Introduction

In the context of the establishment of a strong bio-economy based on biorefineries, heterogeneous and homogeneous catalysis (the so-called ‘chemo-catalysis’) possess an important role. Chemo-catalysis, interwoven with biotechnologies and thermochemistry, enables designing a network of chemical transformations for upgrading biomass-derived compounds to a variety of chemicals, such as in the large scale European project ‘EuroBioRef’ we leaded. In most of the cases, chemo-catalysis is employed to convert the so-called ‘platform molecules’ to added value products and/or intermediates in the biorefinery, which produce not only fuel, but also chemicals, materials, food, feed, etc. These platform molecules, which correspond to the ‘commodities’ in a petro-based refinery, are obtained by more or less extensive preprocessing of biomass raw materials, including fractionation/extraction/purification steps with, when needed, deconstruction of the natural polymers followed by bioprocessing to yield short molecules with most commonly less than 6 carbon atoms. Obviously, in the case of technologies based on fatty compounds, the base molecules are longer, usually up to about C24 (fatty acids, esters, etc.). As suggested above, such technologies are part of the so-called ‘biomass valorization’ concept towards a sustainable society. According, e.g., to the directive adopted by the ‘Industry, Research and Energy Committee’ of the European Parliament on the 11th of September 2008 “Biomass” means the biodegradable fraction of products, waste and residues from agriculture (including vegetal and animal substances), aquaculture, forestry and related industries, the separated collected biodegradable fraction of industrial and municipal waste as well as wastewater sludge. In the context of biorefineries, its valorization consists, in addition to ‘conventional’ food, feed, heat, clothing, etc., applications, in designing more advanced outputs towards chemicals, fuels and materials, etc., based on the development of sophisticated transformations using biotechnologies and/or chemistry.

In this paper, we mainly describe the transformation...
of some C1 to C6 molecules, most of them being actually considered as ‘platform molecules’ in an authoritative U.S. Department of Energy list proposed in 2004 and further updated in 2010. For each family of molecules, which are defined according to the number of carbons of the substrates they are composed of, we review the catalytic transformations we realized in perspective within the global context and the current trends reported in the literature.

Further, in a second part, we give an overview of some important technological bricks we are developing to improve biomass-derived molecules valorization, namely a novel efficient catalytic system for dehydrogenation reactions, which opens interesting perspectives for downstream cascade applications to a variety of chemicals, a new and unique high throughput platform integrating synthesis, characterization and performances evaluation of chemo-, bio- and hybrid catalysts (the REALCAT platform), and, finally, an advanced application of reactive distillation.

2. Chemical Transformations

2.1. C1 Molecules—biogas and methanol

Methanol is conventionally produced by conversion of syngas, which is usually derived from fossil resources such as methane or coal. Recently, some so-called ‘biomethanol’ is synthesized in units using biomass-derived syngas as a raw material. This thus opens the way to the sustainable production of methanol, which can then be considered as a platform molecule with perspectives of downstream chemical applications. We actually developed catalysts for the methanol conversion to 1,1-dimethoxymethane and dimethylether. This will be described in the followings after a first part concerning a new technology we developed to efficiently use biogas as a source of syngas and thus possibly for biomethanol production.

2.1.1. Biogas Conversion to Syngas

Like most alkanes and irrespective of the source of methane—i.e., from biomass or fossil resources such as natural or shale gas—valorization of biogas towards more functionalized molecules must take into account the low reactivity of the starting molecule and the usually stronger reactivity of the products. This results in processes usually exhibiting low yields due to both low activity and low selectivity. This however opens a lot of opportunities for progress in catalytic processes for which two approaches can be undertaken, namely (i) acting on the catalytic active phases, and (ii) acting on the operating conditions and particularly on the way the reactant and the catalyst are contacted. Indeed, structured reactors, membrane reactors or non-steady state operating reactors can bring significant improvements for such reactions.

Biogas is produced by anaerobic fermentation of biomass giving a mixture containing essentially CH₄ and CO₂. According to the nature of the biomass used, it may also contain important amounts of impurities including H₂S, which have to be taken into account in the valorization process. Due to the presence of both CH₄ and CO₂, dry reforming of methane (DRM) is certainly one of the most interesting valorization processes, but also among the most challenging ones. Indeed, DRM being an endothermic reaction, the selectivity and the stability of the process need to be optimal in order to allow it to become a sustainable economic way of valorization of methane towards syngas. Two difficulties need to be overcome. First, the selectivity is often lowered by the reverse water gas shift (RWGS) reaction between the produced H₂ and CO₂. This lowers the H₂/CO ratio, which, in the optimal conditions reaches 1 for the DRM reaction. The second drawback is the low stability of the system essentially due to carbon coking of the catalysts at the needed elevated reaction temperatures.

Our research in this field is oriented in two ways.

Fig. 1 Simplified Transformation Network Gathering Some Catalytic Transformations We Successfully Performed (plain arrows) Also Indicating Transformations We are Not Involved in But that Give Us Substrates for Further Upgrading or Some Possible Interweaved Important Routes (dashed arrows)
The first one consists in developing new or better active phases for dry reforming. In particular, nickel is known to be very efficient for methane activation reactions and, more especially, in DRM, but tends to generate highly coking catalysts. Incorporating Ni\(^{2+}\)-ions in structures such as spinels may result in a better dispersion of the active nickel species leading to interesting compromises between stability and catalytic activity. In particular, we have investigated the NiFe\(_2\)O\(_4\) system, which is an inverse AB\(_2\)O\(_4\) spinel as a precursor of DRM catalysts. While the performances are still limited, we have shown that the preparation method and some pretreatments may considerably affect, and improve, the catalytic activity and stability of such materials\(^{[22,13]}\).

Recently, we have also evidenced that the dispersion, or better incorporation, of such materials in a silica matrix considerably improves the activity, the selectivity and the stability of the catalytic system thanks to the acid properties of the support\(^{[14]}\).

The second way for improving the DRM of biogas is to focus on the reactor design. We have recently developed a new process based on a new non steady state technology, which allows us to radically overcome any RWGS reaction and thus obtaining the nominal selectivity for DRM. The process also continuously regenerates the catalysts, removing any carbon deposition, which leads to remarkably stable performances, which is the object of a patent filing of which the results will be disclosed in due time.

2.1.2. Methanol Upgrading

Methanol is the simplest molecule of the alcohols family with many applications. It can be used, for instance, as a feed for direct methanol fuel cells (DMFC) to power, e.g., laptop computers and electronic devices on aircraft boards\(^{[15,16]}\). In the followings, we describe some possible advanced applications thanks to catalytic upgrading.

