

The field of catalysis is in a state of continuous and chameleonic evolution and expansion, to address the world's socio-economics needs. Since the beginning of the last century, we have observed a strong correlation between industrial needs and research activities focussed on discovering new chemical processes: ammonia synthesis that increased for example, the supply of nitrogen fertilizers thanks to the work of Haber (1919 Nobel Laureate) and Bosch (1932 Nobel Laureate); Fischer-Tropsch synthesis of hydrocarbons; catalytic production of polymers from petrochemicals; and now the new era devoted to green chemistry catalysis. Ostwald (1909 Nobel Laureate) introduced the concept of chemical kinetics and defined a catalyst as “*a substance which affects the rate of a chemical reaction without being part of its end products*”. In the long pathway that has led catalysis to be a more and more predictive science, there are several notable milestones. This new era can probably be traced to the remarkable work of Ertl (2007 Nobel Laureate) which triggered a real revolution. The core of Ertl's revolutionary approach is that catalysis is a science that should be understood, and hence controlled and improved, at the atomic level.

In recent decades, researchers have begun a complete transition towards a deep understanding of catalytic processes at the molecular/atomistic level, based on the concept of active site(s), defined as the region where reactions occur. Moreover, we have assisted in the introduction of descriptors, as quantities which capture (i.e. determine) the catalytic properties of the system. So far, the study of catalytic activity has been related to specific energy mappings, because the adsorption energies of the reactants and the activation energies of the intermediate steps enable the establishment of scaling relationships to be constructed. The reactivity depends on the adsorption strength, showing a ‘volcano’ behaviour, where both a too weak (the reactant desorbs easily) and a too strong (limited by the desorption of product) interaction is deleterious to catalysis. In this view, new descriptors, e.g. the d-band centre and the generalised coordination number, have been introduced to map the energies, leading to a completely new objective in catalysis aimed at a fast screening of materials for acceleration of a certain reaction. This *gold-rush* to find the best catalytic materials often goes under the name of *catalysis-by-design*.

Simultaneously, in the last two-to-three decades, another revolution has taken place arising from the rapid development of the nanoworld or nanoscience. Thanks to advances in microscopic and spectroscopic techniques, miniaturization down to the nm scale and the increasing ability to tune objects (later on called nanoparticles) at such a scale, has offered a variety of new and novel solutions. The alliance between nanoscience and catalysis is focused on achieving a generation of nanocatalysts with both high activity and high selectivity. Furthermore, there is an economic benefit in reducing the amount of precious-metals by developing nano-engineered catalysts. The size-dependence of the catalytic performance of nanoparticles is quite well documented, although not without contradictions. Indeed, there are positive size-sensitivity regimes, where the turnover frequency increases with decreasing nanoparticle size, but there are also negative and neutral-size-sensitivity regimes, for which miniaturization is not of any benefit. Indeed, to meet the main objectives of nanocatalysis, meaning the atomic level control of the complex interaction between nanocatalysts and reactants, we need to unravel not only the size- but also morphology-dependence of catalytic performance. Indeed, employing cluster beams to synthesize and deposit size-selected clusters, it is possible to select single size or a narrow cluster size distribution of metallic nanoparticles and soft-land them onto oxide and carbon-based supports for subsequent tests and characterization.

This Special issue on “*Shaping nanocatalysts*” tries to show some of the efforts researchers are making in this challenging path, manipulating metallic nanoparticles to improve their catalytic performance. In this process, the importance of computational chemistry and physics, as uniquely powerful tools for developing atomistic models for nanostructures, is striking. Indeed, optimising the performance of nanoparticulate based materials requires a detailed understanding of their structures, morphological dynamics and reactivities at the atomic and molecular level. Density functional-genetic algorithm approaches, such as the Birmingham Parallel Genetic Algorithm, can be employed to predict the energetic ordering of metallic nanoparticles. Density functional theory is still the most used and feasible method for sampling the potential energy surface of small

