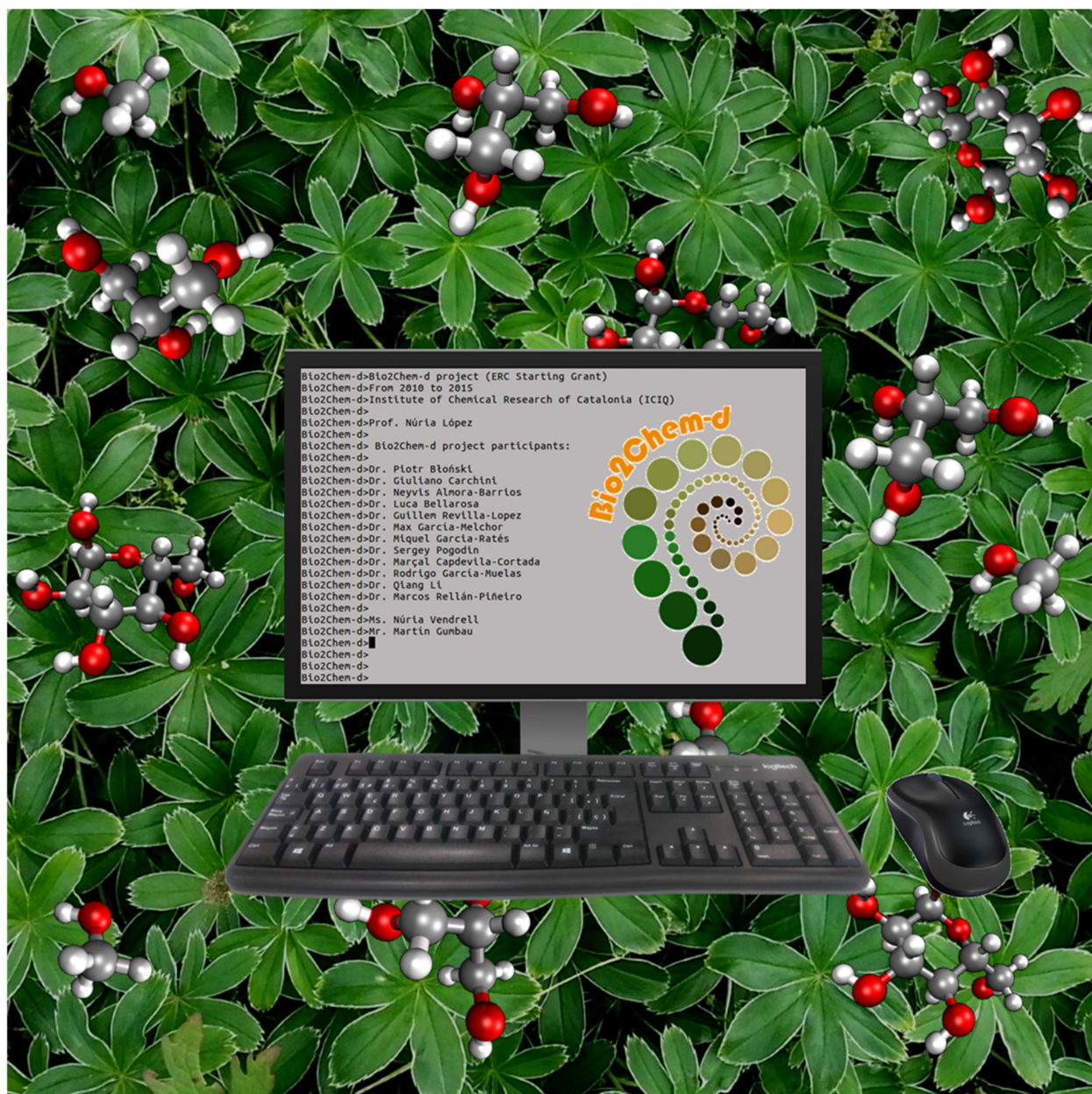# Developments in the Atomistic Modelling of Catalytic Processes for the Production of Platform Chemicals from Biomass

Rodrigo García-Muelas,[a] Marcos Rellán-Piñeiro,[a] Qiang Li,[a] and Núria López*[a]

The transformation of biomass-derived molecules into platform chemicals that can directly be employed by the chemical industry is one of the challenges in catalysis in this century. While some processes are cost-effective and industrially available, the molecular insight has been advancing at a slow pace when compared to other areas (like energy conversion). In the present review we describe the main challenges imposed on the theoretical simulations for the study of these complex molecules and how the most crucial issues are typically addressed. In particular, we focus on technical aspects like the need for London dispersion and solvation contributions. We also deal with the complexity of reaction networks, which requires new approaches and ways to compile the results in the form of databases. This allows the study of large reaction networks for the decomposition of C_2 alcohols, or the plethora of functional groups of cyclic molecules such as lignin and sugars. Finally, we put forward a few applications that show the potential of atomistic simulations in the field.

