

## López Research Group



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### Abstract

The aim of the group is to employ atomistic simulations to understand the mechanisms that govern chemical processes in heterogeneous catalysis and other materials that might be appealing due to their ability to extract, store or provide energy. Both the analysis of reaction networks, activity and selectivity issues and the final tests on the stability of the potential materials are fundamental to establish a solid background to determine the potentialities of catalyst candidates for a given chemical

transformation. As for the new energy materials, their performance and stability are two of the main goals in our research.

Our collaboration with several experimental groups is of fundamental importance to define and compare models that can later be applied to suggest experiments and new materials to be explored. To this end, the use of massive computational resources, as those provided by the RES-BSC is required. We are thankful to them for these resources that help in placing us as players at the European level.

Catalytic activity in heterogeneous catalysis strongly depends on the number of available active sites. Thus nanoparticles, with their high surface to volume ratio, show an enhanced activity. To take advantage of this characteristic, it is important to understand the factors behind gold nanorods. A first principles analysis has uncovered the details behind the anisotropy of these compounds. This phenomenon is caused by the formation of a complex between the surfactant, bromine and silver that preferentially adsorbs on some facets, blocking them from further growth. As a result, open (520) lateral facets appear in the final structure.

Not only the presence of surfactants determines the shape of the nanoparticles, it also greatly affects their selectivity, as it has been investigated in the case of Pd. This material is well known to act as Lindlar catalyst in the partial hydrogenation of triple bonds in acetylenic compounds. For this analysis, the bare, lead-poisoned and ligand-modified systems have been studied. Catalytic performance turns out to be correlated with the accessibility to the active site and with the adsorption configuration and strength, depending on the ensemble size and surface potentials. This explains the role of the ligand in promoting superior performance in the hydrogenation of terminal and internal alkynes, and short-chain alkynes.

An alternative way to improve the properties of nanoparticles is to form alloys. The effect of the composition and metal domain distribution has been evaluated in Au-Pd nanoparticles to understand better the enhanced properties compared to isolated metals. This is a novel study also because of the lack of experimental data, since they are more focused on equimolar nanoparticles. Compounds with varying Au:Pd molar ratios have been prepared by a seed growth method and the selective oxidation of benzyl alcohol was used as a model reaction to study the activity and the selectivity. A strong increase in catalytic conversion when using a 10:1 ratio has been retrieved. This is not casual, since it is the quantity need for Pd to cover the Au cores with a monolayer of Palladium as a full-shell cluster. The key to increased catalytic activity derives from the balance between the number of active sites and the ease of product desorption. According to the calculations, both parameters are extremely sensitive to the Pd content, resulting in a volcano-like activity.

Complexity can also arise from the interaction with the solvent. This problem has been addressed for both metals and porous systems. A typical solvent for reactions on metals is water. Since its influence is rather difficult to take into account explicitly, developing models for its interaction with metal surfaces is of fundamental importance. As an example, water is well known to adsorb on metals in a wide arrange of patterns comprehending several structural motifs like pentagons, hexagons and heptagons. Due to this variety, we have to take into account the

relative stability of the different patterns on the surface. Starting from the already reported structures for the water bilayers, their adsorption energy has been decomposed into their fundamental components: water-water, and water-metal interactions through strain-induced surface metal deformations. From this analysis it is possible to extrapolate the properties of any structure regardless of its complexity. Such properties include likeliness, relative stability, wettability and main patterns.

The effect of the solvent has been also explored in more complex systems such as Metal Organic Frameworks (MOFs). In particular, the influence of the environment has been investigated for the exchange of  $\text{Ni}^{+2}$  into MOF-5 and  $\text{Co}^{+2}$  into MFU-4l. The plotting of the extent of cation exchange versus different solvent parameters yields trends which shed a light on such phenomenon in MOFs and other materials.

Many efforts have been made to improve the present methodology. First, we have focused on the adsorption of molecules on metals. In such systems, van der Waals interaction contribution is dominant and it is still an open problem to correctly take into account. Common density functional theory methods used in the study of adsorption on metals lack dispersion contributions. Formulations like the random phase approximations would mitigate this error, but they are computationally too expensive. Therefore, semiempiric treatments based on dispersion coefficients turn out to be a practical solution. However, the parameters derived for atoms and molecules are not easily transferable to solids. In the case of metals, they cause severe overbinding, as screening is not properly taken into consideration. Alternative ways to determine these parameters for metal surfaces have been put forward, but they are complex and not very flexible when employed to address low-coordinated atoms or alloys. For these reasons, a self-consistent, fast, and costless tool to obtain the dispersion coefficients for metals and alloys for pristine and defective surfaces has been developed. Binding energies computed with these parameters are compared to both the experimental and theoretical values in the literature thus demonstrating the validity of our approach.

