

Editorial

Surface Chemistry and Catalysis

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1. Background

Nowadays, heterogeneous catalysis plays a prominent role. The majority of industrial chemical processes, involving the manufacturing of commodity chemicals, pharmaceuticals, clean fuels, etc., as well as pollution abatement technologies, have a common catalytic origin. As catalysis proceeds at the surface, it is of paramount importance to gain insight into the fundamental understanding of local surface chemistry, which in turn governs the catalytic performance. The deep understanding at the atomic level of a catalyst surface could pave the way towards the design of novel catalytic systems for real-life energy and environmental applications.

Thanks to surface science we can obtain profound insight into the structure of a surface, the chemical state of active sites, the interfacial reactivity, the way molecules bind and react, the role of surface defects and imperfections (e.g., surface oxygen vacancies), and the mode of action of various surface promoters/poisons. To elucidate the aforementioned surface phenomena, sophisticated techniques in combination with theoretical studies are necessary to reveal the composition and the structure/morphology of the surface as well as the chemical entity of adsorbed species. Moreover, time-resolved methods are required to investigate the dynamic phenomena occurring at the surface, such as adsorption/desorption, diffusion and chemical reactions. Under this perspective, it was clearly revealed, based on the recently published review articles by the Guest Editor, that the complete elucidation of a catalytic phenomenon (e.g., metal-support interactions [1]) or the fundamental understanding of a specific catalytic process (e.g., N₂O decomposition [2]) requires a holistic approach involving the combination of advanced *ex situ* experimental and theoretical studies with *in situ operando* studies.

2. This Special Issue

In light of the above aspects, the present themed issue aims to cover the recent advances in “surface chemistry and catalysis” that can be obtained by means of advanced characterization techniques, computational calculations and time-resolved methods, with particular emphasis on the structure-activity relationships (SARs). It consists of 14 high-quality papers, involving: a comprehensive review article on the surface analysis techniques that can be employed to elucidate the phenomenon of electrochemical promotion in catalysis [3]; two theoretical studies (Density Functional Theory, DFT) on H₂O dissociation and its implications in catalysis [4,5]; two mechanistic studies by means of temperature-programmed desorption/surface reaction (TPD/TPSR) and/or operando spectroscopy on N₂O formation over NO_x storage-reduction (NSR) catalysts [6] and on methanol reforming over cobalt catalysts [7]; two articles on H₂ production by the steam reforming of ethanol [8] or diesel [9] over transition metal-based catalysts; two articles on the production of commercial fuels by Fisher-Tropsch synthesis [10,11]; two articles on Au-catalyzed CO oxidation [12] and preferential CO oxidation [13]; and three experimental investigations regarding the structure-activity correlation of NO oxidation to NO₂ over Mn-Co binary oxides [14], cyclohexene oxidation on TiZrCo mixed oxides [15] and alkene epoxidation on silica nanoparticles [16].

Contribution Highlights

The comprehensive review of González-Cobos J. and de Lucas-Consuegra A. [3] addresses the latest contributions made in the field of surface analysis towards the fundamental understanding of the Electrochemical Promotion of Catalysis (EPOC). The authors clearly revealed that the combination of in situ and ex situ surface analysis techniques, such as SEM, XPS, STM, SPEM, UPS, can provide the basis of a better understanding of the alkali-induced promotional effects. This multifunctional surface approach allows the authors to gain insight into the local surface structure of promoter species as well as of back-spillover phenomena taking place under electrochemical promotion conditions. Given the paramount importance of alkali promoters in catalysis, the results presented in this review can shed some light into the underlying mechanism of electrochemical promotion, also paving the way towards the design of highly active conventional heterogeneous catalysts.

Kilin D. and co-workers [4] investigated, by means of DFT calculations combined with density matrix equations of motion, the charge transfer mechanism involved in H₂O dissociation over titanium-doped microporous silica. The results revealed that silica substrates contain electrons and hole trap states, which could facilitate the water splitting. This provided strong evidence towards the key role of the substrate in the electron/hole dynamic processes involved in H₂O dissociation. In this regard, the fine-tuning of metal and/or substrate characteristics could lead to the optimization of (photo)catalytic efficiency.

