (3DFD) technology. The best results were obtained on structured support of 'zig-zag' configuration. The improved heat and mass transfer

properties possibly explain the improved catalytic stability compared to a powder catalyst. Frey et al.<sup>153</sup> worked on  $\beta$ -SiC foam structured support, they studied their hydrodynamic behavior for different morphologies and different surface modifications. They optimized the surface treatment, the coating procedure and the catalyst formulation (Ni-ceria based oxide) to lead to the configuration most active for CO<sub>2</sub> conversion and most selective to methane<sup>154</sup>. They finally developed a tool<sup>155</sup> by infrared thermography to study the exothermicity of the methanation reaction on the surface of foams coated by Ni-ceria-zirconia catalyst. More recently aluminium foams coated with Ni-ceria-zirconia have been efficiently used as structured bed of around 75 cm<sup>3</sup> for the methanation of CO<sub>2</sub><sup>156</sup>. High methane productivity has been achieved without high temperature increase (below 25 °C) showing the good efficiency of the aluminum foams to transfer the heat flow to the reactor wall. Similar conclusions were obtained for Ni-alumina catalyst deposited by dip-coating on aluminum foams<sup>157</sup>. Finally, the first French demonstrator Power-To-Gas project with gas injection in the grid, Jupiter 1000<sup>158</sup> led by GRTgaz, has been officially launched in 2016. It will be implemented in Fos sur Mer and involves an electrolysis power of 1 MW. It is expected to be operational by 2018.

#### 4.1. Dry Reforming of Methane (DRM)

Reforming of methane with CO<sub>2</sub> to produce syngas is considered as an important route for carbon dioxide valorization and abatement of greenhouse gases. Considerable research has been undergone in this area since a couple of decades in order to develop stable and efficient catalysts for this reaction. Until now, few projects have proceeded to industrial application due to several factors. First of all is the strongly endothermic nature of this reaction, thus needing large energy inputs, making this process less sustainable as far as the primary goal of greenhouse gases abatement is considered. Indeed, large amounts of low carbon energy resources (solar, hydro, wind, geothermal, nuclear ...) are needed. On the economical point of view, this process produces syngas that needs then to be transformed to liquid fuel by Fischer-Tropsch synthesis. The viability is thus strongly dependent on the price of traditional fuels.

Furthermore, hydrocarbon reforming by CO<sub>2</sub> suffers several side reactions which alter selectivity (reverse water gas shift reaction) or catalysts stability (coking, typically by hydrocarbon decomposition or Boudouard reaction). Most of these reactions are equilibrated in the DRM conditions meaning that performances are limited by thermodynamic equilibrium especially when more severe conditions are explored - e.g. at high pressure - to meet industrial demand.

Finally, as high temperatures are in any case involved, sintering of both support and active phase need to be controlled to avoid premature deactivation.

Considerable amount of work and several recent reviews have recently been dedicated to DRM<sup>159</sup>. The scope here is to highlight most recent work performed in French laboratories on DRM with a particular attention to some of the critical aspects mentioned above.

#### 4.2. DRM catalysts

##### 4.2.1 Supported catalysts

A wide literature in DRM catalysts concerns supported catalysts. Activity enhancement in terms of reactant conversion cannot be considered as a challenge nowadays as very effective materials allowing to reach thermodynamic limit conversions are rather commonly proposed. Thus, catalysts design for DRM is mainly focused on two aspects: selectivity towards syngas and stability in time.

Ni remains the most common element in DRM catalyst formulations. Its main drawbacks are the tendency to sintering at high temperature and carbon formation. It has been recently shown that the intrinsic activity of silica supported Ni particles is not affected by particle size<sup>160</sup>, in particular at low temperature (500°C). The stabilization of metal nanoparticles is therefore a major field of investigation in order to maintain high performances. Kaydouh et al have proposed the use of ordered mesoporous silica supports (SBA-15) to stabilize Ni (and Ce) nanoparticles<sup>161</sup> and have shown that this contributes to limit particles sintering by providing their better distribution but also to limit the formation of carbon inside the porous structure of the support. Indeed, carbon formation is observed only on the outer surface, as also observed by Galvez et al<sup>162</sup>. A similar approach was used to optimize Co based catalysts using SBA-15 support but the addition of Rh<sup>163</sup> or Ru<sup>164</sup> was necessary to promote both the reduction of Co species and the DRM activity.

The effect of Ni nanoparticles confinement in mesoporous silica substrate was enhanced by doping with LaOx<sup>165</sup> species which further reduce the poisoning of the active site by carbon deposition.

Stabilization of Ni nanoparticles was also achieved by coating nickel nanoparticles with alumina by atomic layer deposition (ALD) on nickel oxide (NiO) and subsequent reduction to Ni<sup>0</sup><sup>166</sup>. Few studies have been devoted to the use of zeolites as support. Most recent work concern ZSM-5 supported Ni and Co catalysts<sup>167</sup> - for which the bimetallic systems showed the best performances - and NaY supported Ni-Rh<sup>168</sup> for which excellent performances are claimed at low temperature (<600°C).

Natural diatomite has recently been proposed as support for Ni based catalysts<sup>169</sup>. Activity and particularly stability is however strongly dependent on the origin of the diatomite and on the pretreatments. Loss of activity attributed to re-oxidation of nickel species is also suggested.

The use of illite clays as support has also been reported recently<sup>170</sup> but doping with cerium and the addition of oxygen (autothermal process) in the reactant stream are necessary to limit carbon deposition and achieve stable performances.

##### 4.2.2 Oxide precursors for DRM catalysts

Another approach for preparing DRM catalysts consists in using oxide precursors, containing the metal active phase (usually Ni), to generate active catalysts by adequate pretreatments.

Spinel based catalysts, have shown good activity for DRM, especially NiAl<sub>2</sub>O<sub>4</sub><sup>171</sup> systems and NiFe<sub>2</sub>O<sub>4</sub><sup>172</sup>. Activity is mainly affected by the size of Ni particles and the reducibility of oxide species. Iron contributes to CO<sub>2</sub> activation at the expense of selectivity as RWGS reaction is also promoted. Introduction of silica<sup>173</sup> helps to stabilize the Ni-Fe catalysts mainly due to the acidic properties of SiO<sub>2</sub> although most of the particles are embedded in the silica matrix.

Perovskite have attracted a lot of attention as precursors for DRM catalysts. Most of the research has been focused on  $\text{LaNiO}_3$  perovskite considering that it associates both Ni as methane activation element and La oxides species which can form carbonates that can act as intermediates in the DRM. A comprehensive review on the subject has been proposed recently by Batiot-Dupeyrat<sup>174</sup>.

Recently Guerrero-Caballero et al proposed  $\text{BaNi}_2\text{V}_2\text{O}_8$  as precursor for DRM<sup>175</sup>. After a reduction treatment under  $\text{H}_2$  at  $800^\circ\text{C}$ , this compound decomposes to form a complex ensemble including Ni and  $\text{Ba}_3(\text{VO}_4)_2$  accompanied by a minor phase  $\text{BaV}_{10}\text{O}_{15}$  which seems to play an important role on catalytic activity and stability.

Ni-Mg-Al catalysts derived from the decomposition of hydrotalcite precursors have been extensively studied by Dębek et al.<sup>176</sup>. These materials showed interesting activities at  $550^\circ\text{C}$  but suffer from deactivation by carbon formation which could nevertheless be limited by La doping<sup>177</sup>.

Generally, catalysts based on oxide modification/decomposition are very sensitive to the precursor preparation methods and the pretreatments.

