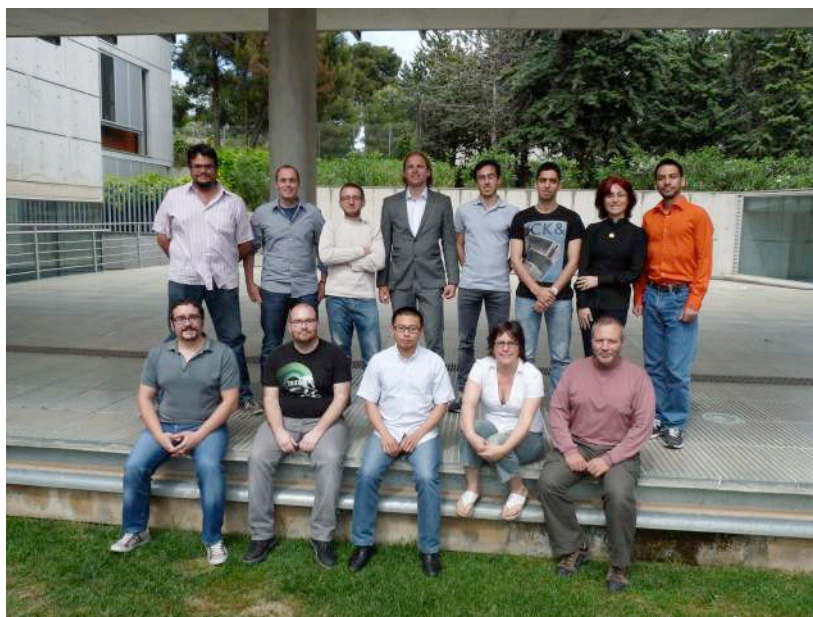


## López Research Group



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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 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.

One of our areas of research in 2013 was that of Metal–Organic Frameworks, which are considered to be the next generation of sorbents both because of their synthetic versatility and their high selectivity potential. In the first generation (IRMOF), the main drawback for commercial implementation is their lack of hydrothermal stability. Although several studies have been conducted to elucidate the reasons behind their structural weakness in humid environments, there is still a need to understand how apparently small changes in the stoichiometry of the building units affect the stability of the lattice. We investigated the reasons behind the different behaviour of several substituted IRMOF-1 structures by using density functional theory and *ab initio* molecular dynamics. We showed that hydrophilic variations in the organic linkers work as new basins of attraction for the incoming water molecules, thus depleting the water content at the metal centre. To confirm this, we performed Monte Carlo simulations to provide insights into the adsorption energies and check the effectiveness of the adsorption sites in the substituted structures for a variety of polar and non-polar molecules. The results showed that linker modification affects molecular adsorption and can improve the overall stability of the lattice in the case of hydrophilic units by redirecting water to the new sites. Three key parameters were singled out to rationalise this behaviour and were then used to predict the favoured adsorption sites in the case of gas mixtures. On the other hand, metal-organic frameworks with open metal sites, such as Cu-BTC, have the potential to improve the separation of molecules with differing polarities. In the Cu-BTC structure, molecules with high dipole moment, such as water, are adsorbed preferentially in the cages containing the open metal sites, whereas less polar molecules, such as alcohols, can be adsorbed in the other cages. We combined Monte Carlo simulations and *ab initio* calculations with the aim of tuning the adsorption properties of Cu-BTC (a) via selective blockage of cages or (b) poisoning the open metal centres. The simulation results propose selective blocking and screening of the active sites as good strategies to enhance the alcohol/water selectivity in the gas and liquid phases, as well as the water resistance of the structure.

With respect to the Deacon reaction, IrO<sub>2</sub> was investigated as an alternative rutile-type catalyst to RuO<sub>2</sub> for gas-phase HCl oxidation. The HCl conversion level over IrO<sub>2</sub> at 723 K was comparable to that of RuO<sub>2</sub> at ca. 170 K lower temperature, in line with the higher computed energy barrier for chlorine evolution over the former oxide. Similarly to RuO<sub>2</sub>, chlorination took place only at the IrO<sub>2</sub> surface, which is predicted to exhibit full occupation of the coordinatively unsaturated iridium sites and replacement of