Introduction

The non-edible fraction of biomass is the most abundant and environmentally-friendly raw material.[1] It can be transformed into platform chemicals by heterogeneous catalysts, which are key processes for the sustainability of the chemical industry.[2] In 2004, the US Department of Energy (DOE) identified twelve target compounds that can be directly obtained from biomass and upgraded into high-value chemicals.[3] This fostered experimental screening for new catalysts and processes. The list was expanded in 2010.[4] Yet, due to the complexity of the systems, the insights about these catalytic routes at a molecular level were lacking. The atomistic simulation of biomass-derived processes has mainly three sources of complexity: the size of the molecules, the non-negligible effects of London dispersion and solvation; and the behavior of the system under operation conditions. These hurdles have been partially addressed in the last years, and the field has reached enough maturity to ensure that reactions can be described accurately for medium sized molecules.

Firstly, even small molecules exhibit an increasing number of conformations. For short-chain C_1–C_2 alcohols this effect is minor, but for larger compounds ($> C_3$) the number of possible rotations increases exponentially, having an important effect in their binding to oxide or metal surfaces. At this point, the chirality and rigidity of the molecules are crucial to understand the catalytic path.[5] Besides, the reaction network that connects reactants and products becomes intricate, as the number of intermediates and transition states increases exponentially,[6] thus limiting the use of the available techniques. For instance, glycerol decomposition on metals consists of 250 intermediates connected by roughly 2000 transition states, while for a typical C_6 the total number is more than two orders of magnitude larger.[6] For such large molecules, the product distribution typically shows poor selectivity and this is one of the challenges of biomass conversion.[7] Moreover, the identification of key transition states is not straightforward as many of them may have a similar degree of rate control for the overall product distribution.[8] For these structures, small energy differences may lead to different product distributions to a large extent[9–10] and therefore, they should be computed accurately. Fundamental electronic structure questions arise from the previous points. London dispersion contributions are key to address the adsorption of large molecules on catalytic surfaces accurately. The seminal theoretical studies on the reactivity of small alcohols neglected these contributions as they were lacking in the computational codes.[11–14] Nowadays, we know that these contributions are important to describe the adsorption energy of large molecules, especially when a carbon tail is present.[15,16] They may change the configuration of the target compounds as well.[17–19] In addition, biomass-derived molecules are rich in oxygenated functional groups, which interact with the ubiquitous water molecules.[20] This interaction is crucial to understand the reactivity, thus the solvation effects need to be included either explicitly,[21] at a very high computational cost, or implicitly.[18] However, the solvation models, which were widely used for homogeneous catalysis, were seldom applied to heterogeneous studies, and thus had to be implemented considering periodic boundary conditions.[22–24] The addition of water implies additional challenges to the simulations as some of the active molecules are acids and new equilibria are established between the catalyst and the surface. Finally, the effect of the reaction conditions should be considered so as to develop suitable models directly comparable to experiments. The contributions can come from pressure, concentration, temperature, pH, and electric potential effects,[25] which may have non-trivial consequences like inducing changes in the state of the catalyst surface.[26]

In the present review, we aim to describe the challenges in the theoretical study of biomass conversion into platform chemicals as well as in the technological challenges that we and others have faced. In particular, we focus on the fundamental issues that were preventing the routine use of computational techniques based on Density Functional Theory to upgrade biomass-derived compounds. As the molecular size increases, so does the difficulty to implement refined techniques such as microkinetics or DFT characterization over the full reaction network, Scheme 1. To foster scientific discussions, all our DFT results are stored and can be retrieved from the ioChem-BD repository,[27] an open database that fulfils the FAIR principles[28] of findability, accessibility, interoperability, and reusability.

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This manuscript is part of the Anniversary Issue in celebration of 10 years of ChemCatChem.
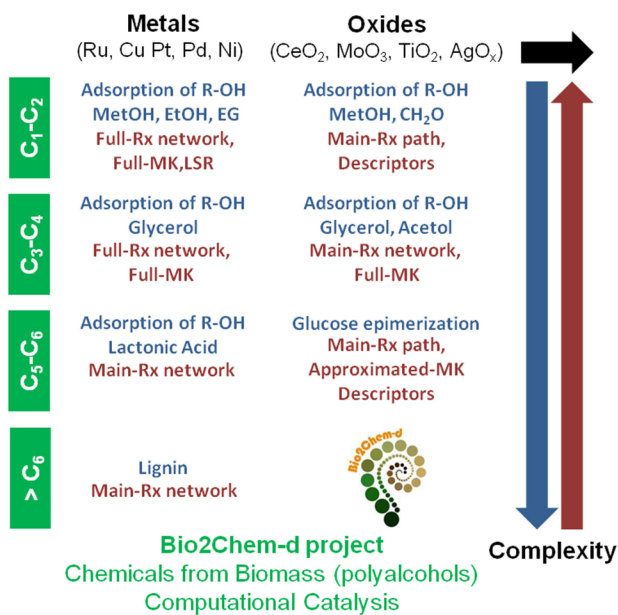
Scheme 1. Summary of the work performed in the Bio2Chem-d project. The studies are divided by the catalyst type (black) and by the molecular size (blue). The analysis performed for each molecular size and catalyst is shown in red. Rx stands for reaction and MK for microkinetics. The arrows on the right side indicate the growth in complexity.