#### 4.3. DRM processes

The development of innovative processes is another mean for overcoming stability and selectivity issues for DRM.

The most active field of research in this respect concerns multiple reforming processes, such as bi-reforming ( $\text{CO}_2 + \text{H}_2\text{O}$ ), tri-reforming ( $\text{CO}_2 + \text{H}_2\text{O} + \text{O}_2$ ) and autothermal ( $\text{CO}_2 + \text{O}_2$ ). Simultaneous vapor reforming is considered in order to limit carbon formation, whereas the addition of oxygen allows to improve the energetic aspects. Bi-reforming has been studied by Jabbour et al<sup>178</sup> on mesoporous alumina Ni based catalysts. Alumina supports proved to be more efficient than silica based supports. Furthermore, the addition of Ca or Mg<sup>179</sup> allows to suppress carbon formation and improve catalyst stability.

Plasma assisted catalytic reforming reactions has attracted a lot of attention in recent years<sup>180</sup>. In particular, Pham et al have studied the use of a dielectric barrier discharge (DBD) plasma reactor with  $\text{La}_2\text{O}_3$  deposited on alumina balls<sup>181</sup>. The presence of the catalysts considerably increased  $\text{CO}_2$  activation at  $400^\circ\text{C}$  whereas it did not contribute to  $\text{CH}_4$  activation but mostly higher hydrocarbons ( $>\text{C}_2$ ) were formed. With a Ni/ $\text{La}_2\text{O}_3$  catalysts (obtained by reduction of  $\text{LaNiO}_3$  perovskite) deposited on a cordierite monolith<sup>182</sup> the yields towards syngas products increased at low temperature ( $500^\circ\text{C}$ ) by improving the activation of  $\text{CO}_2$  thus reducing the amount of higher hydrocarbons formed.

Non-steady state processes can also help to overcome selectivity and stability issues in DRM. Chemical looping process has been studied by Guerrero et al.<sup>183</sup>. This consists in exposing an oxygen vector material to methane and  $\text{CO}_2$  alternatively. During exposure to methane, the solid is reduced and syngas is produced, along with some carbon deposition. The absence of  $\text{CO}_2$  during this step allows to suppress RWGS reaction and thus to reach high selectivity. During exposure to  $\text{CO}_2$ , the solid is re-oxidized and the deposited carbon is removed thus ensuring catalysts regeneration. Ceria supported Ni, and Co catalysts have shown to be very effective for this type of operation which needs however a careful balance between surface reactivity an oxygen supply capacity.

## 5. *In situ / operando* characterization and ab initio calculation of catalytic systems and reactions

### 5.1. General feature

*In situ* and *operando* characterizations as well as theoretical simulations at the atomic scale are pivotal tools to obtain information about the structure and stability of active sites of catalysts, about their reactivity and the kinetics of the reactions.<sup>184</sup>

In order to obtain relevant information on catalytic materials, two approaches have been developed. The *in situ* characterization consists in treating the sample in conditions equivalent (gas flow, T, P) or close to that used to activate the catalyst before the reaction and to avoid any air contact before and during the characterization. The *operando* characterization consists of performing solid characterization during the reaction while measuring simultaneously its catalytic activity and selectivity.

These two approaches are complementary. *In situ* characterization leads to an accurate description of the fresh catalyst. According to the characterization method i.e. bulk or surface specific characterization tools, it can account of the structure of the active phase (structure, morphology, defect) or of the surface sites (nature, concentration, environment) of acidic, basic, redox catalysts as well as of metallic and sulfide ones. However, most of the catalysts present non-uniform surface sites with differences in their local environment and coordination. Moreover, dynamical changes of the nature and structure of the surface sites can occur in the reaction conditions. Thus, the questions to answer are: "Among this variety of surface sites which ones are active in the considered reaction?" and "What are the surface sites in reaction conditions?" *Operando* is a way to answer these questions. Indeed, characterization in reaction conditions is appropriate to identify the active sites, the reaction mechanism, the intermediates of reaction, and the mode of poisons formation.

Important instrumental developments to characterize the catalysts in model conditions or conditions representative of the reaction make French investigation very active and innovative in characterization techniques such as IR, Raman, X-Ray absorption spectroscopy (XAS) and electron microscopy.

Simulations at the atomic scale can also be of great help to obtain information about the structure and stability of active sites, about their reactivity and the kinetics of the reactions under investigations<sup>185</sup>. In France, this was and is still undertaken in the fields of both homogeneous and heterogeneous catalysis. When addressing the formation and breaking of bonds, quantum chemistry remains a method of choice. Several strategies can be chosen to solve the Schrödinger equations, which development is strongly connected to the evolution of supercomputing resources.

Moreover, the general strategy followed to understand and design catalytic systems by quantum chemistry calculations can be summarized as follows:

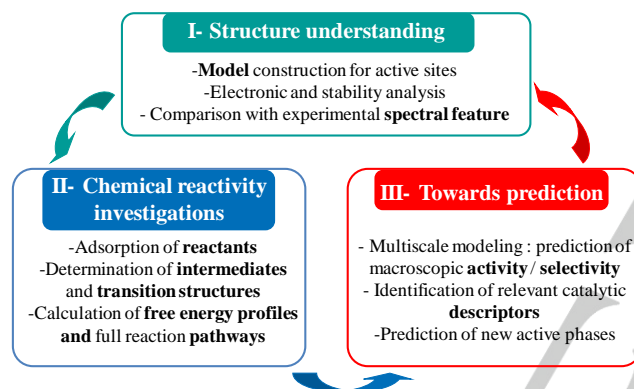
- First, we aim at proposing relevant structural models of complex catalytic materials, to obtain a high level of understanding at the atomic scale (step I, Figure 10). Electronic properties can be deduced, as well as the nature of the most stable systems depending on the operating conditions, based on energetic data and thermodynamic considerations. Then, comparison of well-chosen calculated and experimental spectroscopic features is a key step



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to evaluate the degree of relevance of the model, and also to assign experimental spectra, if the agreement between theory and experiments is satisfactory.

- On validated models, reactivity investigations start by quantifying the coordination/adsorption strength between reactants and active sites, as proposed in the first step of the methodology (step II, Figure 10). The determination of relevant intermediates and transition structures can then be undertaken for the studied reaction. From the calculation of free energy profiles, some insight in the preferred reaction pathways can already be obtained.
- A recent trend is to obtain predictive catalytic data (step III, Figure 10), by integrating quantum chemistry data into higher scales models, so as to predict the activity and selectivity of a given catalyst for a given reaction. If relevant descriptors of the catalyst can be found, by comparing several compositions, one may introduce them in kinetic models and even try to infer new efficient catalyst compositions. To improve the predictability of the model, one may consider some additional sources of complexity which were not invoked in the first round, and this is why the red arrow closes the loop in Figure 10.



**Figure 10.** General methodology followed in the present work for the simulation of complex catalytic systems by quantum chemistry calculations.

All those aspects motivate very active research at several places of the world, and French laboratories significantly contribute to the effort and to the success of the approach (a non-exhaustive list of reviews written by French scientists active in the field).<sup>186</sup> In the following, some chosen studies performed by French teams in both areas of research are mentioned.

