

Research Highlights in the Last 5 Years

Prof. Pérez-Ramírez has been active for 20 years (including a 4-year PhD period and 3 years in industry) in the discovery and understanding of heterogeneous catalysts and reactor concepts devoted to sustainable technologies for the production of chemicals and fuels. He currently heads the group of Advanced Catalysis Engineering (aCe) at ETH Zurich, which works at the interfaces of chemistry, chemical engineering, and materials science and is internationally renowned for the design of novel catalytic materials amenable to industrial implementation. In the period 2013-2018, aCe has made notable accomplishments in challenging timely fields including the valorization of carbon dioxide, natural gas, and renewables, the design of single-atom catalysts, the analysis of pore quality in hierarchically-organized materials, and the development of other novel catalytic systems for various transformations of current and future relevance.

Disruptive catalytic technologies for the valorization of natural gas using halogen chemistry

The “flaring” of natural gas wastes around 3.5% of the global production, a quantity worth around 13 billion USD. To secure the improved utilization of this abundant resource, aCe has led efforts to engineer innovative processes for natural-gas valorization exploiting halogens as activating agents. Unprecedented catalytic systems including titania and europium oxybromide have been identified for efficient halogen recovery via gas-phase HBr oxidation in bromine-based upgrading processes (*Angew. Chem. Int. Ed.* **2017**, 56, 9791). Moreover, cost-effective catalysts based on titania, metal phosphates, and europium oxyhalides have been tailored for the selective conversion of small alkanes via oxyhalogenation chemistry at atmospheric pressure (*Nat. Chem.* **2016**, 8, 803; *Angew. Chem. Int. Ed.* **2016**, 55, 15619; *Angew. Chem. Int. Ed.* **2017**, 56, 13670). An impressive control over the product selectivity to alkyl halides, carbon monoxide, or olefins has been achieved by tuning the catalyst redox potential and halogen type under mild conditions and with a closed halogen loop. The use of advanced *in situ* characterization methods as photoelectron photoion coincidence spectroscopy enabled determination of the mechanism of these complex reactions, with the perspective of establishing structure-performance relationships that allow for rational catalyst design (*submitted*). The processes established constitute a basis for the on-site valorization of stranded natural gas reserves to platform chemicals, positively impacting the energy and chemical sectors with a favorable environmental footprint. Extrapolating our prominent expertise on halogen chemistry we further developed cerium oxide catalysts for ethylene oxychlorination (*Angew. Chem. Int. Ed.* **2016**, 55, 3068) and metal-free nitrogen-doped carbon catalysts for acetylene hydrochlorination (*ACS Catal.* **2018**, doi:10.1021/acscatal.7b03031), which are pivotal steps towards a more sustainable production of plastics.

Catalyst with the potential to realize the conversion of CO₂ to methanol on a commercial scale

A major breakthrough comprises the discovery of indium oxide as a catalyst for the direct hydrogenation of carbon dioxide to methanol (*Angew. Chem. Int. Ed.* **2016**, 55, 6261). Controlling the oxygen vacancies on the catalyst surface, the material can convert a greenhouse gas into a key chemical building block for chemicals and fuels, as an alternative to the classical petroleum-derived syngas route at industrially relevant space-time yields with demonstrated scalability to technical forms by supporting on zirconia extrudates. The selectivity to methanol (ca. 100%), achieved by blocking the reverse water shift reaction, and the stability on stream of at least 1000 hours are unique features of this catalyst, which has been patented in cooperation with the French energy firm Total, with the potential to realize continuous CO₂ conversion to methanol on a commercial scale. The role of CO₂ promotion on the commercial methanol synthesis catalyst was also elucidated through operando synchrotron-based diffraction and spectroscopy studies (*Angew. Chem. Int. Ed.* **2016**, 55, 11031).

Creation of stable single-atom heterogeneous catalysts based on carbon nitride

Designing heterogeneous catalysts in which the active phase is atomically dispersed and fully utilized is a longstanding dream of researchers wishing to fully exploit the exceptional catalytic potential of precious metals, as only a small fraction of the metal is available for catalysis in most commercial materials. Despite intense efforts, previous attempts had failed due to the poor sintering resistance of the resulting materials. Recognizing the unique structural and electronic properties of carbon nitride, we pioneered the first stable single-atom heterogeneous catalyst, featuring isolated palladium atoms entrapped within the cavities of this carrier (*Angew. Chem. Int. Ed.* **2015**, 54, 11265). Epitomizing the principles of green chemistry, the work opens unforeseen avenues in the field of heterogeneous catalysis, and aCe has already extrapolated the synthetic methodology to prepare single-atom catalysts based on various other metals (*Adv. Funct. Mater.* **2017**, 27, 1605785). Closely resembling the structure of the organometallic complexes traditionally applied, the exciting potential of metal centers isolated on carbon nitride to replace homogeneous catalysts in processes difficult to heterogenize was demonstrated for Suzuki couplings (*submitted*).