Fundamental Challenges

London Dispersion

Density Functional Theory (DFT) techniques have been very successful in addressing the reactivity of small molecules on heterogeneous catalysts. And yet, when the Bio2Chem-d project started in 2010, several hurdles were still preventing the consideration of large molecules as those from biomass.[29] The earliest studies on metal catalysts did not include van der Waals interactions.[11,13] Although this is not a problem for small molecules containing one or two carbon atoms,[30] the vdW contribution of each additional methyl group is exothermic by -0.1 eV,[15,31] so this term becomes significant for C_3 or larger molecules. Traditional density functionals did not introduce London dispersion contributions and thus alternatives were sought to mitigate this problem. The first semi-empirical contributions were included in the activation of methane on Ir.[32] Later on, extensive developments in self-consistent functionals, like that of Lunqvist,[33,34] included the non-locality of the London dispersion contributions. However, these functionals were too property-dependent and thus their use was limited. A simpler approach was suggested by Grimme[35,36] employing the C_6 coefficients already used in molecular mechanics. However, when the D2 set of parameters was applied to estimate the adsorption on metals, the results were discouraging as they led to severe overbinding. Simultaneously to our work, Tkatchenko and coworkers derived the C_6 coefficients for atoms and metallic surfaces; however the latter

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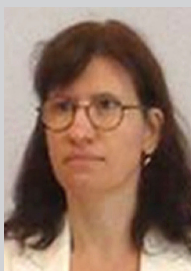
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required some measurements making it difficult to extend.[37,38] In our approach, we simplified the search for the coefficients in the following manner: the C_6 terms are related to the polarizability of the surface, thus different electric fields were used to obtain them.[39] These models can then be employed with enough robustness together with the values for the atoms derived in Grimme's D2. Since then, more advanced schemes have been reported: (i) the D3 extension by Grimme,[40] (ii) the non-local correlation functional vdW-DF[33] that can be combined with several functionals as BEEF-vdW,[41] and (iii) Tkatchenko's full set of DFT-TS,[42] DFT-TS/HI,[43,44] TS+SCS[45] and MBD@rsSCS.[46] All these terms lead to different adsorption energies.[47,48] Besides, in some cases the orientation of the molecule on the surface may change depending on the density functional chosen, thus resulting in different chemical behaviors.[49] An in-depth assessment of these methods can be found in a recent review[50] by Grimme et al.

Increasing the molecular complexity has another side effect: flexible molecules can have multiple conformations and sometimes the most stable gas-phase configuration does not correspond to the adsorbate ground state. This problem has seldom been addressed in the literature. Among our first steps, we develop some rules depending on the relative strengths on intramolecular and metal-adsorbate interactions.[15] We found that the conformational changes can have big impacts on the adsorption of molecules and in their reactivity. For instance, when glucose adsorbs on Ru, a proton is transferred from a hydroxyl to a carbonyl group, which favors the breaking of a C−H bond vicinal to the donating group.[51] The presence of vicinal methanol molecules also affects the preferred reaction path during their decomposition on metals.[21] Thus, the metal reactivity can only be studied provided that the right configurations are identified.

To find the most stable configuration for adsorption is even more complicated on metal oxides due to their multiple adsorption sites with different acid-base and redox character.[52] The difficulty increases if different metal coordinations or vacancies appear on the surface. The adsorption of alcohols and polyalcohols was also studied by us on TiO_2 in which different behaviors were observed for different compounds: primary and secondary alcohols prefer the adsorption on vacancy positions, whereas tertiary or poly-alcohols prefer the Ti_{cus} channels.[53]

Molecular Complexity

An additional side effect of larger molecules is that their associated reaction networks grow exponentially by size and complexity.[6] Therefore, the study of the reactivity for biomass-derived molecules is very computationally demanding. Two main directions have been taken to reduce this burden: (i) to use small surrogates, for which the full reaction network can be sampled; (ii) to search for the preferred reaction path (and maybe one major parasite reaction). Both approaches have significant drawbacks. Small molecules might not properly represent the activity of larger ones since. For instance, they

lack intramolecular hydrogen bonds that stabilize certain conformations. They also are unable to represent the stiffness of large aromatic groups that provide rigidity and anchor them to the catalytic surface, like in lignin. Therefore, surrogates should be used with caution. Simplifying reaction networks has a higher risk as the complexity of molecules derived from biomass cannot be avoided since, in many cases, they contain multiple functional groups in different positions of the molecule, and the desired transformation would encompass both chemo and regioselectivities. Sampling one reaction path does not ensure that the critical selectivity points of the reaction network are considered. In this sense, the modular approaches employed to obtain the contributions from the different units that compose the desired molecule might be effective. Such additive schemes have been used to describe the gas-phase thermochemistry with impressive accuracy.[54] For adsorbates, the existing rules normally span short-sized molecules;[55] although semiempirical equations for the adsorption of large molecules have been put forward.[56,57]

In the foreseeable future, the combined use of databases and statistical learning algorithms will allow generating robust thermochemical models for large molecules.[58] These databases should fulfill the FAIR principles, which require that data is findable, accessible, interoperable, and reusable.[28] In this context, we have created the ioChem-BD repository,[27] in use since 2015, to store all calculations coming from our DFT-based projects.