(a) Methanol conversion to 1,1-dimethoxymethane

Methanol can be used as a starting material in the synthesis of chemicals including dimethylether, methyl t-butyl ether (MTBE), acetic acid, formaldehyde, and olefins. Among them, formaldehyde, MTBE, and acetic acid are major methanol-derived molecules, which contribute to 35, 25 and 9 % of the methanol downstream use, respectively\(^{[17]}\). Formaldehyde is a versatile molecule, which finds a lot of direct applications, e.g., as a solvent, but it is also classified as a carcinogenic, mutagenic and reprotoxic (CMR) substance. In some cases, it can be beneficially substituted by the much safer 1,1-dimethoxymethane or ‘methylal’ (hereafter referred to as DMM). This acetal is currently obtained from methanol in a two steps process. The first one consists in the oxidation of methanol to formaldehyde using conventional FeMo- or Ag-based catalysts, while the second step consists on a reaction between the as-obtained formaldehyde with methanol through a dehydration-condensation reaction\(^{[18,19]}\). In order to reduce the CAPEX and the production costs when envisioning an industrial application, a single step transformation would however be highly desired.

The direct conversion of methanol to DMM actually needs a bifunctional catalyst with redox and acid properties to sequentially combine the aforementioned two steps. Note that, over MoO\(_3\)/TiO\(_2\) model systems, we highlighted the beneficial effect of an adequate balance between redox and acid properties of the catalysts on activity, and showed that it was realized for a MoO\(_3\) species quasi-monolayer\(^{[20]}\). This reaction has driven much attention in the recent years, and a variety of heterogeneous catalytic systems were applied, such as molybdenum-based catalysts\(^{[21–23]}\) heteropolyacids (HPAs)\(^{[25,26]}\), vanadium-based catalysts\(^{[27–31]}\), oxides of rhenium\(^{[32]}\) and of rhenium\(^{[33–37]}\). In a first fundamental approach, we chose the latter systems (the Re-based ones) as model catalysts, and we elucidated the reaction mechanism. We especially evidenced the necessity of the presence of two kinds of rhenium species (Re\(^{+6}\) and Re\(^{+4}\)) spatially close one to another in order to get a high selectivity to DMM\(^{[39]}\). However, while being actually quite efficient, the Re-based catalysts suffer from deactivation due to Re depletion by a reduction/volatilization mechanism. We then identified a more robust catalyst hereafter named as ‘AR01,’ which is an amorphous material of the global composition Mo\(_{12}\)V\(_3\)W\(_1\)Cu\(_1\)Sb\(_3\)O\(_x\). AR01 is and efficient and stable catalytic system in a wide range of conditions (e.g., temperature, methanol concentration, etc...) without any drastic loss in DMM selectivity\(^{[39]}\). In 2008, this catalyst showed the best performances among all the references published in this field, but we discovered later another catalytic system even more efficient. It consists on a material based on iron and molybdenum oxide\(^{[40]}\). This FeMo catalyst is conventionally used in the industry to produce formaldehyde from methanol, with traces of DMM as by-product, which was a hint showing that such a catalyst behaves the ad-hoc properties to also form DMM. After optimization, we discovered that changing the feed composition from the conventional 7 mol% of ethanol industrially used to form formaldehyde to 40 mol% enabled a drastic change in selectivity, which remarkably shifted from formaldehyde to DMM. Such an effect was not observed on other types of catalytic systems. In terms of productivity, the FeMo catalyst is the best ever reported\(^{[41–43]}\).

Figure 2 underlines the particular behavior of the FeMo catalyst compared to other catalytic formulations so far known for their efficiency in the methanol direct acetalization reaction. We investigated deeply the FeMo system, and LEIS allowed us to evidence that both Mo and Fe atoms are exposed to the upmost surface of the catalyst. In addition, EPR suggested that the redox properties of the system could be attributed to
the Fe species, which most probably act in the reaction through a Mars-van Krevelen mechanism44). Further, we also found that the acid properties of the catalysts were created in Operando by dehydroxylation of the surface with further creation of anionic vacancies acting as Lewis acid sites.

(b) Methanol conversion to dimethylether

Dimethylether (DME) can find applications, e.g., as a blend in diesel fuels and gasoline, or as a propellant in sprays. It is conventionally obtained from syngas-derived methanol, which is further condensed to DME over an acid catalyst, even if some research efforts concentrate on its direct synthesis from syngas over bifunctional catalysts.

We demonstrated that mesostructured aluminosilicates are efficient in the reaction of DME synthesis from methanol45). We evidenced a correlation between the reactivity of the solids and their structural features and their acidic properties, and we could obtain the remarkable performance of a 80 % methanol conversion at 598 K with 100 % selectivity to DME.

2. 2. C2 Molecule —ethanol

Ethanol is currently produced both as a petrochemical, through the hydration of ethylene and, via biological processes, by fermenting sugars with yeast. Ethanol, the most important C2 platform molecule issued from biomass, is massively produced at the commercial scale starting from renewable feedstock46),47). Therefore, it can be considered as a key compound in biorefineries. Even if the main part of the production is currently obtained by a 1st generation fermentation process, ethanol can also be produced from abundant lignocellulosics biomass such as municipal or agricultural wastes (cereal straws, sugarcane bagasse, rice hull, timber species, etc.), forest residues, fast growing trees, or grasses grown in marginal lands, and could then be produced in even more substantial amounts than today48),49). There are three markets for ethanol: beverages, fuels and chemical products with numerous industrial applications (pharmaceuticals, cosmetics, inks, paints, etc.). It has a long history as a fuel for heat and light, and, more recently, as a fuel for internal combustion engines. Ethanol has a widespread use as a solvent of substances intended for human contact or consumption, including medicines, flavorings, scents, and colorings. In chemistry, it is both a solvent and a feedstock for the synthesis of other products. While being a very simple molecule, a very rich chemistry can be derived from ethanol used as a platform molecule. In our research, we are targeting various products: hydrogen (together with carbon structures), 1,1-diethoxyethane by acetalisation, butanol and higher alcohols through the so-called ‘Guerbet reaction’ among others. Our main findings are summarized hereafter.

2. 2. 1. Hydrogen Production from Ethanol

H₂ is the gas that is the most widely used, mainly in refining processes and for ammonia synthesis. However, H₂ economy could be clean and sustainable only if this compound could be produced from renewable sources. In such a context, the ethanol transformation reaction is a useful way that is being extensively studied. So far, hydrogen has been produced from ethanol by steam reforming (SRE), partial oxidation, oxidative steam reforming (OSRE), and autothermal reforming50) reactions51)–53). The endothermic SRE reaction (673-973 K) extracts more hydrogen atoms
from ethanol and water, but needs an additional energy supply. One alternative way of supplying heat is to add oxygen or air to the feedstock and, simultaneously, to burn a portion of ethanol.

For this purpose, Ni-based catalysts are extensively studied, owing to their fairly good activity in the cleavage of the C-C and C-H bonds. Different types of nickel-based catalysts such as CeNiO₃ (0 < x ≤ 5) and NiₓMg₂AlO₇ (0 < x ≤ 12) compounds we developed revealed as particularly efficient at low temperature. Well tuning the catalyst preparation, formulation, as well as the activation procedure and the reaction conditions enable obtaining a high and stable activity even when some solid carbon is formed. The influence of different parameters was analyzed, such as the concentration of ethanol, the reaction temperature, the Ni content and the in-situ pretreatment in H₂ of the catalyst.