## 5.2. *In situ* and *operando* characterization

### 5.2.1. *In situ* characterization

Depending on the method i.e. bulk or surface specific techniques, *in situ* characterization account for the structure of the active phase (structure, dispersion, morphology, defect) or on the surface sites (nature, concentration, environment) of the catalysts.<sup>187</sup> A powerful and widely used method that informs specifically on the catalyst surface is IR spectroscopy.<sup>93,188</sup> Surface properties can be probed either directly through the IR signal of hydroxyl groups or of residual surface impurities, or indirectly by monitoring probe molecule adsorption. According to the probe molecule, an accurate description of the acidic, basic, redox sites as well as of the metallic or sulfide sites can be obtained. As for the acidity, 2,6-

dimethylpyridine and CO (when adsorbed at very low temperature) are the most powerful probe molecules used to determine the nature, strength and amount of acidic sites on a large variety of materials such as oxide supports and catalysts, zeolites, sulfides, metal organic framework materials.<sup>188,189</sup> Regarding basicity, CO<sub>2</sub> is the most largely used probe even if C-H acid molecules like methylacetylene or chloroform can be also very useful to assess the strength of basic sites.<sup>188a,190</sup> Note that quantification and structure of different basic sites in oxides could be recently extracted from the complex IR spectra of adsorbed CO<sub>2</sub> using 2D IR spectroscopic methods.<sup>191</sup> NO and even more CO are the most suited molecules to probe surface of metal and sulfide phases since they inform on the nature, oxidation state, dispersion, defect and morphology of these particles.<sup>192</sup> However, the operating conditions can deeply modify the structure and the surface properties compared to fresh catalysts. As common features occurring during the catalytic reaction, one can quote coke deposition, sintering of the active phase, change of the nature of the surface site in presence of reactants or products as water.<sup>193</sup> Obviously, characterizations of fresh and working catalysts are required to reach a complete understanding of the catalyst behavior.

### 5.2.2. *Operando* characterization

Characterization techniques can be classified into two groups: those that are based on interaction of an electromagnetic radiation with matter (as IR, Raman, UV-vis, XAS spectroscopy) and that can be performed under atmospheric condition, and those that required high-vacuum (as electron microscopy, XPS).

#### Characterizations based on electromagnetic radiation-matter interaction

The first *operando* characterizations were published in the early nineties.<sup>194</sup> At that time, different terminologies were used as dynamic *in situ* or *in situ* on-line. *Operando* appeared very rapidly as a methodological breakthrough allowing to discriminate active sites, spectators species and even intermediates ones.<sup>93b</sup> The design of the spectroscopic reactor-cell is a key point that required inlet connected to gas flow system, outlet to analytical tools as gas chromatography and mass spectrometer, and reactor-cell allowing obtaining high quality spectroscopic data of the pellet in conditions relevant for catalysis (T, P). The *operando* cells often results from a compromise between catalytic and spectroscopic requirements. This makes difficult obtaining ideal plug flow reactor conditions. Thus, a good practice (but scarce) is to compare activities measured in an *operando* reactor-cell to those obtained in a traditional reactor.<sup>195</sup> Recent papers report kinetic modeling studies in *operando* system some having even led to optimization of the *operando* spectroscopic cell.<sup>195, 196</sup>

As for vibrational spectroscopies, *IR operando* spectroscopy has been early and largely developed in France. One can quote the IR platform of LCS (Laboratoire Catalyse et Spectrochimie, Caen) that gathers 22 FTIR spectrometers devoted to *in situ* and *operando* studies of catalysts. *Operando* Raman spectroscopy was firstly developed by Banares group of CSIC (Instituto de Catálisis y Petroleoquímica, Madrid)<sup>197</sup> and closely followed by French teams.<sup>198</sup> All these groups work actively to the development of reactor-cells for getting closer to industrial reaction conditions as well as to the development of cells and equipment for the coupling

of techniques as IR-thermogravimetry<sup>199</sup>, IR-Raman and Raman-UV-RPE.<sup>200</sup> The achievement of IR *operando* cells that can reach temperature up to 1073K and pressure up to 4 MPa<sup>201</sup> or can allow analysis of catalyst in its industrial form (as deposited on monolith<sup>202</sup>) leads to a development of the applications fields. Moreover, the high sensitivity, good time resolution, easy implementation make these spectroscopies largely used in refining<sup>203</sup>, fine chemistry<sup>204</sup> or pollution abatement.<sup>205</sup>

The use of synchrotron radiation for *operando* studies is also in strong development particularly due to the 3rd generation synchrotrons that are now more accessible (SOLEIL (Paris-Saclay) and ESRF (Grenoble) in France). Their high brightness makes them perfectly adapted for obtaining high temporal and spatial resolutions for most of the synchrotron techniques (X-ray absorption spectroscopy – EXAFS and XANES, wide and small angle X-ray scattering - WAXS and SAXS, X-ray diffraction XRD).<sup>206</sup> This has open many possibilities for the characterization of catalytic materials both during the activation process and in reaction conditions. Time resolution from a few milliseconds to a few microseconds (according to the detection mode) makes relevant the XAS *operando* monitoring of structural and electronic modifications of catalysts<sup>207</sup>. In the same way, the quality of the beam lines and of the optics that allows obtaining micronic resolutions, has open new routes as the study of the structural changes at the scale of one particle during catalytic reactions<sup>208</sup>. The coupling of synchrotron techniques with Raman or UV spectroscopies, is very fruitful to obtain complementary information during the limited beam line time.<sup>209</sup>

#### Adaptation of ultra-high vacuum instruments to environmental conditions

This section concerns characterization techniques that requires ultra high vacuum to obtain good spatial resolution and reliable spectral data.

Regarding electron microscopy, two options have been developed. The sample can be placed in an *operando* micro-cell that possesses windows thin enough to be transparent to the electron beam although strong enough to be resistant to gas or liquid pressure (up to one bar). Using standard high-resolution transmission electron microscope (TEM) with aberration correction system, high quality images can be obtained in environmental conditions. The second approach concerns dedicated electron microscope with an environmental chamber and a differential pumping system. These microscopes are commonly called ETEM (Environmental Transmission Electron Microscope) or ESEM (Environmental Scanning Electron Microscope) and are dedicated to imaging in gaseous conditions. They possess a set of diaphragms and differential pumping making possible generating a reduced vacuum where the sample is located while maintaining a high vacuum in the others parts of the microscope. One has to mention the difficulties to analyze on these systems the reaction products that are formed in very small amount. Nevertheless, cutting-edge observations have been obtained in environmental conditions as the changes of the morphology of metal nanoparticles under gas environment<sup>210</sup> or the structure of the active phase under reaction conditions.<sup>211</sup> The French national network METSA (Microscopie Electronique et Sonde Atomique) strongly facilitates the access to these highly specific electron microscopes.

Other techniques that normally require ultra-high vacuum conditions, have been adapted to environmental conditions as near ambient pressure X-Ray photoelectron spectroscopy (NAP) that allows qualitative and quantitative measurements under submilli-bar pressure range.<sup>212</sup>

#### 5.2.3. Current challenges

Interest in liquid-phase reactions over heterogeneous catalysts is growing rapidly, particularly due to the development of processes for biomass conversion into renewable fuels and chemicals. However, the state of working catalyst in liquid phase is in many cases unknown. Most of the efforts in the *operando* and *in situ* spectroscopy have been devoted to gas-solid reaction systems, and study of liquid-solid systems is almost in its infancy. One of the important difficulties is that liquids generally strongly absorb the incident radiation. However, specific liquid phase cells have been developed for different techniques as Raman spectroscopy and TEM allowing identification of the structure of the active phase in liquid condition<sup>213</sup>. Different authors report that IR spectroscopy using Attenuated Total Reflection accessory (IR-ATR) is a possible way to visualize the solid-liquid interface during liquid phase reaction.<sup>214</sup>

The development of chemiometric methods have to be enhanced in order to go further in the analysis of the characterization data to obtain more accurate information from complex spectra<sup>215</sup>, to perform combine analysis issues of several techniques<sup>191</sup> and to analyze more rapidly and more systematically the numerous data issued from the different analytical tools of the *operando* experiments.