Advanced methods to assess complex pore architectures in hierarchically structured catalysts

The engineering of multilevel pore architectures is increasingly pursued to combine the unique chemical functionality of catalytic solids with efficient molecular transport. aCe is world leading in the synthesis, structural

analysis, application and scale up of hierarchically-organized zeolites. A major recent achievement has been the identification of powerful advanced tools to gain insight into the architecture of complex pore networks and the impact on transport processes, which is essential to optimize their integration. For example, positron annihilation lifetime spectroscopy (PALS) was demonstrated to have unprecedented sensitivity to the global connectivity of pores in hierarchically-organized zeolites and their related effectiveness at enhancing the diffusion, which were found to govern the catalyst lifetime in coke-forming reactions, such as the acid-catalyzed conversion of methanol to olefins (*Nat. Commun.* **2014**, 5:3922; *Angew. Chem. Int. Ed.* **2015**, 54, 1591). Similarly, the scope of the widely applied technique of gas sorption was greatly extended through the development of differential hysteresis scanning approaches to map the mesopore geometry, enabling unprecedented insights into the impact of widely practiced demetallation treatments on the porosity evolution (*Adv. Funct. Mater.* **2016**, 26, 5621). These efforts have contributed to a paradigm shift in the way in which zeolite catalysts are manufactured and applied that has been recognized by both academia and industry alike.

Design of metal compounds with controlled vacancy chemistry for selective hydrogenations

Heterogeneously catalyzed hydrogenations are key transformations applied industrially at different scales, ranging from the multi-ton purification of olefin streams to the smaller batch preparation of fine chemicals. Intensive efforts have been devoted to breaking away from the reliance on scarce noble metals (Pd, Pt, Ru) employed in the traditional formulations through the precise control over the catalytic ensemble. By tailoring the nanostructure of various metal compounds, the group has identified highly selective materials for alkyne semi-hydrogenation. Understanding and controlling the chemistry of oxygen vacancies was shown to be critical to develop catalysts based on metal oxides. While their formation was found to adversely affect the performance of cerium oxide (*Angew. Chem. Int. Ed.* **2014**, 53), the surface reduction of indium oxide led to the creation of well-defined vacancies and surrounding In_3O_5 ensembles exhibiting outstanding selectivity in acetylene hydrogenation under industrially-relevant conditions (*Angew. Chem. Int. Ed.* **2017**, 56, 10755). Similarly, shape-controlled syntheses were found to be fundamental to maximize the performance of metal sulfides (*submitted*). The insights obtained provide design rules to tap the unexploited potential of non-toxic compounds and preferably abundant metals.

Catalyst and process design for the sustainable manufacture of biochemicals

The identification, development, and implementation of processes to convert renewable feedstocks into chemicals is a vibrant field of research rooted on mitigating global warming and transitioning to a post-petroleum future. In this context, aCe has pioneered the concept of process-driven catalyst design integrating modelling and assessment through life-cycle analysis as an early-stage evaluative tool of the economic and environmental perspectives of future biorefineries. This is demonstrated for the sustainable valorization of glycerol a burgeoning waste product from the bioenergy sector, into the most appropriate portfolio of value-added chemicals (*Energy Environ. Sci.* **2015**, 8, 558; *submitted*). This innovative and versatile approach holds the potential to guide both fundamental chemical research and process design in the development of biorefineries based on CO_2 and other perspective renewable feedstocks.

Facile routes for the large-scale manufacture and regeneration of metal organic frameworks

Metal-organic frameworks (MOFs), porous coordination polymers possessing extremely high surface areas, have flourished since their introduction into a wide variety of compositions and more than 15000 structures. Currently, the most important factors influencing their industrial implementation concern the limited cost efficiency in terms of space-time-yield, the frequently high cost of raw materials and complex character of the synthesis, coupled to the existence of and stability in applications justifying their large-scale production. To tackle this, we have developed a scalable room-temperature route for the conversion of widely available copper hydroxide into HKUST-1, one of the most promising MOFs for catalytic and adsorption applications (*Adv. Mater.* **2013**, 25, 1052). The group also introduced the possibility of reconstructing this MOF following degradation due to contact with water, via a facile, one-step, solvent-assisted treatment (*Adv. Funct. Mater.* **2014**, 24, 3855).

Sustainable manufacture of chemicals on capped nanoparticles

The controlled capping of metal colloids with ligands can enable the development of catalysts with unique functionality. Inspired by this, aCe has illustrated the importance of understanding the interfacial effects related to the metal-ligand interaction in order to maximize the potential performance enhancements, which was demonstrated for hybridized metal nanoparticles modified by the water-soluble ligand hexadecyl(2-hydroxyethyl)dimethylammonium dihydrogen phosphate and supported on suitable carriers. In particular, the intrinsic acidic properties at the ligand-metal interface of capped ruthenium nanoparticles permitted a less energy demanding path in the hydrogenation of levulinic acid to gamma-valerolactone one of the top 10 most promising renewable platform chemicals (*Green Chem.* **2017**, 19, 2361). The presence of the organic shell was also shown to be key to changing the adsorption mode of reaction intermediates on palladium nanoparticles, resulting in highly efficient catalysts for the direct synthesis of hydrogen peroxide, which attracts growing attention as a green oxidant (*Angew. Chem. Int. Ed.* **2017**, 56, 1775).