Under steam reforming conditions (mixture of ethanol and water with H₂O/C₂H₅OH = 3), the highly loaded well-dispersed Ni₁₂Mg₂AlO₇ catalyst allows obtaining a total conversion of ethanol at only 523 K with the formation of H₂, CH₄ and CO₂ without formation of CO. At 923 K, very high H₂ yields of 4.6 mol mol⁻¹EtOH⁻¹ and of 5.0 mol mol⁻¹EtOH⁻¹ can be obtained over the CeNi₁O₃ and the NiₓMg₂AlO₇ catalysts, respectively.

In the presence of oxygen in the feed, we developed particularly efficient catalysts at room temperature, as well as a new technology. H₂ is produced from ethanol in a sustainable way by taking advantage of the chemical energy produced by the reaction between hydride species stored in the nano-oxyhydride catalysts and O₂ in complement to the exothermic reaction between ethanol and O₂. Not only the CeNiH₃O₇ (20 wt% Ni) nano-oxyhydride catalyst, but also the CeNiₓH₁O₇ oxyhydride family exhibited a catalytic activity in the OSRE reaction, which depends on the Ni content. Ethanol is completely converted on the CeNiₓH₃O₇ catalysts with various Ni contents. The H₂ molar fraction varies with the Ni content and 45 mol% are obtained on the CeNi₁H₃O₇ catalyst with an excellent catalytic stability after 75 h of reaction even if some carbon is formed. The catalyst preparation and the reaction conditions were further optimized and the obtained results were patented.

A correlation between the catalytic activity and the physico-chemical characterizations allowed us to evidence that the active nickel species are in strong interaction with other cations. We proposed an active site involving Ni cations and anionic vacancies, and a mechanism involving heterolytic abstraction of hydride species from ethanol (Fig. 3).

2.2. Ethenol Acetalization to 1,1-Diethoxyethane

Acetalization is one possible way of ethanol valorization. This topic joins the formation of DMM previously described in 2.1.1. (a). The different possible products obtained when ethanol molecules react on redox and acidic catalysts are depicted in Fig. 4. Even if this scheme is very close to that assigned to methanol, the literature on ethanol direct acetalization is extremely scarce. However, 1,1-diethoxyethane (DEE) is considered as a promising oxygenated additive to diesel blends, and it is a raw material used in pharmaceutical products and in the fragrance industry. Like in the case of DMM, DEE is industrially produced in two steps. The first one is the formation of acetaldehyde through the Hoechst-Wacker process involving the oxidation of ethylene by oxygen.
in water using PdCl2/CuCl2 catalysts\textsuperscript{(69), (70)}. The second step is the reaction between the so-formed acetaldehyde molecules with ethanol. All these reactions take place in the liquid phase leading to some issues, such as reactor corrosion. To overcome this kind of problem, the one step gas phase ethanol acetalization reaction has been studied by a few teams. The first study has been carried out by Liu \textit{et al}.\textsuperscript{(32)}. They used RuO\textsubscript{2} supported on SiO\textsubscript{2} and SnO\textsubscript{2}, and the best performances observed over RuO\textsubscript{2}/SnO\textsubscript{2} were assigned to a better reducibility of the Ru atoms when deposited on the SnO\textsubscript{2} support. Applying the same philosophy as that for DMM synthesis, we ranked different industrial catalysts according to their activity and compared their performances with those of model Re/TiO\textsubscript{2} catalysts\textsuperscript{71}. The optimization of the reaction parameters (\textit{i.e.}, GHSV, temperature, feed composition) allowed us to obtain the best DEE productivity ever reported (\textit{i.e.}, 0.7 kg DEE kg\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1}) over AR01 and Re/TiO\textsubscript{2} catalysts. However, the latter ones deactivate with time on stream due to the volatilization of Re species via reduction under ethanol atmosphere while AR01 is stable and would thus be preferred when envisioning industrial applications.

As a general issue, the presence of acid sites induce the formation of ethylene, which can further react on the catalytic sites present at the surface of the catalysts, namely acid and redox, but also over basic sites that are unavoidably present. Numerous by-products are then formed consecutively to ethylene formation, but other side reactions are also possible. Indeed, on such multifunctional catalysts, the so-called ‘Guerbet’ reaction\textsuperscript{(72)} can then occur to complicate even more the composition of the obtained products’ blend.

\subsection*{2.2.3. Ethanol Conversion to Butanol and Higher Alcohols}

Marcel Guerbet gave his name to the eponym reaction, which globally consists on dimerizing an alcohol to a β-alkylated compound. It has been first proposed that the Guerbet reaction proceeds through a sequence of 4 steps, with first a dehydration of the alcohol on basic sites (or oxidation over redox sites) to the corresponding aldehyde, followed by an aldol condensation of two aldehyde molecules on basic sites and further dehydration of the as-obtained aldol over acid sites to a α-β unsaturated aldehyde or ketone that is lastly hydrogenated over redox-acid-base sites to finally form higher alcohols\textsuperscript{(73)}. However, some recent literature suggests that at a fraction of the final alcohol is a primary product and the other fraction may be formed by reaction between the alcohol and the corresponding aldehyde\textsuperscript{(74)}.

We developed different strategies to realize the ethanol conversion to butanol and higher alcohols blends, based on the optimization of different families of catalysts. We used hydroxyapatites, hydrotalcites and perovskites:

1. Hydroxyapatites: We synthesized [Ca\textsubscript{30}(PO\textsubscript{4})\textsubscript{14}(OH)\textsubscript{2}]\textsubscript{x} solids with different Ca/P ratios and thoroughly characterized them to determine their structural, textural and acid-base properties\textsuperscript{(75)}. These catalysts were then tested in the Guerbet reaction of ethanol in the gas phase. A good correlation was found between the catalytic properties of the synthesized hydroxyapatites and their acid-base properties. In particular, an optimal ratio of the quantity of the acid sites to the quantity of the basic sites of 5 was evidenced. Optimization of the catalytic system finally enabled obtaining a yield of heavier alcohols of 30 % at an ethanol conversion of 40 \%\textsuperscript{(76)}.

2. Hydrotalcites: We also attempted the use of Mg\textsubscript{6–x}Cu\textsubscript{x}Al\textsubscript{2}(OH)\textsubscript{16}CO\textsubscript{3}.4H\textsubscript{2}O solids\textsuperscript{(77)}, which were synthesized and calcined to obtain a fine mixture of oxides with acid and basic properties needed in the Guerbet reaction. Indeed, upon calcination, MgO and Al\textsubscript{2}O\textsubscript{3} were formed together with some copper-containing phases when the Cu content increased. As a remarkable feature, we could evidence the Mg atoms substitution by Cu atoms thanks to the observation of a rare “Fermi contact effect” considerably modifying the \textsuperscript{27}Al NMR spectra. The Cu-doped solids exhibited a higher reactivity towards ethanol with improved dehydrogenation properties yielding acetaldehyde as a main product.