#### 5.3. *Ab initio* calculation

##### 5.3.1. Homogeneous catalysis

Regarding homogeneous catalysis, the systems under investigation are generally well characterized, so that crystallographic structures can be chosen as the starting point for a reactivity study. Numerous groups work in the field of theoretical coordination chemistry in France, but catalytic reactions by transition metal complexes, after precursor work in the 80's with the extended Hückel method,<sup>216</sup> were deeply investigated under the impulsion of Odile Eisenstein at University Paris-Sud (Orsay) then in Montpellier,<sup>186d</sup> at higher levels of theory. A large set of reaction (C-H bond activation,<sup>186d</sup> C-C coupling,<sup>217</sup> C-N coupling,<sup>186f</sup> alkene metathesis,<sup>218</sup> CO<sub>2</sub> activation<sup>219</sup> inter alia) with d-block metal catalysts and lanthanides were then investigated by *ab initio* calculations in several French teams inspired by this approach. *Ab initio* calculation in this field are able to elucidate reaction mechanisms and explain selectivities, metal and ligand effects.

##### 5.3.2. Heterogeneous catalysis

In the field of heterogeneous catalysis, the first question to be addressed is the structure of the surface itself, in particular under reaction conditions. Despite the achievements of state-of-the-art characterizations, defining the atomic arrangement at the active site is still an issue, due to the complexity of heterogeneous catalysts. Similarly to homogeneous catalysis, precursor works were performed (in particular in France) in the 80's and 90's,<sup>220</sup> mainly by extended Hückel methods, but the real breakthroughs came

once Density Functional Theory (DFT) and periodic planewaves methods were born. These methods made possible the construction of rather complex models, for a reasonable computational cost, taking into account long range interactions, which are important to be considered at the surface of solids. Of course, such progress was also made possible thanks to the increase of computational resources with advances in the field of supercomputing. In France, such approaches were promoted by CNRS through the Groupement de Recherche (GdR) 12090 (1996-2003) "Dynamique moléculaire appliquée à la catalyse", held by Hervé Toulhoat from Institut Français du Pétrole (now IFP Energies nouvelles), and several partners. One of these was the University of Vienna, namely the group of Prof. J. Hafner, who is at the origin of the popular VASP program.<sup>221</sup> This support from the GdR is probably one of the reason why this code is widely used in the field of heterogeneous catalysis, at an international level. Total and CNRS labs participated to the story of the GdR and are still now very active in the field. Since then, the structure of the surface sites have been investigated in details by French teams for systems like metals (ideal surfaces,<sup>222</sup> supported metals<sup>223</sup>), oxide supports and catalysts,<sup>224</sup> transition metal sulfides,<sup>186a, 186c</sup> in realistic chemical environments. Some of these models serve as reference at an international level.

The calculation of spectral feature appeared to be key to validate the model and assign experimental spectra, in particular in combination with *in situ* and *operando* experiments evoked before. Noticeable are in particular advances made for the characterization of the surface of oxides by infra-red or Raman spectroscopy<sup>224a, 224j, 225</sup> or NMR<sup>224j, 226</sup> for a great variety of surface species. The spectral feature of adsorbed probe was also calculated, providing preliminary insight in the surface reactivity (acido-basicity, redox properties).<sup>222c, 227</sup> The DFT calculation of XANES feature for supported metallic particles<sup>223c</sup> (platinum) or oxide particles<sup>228</sup> (molybdenum oxide) led to the monitoring at the atomic scale of the morphology of the deposits and their adsorption properties.

The reactivity of the surface sites revealed by such approaches was also investigated by DFT calculations for a variety of reactions, with practical applications in refining,<sup>18, 191a, 191b</sup> petrochemistry,<sup>229</sup> fine chemistry,<sup>223d, 230</sup> biomass conversion<sup>231</sup> and pollution abatement.<sup>232</sup> The level of understanding of reaction mechanisms and the still improving quantification of rate constants<sup>233</sup> reached thanks to *ab initio* calculations now makes it a relevant tool in mechanistic investigations. This also holds true for less conventional fields such as photocatalysis,<sup>234</sup> electrocatalysis,<sup>235</sup> catalysis by Metal Organic Frameworks<sup>236</sup> and for supported organometallic chemistry.<sup>186e, 237</sup>

### 5.3.3. Current challenges

Parallel to the challenge of *in situ* and *operando* characterization of catalysts, some current challenges for *ab initio* calculations applied to catalysis are:

- The accurate simulation of the behavior of the catalysts (both heterogeneous and homogeneous) in a solvent. "Implicit" solvation models are often employed to represent the role of the dielectric constant of the solvent on the stability of the catalyst and reaction intermediates, but an explicit simulation is often thought to be required to accurately take into account the effects of specific solute/solvent and surface/solvent interactions. This requires however to perform very costly molecular dynamics calculations,

which were so far performed with success with rather model systems,<sup>238</sup> and give rise to intensive work for transposition to more complex systems.

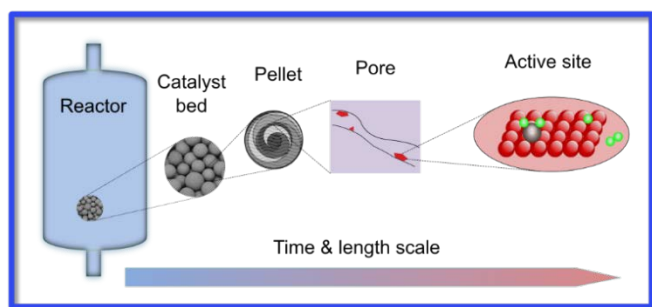
- The accurate estimation, at "chemical accuracy" of rate constants of elementary steps, to make the construction of predictive kinetic models possible, starting from *ab initio* calculations.<sup>239</sup> On simple cases again, the construction of such relevant multi-scale models was shown to be possible,<sup>240</sup> thanks to the comparison with experimental feature. Here again, the transposition to more complex reaction networks needs additional work.

When dealing with prediction of optimal catalysts, a complementary computational approach is to check if the experimental rate constant can be correlated to simple descriptors of the catalyst and of its interaction with the chemical environment. This very active field of research at the international level<sup>241</sup> was successfully initiated by French teams in the 90's<sup>242</sup> and gave conclusive results since then for a large set of reactions, very often catalyzed by metals and transition metal sulfides.<sup>243</sup>

Theoretical simulation can modelize the structure of the active sites, their reactivity and their evolution with the reaction conditions. Hence, parallel between characterization and calculation has a strong added-value because it is of great help to interpret the experimental data, as well as because it confirms the relevance of the calculated models. Tight relationships between experimental and theoretical groups have being developed.