clusters and to estimate the most stable chemical orderings as shown in Guerrero-Jordan, et al. in "Theoretical Investigation of the Structures of Unsupported 38-atom CuPt Clusters". The catalytic performance of nanoparticles can be understood by determining the reaction mechanisms that lead to the different intermediates and products. These mechanisms often consist of many steps, making the analysis of each mechanism for the different catalysts excessively demanding by standard computational tools, although employing descriptors, could accelerate the evaluation of the catalytic performance by analysing specific features of the active sites and the reacting molecules. Indeed, proposing new geometrically sensitive scaling relations between the adsorption energy of adsorbates that are valid for all metals and for all surface sites, by introducing simple descriptors, such as the generalized coordination number, have a strong predictive potential. Applications and limitations of the generalised coordination number as a descriptor have been discussed by Vagner Rigo et al., in "Ethanol chemisorption on core-shell Pt-nanoparticles: an ab-initio study". It was noted that, for relatively long molecules, the distortion of the underlying nanoalloys should be taken into consideration as part of the geometrical descriptor. Nonetheless, the use of geometrical descriptors may turn out to be extremely helpful to account for isomeric fluctuations. We should indeed stress that metallic nanoparticles undergo frequent structural transitions which are thermally activated already at room temperatures, making the hypothesis of a static lattice an oversimplification. In the manuscript authored by K. Rossi et al., entitled "The effect of size and composition on structural transitions in monometallic nanoparticles", Metadynamics and Iterative Molecular Dynamics are applied to address the temperature-dependence of structural changes, and how concerted mechanisms depend on the chemical species.

However, size, shape and temperature are not the only parameters to play with to optimise the catalytic properties of metallic nanoparticles. In the case of multicomponent nanoparticles (nanoalloys), they may present distinct chemical ordering which is not usually available in their bulk counterparts. Indeed, the mismatch between the two metals might lead to a series of size-dependent structural transitions, which can be rationalized in terms of symmetry-breaking, caused by the accumulation of stress at the atomic level and its subsequent release. Density functional based methods to optimize chemical ordering in nanoalloys are under investigation, with the objective of enabling the generation of databases of structures and energies of bimetallic nanoalloys spanning the Periodic Table. Improving the performances of metal catalysts through nanoalloying is also confirmed by experiments. For example, bulk-immiscible bimetallic systems, such as Pd-Ir, at the nanoscale form segregated Ir@Pd core-shell structures, which are active for the preferential oxidation of CO (PROX) in the presence of hydrogen. Aslan and Johnston in their paper "Pentameric PdAu and PdPt Nanoparticles on the MgO (100) Surface and their CO and O₂ Adsorption Properties", also address the effect of the substrate on the catalytic activity of Pd-based nanoalloys using density functional theory.

The Thomas-Young Centre London, jointly with the Toucan critical mass group (EPSRC Critical Mass project "Towards an Understanding of Catalysis on Nanoalloys", EP/J010804/1, a UK network for the modelling and the design of multimetallic nanoparticles for target reactions) organised the 4th TYC Energy Materials Workshop, held on 14-16 December 2016 at King's College London, UK. This workshop brought together leading experts from across the world on the design of nanocatalysts and plasmonic nanoparticles for catalytic applications. The workshop showcased the very best of current research in the area of nanoparticle design for catalytic applications, with an overview of the most recent developments, such as plasmonic nanoparticles for accelerating catalytic reactions. Psi-K, CCP9, Springer, and IoP sponsored the event, which enabled fees for early career researchers to be halved, resulting in 43% of the audience being made up by PhD students and research assistants. Overall, 79 participants, from institutions spread over 14 different countries, attended the conference and at least 20% were female scientists. The workshop provided a forum for the exchange of best practice and discussion of future directions of this growing field of computer simulation. Furthermore, thanks to the warm and supportive atmosphere, delegates shared their scientific views, and techniques and boosted their collaborations. As Gianfranco Pacchioni (Bicocca-Milano) highlighted in his closing remarks,

“we have learnt something new in these days, and this is not so common”. We hope that this Special issue helps you all to get a flavour of that learning.