3. Perovskites: We further investigated the catalytic behavior of mixed-oxides exhibiting the perovskite structure (ABO\textsubscript{3}) by tuning up their composition. Series of samples, either stoichiometric or non-stoichiometric, were synthesized using the auto-ignition method, which allowed us studying the influence of the different surface chemical properties required to this realize the Guerbet reaction: acidity, basicity, as well as dehydrogenation, hydrogenation and redox characters. Among all the prepared samples, La\textsubscript{3}FeO\textsubscript{4}, which exhibited the most pronounced basic character, was also the solid over which the highest conversion of ca. 32 \% was observed.

Among the three above-described systems, we obtained the best performances on the hydroxyapatites system, which clearly appears as a promising catalyst for the production of butanol and/or higher alcohols from ethanol, even if some optimizations are still needed.

Further, we patented a variation of the Guerbet reaction for synthesizing acrolein or methacrolein directly from a mixture of methanol and ethanol or propanol. This includes two successive steps: oxidation in the presence of a selective oxidation catalyst of the light alcohols in the feed and aldol condensation of the so-formed aldehydes in the presence of a second catalyst. The two steps can be combined in the presence of a single catalyst, and, in particular, some molybdenum-based selective oxidation catalysts were identified as efficient. Obviously, these two steps can be conducted in a single reactor or in two cascade reactors\textsuperscript{(78)}. On a FeMo catalyst, remarkable performances were observed.
with a yield of acrolein of 67.1% by reacting equimolar fractions of methanol with ethanol at 598 K using diluted oxygen as an oxidant.

2.3. C3 Molecules —glycerol and lactic acid

Glycerol and lactic acid are C3 biosourced molecules available on the market. The former is co-produced with biodiesel, while the demand of the latter, which can be derived from glycerol among various possible substrates, is increasing due to the developing polylactic acid market.

2.3.1. Glycerol Conversion

Since the biodiesel boom in the end of the 20th century, the amount of glycerol available on the market has literally exploded. Various applications of glycerol can be found in the literature, such as dehydrogenation, oxidation, condensation, ... Hereafter, we will discuss about glycerol conversion to acrolein and acrylic acid in the gas phase, before describing glycerol upgrading to fine chemicals as well as to H2 in the liquid phase.

(a) Glycerol conversion to acrolein

One of the most promising valorization ways for glycerol consists on its dehydration to acrolein. Acrolein is used as an intermediate for the synthesis of DL-methionine as well as for polycarbonate-based polymers. Glycerol dehydration to acrolein can proceed over various solid acid catalysts, such as zeolites, supported inorganic acids or mixed metal oxides (i.e., WO3). The main drawback of acid catalysis is the deactivation by coking. This issue can be tackled from two strategic angles, either by optimizing the catalysts or from the process side. Concerning the optimization of the catalysts, the crucial parameters are pore diffusion and acid strength. It is well agreed in the literature that medium acid sites and rather large pores are favorable for increased long-term stability. Hence, we focused on silica-supported silicotungstic acid (STA) and optimized the catalytic long-term stability by (i) choosing SBA-15 as a support with a tailor-made pore-size of 8 nm and (ii) introducing zirconia nanoparticles in SBA-15 in order to moderate the acid strength of the subsequently supported STA by modulated electronic interactions.

These tailor-made properties resulted in outstanding long-term performances with an acrolein yield of 69% after 24 h with only slight deactivation (initial yield of 74%) versus only 24% for the ZrO2-free catalyst.

Furthermore, the regeneration of the SBA-15-supported catalytic systems was studied, by burning the carbonaceous species in oxidative atmosphere. Over STA/SBA-15, the regeneration under air led to a significant loss in acrolein yield (30%) due to the thermal destruction of STA. On the other hand, the catalyst based on zirconia-grafted silica fully recovered its performances due to an increased thermal stability of the active phase, which was ascribed to the strong electronic interaction between STA and zirconia. This specific interaction was also responsible for the slight decrease in the acid strength of the supported STA, just sufficient to avoid coking while still enabling the realization of the glycerol double dehydration reaction. Finally, the cyclic regeneration of the catalysts was performed using periodical switching between a glycerol feed and an air feed with 10 min for each cycle. Surprisingly, the catalyst based on zirconia-grafted silica exhibited poor performances (35% acrolein yield) whereas the catalyst based on bare silica exhibited high and stable performances (74% yield in acrolein). These results can be understood considering the initial performance of these two catalysts. In fact, while the zirconia-grafted catalyst exhibited outstanding long-term performance, it requires an activation period of about 1 h. In the beginning (0-1 h), the zirconia-grafted catalyst exhibits a poor selectivity to acrolein of no more than 38%, against 79% for the catalyst based on bare silica. This type of activation period is well reported for Lewis acid catalysts in the dehydration of glycerol. In fact, Lewis acid sites present on the fraction of zirconia that is not covered by STA first catalyze the selective formation of acetol. Thereby, pseudo-Brønsted sites are formed by hydroxylation, which can then catalyze the selective dehydration to acrolein. As a conclusion, whereas the zirconia-grafted catalyst was adapted to long runs due to a slowed down deactivation and a high thermal stability, the catalyst based on bare silica was adapted to short run/regeneration.

With respect to the possibility of using the catalyst based on bare silica in short reaction/regeneration cycles, we then focused on the process. As aforementioned, the problem of catalyst deactivation can also be tackled from the process side, meaning, i.e., the use of a moving bed reactor or a fluidized bed reactor.
Glycerol was notably studied by Corma et al., and is comparable to the technology employed in the fluidized catalytic cracking process\(^{91}\). The main disadvantage of such a concept is the need for two reaction vessels: one for the reaction itself, one for the regeneration. Thus, we focused on a fluidized bed enabling — at the same time — the reaction and the regeneration in the same reaction vessel. The corresponding concept is referred as the two zones fluidized bed reactor (TZFBR) and is depicted schematically in Fig. 6\(^{92}\). The catalyst is fluidized by means of a pre-heated fluidizing gas (nitrogen or air). Inside the fluidized bed, glycerol can be introduced via a distributor located at the end of a plunging cane. Since glycerol is dragged with the fluidizing gas, the catalytic bed contains two zones. The zone over the glycerol injector is referred as the reaction zone, where the glycerol is catalytically converted to acrolein, and the zone lower than the glycerol distributor is used as a regeneration zone. In this latter part, the deposited carbonaceous species are oxidized with the oxygen co-injected with the carrier gas. With respect to the high cross-mixing of the catalyst in the fluidized bed, the as-regenerated catalyst is constantly exchanged with the catalyst from the reaction zone, allowing thus continuous and efficient regeneration.