## 6. Catalysis: a kinetic phenomenon

Catalysis is used in the majority of processes in the chemical and petrochemical industry. Inside a catalytic reactor multiple chemical and physical processes take place. They occur at different length and time scales and often in different phases, as depicted in Figure 11 in the case of a fixed bed reactor. The reactants that enter the reactor need to be transported to the active site, where they are transformed into products. This might include transfer from one phase to another and even phase transformations (e.g. condensation, evaporation). This leads to concentration gradients at the reactor and pellet level. The products need to be transported from the active site to the reactor outlet, avoiding their transformation into undesired products. At the same time, heat needs to be supplied or removed from the active site all the way through the reactor wall. These aspects are exemplified in a case study of a mathematical reactor model of a complex three phase reactor.<sup>244</sup> The reactor model serves in further process development as shown in a recent example on the development of an industrial process for the Fischer-Tropsch synthesis.<sup>245</sup> The interplay of the different processes, physical and chemical at different length and time scales is very complex and are often subjects of different disciplines. Traditionally, chemical engineers and physicists have studied heat and mass transfer on the reactor and pellet scale. Researchers in chemical reaction engineering, catalysis, surface science and physical chemistry have studied the kinetics on the macro and micro scale. At the smallest scale surface scientists and theoretical chemists have studied the kinetics of sorption and surface reaction. In the last decades multi-scale approaches have been developed that link the processes at the different length and time scales.<sup>246</sup> Today, Computational Fluid Dynamics (CFD) models containing detailed kinetics on one side and DFT based microkinetic models on the other side of the spectrum are more frequently reported.<sup>247</sup>



**Figure 11** Scheme of a fixed bed reactor showing the different length scales present in a catalytic process.

However, many challenges from better fundamental understanding of the physical and chemical processes at the different scales to the development of numerical models remain, before reactor design integrating all the various length and time scale will become reality.

The need for sustainability in the chemical and petrochemical industry, accompanied by changes in raw materials both fossil and biomass based, drives the development of new, better integrated and intensified processes. For this, more sophisticated reactor models are needed, based on accurate kinetics and transport phenomena.

The proper design of a catalytic reactor requires the knowledge of rate of reaction and selectivity as a function of the operating conditions as well as knowledge of physical transport of heat and matter. Rate expressions based on the *intrinsic* reaction kinetics are used to upscale laboratory data to pilot plant level and industrial units. Kinetic studies do not only aim for reactor design but also aim at the understanding of the reaction mechanism and the design of improved catalysts.

Industrial reactors are nearly always operated in a regime where mass or energy transport affects the product distribution. Thus an understanding of the coupling between transport processes and chemical reactions is essential for the design and scale-up of an industrial reactor. In the last decades computational fluid dynamics has become an important tool in the field of chemical engineering and can allow for the understanding of the coupling between transport processes and chemical reactions. CFD models solve for the spatial distributions of the velocity, concentration, and temperature fields. The full solution of the underlying Navier-Stokes equations is generally computationally too expensive for industrial reactors and simplifications and new numerical schemes are being developed for heterogeneous catalytic reactors, for example on the flow distribution in a catalytic converter.<sup>248</sup> One should not only study the kinetics for the transformation of reactants into products, but also the change of the catalyst itself as a function of time, e.g. catalyst (de)activation. Catalyst lifetime is an important process design variable that often determines the specific reactor or process technology. The modeling of the kinetics of deactivation is increasingly described by more and more fundamental models, which are incorporated into microkinetic models.<sup>249</sup>

The continuous increase in computational power allows for more sophisticated mathematical tools and thus faster and better pro-

cess design. Computational methods are more and more prominent in reactor and kinetic modeling, including catalyst design. On one hand, theoretical chemistry allows mechanistic ideas to be pursued together with the prediction of physical and thermodynamical properties of reactants and products.<sup>240, 246, 247c</sup> On the other side of the spectrum, CFD are used to get an understanding of the role of the hydrodynamics and the heat transfer on the overall reactor performance.<sup>246, 247b</sup> Experimental methods for kinetics and heat- and mass transfer measurements have also strongly evolved over the last decade.

Chemical kinetics is a complicated process, where transport of heat and matter takes place at the same time as the chemical reactions. In order to measure the intrinsic chemical kinetics it is important to choose the reactor design and operating conditions such that the rate of the physical processes are fast compared to the rate of reaction and one can neglect these processes. This becomes quite challenging for fast reactions especially those that take place at high temperatures where additional material constraints occur.<sup>250</sup> Microstructured reactors and other reactor designs with small dimensions and well defined hydrodynamics, such as the annular reactor, have been used to acquire accurate kinetic and transport data for fast or strongly endo- or exothermal reactions.<sup>250, 251</sup>

Two distinct objectives can be identified when a kinetic study is started depending on its use. Firstly, kinetics should provide a "simple" model that can be easily included into a chemical reactor model. This could be called a "chemical engineering" approach where priority is given to an accurate prediction of the "usual" operating conditions and to be able to represent (at least) the experimental data. They can be complex, but usually they are based on pseudo-first order or power law single rate equations<sup>252</sup> or on a full set of mass balance equations.<sup>253</sup> These models can be selected in case of lack of detailed data as often observed in raw biomass conversion.<sup>254</sup> They can be also helpful to determine relations between catalytic structure and catalytic activity.<sup>255</sup>

Secondly, the development of a full comprehensive kinetic model can be pursued to obtain a deeper comprehension of the mechanism. This requires usually more complex experimental tools (dynamic experimentation, isotopic labeled substrates, ...) and mathematic methodologies (integration, parameters adjustments, statistical analysis ...). At the same time, a better predictability of such models is expected.

Steady-state kinetics mainly give information on the rate-determining step, providing little or no information on the faster quasi-equilibrated steps. Transient experiments provide much more detailed information. Their drawback is the need for more dedicated experimental tools and more advanced kinetic modeling. Several transient experimental approaches have been developed, such as TAP and SSITKA,<sup>256</sup> but they are mainly restricted to gas/solid reactions. Recent examples are methanol to olefins,<sup>257</sup> deNO<sub>x</sub><sup>258</sup> and Fischer-Tropsch synthesis.<sup>259</sup> Modeling of transient kinetic data is generally based on sequences of elementary steps without any a priori assumptions on the rate determining step, or other simplifications.

This modeling approach is more and more applied also to describe catalysts performances under steady-state conditions, known as microkinetics.<sup>246,248</sup> It provides detailed insights into the reaction mechanism and can be very helpful in catalyst development. As no rate-determining step is assumed, these models will be more robust over a larger range of operating conditions and will better predict the reaction dynamics. These models allow to

incorporate kinetic information from different experiments, such as surface science or temperature-programmed experiments, or from computational chemistry. Examples of this approach are DeNO<sub>x</sub> by NH<sub>3</sub><sup>260</sup> and CO oxidation in catalytic converters.<sup>261</sup> Microkinetics is also applied increasingly by theoretical chemists to link DFT studies with experimental kinetic data.<sup>240,257,262</sup> Similar to microkinetic modeling is the single event method, especially oriented towards complex networks involving reactions of hydrocarbons.<sup>263</sup> However, alternative approaches are also still being developed to deal with large complex reaction mixtures.<sup>264</sup>

Microkinetic modeling also provides a link with rational catalysts design. By correlating the kinetic parameters with specific catalyst descriptors structure-performance relationships can be established giving then a feedback to catalyst synthesis. This approach has been applied for the development of catalysts for the oxidative coupling of methane<sup>265</sup> as well as for hydrogenation or HDS.<sup>243b,266</sup> Combined with high-throughput catalyst testing it can be a powerful tool for accelerated catalyst development. Two national projects are devoted to the efficient developments of new catalysts: 1) the platform REALCAT<sup>71</sup> is actually equipped with robots for automated synthesis of catalysts and biocatalysts, rapid characterization tools, and ultra-fast tools for catalytic performance evaluation. This integrated combination of skills and technologies enables high-level R&D catalysis development programs on hot topics including environmental and economic issues. The versatility of the platform also offers the possibility to run projects in the field of materials development; 2) the SYSPROD<sup>267</sup> project (Systemic multi-scale approach for industrial production processes), part of the AxelOne platform aims to cover the complete spectra of tools essential to span the entire innovation cycle from fundamental scientific research to industrial scale-up. The SYSPROD project combines innovative tools from discovery (TRL 1-3) to up-scaling (TRL 4-6) in order to boost innovation in the development of catalysts from conception to pilot scale preparation and testing in real conditions. Within this platform, a structure/activity correlation between catalyst activity (including kinetic parameters) and descriptors will be established to optimize the design of the catalysts at the lab scale, before extrapolation of the production.