Microkinetics

Even when the reaction networks are fully characterized in terms of their thermodynamic and kinetic parameters at the DFT level, their predictability is limited. As we have explained above, many functional groups are present in different parts of the molecule. In many cases, we have found that the barriers of several parallel paths are comparable, thus they might be active simultaneously.[77] This means that a successful analysis of the reaction network requires the use of microkinetic models so that the molecular insight obtained for all elementary steps can be mapped to experimental data like reaction orders, activation barriers, activity of catalyst, and product selectivity.[59] Many reactivity descriptors and volcano plots are based on microkinetics.[60,61] Still, due to its simplicity, the molecular interpretation based on energy profiles is more common, at least for simple reaction networks.

Microkinetic models can have different levels of simplification. For instance, many differential equations can be grouped to represent a single-rate determining step,[62] as the energies of intermediates and transition states are highly correlated.[9] This reduction is very convenient to optimize reaction conditions. However, this approach cannot be used to screen catalytic systems, as the potential catalysts might prefer different reaction paths, e.g., the reforming of ethanol on Pd and Pt.[77] Another approach is to consider flow reactors to be in quasi-equilibrium. Despite removing the dependence on time, this simplification may yield unphysical results as flow reactors

may operate in a pseudostationary state.[63,77] Several simplifications are common during the obtention of the free energies; therefore, the accuracy can be increased with a correct description of the entropy terms.[64] Finally, it is common to assume a constant adsorption energy for each intermediate, by neglecting coverage effects and lateral interactions. For some intermediates, like water or carbon monoxide, this simplification may lead to large deviations. For water, cooperative effects mediated by hydrogen bonds appear at medium concentrations, which in turn vary the relative binding energies of the different substrates to the active sites. For carbon monoxide, the repulsion is very high, so the binding energies should be lower at large coverages. Repulsive effects may be included as a linear function from the coverage, such as in Ref. [65], at least for the common poisons CO, C, and O. As these contributions are repulsive, a refinement of the technique is to include lateral interactions above a threshold surface concentration, i.e. 1/3 for hexagonal surfaces.[66] Below this value, the adsorbates do not "feel" each other. In any case, the repulsive interactions mediated by metal surfaces are inversely proportional to the cube of the distance,[67] thus next-neighbor interactions are seldom included.[68] Finally, the full set of lateral interactions can be considered altogether through Kinetic Monte Carlo (KMC) simulations. KMC boosts the accuracy of kinetic measurements, but it is considerably more expensive than microkinetic modeling. As other groups,[69–73] we have also been active in reporting KMC codes and applications.[74] Refinements in the accuracy of DFT and the way lateral interactions are treated will be the object of future research, where again statistical learning techniques can improve our models.

For biomass conversion, microkinetics has been typically applied on the full reaction network of small alcohols, such as methanol,[75] ethanol,[9] or ethylene glycol.[76] Particularly in our group we computed the full set of reactions encompassing the decomposition of all these species on four different metals (Cu, Ru, Pd, and Pt), comprising 75 intermediates and 250 transition states for each metal. This allowed us to unveil the activity of these materials for hydrogen production under four reaction conditions.[21,77] We focused on the direct decomposition to compare our results with surface science data, as well as three emerging technologies: autothermal reforming, steam reforming, and aqueous phase reforming. For such a complex reaction network, a genomic notation was implemented to allow the systematic identification of intermediates, as described below. The 1000 transition states of our reaction database are openly available. They can be easily extended to include larger molecules or lateral paths like oxidation reactions via the linear scaling methods based on Brønsted-Evans-Polanyi (BEP)[78–80] and Transition State Scalings (TSS).[81–83] In our study, the TSS were used to estimate the 1697 C_3 related transition states of glycerol decomposition on a Ru surface which are used in the microkinetic study to predict the most suitable technology for H_2 production. By combining the linear scalings for the intermediates and the BEP relationships for the transition states, Greeley et al. investigated the thermochemistry and kinetics in the free energy diagram of glycerol decomposition on: (i) Pt(111),[84] (ii) a series close packed transition metal surfaces,[85]

and (iii) on a Pt–Mo alloy.[86] The O–H, C–H, C–O and C–C competition in different dehydrogenation stages has been well described. For oxides, we also computed the reaction network for glycerol hydrodeoxygenation (HDO) to propylene catalyzed by MoO_3[87,88] and analyzed it through a microkinetic model. The main reaction path, the apparent activation energy, and the reaction order of H_2 were obtained from the microkinetic analysis.[89]