(b) Glycerol conversion to acrylonitrile

The drastic increase in catalyst lifetime motivated us studying the use of “green” acrolein from glycerol dehydration in cascade reactions, and, especially in the ammoxidation of acrolein to acrylonitrile. The synthesis of acrylonitrile from glycerol can proceed either via a direct or an indirect pathway, whereby in the latter case, two independent coupled reactors (tandem reactor concept) must be employed. Although the direct ammoxidation of glycerol appears as advantageous since it requires only one reactor and one catalyst, the subject is discussed controversially in the literature\(^{93,94}\). In fact, whereas Bañares et al. claimed a high yield over antimony–vanadium catalyst (48 %)\(^{95}\), Liebig et al. could not achieve the same results\(^{94}\). We focused on the indirect ammoxidation of glycerol using tungsten oxide on titania as a catalyst for the dehydration of glycerol to acrolein and antimony–iron mixed oxide as a catalyst for the ammoxidation of acrolein to acrylonitrile. After optimization of the reaction conditions, a high and stable yield of 40 % was achieved\(^{96,97}\). Surprisingly, this yield in acrylonitrile using the tandem reactor setup was even higher than that theoretically predicted from the performances of the two reactions taken independently (40 % versus 28 %), suggesting that by-products from the glycerol dehydration step were also ammoxidized to acrylonitrile. An enlarged study indeed revealed that notably allyl alcohol can give a yield in acrylonitrile as high as 84 % over the antimony–iron oxide catalyst\(^{98}\). These results are very promising when considering allyl alcohol as a new platform molecule, which can be actually derived from glycerol even if some optimization is still required to reach high yields\(^{99}\).

2.3.2. Glycerol Conversion to Fine Chemicals in the Liquid Phase

The production of a large variety of chemicals from glycerol is well documented. Nevertheless, the liquid phase valorization of glycerol by oxidation over heterogeneous catalysts is not an easy topic. Indeed, the reaction network is quite complex with many possible products. Obtaining a specific target molecule and understanding the associated reaction mechanism motivated different research groups to develop various methodologies as well as different reaction processes\(^{100}\). Many experts were then independently established for different sets of operating conditions. This sometimes makes it difficult to compare catalysts and catalytic results from a research team to one another due to the diversity of approaches. However, a consensus is clearly established on some general behavior, i.e., on the efficiency of some metallic active phases. In early works, the supported metallic Pt\(^{101}\) and the derivative catalytic systems such as Pt-Bi\(^{102}\) and Pd\(^{103}\) were identified as efficient for converting glycerol. Extended works were also focused on the use of gold-based catalysts. Indeed, gold, being more resistant to oxidation, much active at low temperature, but operating only in alkaline medium\(^{104}\) is, at least from a fundamental point of view, a promising metal to realize this reaction. We also recently supported AuPd nanoparticles on a
TiO₂ support to benefit from the Au activity while suppressing C–C bond cleavage thanks to the presence of Pt₁⁰⁵.

As an important point, it must be kept in mind that the glycerol molecule is stable, but may be degraded in alkaline medium at low temperatures. This non-catalytic transformation of glycerol was first ignored in the literature dealing with glycerol partial oxidation. Thus, we studied the real impact of the alkaline conditions and distinguished between the actual gold catalytic contribution and the non-catalytic conversion induced by pH conditions₁⁰⁶. To do so, and to avoid the influence of any support effect also well described in the literature₁⁰⁷, a quasi-homogeneous solution of gold particles was used as a catalyst in the liquid phase oxidation of glycerol. A parallel study of two alkaline (NaOH/glycerol = 4 mol/mol) glycerol solutions (0.3 M, 1 M = 1 mol L⁻¹) with or without the presence of the gold nanoparticles (≈16 nm diameter) evidenced a critical temperature effect. At 373 K, a conversion over 90 % was obtained in both cases, with a high productivity for glyceric acid, and it is then not possible to distinguish between the base-induced and the catalytic effects. However, at, e.g., 333 K the conversion in the absence of a catalyst was 15 % versus 65 % when the catalyst was also present. The experimental results were backed up by a DFT study, and we could then propose a comprehensive glycerol conversion mechanism taking into account both effects.

In addition to fundamental studies aiming at understanding the reaction mechanism, it is necessary to address and optimize the various factors influencing the reaction performance. Indeed, the catalyst must be efficient, resistant in the reaction conditions (highly alkaline) and robust over time. To this purpose, we stabilized Au–Pd nanoparticles in an ion-exchange resin₁⁰⁸. This solid was then used as a catalyst for the liquid phase oxidation of glycerol (0.3 M) with oxygen (1 MPa) under basic conditions (NaOH/glycerol = 4 mol/mol) first in a batch reactor and also in a fixed bed flow type reactor. The preparation of such catalysts is based on the use of gold (HAuCl₄) and palladium (PdCl₂) precursors, which come to exchange with the Cl⁻ anions on the resin surface. After a reducing treatment with NaBH₄, the bimetallic nanoparticles are formed. A systematic study highlighted at 333 K in a batch reactor that the most efficient catalytic formulation, leading to a 85 % conversion and 88.5 % selectivity to glyceric and tartaric acids, is an equimolar Au/Pd mixture particles (1-3 nm). For long term reaction test (flow reactor), this system was stable over 4000 min, with 50 % of conversion and selectivities to glyceric and tartaric acids of 60 % and 30 %, respectively.

Another important point relies in the possibility of using crude glycerol instead of using purified glycerol when envisioning industrial applications with thus economic viability as a driver. In fact, only a few studies have reported the catalytic transformation of crude glycerol₁⁰⁹–₁₁₂. For our studies, we used several samples of crude glycerol taken at various stages of purification in a biodiesel refinery (Trezbinia, S. A., Poland) as raw materials for the liquid phase oxidation₁₁³,₁₁⁴. Our rational approach consisted initially on determining the crude glycerol components, and second on identifying the impact of each impurity on the catalytic process and, in a last stage, on determining the resistance to each impurity of various noble metal catalysts. The analysis result of various crude glycerol fractions shows the main presence of, obviously, glycerol, MONG (matter organic non-glycerol, mainly unreacted fatty acid derivatives), methanol, water, ash (mineral salts), MONG-NM (matter organic non-glycerol and non-methanol, mainly mono-, di- and triglycerides) and organic sulfur derivatives (OSD). In this work, several solutions of purified glycerol (0.3 M) in which we added a selected impurity (additive/glycerol weight ratio from 0 until 2) were prepared and used as feeds in catalytic tests under oxygen (5 bar, 1 bar = 1 × 10⁵ Pa) with a 1 wt% Pt/Al₂O₃ commercial catalyst (Pt/ glycerol molar ratio of 2510). In this systematic study, we have shown that some impurities (or additive) would rather have a beneficial effect, such as methanol, which would allow a better solubility of oxygen and thus promote the catalytic activity. Similarly, the presence of residual bases after biodiesel production facilitates reaching the adequate pH range to realize the reaction. While the presence of minerals salts does not significantly influence the catalytic activity, the MONG-NM compounds have a devastating effect on the catalytic activity, mainly by sticking to catalytic active sites. Nevertheless, choosing to realize the reaction with purified glycerol or with crude glycerol with then a purification procedure to separate the product is not straightforward and more related to techno-economic considerations.