Structure-performance relations are important for better understanding and rational design of catalysts. In the last decades, efforts have been made to perform simultaneously catalyst characterization with activity testing to establish structure-reactivity relationships. *Operando* studies combine characterization of catalytic materials under reaction conditions with simultaneous monitoring of reaction kinetics. However, a large number of these combined studies concentrate more on the characterization perspective than on the validity of the obtained kinetic information.<sup>268</sup> Proper design of spectroscopic cells that are suited for intrinsic reaction kinetics is a challenging task.<sup>269</sup> It is important to check the kinetics measured in an *operando* cell with those of a better suited kinetic reactor, before quantification of the rate of surface intermediates can be performed.<sup>270</sup> An example of spatially resolved IR analysis for the kinetics of CO oxidation is reported by C. Daniele et al.<sup>271</sup>

From the above analysis it is clear that kinetic studies are key to mechanistic understanding, catalyst optimization and reactor design, and it should go hand in hand with detailed characterization and advanced synthesis. However, detailed kinetic studies are rather rare in the literature. A search of the Scopus database with

the keywords “kinetic modeling” or “kinetic study” or “microkinetics” and “catalyst” from 2006–2017 lists approximately 6000 publications, presenting only 2% of the total list of catalysis papers. A part of these studies presents only very limited kinetics (just an apparent activation energy, or a reaction order). The statistics per country show that France contributes 4.5% to research on kinetics in catalysis. Research on reaction kinetics of catalytic reactions can be found in all major catalysis and most chemical engineering laboratories, both industrial and academic, throughout France. The importance of chemical kinetics from an industrial perspective in Europe is reflected in the Eurokin consortium, active in the field of chemical kinetics since 1998 and including two French members.<sup>272</sup>

In term of perspectives, new challenges for kinetic as a disciplinary and/or as tools, from our point of view, are:

- Better predict *in silico* kinetic constant as developed decades ago with gas-phases kinetics (combustion for example where automated network can be generated and tested). This could be done in line with recent works presented earlier in the paper based on DFT/molecular dynamics approaches for example. Progress is expected also from *in operando/in situ* experiments able to provide quantitative estimation of “active sites”.
- Improve physico-chemical interaction between substrates and catalytic surface or active sites for micro-kinetic modeling issues. This is more critical when the reaction is involving three-phase media requiring new dynamic tools for kinetic investigations able to deconvolute mass transfer, residence time distribution of separators and chemical kinetics.
- Biomass deconstruction and catalytic conversion requires deeper analysis in term of kinetics to find new descriptors and stop to limit kinetic analysis to pseudo-first order approach. This could be inspired by studies done in petroleum fractions hydrotreating for example with continuous lumping approaches<sup>264</sup> or also structural kinetic based on NMR quantitative data. A closer interaction with analytical sciences could then be very helpful.

## 7. Complementary approaches to conventional heterogeneous catalysis aiming at improving the efficiency and re-use of catalysts

After the previous overlook of several key facets of heterogeneous catalysis, this part rather aims at briefly highlighting some complementary approaches mostly developed in the field of liquid-phase catalysis. Homogeneous processes generally allow higher activities, better selectivities and milder reaction conditions in terms of temperature and/or pressure compared to their heterogeneous counterparts. The mechanistic studies are also generally much easier which is of great concern for the optimization of catalytic systems. Despite this, it has to be reminded that homogeneous or quasi-homogeneous catalysts are less widely used in industry for large scale production than heterogeneous ones specially in the refining industry. In chemistry, the main reason for such discrimination has long been primarily related to an easier implementation of the catalyst recycling and/or continuous operations in heterogeneous conditions.

However, homogeneous catalysis plays a crucial role, especially as far as the preparation of fine chemicals is concerned. Due to their higher overall cost, homogeneous processes are of particu-

lar relevance for the preparation of higher added-value compounds such as pharmaceuticals or agrochemicals but can also be used for some bulk chemical synthesis due to their differentiated performances. Metathesis is one of the good illustration. Hence, some homogeneous catalytic systems found applications in vegetable oil transformation combining high productivity and high selectivity. In this field, the main objectives are the direct transformations of abundant natural products represented by C18:1 fatty acid (oleic acid) derivatives and unsaturated terpenes into valuable monomers for polymer production, and the synthesis of high added-value fine products upon cross-metathesis with ethylene (ethenolysis),<sup>273</sup> electron-deficient olefins such as acrylonitrile,<sup>274</sup> acrylates,<sup>275</sup> methacrylates and acrylamides,<sup>276</sup> and alkynes.<sup>277</sup> The preparation of new robust ruthenium complexes including sterically encumbered catalysts for application in membrane separation in organic solvents is also sought.<sup>278</sup> It also noteworthy that two relevant olefin metathesis processes have been recently reported. The first one concerns a soluble ruthenium olefin metathesis catalyst<sup>279</sup> that performs the conversion of linear alpha-olefins to longer internal linear olefins with high selectivity (>99%) under neat conditions at low loadings (50 ppm) and without the need of expensive additives such as benzoquinone derivatives.<sup>280</sup> This robust catalytic process allowed to efficiently and selectively re-equilibrate the naphtha fraction (C5–C8) of a Fischer–Tropsch feed derived from non-petroleum resources to a higher-value product range (C9–C14), useful as detergent and plasticizer precursors.<sup>281</sup> The second one concerns a commercially available homogeneous ruthenium olefin metathesis catalyst<sup>282</sup> that performs the transformation of methyl oleate at 85% technical grade (isolated from very high oleic sunflower oil) into corresponding metathesis products (9-octadecene and dimethyl 9-octadecenedioate, respectively) with only 5 ppm of catalyst loading, in neat condition, within 15 min. of reaction in the presence of 1 mol% of bleaching earth.<sup>283</sup> This efficient process was successfully conducted up to 200 kg scale with a remarkable TON of 200 000.<sup>284</sup>

Homogeneous catalysis represents a vast and extremely rich and versatile field of research that will not be dealt with in details in this review dedicated to heterogeneous catalysis. Only two recent breakthroughs of particular concern for pharmaceutical applications will be discussed here. Both target to the reduction of the contamination of reaction products by metals for economic, health and/or environmental reasons which constitutes a common interest with the field of heterogeneous catalysis. Since the early 2000s, there is indeed a downward tendency to develop homogeneous catalysts based on using abundant, low-toxic and cheap metals. Catalysts developed with these metals are indeed much more relevant and attractive for large-scale applications than systems involving precious metals. Therefore, a large panel of homogeneous catalytic systems based on transition metals such as copper,<sup>285</sup> iron,<sup>286</sup> manganese<sup>287</sup>... or based on alkaline earth metals (e. g. calcium)<sup>288</sup> were reported to promote a wide range of transformations including cross-coupling reactions<sup>289</sup> and arylations of *N*-, *O*-, *C*-nucleophiles,<sup>290</sup> alkene or ketones hydrofunctionalisations,<sup>291</sup> various reductions (ketones, nitro compounds, CO<sub>2</sub><sup>292</sup>...), C-H functionalisations,<sup>293</sup> polymerizations (olefins, cyclic esters<sup>294</sup>), radical processes<sup>295</sup> and many other transformations possibly in their asymmetric versions following Kagan's pioneering work.<sup>296</sup> Noteworthy, while some of these reactions are already applied on the industrial scale (e. g. arylations of nucleophiles<sup>290</sup> and polymerizations<sup>294</sup>), other are still in their infancy

at the laboratory scale and will certainly, at least for some of them, know a strong development in a near future.