Solvation

Another important particularity of biomass is the need to include the effects of water in the simulations. Water is ubiquitous in raw biomass. It is also generated from bond-breaking reactions that eliminate oxygen in the form of water from sugars and other biomass compounds. Metal-water interactions have been extensively investigated in the contexts of heterogeneous catalysis and electrochemistry, both by experimental and computational techniques. Detailed reviews on the state-of-the-art of this extensive topic are available in Ref. [90] and [91]. The main results concern the wetting/non-wetting character of the layers;[92,93] the stability of different water arrangements on the surface,[91,93] as distinctive patterns appear at sub-monolayer coverages depending on the metal; and the possibility of fitting new potentials that could be used in electrochemical simulations.[94] There are two ways of including the effect of solvation on theoretical simulations, either by explicit water molecules, or by replacing the vacuum region with an implicit solvation, Scheme 2.
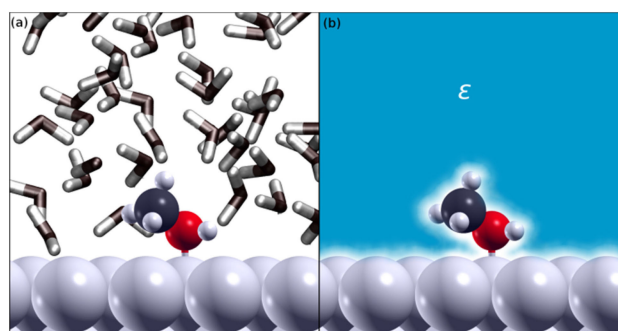
Scheme 2. (a) Explicit solvation model, where the liquid water molecules are placed in the simulation box.[96] (b) In the implicit model, the vacuum is replaced by a continuum with electric permittivity ε delimited by a smooth frontier.[19]

Most of the studies with explicit water molecules were based on low water coverages (1 bilayer)[14,95] or in small cells where lateral interactions were non-negligible.[13] Extended dynamics on metal systems have been possible just recently.[96] Neural network potentials based on DFT may further expand the complexity of the systems that can be studied at a reasonable computational cost.[97] Our early simulations on the dynamics of the metal-water interface identified that, depending on the nature of the metal (reactive or unreactive), the

metal-water interfaces differ. For instance, the wetting layer of Pd and Pt is denser than the bulk liquid. Besides, the interface shows low ordering as five- and seven-membered rings appear, in good agreement with experiments done at lower coverages.[98] On Ru, half of the water molecules dissociate, and form a very rigid structure containing mostly hexagonal patters.[99,100] However, there is no explicit pH variation at the interface as protons and hydroxyls are trapped on the surface.[96] On oxide surfaces the situation is more complex. Wetting and dewetting behaviors have been found to correlate with the acid-base properties of the surface, such as the presence of hydroxyl groups,[101] and geometric factors. The acid strength promoted the wettings of the surface, but the geometric match between the oxygens of the ice structure and the adsorption sites on the surface were shown to be the most important factor that controls wettability.[102]

However, water-containing simulations are complex as the dynamic and cooperative effects with solvent are very important. In homogeneous catalysis, implicit water solvation models[103] have been applied extensively. Typically, the best schemes are the explicit consideration of one or two water molecules surrounded by a continuum of constant polarizability. Including more than two explicit waters induces additional problems related to the configurational entropy (that is blocked) whereas not including them implies considering very specific and directional bonds.[104] However, continuum models are only recently being implemented in periodic boundary conditions codes.[22–24] The solution to the Poisson equation can be done in different ways, and in our particular case we used a multigrid algorithm to solve the underlying Poison equation,[23] an approach that was later used by other groups.[24] Our tests demonstrated that solvation values are in good agreement with the molecular implementations. Besides, the same scheme can be used to investigate transition states.[19] However, many developments are needed in this area so that such approaches become the standard in the field.

Complex Electronic Structure

In parallel, the study of the reactivity of biomass on oxide surfaces has many more fundamental problems arising from the complexity of the electronic structure of these materials[105] but also for the much wider variability in the types of elementary steps that they allow. For instance, ceria and molybdenum oxides have been described as active in the transformation of methanol (a byproduct of several biomass conversion processes)[106] into formaldehyde.[107–114] For CeO_2, the structure sensitivity drives the selectivity: the closed-packed (111) and (110) surfaces produce formaldehyde, which on the (100) surface is further oxidized to CO.[115] For molybdenum oxides, the influence of Mo oxidation state and the degree of surface reduction were analyzed. It was shown that only the fully oxidized MoO_3 is selective for formaldehyde production. In addition, the role of Fe as dopant, which was experimentally found to increase the catalytic activity,[116] was unraveled. Iron atoms act as electron buffer in redox steps decreasing the