After this preliminary study, we decided to compare the resistance of 4 noble metals to the various glycerin impurities. We used commercial catalysts (Pt/Al₂O₃, Pd/Al₂O₃, Au/Al₂O₃) and a homemade Ag/Al₂O₃ catalyst and first compared their behavior with pure glycerol or crude glycerol (333 K, 0.3 M glycerol, NaOH/glycerol = 4 mol/mol, 5 bar O₂). Based on the initial rate of reaction, selectivity (at 10 % isomconversion) and the global performances over a period of 100 min, we obtained the following interesting conclusions:

- First, the most paradoxical feature is that the Au/Al₂O₃ and Pt/Al₂O₃ catalysts, the most efficient with pure glycerol and the most studied systems in the recent years, become drastically less active when contacted with crude glycerol. This is due to MONG-NM and OSD developing a strong affinity with the active sites thus preventing adsorption glycerol. This observation

is confirmed by a previous work dealing with the use of (3-mercaptopropyl)trimethoxysilane (MPTES) as a stabilizing agent of the gold nanoparticles on the support, but also actually acting as a catalyst poison;

- The Pd/Al2O3 and Ag/Al2O3 catalysts while losing some of their activities, are the most resistant in the case of crude glycerol use. These metal phases are therefore the most promising ones;

In addition to these rather fundamental and conceptual approaches, our group meets the latest industry issues in terms of development of catalyst formulations with specific characteristics. Thus, in partnership with the ITE PIVERT, we have developed and patented a supported silver catalyst enabling, in our conditions, a yield of 70 % glycolic acid, an important target molecule with a high added value.

2.3.3 Glycerol Aqueous Phase Reforming

Hydrogen production from bioalcohols using the aqueous phase reforming (APR) method presents attractive advantages. It can be carried out at relatively low temperatures (473-553 K) and at a moderate pressure (15-70 bar). As it operates in the liquid phase, the aqueous solution used has not to be evaporated, thus enabling energy savings. We developed a sol-gel PtNiAl catalyst containing well dispersed active phases. The effect of the preparation method, the operating conditions, the presence of different non-noble incorporated metals, as well as the factors behind the deactivation were analyzed. The enhancement of textural properties, and cooperative effect between Pt and Ni leads to a high resistance against sintering with better and more stable catalytic activities in the aqueous phase reforming of glycerol, especially at moderate temperature/pressure conditions, together with higher reforming rates to gaseous products.

2.3.4 Lactic Acid Conversion

Lactic acid (LA) is one of the renewable bio-based feedstocks that have already a proven potential in industrial applications, notably for the production of polylactate polymers. It can be produced by fermentation of various renewable resources such as refined carbohydrates (sugars and starches) derived from agricultural crops; carbohydrates derived from waste streams (i.e., cheese whey and wood molasses). Lactic acid is extremely reactive as it contains both a hydroxyl- and a carboxyl group, whereby it can potentially undergo a variety of reactions including dehydration to acrylic acid, oxidation and decarbonylation.

Recently, we have notably studied the oxidation of lactic acid to pyruvic acid. Pyruvic acid is a desired commodity chemical widely used in the chemical, pharmaceutical and agrochemical industries. We have performed the oxidation of lactic acid over Ni/Nb mixed oxide catalysts with varying the Ni/Nb ratio with the idea to tune the acidity and the redox properties of the catalysts at the same time. The corresponding properties were probed by temperature-programmed desorption of ammonia (NH3-TPD) and temperature-programmed reduction (TPR), respectively, showing that the hydrogen uptake increased with the amount of nickel, whereas the acidity increased with the amount of niobium. The optimum ratio between acidity and redox character was found for the catalyst with a composition of Ni0.85Nb0.15, exhibiting a 15 % yield in pyruvic acid at 523 K (30 % conversion). The use of higher temperature was found unfavorable for the selectivity in pyruvic acid, since the total oxidation was promoted.

The second main reaction studied in our team was the dehydration of lactic acid to acrylic acid. As aforementioned, acrylic acid is a valuable intermediate for the polymer industry. It can be obtained from lactic acid by selective dehydration. Thus, several catalytic systems are reported in the literature, such as sulfates, zeolites and phosphates. We recently developed a catalytic system efficient in this reaction, for which a patent has just been filed.

2.4 C4 Molecules — butanediols

Butanediols can be obtained by fermentation of waste and biomass. In the recent years, butanediols have thus become a promising starting material for chemical industry. For example, we can mention the conversion to 1,3-butadiene (BD), which is the main building block for the synthesis of synthetic rubbers and resins. Starting from 1,3-butanediol, BD can be obtained by catalytic dehydration over acid catalysts, i.e., zeolites. We also recently filed a patent on a new catalytic system efficient and stable for realizing such reaction.

Further, we developed the specific reaction of oxidative dehydration of but-3-en-1,2-diol (BDO) to hydroxybut-3-en-2-one (HBO) over specifically designed Pd-Au and Pd-Pt bimetallic systems. These catalysts are active and selective in the liquid phase at the low temperature of 323 K using O2 as an oxidant. We obtained the best performances over the PdPt catalyst supported on titania with a 77 % yield, without any metal leaching.