The other breakthrough aims at avoiding metals through the development of organocatalysts, i.e. the use of usually small organic molecules to catalyze reactions normally needing metallic species. These types of, mostly homogeneous, catalysts provide a much safer way of obtaining fine chemicals without the risk of metal contamination of the end-product for specific applications as pharmaceuticals. It also avoids the frequent high cost of ligands and/or metals necessary to obtain active catalytic systems. This particular field of research has tremendously grown for the past 20 years leading to a fast and extremely large development of these catalysts, illustrated by the increasing number of published reviews and books.<sup>297</sup> Many types of organocatalysts have been developed and reported: Lewis bases and acids, Brønsted bases and acids.<sup>298</sup> These catalytic systems were proven very active in a large range of reactions including the Mannich reaction<sup>299</sup> or the direct transformation of CO<sub>2</sub> into cyclic carbonates<sup>300</sup>, reduction to aminals<sup>301</sup> or hydroboration via the formation of frustrated Lewis pairs<sup>302</sup>. Organocatalysis is also emerging in polymerization reactions either for polymer synthesis thus avoiding the use of isocyanate in polyurethane synthesis<sup>303</sup> or to permit metal-free synthesis of polyethers for example.<sup>304</sup> One of the strongest area of organocatalysis has become its use in enantioselective transformations where organocatalysts advantageously replace costly precious metal ligands and numerous examples can be found in the literature.<sup>305</sup> The extremely rich field of organocatalysis also allowed the emergence of new types of catalysts such as silylene-based catalysts able to act like metal centers to perform oxidative additions,<sup>306</sup> or new heterogeneous or supported organocatalysts which conjugate the advantages of heterogeneity with metal-free materials.<sup>307</sup>

In addition, the combination of homogeneous chemocatalyst together with biocatalyst (hybrid catalyst) has been recently reported to valorize biobased saccharides into value-added chemicals.<sup>308</sup>

Apart studies on catalytic systems involving safer and cheaper metals and organocatalysts,<sup>309</sup> another common challenge for researchers of the homogeneous and heterogeneous catalysis communities is the search for greater catalyst efficiency while ensuring a strong re-use potential. While researchers in homogeneous catalysis tend to implement immobilization pathways for efficient soluble species leading to their definitive or temporary heterogenization, researchers in heterogeneous catalysis will tend to use active phases which have already proved their efficiency in solution in order to develop more efficient heterogeneous catalysts. This part will focus on the main immobilization strategies implemented and will shed light, when possible, on collateral advantages that can be targeted such as support effects or the influence of the respective location of the active phases on the global performance of the resulting catalyst.

### 7.1. Biphasic catalysis with nanoreactors

Biphasic catalysis is based on the use of a catalyst that is soluble in one of the phases while substrates and products are mainly soluble in the other. Under these conditions, simple decantation allows the re-use of the catalyst quite easily. The most known industrial process is the "oxo process" developed by Ruhrchemie / Rhône Poulenc. This relies on the use of a water-soluble rhodium complex and affords butanal from the reaction of propene with syn

gas. Unfortunately, the low affinity of longer alkenes for the aqueous phase limits the development of purely biphasic systems for these substrates. Progress has recently been obtained with new solvents, in particular with ionic liquids (Difasol® process)<sup>310</sup> and fluorinated solvents. The introduction of surfactants has also been considered but oil/water micelles are self-assembled nano-objects suffering from their fluctuating nature and the fact that they can over-swell giving rise to stable emulsions leading to complications for the final separation and loss of catalysts. An interesting approach recently developed aims at using stable spheric nano-objects (core-crossed-linked micelles), based on one polymer molecule, made of a hydrophobic core and a hydrophilic periphery compatible with the reaction medium, essentially water.<sup>311</sup> These structures as opposed to micelles which exchange their contents upon inelastic collisions allow an efficient partitioning between the catalyst and the reactants similar to that obtained in conventional biphasic system. In this case, the authors have shown that it is possible to control the size of the thus formed nano-objects, the thickness of the hydrophilic crown and the quantity of phosphine ligands to be integrated outside on the periphery or just within. Tested in the hydroformylation of 1-octene which is a reaction difficult to carry out according to the purely biphasic process (no surfactant added), these new catalysts allowed TON values of 700 h<sup>-1</sup> without excessive leaching of the metal and have mainly led to the linear isomer of nonanal. Reactants could be recovered by phases separation at the end. Other uses of these nano-objects may involve different catalysts with antagonistic properties immobilized inside and outside.

## 7.2. Recyclable homogeneous catalysis

Unlike the previous approach, reactions are performed here in one-phase system keeping the advantages of homogeneous catalysis and, at the end, separation is induced by an external stimulus such as the variation of temperature (thermomorphic catalysis) or the addition of a non-solvent. Either soluble catalysts precipitate without prior modification (for example, multi-charged polyoxometalates) or they need to be immobilized on structures like polymers or dendrimers whose separation through precipitation is more efficient. Examples of thermomorphic catalysts recently developed by French teams include the anchoring of an iridium carbene ((NHC)IrCp\*Cl<sub>2</sub>) on polyethylene<sup>312</sup> which is soluble in hot polar solvent and insoluble upon cooling. The resulting entity was shown to be effective for catalytic hydrogen/deuterium exchanges in organic compounds targeted for *in vivo* studies. Such thermomorphic catalyst showed similar behavior to its constitutive carbene and could be recycled twice without loss of activity and of iridium.

Functionalized dendrimers concentrate in a single place of nanometric size a large quantity of organic functions which can act as so many potential organocatalysts<sup>313</sup> or ligands for metallic complexes<sup>314</sup> or nanoparticles.<sup>315</sup> For these reasons, they have recently been the subject of numerous studies dealing with catalysis. Another advantage of such nano-objects deals with their dimensions which are suitable to envisage their recovery by nanofiltration. However, the most frequently used method remains their precipitation by the addition of a non-solvent.<sup>316</sup> Besides, another advantage, called catalytic dendritic effect, could be emphasized in many applications.<sup>317</sup> This is apparently related to the proximity or to the pre-organization of the active phases as evidenced through positive spillovers on the yield, the selectivity or on the

reaction rate. Demonstration of this effect is often carried out by comparative tests involving the same number of free metal or organo-catalysts in solution. It should be noted, however, that in other examples, the dendritic effect may result in negative consequences, the nature of the effect being for the moment difficult to predict.

Another possibility leading to an easy recycling of the homogeneous catalysts consists to use them in expanded supercritical fluids, *i.e.* mixtures with organic solvents. Separation of the catalysts and reactants at the end of the reaction is then induced by lowering the pressure which indirectly modifies the polarity of the reaction mixture.<sup>318</sup>

## 7.3. Supported catalysis

The other important trend in liquid phase reactions aims to develop heterogeneous catalysts through the immobilization of soluble complexes,<sup>319</sup> enzymes,<sup>320</sup> pre-formed metal nanoparticles<sup>321</sup> or organic functions (organo-catalysts<sup>322</sup>) on solid supports. Such concept is not new. It has been considered for a long time that this approach could lead to more defined heterogeneous catalysts. Recycling of the anchored species is usually facilitated but very often results in some deactivation compared to the non anchored ones.