Once the adsorption energies are retrieved with enough accuracy, it is possible to employ such values to predict the behaviour of more complex molecules. This is done by linear-scaling relationships, which are powerful tools in the rational design of new catalysts. At the moment, only few of these thermodynamic relationships consider multifunctionalised molecules, and none deals with intramolecular interactions such as hydrogen bonds, which are widely present in polyoxygenated molecules obtained from renewable sources. To fill this gap, we have completed an adsorption database with 14 mono- and polyalcohols up to four carbon

atoms, on clean Pt and Pd(111) surfaces, using periodic density functional theory, and including van der Waals terms, and we have obtained results that are in good agreement with experimental data. With this data, we have proposed a robust multifactorial linear-scaling relationship, which is an additive function of the contributions from hydroxyl and  $\text{CH}_x$  groups and the hydrogen bonds. We have validated the model by comparison with experiments and by the prediction of adsorption energies of C4–C7 sugar alcohols on both surfaces. Our study paves the way for large multifunctionalised molecules, like those derived from biomass.

Unfortunately, such approach is not easily extendable to metal oxides, especially when the corrugation of the surface is comparable with the length of the adsorbates involved. For this reason we have systematically studied the interaction of small chain alcohols with up to four carbons and three hydroxyl groups on the  $\text{TiO}_2(110)$  rutile surface with different reduction degrees. Adsorption takes place through an acid–base interaction that can lead to both molecular and dissociated species. The latter are energetically preferred. Bulk reduction does not provide any significant change, either in the structure or in the adsorption energies, because the electrons are delocalised to a great extent. If vacancies are present at the surface these are the best adsorption sites for primary and secondary monoalcohols. In the case of bulky alcohols, steric hindrance is the main adsorption-controlling factor, while templating effects of the basic (oxygen) sites on the surface are the key parameters to understand the adsorption of poly-alcohols. Vicinal polyalcohols behave even in a more complex way, they prefer the vacancy position only when dissociated. Our results warn about the use of small surrogates to investigate the chemistry of large alcohols as the adsorption patterns are not only quantitatively but also qualitatively wrong.

$\text{RuO}_2$ , a rutile-like compound, has also been employed in the investigation of nano-scale processes. In fact, for a complete description of the catalytic processes, an extension to the nanoscale range of surface reactions is needed. To date, this has been only qualitatively achieved by means of kinetic Monte Carlo coupled to density functional theory, KMC-DFT. To understand the reasons behind this, a widely employed model for oxygen interaction with the  $\text{RuO}_2(110)$  surface, has been explored. Our analysis reveals several covert problems that render the model's predictions questionable. An advanced approach that considers all the relevant elementary steps and configurations has been suggested, along with the smoothing of the intrinsic errors in the DFT description of oxygen. Under these conditions, KMC provides quantitative agreement to temperature-programmed desorption experiments. These results illustrate how KMC-based simulations

can be pushed forward so that they evolve toward being the standard methodology to study complex chemistry at the nanoscale.

Finally, an important part of the work has been devoted to the study of reactivity of metal oxides. First, we have examined the limited activity of  $\text{TiO}_2$ , which strongly limit its use in the industry, despite having been deeply investigated. Concerning oxidation processes, this phenomenon has been related to the inability of  $\text{TiO}_2$  to dissociate molecular oxygen. In the oxidation of HBr to  $\text{Br}_2$ , the catalyst works through defect states that are introduced during the reaction. The identification of active, stable, and abundant materials for bromine production is the key to the future implementation of  $\text{Br}_2$ -mediated alkane functionalization processes. A comparison with expensive rutile-type oxides, such as  $\text{RuO}_2$  and  $\text{IrO}_2$  has been carried out, on the basis of surface characterisation and molecular modelling.

Another important process on metal oxides is  $\text{H}_2$  dissociation, whose mechanism is usually inferred from the infrared spectra of reaction products, on the basis of the presence or lack of M–H fingerprints. A deeper understanding of this reaction has been achieved by means of DFT. In fact it has been found that oxides with polar M–O bonds might favour heterolytic dissociation. Moreover, the resulting heterolytic product can evolve further to the homolytic one, provided that metal ions are reducible. Hence, it follows that the redox capacity of the metal determines the reaction outcome. This finding sheds light on why both M–H and O–H bands appear in the infrared spectra of nonreducible oxides such as  $\text{MgO}$  or  $\gamma\text{-Al}_2\text{O}_3$ , while only O–H bands are observed for reducible oxides like  $\text{CeO}_2$ . A unified mechanism for polar oxides results that can be generalised to other materials exhibiting significant charge separation. Importantly, the low activity of  $\text{CeO}_2$  toward  $\text{H}_2$  can be improved by enhancing the basicity of surface O atoms upon lattice expansion. This may pave the way for the efficient use of  $\text{CeO}_2$  in selective hydrogenation reactions and for the further advance on processes involving dissociation of nonpolar bonds like C–H.

$\text{CeO}_2$  is also used in the semihydrogenation of propyne. Interestingly, this reaction turned out to be characterised by a concerted mechanism. Compared to homogeneous and enzymatic catalysis, the study of heterogeneously catalysed reactions is far behind when considering concerted mechanisms. By means of DFT it has been demonstrated that the high surface H coverage imposed by the experimental hydrogenation conditions induces site isolation and drives the reaction through a six-membered ring transition state. This unprecedented pathway accounts for many of the experimental observations, such as the unique syn-stereoselectivity, the excellent

alkene selectivities, or the high temperature and large H<sub>2</sub>/alkyne ratios required.

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