



Preface on recent advances on surface and interface functionalization in Nano-Catalysis (SUR-INTER-CAT)



Heterogeneous catalysis constitutes an indispensable part of our society, receiving ongoing attention from both the academic and industrial community. It is massively involved in numerous energy and environmental processes of paramount importance, including, the production of high quality chemicals and fuels, hydrocarbons processing, fuel cell applications, photocatalytic degradation, abatement of hazardous substances, among others. In this regard, the rational design and development of cost-efficient catalysts with adequate activity and durability constitutes one of the main research pillars in catalysis [1–4].

Towards this direction, the fine-tuning of size, shape and electronic state at nanoscale by means of advanced synthesis procedure and surface/interface functionalization strategies (e.g., surface promotion, aliovalent doping, chemical modification, special pretreatment protocols, organic ligands, etc.) can exert a profound influence not only to the surface reactivity of metal sites in its own right, but also to metal-support interfacial activity, offering extremely active and stable materials for real-life energy and environmental applications, such as the CO oxidation [5–9], NO_x abatement [10–12], CO₂ hydrogenation to value-added products [13–15], degradation of organic contaminants [16–20], etc.

The present themed issue is focused on the recent advances in relation to the synthesis and the surface/interface functionalization of catalysts composites. It consists of six high quality papers, in which advanced synthetic and/or modification routes were employed towards the development of highly active and stable nanocomposites for various energy and environmental applications.

Dong et al. [21] prepared by electrospinning highly efficient and stable La_{0.8}Ce_{0.2}Fe_{1-x}Ni_xO₃ perovskite-type nanofiber catalysts for CO oxidation. Interestingly, calcination temperature notably affects crystal structure and oxygen storage capacity, with the optimum performance to be obtained at 800 °C. Moreover, Ni-doping facilitates oxygen vacancies formation resulting in an enhanced oxidation performance. These findings clearly revealed the key role of synthesis procedure and pretreatment conditions towards modulating the solid state properties and in turn the catalytic performance.

In a similar manner, Benzbiria et al. [22] revealed the pivot role of copper surface pretreatment (pre-reduced, passivated and covered with PDTC ammonium salt) on the oxygen reduction reaction (ORR) in 0.5 M NaCl solution. In particular, ORR rate is markedly affected by the surface treatment, following the order: PDTC covered < reduced < passivated. The beneficial effect of passivation was attributed to the partial reduction of copper oxide, which enhances ORR kinetics. On the other hand, PDTC inhibits the ORR, due to the formation of a protective layer which limits the O₂ access to the surface. Moreover, in a pre-reduced

copper surface, the ORR is controlled by the oxygen diffusion in the solution.

Moreno et al. [23] synthesized a mixed-structure silica by SiCl₄ hydrolysis through nanoparticles growth on a micrometric surface, which generates a local heterogeneity with nano- and micro-metric domains on the surface. Both silica nanoparticles and mixed-structured silica with Si-Cl surface groups were employed as carriers to prepare titania/silica photocatalysts. The as-obtained composites exhibited high photocatalytic activity for the degradation of RhB dye, which can be attributed to the fine-tuning of structural topology induced by the synthesis route.

Kannan et al. [24] revealed the effectiveness of rare-earth doping towards obtaining NiO-Ce_{0.9}Y_{0.1}O_{2-δ}-Ce_{0.9}Sm_{0.1}O_{2-δ} nanocomposites, which can be employed in various energy and environmental related processes. In particular, rare-earth doping notably alerts the physico-chemical properties of parent oxides, which then is reflected in their photo-catalytic and antibacterial activity.

Avalle et al. [25] explored the possibility to fine-tune the reactivity of electro/electrolyte interface in energy conversion processes, such as the hydrogen evolution reaction (HER). More specifically, the impact of the geometry of silver crystalline facets (111) and (100) on the phosphate species adsorption as a function of the potential was explored. Significant face-induced differences on the electrochemical properties were disclosed; for instance, the onset potential of HER reaction in Ag(111) was about 100 mV more negative compared to Ag(100).

Finally, Rives et al. [26] reported on the functionalization of sepiolite clay mineral by (3-chloropropyl)triethoxysilane (CIPTES) or 3-[tri(ethoxy/methoxy)silyl] propylurea (TEMSPU) alkoxides. The obtained solids were tested as adsorbents for pollutants adsorption, such as herbicide glyphosate and caffeine. It was found that silane functional groups blocked the active sites, thus adsorption is mainly taking place within the zeolitic channels and on the surface of the functionalized solids. To this end, pollutants effectively interacted with urea groups from grafted alkoxide, which could lower the mobility of the adsorbed contaminants.

In summary, this special issue highlights the ongoing importance of “surface/interface functionalization”, towards fundamental understanding and rational design of highly active and robust composites for numerous energy and environmental applications. We are very pleased to serve as Guest Editors on this thematic issue involving six high quality studies. We would like to express our gratitude to the Editorial staff of Applied Surface Science Advances for the invitation and continuous support. We are also most appreciative to all authors and reviewers for their efforts towards obtaining the current special issue.

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Guest Editors of the Special Issue “Recent Advances on Surface and Interface Functionalization in Nano-Catalysis (SUR-INTER-CAT)”.

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