Examples of catalysts immobilization on silica supports using a covalent route are the most described. Materials with rather large specific surfaces are sought for this application, especially silica with structured mesopores with often the idea to get some benefits of the confinement in addition to the recycling aspects. Regarding the grafting procedures, these generally involve the functionalization of the starting complexes or their ligands by trialkoxysilane groups that react with the surface silanols.<sup>323</sup> The anchoring process can also be carried out according to a two-step procedure involving first a pre-functionalization of the support and of the complex and then the reaction of both functions. For the latter strategy, stable amide-type bonds<sup>324</sup> or triazoles<sup>325</sup> obtained through click chemistry are the most used to generate a linker. In many examples, the catalytic tests of the heterogenized catalysts emphasize their relative stability through the implementation of several runs carried out consecutively in batches. In general, comparisons of the reactivity between the supported species and their analogues in solution are also proposed. One of the benefits of heterogenized catalysts lying in the possibility to carry out reactions in solvents where the catalyst precursor is not soluble alone,<sup>319b</sup> such comparisons are sometimes not possible. Otherwise, this type of comparison (with the same solvent) very often indicates a lower reactivity on support often attributed to problems of diffusion of the reactants. This is particularly true when bulky entities are anchored. Unfortunately, such conclusions are not always supported by comparisons of different silica supports with variable two- and three-dimensional porosities. Other factors may be suspected, for example a more difficult access to the active site than in solution. Indeed, the relative location of the grafted entities with respect to the surface is essential for example in the case of enzymes and has to be tighter controlled. The confinement of active species does not lead always to an improved selectivity, as observed recently during the grafting of cyclopropanation catalysts based on copper(I) complexes.<sup>319b</sup> Indeed, irrespective of the type of silica on which they were grafted (Aerosil 380 and Davisil or silicas with structured mesopores), the immo-

bilized Cu(I) catalysts afforded quasi-equivalent enantio- and diastereo-selectivities in the reaction of a prochiral alkene with ethyl diazoacetate used as a source of prochiral carbene. The effects of the concentration and organization of the positioning of the active phases in the manner described above with the dendrimers has also been emphasized with heterogenized catalysts too. Comparing epoxidation catalysts obtained by grafting polyoxometallates either in an ordered manner on silica supports with an hexagonal distribution of the porosity (SBA-15 type materials) or in a more disordered one, on meso-cellular foams, it turned out that the first materials gave rise to better performances despite their expected lower diffusing properties.<sup>319a</sup> On a case-by-case basis, the presence of residual silanol groups on the surface of the grafted silica can be detrimental. In these latter cases, it can be necessary to substitute H atoms by SiMe<sub>3</sub> groups<sup>326</sup> in order to adjust the hydrophobic / hydrophilic balance as a function of the chosen reaction solvent. In other words, the reagents must be able to access the active sites and the products to be desorbed as soon as possible for selectivity issues.

Other approaches consist in the deposition on similar solid supports of stationary phases in which homogeneous catalysts are soluble but not the solvent (mobile phase). In this case, the reagents diffuse into the stationary phase and, after reaction, the products are extracted by the mobile phase.<sup>327</sup> This concept has been successfully applied with stationary phases such as water<sup>328</sup> (Supported Aqueous Phase Catalysis / SAPC) and especially ionic liquids (Supported Ionic Liquid Phase Catalysis / SILP<sup>329</sup>). An important advantage in the second case is the minimization of the quantities of ionic liquids used. Numerous examples of the SILP version involve CO<sub>2</sub> under pressure as a mobile phase.<sup>330</sup>

In liquid phase applications, the stability of the support with respect to leaching is an essential parameter as well as its ability to be functionalized, but other effects can be sought, hence the use of the term "non-innocent" supports. In surface organometallic chemistry<sup>331</sup> approaches where metals are directly coordinated with surface silanol groups (case of silica), the support will truly act as a ligand. The influence of the support can also manifest in a less direct manner on complexes associated via organic linkers. Such an example has been described recently in the case of nickel (II) complexes grafted via amide bonds onto multilayer carbon nanotubes that are used as catalysts for the polymerization of ethylene.<sup>332</sup> Clearly, the resulting materials proved to be much more efficient than the corresponding soluble complexes and also allowed the production of polymers with much higher molecular weights. These effects are not related to the modification of the starting complexes for the purpose of immobilization. In fact, the support was shown to tune the stability of the supported complexes by both electronic and steric effects. In other interpretations, it is even argued that the very good thermal conductivity of the carbon nanotubes allows to counteract local heating related to the exothermicity of the polymerization reaction.

Decantation methods based on sedimentation or centrifugation pathways are logically those most used in the case of immobilized catalysts. However, the low density of some of these supports is an important drawback. In the recent literature, one important way to improve separation is to consider supports having magnetic properties. The most commonly described are superparamagnetic iron oxides particles characterized by low remanent magnetization (magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>)), but it is also possible to find some papers directly exploiting metal particles, for

example Fe(0) or Co(0) particles, more sensitive to magnetic fields. The oxides are handled directly or coated with a layer of silica while the metals are typically surrounded by carbon layers. Different types of catalytically active phases (metal nanoparticles,<sup>333</sup> organocatalysts, metal complexes, etc.) have been anchored on these supports, including dendrimers or polymers<sup>334</sup> whose advantage consists in increasing the catalysts loading. Immobilization strategies are often based on covalent bonds with the particles but weaker links can be exploited such as reversible π-π interactions between e.g. pyrene-tagged dendritic Pd based catalysts and Co/C nanoparticles.<sup>335</sup> In that case, catalysis was shown to proceed in the homogeneous phase at elevated temperatures but upon cooling, functionalized dendrimers were stacked again to the nanoparticles and the entire system could be recovered easily by magnetic decantation. According to the authors, up to 12 iterative runs could be performed without significant loss of activity.

Reduced energetic expenses related to separation operations are highly desired for chemical industry applications. One interesting solution is based on the transposition of batch processes into continuous flow ones. The latter are less widespread in solid/liquid than in solid/gas catalysis processes but enormous progress have been made in recent years in this area as reported by very recent reviews.<sup>336</sup> Large scope of reactions has been considered up to now and prototypes of micro-reactors are even used in the pharmaceutical sector. These reactors present very interesting advantages such fast heat and mass transfer allowing the safe implementation of reactions known to be ultrafast, exothermic and/or to involve unstable intermediates. Organocatalysts, organometallic complexes, metal nanoparticles or enzymes have already been implemented using strategies based either on packed-beds, monoliths<sup>337</sup> or wall-coating but a lot of work is still needed in order to increase the lifespan of the supported catalysts and to combine different micro-reactors together. Some examples also involve soluble forms of catalysts.<sup>338</sup>

## Conclusion

Catalysis is a crucial discipline that is closely interwoven with numerous scientific disciplines and within the last past 10 years, the French catalysis community has been deeply reorganized to tackle the new scientific, technological and environmental challenges faced by catalysis. As described in this review, novel institutes and networks were thus created and catalysis is now often approached from a systemic and multidisciplinary point of view. In addition, the relationship between academia and industry (SME's and large companies) has been strongly strengthened not only to better identify the scientific hurdles faced by catalysis at a fundamental level but also to facilitate or accelerate the implementation at a larger scale within collaborative innovation platforms. This new positioning of the French community offers great opportunities to develop collaborative and innovative researches in the context of an international competitiveness and growth and fits well with the European Roadmap on Catalysis developed by the European Cluster on Catalysis.<sup>339</sup>

Beside research, much effort is also paid to education, scientific events and opening to a general public in order to attract young scientists and to form the next generation who will work on the future challenges facing by catalysis and more largely by our Society.



**Keywords:** Catalysis • French roadmap • Chemicals • Energy • Environment.

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