In a similar manner, Wang W. et al. [5] explored, by means of DFT calculations, the adsorption of H₂O and its dissociation fragments (OH, H and O) on clean and O-pre-adsorbed Fe(100) surfaces. It was demonstrated that interactions between the different adsorbates and catalyst surface followed the order: H₂O < OH < H < O. More interestingly, it was revealed that both the H abstraction from the H₂O molecule and the subsequent OH dissociation are favored over O-pre-adsorbed Fe(100) surfaces. The results confirmed that the presence of pre-adsorbed oxygen on the catalyst surface can notably enhance the H₂O dissociation, opening new horizons towards the development of more efficient catalysts.

In a comprehensive mechanistic study by Forzatti P. and co-workers [6], the origin of N₂O formation over Pt-BaO/Al₂O₃ and Rh-BaO/Al₂O₃ model NSR catalysts was investigated by micro-reactor transient reactivity experiments and operando Fourier transform infrared (FT-IR) spectroscopy. It was clearly revealed that N₂O formation involves the coupling of undissociated NO molecules with N-adspecies formed via NO dissociation onto the reduced metal sites. In this regard, the N₂O formation is dependent on the oxidation state of the metal sites. At high temperatures, where the reductants effectively keep the metal sites in a fully reduced state, complete NO dissociation is achieved, thus hindering the N₂O formation. In contrast, at low temperatures, where the reductants start to reduce the active sites, the N₂O formation is favored.

The adsorption characteristics of methanol and its reforming products over Co-Mn catalysts were systematically investigated by Papadopoulou E. and Ioannides T. [7] through temperature-programmed desorption (TPD) studies. The influence of various parameters, in relation to the synthesis procedure and the Co/Mn ratio, into adsorptive properties was systematically explored in order to gain insight into the structure-activity relationships. The results indicated that the activity differences can be mainly related to the relative population and the nature of active sites. In particular, Co and Mn sites were considered to be responsible for H₂ desorption at low and high temperatures, respectively, whereas the interfacial sites can be considered for the intermediate temperature H₂ desorption.

Konsolakis et al. [8] reported on the Ethanol Steam Reforming (ESR) of various transition metals (Ni, Co, Cu, Fe) supported on CeO₂ with particular attention to surface chemistry aspects. A complementary surface characterization study was undertaken to reveal the impact of metal entity and/or metal-support interactions on the reforming activity. The results revealed the excellent reforming performance of Co/CeO₂ catalysts, both in terms of H₂ yield and life-time stability. The latter was attributed, inter alia, to the high oxygen mobility of cobalt-ceria binary oxides, mainly linked with

the high population of lattice oxygen species. This factor can be considered responsible for the facile gasification of the carbonaceous species, thus preventing catalyst deactivation.

The impact of structural promoters (La, Ba, Ce) on the Diesel Steam Reforming (DSR) of Ni/Al₂O₃ catalysts was explored in detail by Tribalis A. et al. [9]. Incorporation of dopants into the Al₂O₃ carrier was found to be always beneficial, but to a different extent, depending on the nature of the promoter. The optimum performance, in terms of activity and stability, was obtained by simultaneously doping the Al₂O₃ support with Ba and La modifiers. On the basis of a complimentary surface characterization study, the latter was attributed to the increase of dispersion and reducibility of the Ni phase in conjunction with the decrease of the support acidity.

Lopez L. et al. [10] comparatively explored the catalytic performance of Rh/MCM-41 and Rh/SiO₂ catalysts for ethanol synthesis from syngas. The obtained differences in activity and selectivity were attributed, on the basis of complementary catalytic and surface characterization studies, to the different concentrations of water vapor in the pores of Rh/MCM-41. The latter was considered responsible for the enhanced formation of CO₂ and H₂ over Rh/MCM-41 catalysts through the water-gas-shift-reaction (WGS).

De la Osa A.R. et al. [11] investigated Fisher-Tropsch synthesis (FTS) over Co/SiC catalysts with particular emphasis on the impact of cobalt precursor (nitrate, acetate, chloride, citrate) on FTS activity. Surface titration techniques along with an extended characterization by TPR and TEM were employed to gain insight into the structure-activity correlation. It was found that the nature of the precursor notably affects the acid/base properties as well as the metallic particle size, with great consequences on the FTS activity and chain growth probability. Cobalt nitrate provided the optimum activity and selectivity to C₅⁺, which was attributed to the higher particle size, degree of reduction and basicity as compared to the other precursors.