energy barriers thus accelerating the process.[117] On the other hand, for many metal oxides, fundamental questions such as the way hydrogen is activated on the surface were only partially understood.[118,119] As several reactions involving biomass are dedicated to reduce the oxygen content via hydrodeoxygenation (HDO) processes,[120] which are carried out with the help of hydrogen,[121–124] the question of how H_2 interacts with the surface remains crucial to assess the catalytic capabilities of the surface. On $CeO_2(111)$ we observed that H_2 is activated heterolytically; thus, at the transition state, a proton and a hydride are formed,[125] but due to the surface reducibility the whole reaction ends up in the formation of two surface hydroxyls and the reduction of two cations. The use of the same surface in methanol conversion is the perfect example that demonstrates the limitations of standard DFT when investigating reducible oxides. The adsorption of hydrogen and formation of a surface vacancy by water releasing was studied for MoO_3.[89] Acid-base reactions are easily described by standard GGA methods. The main issue is that reactions that reduce/oxidize the surface require the use of GGA+U approaches[126,127] where the U stands for a local fix of the electron self-interaction that appears for strongly correlated materials.[128] This problem has been reported in the literature for years but there are further implications. The GGA+U approximation works for static problems (i.e. electronic structure) but when reduction (oxidation) processes take place, the best performing U value for the total reaction energy is not the best performing for the kinetic evaluation (transition state).[129] This is due to the different electron localization and imposes severe constrains when addressing the reactivity on oxides in complex reaction networks. While acid-base reactions are stable against the U term, the redox ones need to be benchmarked.[126–131] In addition, we have observed that the electronic structure can be very dynamic for reducible oxides. For oxides with more than one consecutive oxidation state, defects like oxide vacancies can provide two electronic structures that are dynamically interconnected, and thus both can be active parts of the catalytic cycle.[126] All these fundamental problems are also likely to emerge in the context of energy production[132,133] and storage[134,135] as many of them are based on small energy differences between different oxidation and spin states that can be easily masked by the inaccuracy and deficiencies that we have described above.

As electronic structure complexity increases the use of simple energy descriptors (like the adsorption energies of key species employed in metals) is no longer an option and more chemically adapted terms can be more suitable. We developed a new series of descriptors which are not based on adsorption energies and can be directly mapped to experimental observations. They encompass geometric, redox and acid-base terms, leaving out second order contributions such as phase cooperation, multifunctionality of active sites, and site isolation.[136] Our results show that elementary steps on different surfaces and in doped materials can be traced back to these parameters, particularly the redox terms, thus establishing a robust framework for future studies.[137,138]

Case Studies

In the following we present three case studies that have been at the core of the research:

Decomposition of C_1–C_2 Alcohols on Metals

The decomposition of methanol, ethanol and ethylene glycol was studied on different metals to analyze how the external conditions affected the activity and selectivity of the catalysts. Initially we searched for the most stable adsorption configurations extracting a new set of rules for adsorption on the pristine surfaces.[15] In parallel, the adsorption of water and its interaction with coadsorbed alcohols was investigated.[17] In both cases, the London dispersion contributions were found to be necessary to reproduce experiments. Taking these structures, we considered all the possible decomposition pathways arising from C–H, O–H, C–C, and C–O breakings, as well as the water-gas shift reaction. The resulting reaction network contains 75 intermediates and 250 transition states.[21,77] Due to its complexity, a genomic notation was developed to label the intermediates and easily account for the different decomposition routes of C_1 and C_2 alcohols on the metals under study. For example, $CH_3OH \rightarrow CH_2OH \rightarrow CH_2O \rightarrow CHO \rightarrow CO$ was denoted as: $1411 \rightarrow 1312 \rightarrow 1211 \rightarrow 1111 \rightarrow 1011$. In each notation, from left to right, the first three digits stand for the number of C, H, and O atoms in the given species. The last one is used to label possible structural isomers, which are typically 1–2 for C_1, 1–5 for C_2, and 1–9 for C_3. These genomic strings are well suited for automation procedures of C_1–C_3 molecules and were key to develop fast robust Density Functional Theory inputs. However, for larger molecules, other frameworks such as SMILES should be considered.[139] Similarly, all the transformations between fragments can be encoded. These provide a complete matrix of reactivity that can be downloaded as a csv file from the ioChem-BD database[27] to be further processed and then new elementary steps can be added if required. Since they are stored according to the FAIR[28] database principles, the data can be employed by other researchers in the field of Catalysis to reduce the computational and human burden of calculating such large networks. Besides, the database is openly available to be further analyzed by anyone through statistical-learning algorithms.

The database was then interrogated by a microkinetic model, to describe the catalyst behavior for H_2 production from alcohols under four different reaction conditions. These include steam reforming along two emerging alternatives, namely the aqueous-phase reforming and autothermal reforming.[77] In all cases, the reaction network for the decomposition plus the water-gas shift reaction are sufficient to describe the reactivity. However, in some cases, a few additional reactions were included to address particular issues such as CO elimination by oxidation and water assisted processes. Then, we were able to predict the activity of Ru for the reforming of glycerol by using linear scaling relationships (LSR). We have also found that LSR hold for solvent environments, as shown in Figure 1.[18,77] This
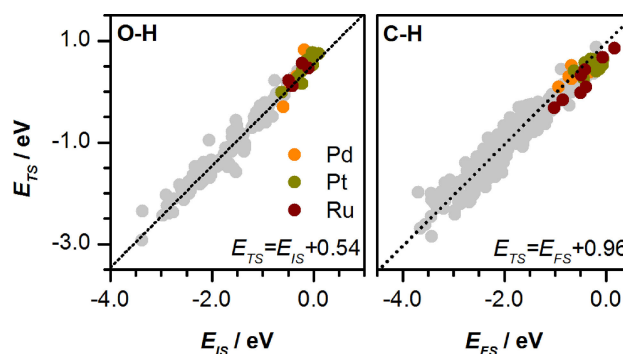