2.5 C5 Molecules — xyllose, furfural and furfuryl alcohol, levulinic acid, isoprene

Pentoses (C5 sugars) are obtained by cleaving hemicellulose via hydrolysis based on diluted mineral acids like phosphoric or sulfuric acids. The most important molecules that can be obtained through this process are xyllose and arabinose. Xylose has only a few direct applications, but could be transformed to various important chemicals such as xylitol and furfural. Xylitol obtained by hydrogenation of xyllose on Raney nickel catalysts has a high sweetening capacity and possesses non-diabetic and anti-caries properties. However, some drawbacks must be mentioned: a rapid catalyst deactivation due to accumulation of organic impurities (from the starting material) on the catalyst sur-
face, leading to poisoning of the active sites, and metal leaching as well as difficulties in terms of post reaction separation\textsuperscript{135}. The annual xylitol market is estimated to be around $340 million with a price of $5/kg indicating its significance in many value added chemical industries\textsuperscript{136}. Furfural is a promising renewable platform molecule and it is a natural precursor to furan-based chemicals. It could be produced from the acid-catalyzed hydrolysis and dehydration of lignocellulosic pentoses\textsuperscript{137}. It is also starting molecule to produce maleic anhydride (MA-C$_4$H$_2$O$_3$), an important building block in the petrochemical industry. MA is a precursor of several valuable products such as succinic acid, tetrahydrofuran, saturated polyester resins and 1,4-butanediol or furfuryl alcohol. Even if industrially, maleic anhydride is mostly synthesized via catalytic oxidation of benzene, o-xylene or n-butane, it can be also produced from bio-based compounds. We recently proposed a review article on MA synthesis from renewable chemicals. We summarize in it the most valuable methods to obtain MA from bio-based furan derivative [furan, furfural and 5-hydroxymethylfurfural (5-HMF)]\textsuperscript{138}. Furfural oxidation to MA constitutes a green alternative to this process. It has been shown that the best results in terms of MA selectivity were obtained in the liquid phase using homogeneous H$_3$PMo$_{12}$O$_{40}$ and VO(acac)$_2$ catalysts. In the case of heterogeneous catalysts, the best results reported so far are obtained by vapor phase oxidation using vanadium oxide or vanadium-molybdenum mixed oxides supported on Al$_2$O$_3$\textsuperscript{139}. The liquid phase oxidation using heterogeneous catalysts still needs improvement. Especially, the leaching of the active phase should be avoided. Furfuryl alcohol could be synthesized over Ni-Sn alloy catalysts enables furfuryl alcohol yields over 97 %\textsuperscript{140}. Levulinic acid is a by-product in the dehydrogenation of fructose to 5-HMF. It can be obtained in high yields by acid treatment of glucose, fructose or cellulose but also directly from lignocellulose\textsuperscript{141} or catalytically from glucose on solid metal(IV) phosphate catalysts\textsuperscript{142}. Levulinic acid itself has no direct application, but can be converted to other valuable compounds like y-valerolactone (a first step towards the production of 2-methyltetrahydrofuran) via hydrogenation over Ru of Pt-based noble metal catalysts\textsuperscript{143} or via hydrogenolysis over y-alumina-based nickel-copper bimetallic catalysts\textsuperscript{144}. Isoprene is a valuable monomer for the rubber and most chemical industries. Industrially, it is obtained via various methods such as dehydrogenation of isopentane, liquid phase oxidation of hydrocarbons or liquid phase catalytic synthesis from isobutylene and formaldehyde\textsuperscript{145}. Isoprene could be produced from glucose using some family of bacteria (Escherichia coli). Even if the glucose conversion yield to isoprene at the level of 7-10 %\textsuperscript{146,147} is too low for the industrial application, some patents are already deposited. The current utilization of renewable biomass-carbohydrates in general, and sugars in particular, as a feedstock for the chemical industry is modest when considering their unexploited potential. Glucose could be obtained from cellulose and starch and then converted to fructose via isomerization. The oxidation of low molecular weight carbohydrates is a highly attractive process and produces sugar acids, which have many applications in food industries, pharmaceutics and cosmetics. Gold catalysts were found to have a clear advantage in terms of activity and selectivity compared to platinum and palladium-based catalysts used so far for carbohydrate oxidation. The same gold catalyst is able to completely convert all different aldoses (e.g., glucose, lactose, maltose, fructose, arabinose) to their corresponding aldonic acids (e.g., gluconic acid). It was found that unsupported gold particles in aqueous solution (3-5 nm) show very high activity in the aerobic oxidation of glucose, not far from that of enzymatic systems\textsuperscript{149,150}. A linear correlation between activity and number of exposed gold atoms was demonstrated. Even though these systems are very active and selective, the catalysts described in the literature do not have a sufficient long-term stability, as the activity decreases of about 50 % within only four repeated batches\textsuperscript{151,152}. The hydrogenation of sugars gives alcohols such as sorbitol used largely in the food industry for diabetic diet. Indeed, its ingestion does not yield any increase in the blood sugar level as compared to sucrose. More recently, sorbitol has been used for the synthesis of isosorbide\textsuperscript{153}. Sugars could be also transformed to other major products such as 5-hydroxymethylfurfural (5-HMF) or glycosides. 5-HMF could be obtained directly from sugars using aluminosilicates. High yields (about 80 %) have been reported for fructose and glucose. However, there are still some drawbacks concerning the rapid degradation of 5-HMF to levulinic acid (in the presence of water) and the use of organic solvents (purification and separation issues). Recently, we have developed catalysts for the selective oxidation of 5-HMF to 2,5-diformylfuran (DFF)\textsuperscript{154,155} and some groups were focusing on FDCA synthesis (2,5-furandicarboxylic acid), a green alternative to terephthalic acid\textsuperscript{156}. Most of the catalytic systems are based on noble metals, with FDCA yields over 95 % and on vanadium phosphate oxides with DFF yield of 83 %. Available and (relatively) cheap carbohydrates (glucose, fructose, maltose, cellulose, and lactose) can be used as raw material for biodegradable surfactants synthesis.
The alkylpolyglycosides (APGs), non-ionic surfactants, are of a growing use because of their good foaming properties, as well as synergy with other surfactants. They have found application in dishwashing and laundry detergents, and in other cleaning products\(^{157}\). The most important carbohydrate-derived surfactants produced on an industrial scale are (ethoxylated) sorbitan, sucrose fatty acid esters, fatty acid glucamides, and alkyl polyglucosides\(^{158}\). Glycosylation of simple alcohols with D-glucose can be performed by strong acids like HF\(^{159}\), BF\(_3\)-etherate\(^{160}\), HCl\(^{161}\), p-toluene sulphonic acid (PTSA)\(^{162}\) and H\(_2\)SO\(_4\)\(^{163}\) to give both \(\alpha\)-and \(\beta\)-anomers with high degree of polymerization of glucose unit. This reaction could be also performed using solid acids such as Amberlyst and Nafion\(^{164},165\).

### 3. Toolboxes

In addition to targeted chemical transformations for which we develop catalytic systems, we are also involved in the design of broader concepts and technological bricks, such as the TZFBR described in 2.3.1. (a). Hereafter are described our advances concerning the development of an innovative and very efficient dehydrogenation catalytic system, our vision and implementation of high throughput technologies to assist catalysts discovery, as well as our latest results on reactive distillation.

#### 3.1. Dehydrogenation Reactions

Most of the biomass-derived molecules are largely functionalized with alcohol functions. Moreover, simple alcohols such as ethanol and butanol can be easily obtained by biomass fermentation. Therefore, transformation of the alcohol functionality constitutes a strategic transformation for the conversion of biomass-derived molecules to high value added products. Acceptorless dehydrogenation of alcohols catalyzed by transition metal complexes constitutes an attractive transformation that enables producing reactive carbonyl compounds (aldehydes or ketones) while releasing hydrogen as a valuable co-product\(^{166}\). Moreover, depending on the reaction conditions, the produced carbonyl compound can be further transformed in-situ by multiple condensation, dehydrogenation, dehydration and hydrogenation reactions into a wide variety of chemicals such as esters, amides, carboxylic acids, heavier alcohols and amines (Fig. 7).