50% of the oxygen bridge positions by chlorine. Advantageously, IrO<sub>2</sub> is more resistant to oxidation than RuO<sub>2</sub>, since the latter forms volatile RuO<sub>4</sub> species at high temperatures. We have also studied the modification of CeO<sub>2</sub> to improve this material in the Deacon reaction. The role of trivalent (La, Sm, Gd, and Y) and tetravalent (Hf, Zr, and Ti) dopants in the catalytic, structural, and electronic properties of ceria was investigated. Promoted ceria can be improved by a factor of 2 when doping with Hf and Zr in appropriate quantities, whereas trivalent dopants are detrimental. Although both oxidation reactions rely on the existence of oxygen vacancies, the order of reactivity in HCl and CO oxidation is not completely parallel. The effects of promoters on the electronic conductivity and the vacancy formation energy were studied by contactless conductivity experiments by using the microwave cavity perturbation technique and density functional theory calculations. Furthermore, transport properties were also assessed on the basis of theoretical calculations. The order of oxygen vacancy formation energy follows well the order of conductivity (polaron mobility) (trivalent > tetravalent > undoped) observed under inert and oxidizing conditions. This implies that none of these properties correlates with the reactivity. On the other hand, reducing conditions strongly enhanced the conductivity of Hf- and Zr-doped ceria. In HCl oxidation, only the balanced reduction of both Cl and O vacancy formation energies allows for an enhanced reactivity. Promoters give rise to lattice contraction-expansion modifying vacancy formation energies, adsorption properties, and surface coverages.

Another line of research was the study of selectivity in the area of hydrogenation. The gas-phase partial hydrogenation of propyne was investigated over supported Ag nanoparticles (2–20 nm in diameter) prepared by using different deposition methods, activation conditions, loadings, and carriers. The excellent selectivities to propene attained over the catalysts, exceeding 90%, are independent of the size of the particle size, but the activity is maximal over approximately 4.5 nm Ag particles. Certain kinetic fingerprints of Ag, such as the positive dependence on the alkyne pressure, the relatively low reaction order in H<sub>2</sub>, and the low apparent activation energy, deviate from those of conventional hydrogenation metals such as Pd and Ni, thus questioning the applicability of the classical Horiuti–Polanyi scheme. Periodic dispersion-corrected density functional theory (DFT-D) calculations and microkinetic analysis demonstrate the occurrence of an associative mechanism, which features the activation of H<sub>2</sub> on the adsorbed propyne at structural step sites. By using the atomistic Wulff model, the number of B5

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sites available on the Ag nanoparticles was estimated to be maximal, in the size range of 3.5–4.7 nm. The rate of propene production correlates with the density of B5 sites, which suggests that the latter are potential active centres for the reaction. This alternative pathway broadens the mechanistic diversity of hydrogenation reactions over metal surfaces and opens new directions for understanding metals that do not readily activate H<sub>2</sub>.

With respect to the architecture engineering we developed a method for understanding synthetic processes. Seed-mediated growth is the most efficient methodology to control the size and shape of colloidal metal nanoparticles. In this process, the final nanocrystal shape is defined by the crystalline structure of the initial seed as well as by the presence of ligands and other additives that help to stabilize certain crystallographic facets. We analysed the growth mechanism in aqueous solution of silver shells on presynthesized gold nanoparticles displaying various well-defined crystalline structures and morphologies. A thorough three dimensional electron microscopy characterisation of the morphology and internal structure of the resulting core-shell nanocrystals indicates that {100} facets are preferred for the outer silver shell, regardless of the morphology and crystallinity of the gold cores. These results are in agreement with theoretical analyses based on the relative surface

energies of the exposed facets in the presence of halide ions.

Finally we completed a long project concerning mobility in oxides. Oxides at the nanometric scale show a markedly different behaviour from that of their bulk counterparts. Ultrathin oxides grown on metals do not reach the full insulator regime, and they cannot decouple the electronic clouds of incoming adsorbates from those of the metal substrate. Although oxygen vacancies control the chemical and physical properties of ultrathin oxide films, the role of intrinsic defects has been overlooked so far. By means of density functional theory methods, we showed that the addition of atoms with high electron affinity, such as Au, to ultrathin MgO, grown either on a Ag or Mo support, has a threefold effect: reverses the preferential positions of oxygen vacancies completely, decreases their residual charge, and enhances their mobility. Oxygen vacancies behave in a completely different way for the MgO/M systems compared to the Au/MgO/M systems, which opens a new way to tune the reactivity of adsorbates.

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