Figure 1. Initial and final states can be used to predict the energy of the transition states of O–H and C–H breakings, respectively. The corresponding scaling lines were deducted from data taken from Ref. [21] and [77]. Note that, these scalings are preserved for the reactions taking place in solvated environments, [19].

means that once solvation effects are considered for the intermediates, their effect on the activation energies can be predicted. Recently, a thermochemical model based on group additivity quantified the solvation effects.[94] Moreover, the scaling relationships drawn for surrogates can be transferred to higher alcohols provided that a few rules are preserved. Firstly, the adsorbates should not change their orientation due to large anchoring effects. Secondly, the molecule should have enough flexibility so that the reaction centers can interact with the surface without hindrance. Conjugation and aromaticity within the adsorbate molecule should be considered apart, *vide infra*. Finally, the surface-mediated interaction between functional groups should be mild. These conditions allow the formulation of a compact model for large molecules.

Epimerization and Nanoselect™ Ru

Biomass-derived molecules can also have a large impact on the food industry, where molecules as polysaccharides can be converted into high-value products like sweeteners and other food additives.[140] Nature generates sugars that differ from interesting precursors by the orientation of only one chiral CHOH center. The reaction that inverts the stereochemistry of a single stereocenter is called epimerization.[141] Mo-based catalyst, either in molecular or solid forms, were reported to catalyze the C2 epimerization of aldoses through a 1,2 C-shift.[142–144] We investigated the reaction path and the ability of different Mo-materials to carry out the reaction[145] and found that the same computational scheme can be used for both types of catalysts, linking their properties and showing that a unified theory in catalysis could be developed irrespectively the nature of the catalyst. The solvent contributions were obtained for the key step by applying implicit VASP-MGCM[23] code and by adding explicit molecules, thus helping into the formulations. The most relevant catalytic properties are related to the ability of Mo centers to cycle between different oxidation states, which can be modulated by the lattice, or the scaffold in molecular catalysts. Thus, reducibility, calculated as hydrogen

addition energy (HAE),[146,147] was found as the single descriptor of the activity, which shows a volcano-shape dependence on reducibility, see Figure 2. Finally, a better catalyst able to perform the reaction four times faster was identified.
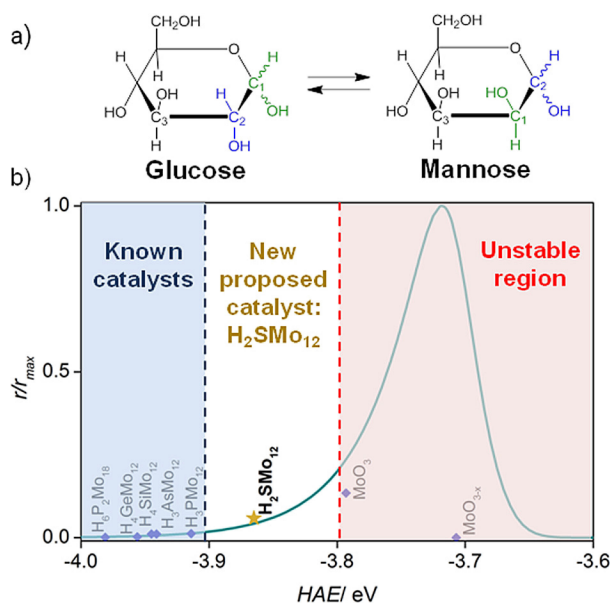

Figure 2. a) Schematic representation of the glucose C2 epimerization to mannose though a C-shift. b) Normalized reaction rate as a function of the hydrogen addition energy, HAE. Blue dots mark the rate calculated for the experimental catalyst.

The epimerized sugar feedstock can then be hydrogenated to produce the desired sugar alcohols. In this case, we studied the sugar (mannose and glucose) hydrogenations on the Ru catalyst.[51] Each of them has different isomers with linear and cyclic structures (α and β).[148] The concentration and adsorption energies of these isomers in the solution and on the surface, combined with the different rate-limiting steps (the water assisted ring opening and C—H bond formation) in hydrogenation network, determine the differential hydrogenation rates. The kinetic model based on the Langmuir-Hinshelwood mechanism[149] was used by considering the factors above. The reaction order of mannose and glucose hydrogenations from this model agrees well with experimental results.