Cui H.-Z. et al. [12] studied low-temperature CO oxidation over Au/FeO_x catalysts, employing two different types of iron oxide supports, i.e., hydroxylated (Fe-OH) and dehydrated (Fe-O) iron oxides, and different preparation procedures (precipitation pH, calcination temperature). Surface characterization by a series of advanced characterization techniques, i.e., high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES) spectroscopy, was carried out to explore the relationship between the nature of the oxide matrix and the catalytic activity. The results revealed that the surface chemistry of Au nanoparticles can be notably influenced by the nature of the support as well as by the preparation procedure following, with vast consequences on the catalytic activity. Metallic gold particles strongly interacting with the oxide carrier were determined as the active sites for CO oxidation.

Widmann D. and co-workers [13] explored, in a comprehensive manner, the underlying mechanism of the CO-PROX reaction over Au/TiO₂ catalysts by means of quantitative temporal analysis of products (TAP) reactor measurements. The authors concluded that CO and H₂ are oxidized by the same active oxygen species under PROX conditions, independently of the CO/H₂ ratio; both CO and H₂ compete for TiO₂ surface lattice oxygen located at the perimeter sites of the metal-support interface. In light of these findings, the authors suggested that the strategies for more selective Au catalysts should focus on the fine-tuning of the support material and/or the metal-support interface perimeter sites.

Qiu L. et al. [14] investigated the low-temperature oxidation of NO to NO₂ over Co-Mo/TiO₂ catalysts with particular attention to the impact of Co loading and the calcination temperature. Cobalt incorporation into Mo/TiO₂ catalysts in conjunction with calcination at moderate temperatures (300–400 °C) resulted in the optimum oxidation performance. By means of various surface characterization techniques, a close correlation between the redox characteristics (Mn oxidation state, amount of surface adsorbed oxygen) and the NO oxidation performance was revealed.

Liu T. et al. [15] investigated the aerobic oxidation of cyclohexene to value-added chemicals over TiZrCo metallic catalysts. High conversion of cyclohexene (>90%) accompanied by high selectivity to 2-cyclohexen-1-one (ca. 58%) was obtained by this particular catalyst, and these are among the

highest values reported. Surface characterization revealed that CoO and Co₃O₄ are the active sites contributing to the superior performance of TiZrCo catalysts.

Finally, Li X. et al. [16] examined the cyclooctene epoxidation over phosphotungstate-based ionic silica nanoparticles. The novel synthesized silica network was extremely active for cyclooctene epoxidation, offering almost complete conversion and selectivity to epoxy-cycloocten at 70 °C. The superior efficiency of the as-synthesized material as compared to bare SiO₂ nanoparticles was ascribed, based on an extended characterization study, to their optimal textural and structural/morphological characteristics.

In summary, the aforementioned special issue highlights the ongoing importance of the “surface chemistry approach”, from both theoretical and experimental points of view, towards the fundamental understanding of catalytic phenomena. I am very pleased to serve as the Guest Editor of this thematic issue involving 14 high-quality studies on the interfacial discipline of “surface chemistry and catalysis”. Firstly, I would like to express my gratitude to Professor Keith Hohn, Editor-in-chief of the *Catalysts* journal, for his kind invitation to organize this thematic issue. Special thanks to the editorial staff of *Catalysts*, particularly to Senior Assistant Editor Ms. Mary Fan, for their efforts and continuous support. Moreover, I am most appreciative to all authors for their contributions and hard work in revising them as well as to all reviewers for their valuable recommendations that assisted authors in upgrading their work to meet the high standards of *Catalysts*. I hope that this special issue will be a valuable resource for researchers, students and practitioners to promote and advance research and applications in the field of “surface chemistry and catalysis”, since the fundamental understanding of catalysis will definitely be the vehicle towards the rational design of highly efficient and low-cost catalysts.

Conflicts of Interest: The author declares no conflict of interest.

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