Ruthenium and, more recently, iron pincer complexes have been reported as efficient catalysts for these dehydrogenation, dehydrogenative coupling and hydrogen borrowing reactions\(^{167}\). However, most of the reported catalysts show little activity for light primary alcohols such as ethanol and usually require a base-assisted activation. We recently developed several ruthenium aliphatic PNP pincer complexes that display very high activity, productivity and stability for the dehydrogenative coupling of primary alcohols toward esters under base-free conditions\(^{168}\). For this reaction, turnover frequencies up to 8000 h\(^{-1}\) can be obtained with selectivities over 99 %. For the first time, ethyl acetate could be efficiently produced from ethanol under neat and neutral conditions. With similar catalysts, primary alcohols could be efficiently dehydrogenated to carboxylic acid salts and the catalyst could be recycled using a biphasic system.

Finally, these complexes could also be efficiently used for an original hydrogenation-dehydrogenation reaction cascade enabling producing fatty esters such as myristyl myristate, used as an emollient ester in skin care applications, from readily available fatty acid methyl esters (FAMEs) (Fig. 8)\(^{169}\).

#### 3.2. High-throughput Technologies

The \(a \, priori\) theoretical design of the “best” catalyst for a desired reaction is unfortunately not yet possible.
and a time- and money-consuming experimental approach is still needed for developing new catalytic processes. Hence, with the aim of shortening this experimental phase and, therefore, of accelerating the discovery cycles, our team has imagined the REALCAT platform\(^{170}\), which was accepted and funded by the French Government in the frame of the “Equipment of Excellence” leg of the ‘Future Investments’ program (PIA) in December 2011. REALCAT is an acronym standing for the French denomination « RÉacteurs Avancés pour le cribLage en CATalyse appliquée à la valorisation de la biomasse », which can be translated by “Advanced High-Throughput Technologies Platform for Biorefineries Catalysts Design.”

The REALCAT platform, which was inaugurated in May 2014, is now fully operational. It consists in a completely unique in the world, integrated and top-level ensemble of high-throughput (HT) technologies including (i) robots for the automated synthesis of chemo- and bio-catalysts, (ii) rapid characterization tools and (iii) a series of versatile parallel continuous and batch reactors and fermentors—for gas phase, liquid phase or multiphase reactions—combined with ultrafast analytical tools at the top of the state-of-the-art for the analysis of the products in the reactors effluents. All kinds of catalysis can be addressed by REALCAT: heterogeneous, homogeneous, biocatalysis or even their combinations. A detailed description of the equipment and functioning of the platform can be found elsewhere\(^{171}\).

REALCAT has been designed for the development of biorefineries catalysts (for instance, Keggin-type heteropolyacid-based catalysts for glycerol dehydration to acrolein\(^{172}\)) but, obviously, it can also be used for the development and optimization of catalytic processes based on fossil resources. For example a recent work has been carried out on the well-known Fischer-Tropsch process\(^{173}-175\).

Up to now, one of the biggest successes of REALCAT has been obtained in the frame of the French-Japanese International Associate Laboratory CAT&P4BIO (standing for ‘Innovative Catalysts and Processes for Oxidation Reactions; Biomass Conversion’) just a few months after its inauguration. As a matter of fact, a collaboration between Professor Ueda’s team at the Catalysis Research Center of Sapporo (CRC, Hokkaido University) and French researchers of the present team has led to the discovery of a new very efficient heterogeneous catalytic process for the production of renewable acrylic acid. This process, which opens the way to renewables acrylates is now being jointly patented by the respective French and Japanese institutions.

REALCAT is open to external users. At full capacity, the platform aims at running 20 projects per year involving worldwide users from both academic and industrial areas. Among these 20 projects, it is estimated that half of them will be performed in the frame of industrial collaborative projects; 20 % in the frame of academic collaborative projects (including the projects led by the members of the REALCAT consortium only), and 30 % in the frame of pure provisions of services.

Further, the technological developments we are achieving to improve high throughput technologies will be soon commercialized through a startup company, TEAMCAT Solutions\(^{176}\), which will be launched mid-end 2015.

### 3.3. Reactive Distillation

Reactive distillation is one of the outcomes of process intensification, where the reaction and the separation of the products can be achieved in the same operation unit. This alternative—often proposed for reversible reactions—increases the products yield by removing continuously one of the products, and simplifies or eliminate the separation system, yielding a significant reduction of the capital and/or the operation cost\(^{177},178\).

One of the characteristics in the production of bio-based platform molecules is the highly diluted reaction mixtures obtained from the chemical/biological treatment of biomass. The purification of these molecules can be highly energy consuming, making this an important issue for the later scale-up of the process. In the case of glycols—ethylene glycol (EG), propylene glycol (PG) or sorbitol—traditional distillation is used so far as a purification step meaning that all the water present in the system must be evaporated. In reactive distillation, new intermediary compounds can be produced, with boiling points lower than water, thus avoiding the evaporation of all the water in the solution and then reducing the total energy consumption\(^{179}\).

Cyclic acetalcs can be produced by reversible acetalization of glycols with aldehydes or ketones. The reaction is catalyzed by acids\(^{180}\), optionally in the presence of ion exchange resins (Amberlyst)\(^{181}\), and the boiling point of the produced cyclic acetal is considerably lower compared to the corresponding glycol. For instance, PG produces 2,4-dimethyl-1,3-dioxolane (24DMD), after reacting with acetaldehyde, with boiling points at atmospheric pressure of 470 K and 355 K, respectively. Once the equilibrium data of the system is known\(^{182}\), different scenarios of separation can be imagined depending on the composition of the mixture of glycols\(^{183}\). Then, energy savings per kg of purified glycol can be easily calculated using process simulations software. Depending on the purification scenario, not only the operation cost could be reduced, but also the capital costs by reducing the number of separation units compared to purification system based on traditional distillation (note that we did not publish these results yet).

The reactive distillation technology is compatible with the regularly used equipment (distillation columns)
making easier the transitions in between. The implementation of this kind of technology can make the production of glycols from renewable resources a competitive pathway compared to the petrochemical ones.

4. Conclusion and Perspectives

Biomass and biomass-derived platforms molecules conversion by chemo-catalysis, and also by bio-catalysis, is an abundant field of investigations with many perspectives and possible transformations. Beside the adaptation of conventional approaches to design the catalysts that will operate in biorefineries, the largely renewed interest towards catalysis due to bioresources advanced exploitation participates to a so-to-speak re-activation of the field, which is also now much more resource with new concepts and new fundamental approaches. Among them, a new field in catalysis we mention as 'hybrid catalysis' is emerging taking advantage of two worlds that were long separated, namely chemo- and bio-catalysis. A pragmatic, rationalized and humble concerted approach between these two fields will undoubtedly yield to synergetic effects enabled by smart one-pot cohabitation of both kinds of catalysts. We are involved in the development of a few hybrid catalysis strategies, one of them being the object of a patent we recently filed, but other groups are also successfully developing such an approach, which was considered as impossible a few decades ago.

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