Conversion of Acids and Lignin Derivatives

Increasing the complexity of the reactants leads to several issues. For instance, levulinic acid (LA) and γ-valerolactone (GVL) were labeled in the target list by DOE. LA can be derived from the Levulinic acid hydration process of 5-hydroxymethyl-furan (HMF) from cellulose and hemicellulose.[150–152] And GVL can be obtained from LA conversion. Several indications pointed out to the need for a catalyst with acidic properties to increase the rate of the catalysts. Experimentally, it was found that a new class of materials based on surfactant-decorated metals, in this case Ru, were able to perform the reaction with a

high activity and higher robustness. The reaction network leading from LA to GVL is a complex one and encompasses intramolecular ring esterification and hydrogenation steps. A domino reaction was earlier proposed in which the full LA was firstly protonated to $R-C(OH)_2^+$ and then followed by the ring formation and water elimination.[153] The final product, GVL, would be produced from the hydrogenation of the unsaturated ring intermediate. Our mechanistic investigation[154] described that to achieve full conversions into the final products the domino reactions are the C—O bond scissions from the COO— or COOH group on Ru surface as shown in Figure 3. In addition,
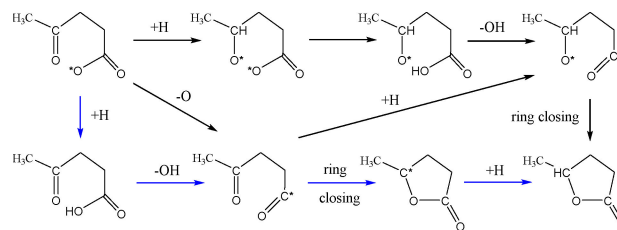
Figure 3. Mechanism of levulinic acid conversion to γ-valerolactone from DFT calculations.

our simulations showed how for the ligand-decorated Ru nanoparticles the reaction could be promoted by the interface high acidity, which can also be used for interpreting the similar behavior of graphene when it is used as the support for metal catalysts in LA conversions.[155,156] As we have mentioned before, acidity promotes a route where the reaction is speeded up about four times because it tips the balance in the starting point for the reaction networks. The complexity of both the catalyst and the reaction mechanism, as well as the of pH effects in decorated nanoparticles discussion for the first time present a new perspective that highlights the need to study decorated nanoparticles by tailoring their interfaces rather that the separated units (metal and ligand) independently. Recently, we have been able to use a similar approach to investigate the decarbonylation transformations of acids to alkenes on phosphine-decorated Pd catalysts.[157] Monodentate phosphines cover the surface and lead to the poor activity whereas bidentate ligands would break the ice by creating the transient cavities via their inherent dynamics, thus increasing the activity. Besides, the presence of the ligands also prevents the surface poisoning derived from the strong binding molecule, C, in a similar behavior as that of the ligand that prevents Ru oxidation by reducing oxygen adsorption.

The ultimate frontier in reactant complexity comes from lignin.[158] Lignin is a widely available biomass resource accounting for 15–30% of weight and up to 40% of the energy of lignocellulose.[159,160] Its rigidity and strength originate from the variable composition of polymer structures formed via C—C and aryl-ether linkages[161] and thus model systems need to be used to address the most fundamental questions like bond breaking mechanisms.[162] In particular, for theoretical research on the most common linkage β-O-4, dissociation mechanisms have been proposed by using simple surrogate models such as 2-

phenoxyethanol on Pt(111)[163] and 2-phenoxy-1-phenyletha-nol[164] on Pd(111). We have studied the role of chirality, conjugation and rigidity for dimers reacting on Ni and doped Ni. We have found that the surrogate approximation that has been so successfully applied for small molecules fails here due to the *sergeants and soldiers principle*.[165] Besides, rigidity inhibits the reactions on the C—C and C—H bond breakings. Conjugation and chirality can be potentially used to design catalysts for the β-O-4 bond selective breakings. In addition, single-atom catalysis (in this case as dopants in metals) shows a preeminent ability to selectively cleave and depolymerize such complex compounds.

Conclusions

During the last years many research groups have been trying to study by theoretical means the transformation of large biomass-derived molecules, mainly alcohols and polyalcohols, into molecules that can serve as chemical platforms. In this context we have contributed to solve fundamental problems by: (i) estimating new approximated parameters for the London dispersion contributions, (ii) building an implicit solvation model for periodic systems, (iii) identifying new linear scaling relationships on metals, (iv) determining conformational contributions for large molecules, and (v) automatizing the search of transition states. Metals and oxides were among the materials employed as catalysts. The largest challenges were related to: (i) the complexity of the electronic structures, like the dynamic oxidation states found for molybdenum oxides; (ii) the appearance of alternative non-conventional reaction paths such as the heterolytic cleavage of hydrogen on ceria; and (iii) the need for descriptors that address both redox and acid-base chemistry. In many cases, microkinetics was needed to understand the behavior of large reaction networks, such the ones arising from the decomposition of alcohols on metals. However, the comprehensive treatment of lateral interactions is still difficult and Kinetic Monte Carlo codes are not yet fit for this purpose. Despite the advances made so far, there are plenty of challenges and opportunities ahead. The intensive search for novel materials that can serve as catalysts will require their detailed electronic structure characterization. Biomass conversion is an area where the emerging techniques of statistical learning could reduce the computational burden and speed-up the discovery of new materials. However, sufficiently large and open data is needed to get reliable results from such algorithms. Therefore, the openness of the work performed by our group is one of the most encouraging aspects as newer models can be derived from our data. We hope that our studies may be helpful for the future modeling of catalytic systems with higher complexity. These models, combined with experimental data, shall provide valuable insights to keep building a sustainable chemical industry.

Conflict of Interest

The authors declare no conflict of interest.

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