Functional materials for eco-catalysis of small molecules

Catalysis is facilitating the development of our society due to its critical role in the fields of energy conversion, environmental remediation, human health care, and so forth. With the diminishing of the fossil fuels and the increasing carbon emission year by year, the exploration of novel catalytic systems for eco-catalysis of small molecules, such as N₂, O₂, H₂O, CO₂, and light alkanes, into value-added chemicals with high efficiency and low carbon emission is attracting more and more attention. The eco-catalysis of small molecules relies heavily on the rational design of functional catalysts and the clever choice of energy suppliers (thermal/photo/electro-based) to overcome the activation barriers of nitrogen-nitrogen, carbon-hydrogen, carbon-oxygen bonds, as well as to achieve highly efficient carbon-carbon coupling for long-chain hydrocarbons synthesis from small molecules. In the past decades, tremendous progress has been made in the field of eco-catalysis of small molecules, for example, but not limited to, the ammonia synthesis via electro-catalysis of N₂, the electro/photo-driven overall water splitting for H₂ or O₂ evolution, and the hydrogenation of CO₂ into basic chemicals (light olefins or aromatics). However, the large-scale utilization of the aforementioned eco-catalysis technologies is still hampered by the low transformation efficiency (conversion rate and target products selectivity), ambiguous reaction mechanism, the lack of appropriate engineering equipment, and so forth. Thus, to drive the eco-catalysis of small molecules going forward, this special issue highlights the recent advancements in the relevant research areas, especially the tailor-made functional catalysts that boost the highly efficient conversion of small molecules, including oxygen vacancy-rich metal oxide or metal phosphide-based catalysts for photo/electro-catalytic water splitting, highly efficient catalysts for thermo-catalytic hydrogenation and photo-catalytic conversion of CO₂ respectively into aromatics or methanol, transition metal/carbon composites as electro-catalysts for oxygen electro-catalysis, advanced catalysts for light alkanes upgrading, halide perovskites for photo-synthesis, and so forth.

H₂ evolution from photo/electro-catalytic water splitting is a promising H₂ synthesis strategy with less carbon footprint and energy consumption compared with the traditional coal-steam reforming process. Currently, different kinds of catalysts have been investigated in the photo/electro-catalytic water splitting for H₂ production. Zou et al. summarized the recent development of metal phosphides as outstanding electro-catalysts to lower the overpotential of electro-catalytic water splitting and co-catalyst during the photo-catalytic water splitting process to accelerate the transfer and separation of charge carriers. Although some progress has been made, the actual rate of H₂ production is still too low to meet the demand of industrial applications. The ultimate goal is to explore stable, efficient, and low-cost metal phosphide-based catalysts or co-catalysts for commercial electro/photo-catalytic H₂ evolution from water splitting. Furthermore, vacancy-rich metal oxides have also been widely employed as efficient catalysts for H₂ production by photoelectro-chemical water splitting. Wang et al. comprehensively summarized the influence of oxygen vacancy on the photo-electrode in two aspects that is the optoelectrical property of semiconductor and surface electro-catalysis. However, due to the complicated nature of oxygen vacancy, the knowledge about oxygen vacancy is far from sufficient to fully utilize oxygen vacancy in tailoring photo-electrodes. In-depth understanding and rational engineering of the defects, especially oxygen vacancy, in the semiconductors could lead to potential breakthroughs in this promising research field.

CO₂, as an important greenhouse gas, has brought great environmental issues, such as ocean acidification, climate change, and global warming. The highly efficient conversion of CO₂ into value-added chemicals will shed new light on the resource utilization of CO₂ and the alleviation of its environmental concerns. CO₂ conversion can be realized by various strategies, including electro-chemical, photo-chemical, and thermo-chemical processes, among which thermo-chemical CO₂ hydrogenation strategy has attracted tremendous attention due to its high efficiency, controllable selectivity, and tremendous potential for industrial application. Tsubaki et al. systematically investigated the advanced bifunctional or multifunctional catalyst for the direct hydrogenation of CO₂ into aromatics via the methanol...
mediated pathway or the modified Fischer-Tropsch synthesis process. It should be noted that the development of CO$_2$ hydrogenation technology should not neglect several important points, such as the cost of CO$_2$ capture and H$_2$ supply, carbon-neutral strategy for H$_2$ production, and the integration of the related processes. The multiple collaborations and interplay between various research endeavors are needed to speed up the progress of CO$_2$-to-aromatics systems toward industrial applications. In addition to the thermo-catalytic CO$_2$ hydrogenation process, the solar-driven conversion of CO$_2$ into methanol is an effective solution to the global energy shortage and the current greenhouse gas issue. Zou et al. gave a comprehensive overview of the recent research progress in the solar-driven catalytic synthesis of methanol from CO$_2$ and briefly outlines the relationships among the traditional photo-catalysis, photoelectron-catalysis, and photothermal-catalysis. The unique strategies for the design of catalysts are summarized and discussed.

The wide and huge reservation of shale gas around the world and the successful exploitation of the burning ice have drastically altered the global energy and chemicals market. The discovery of alternative pathways for the direct conversion of light alkanes into target products with long-term stability is a key step for the utilization of shale gas and burning ice. Chen et al. summarized the important progress in the catalytic conversion of light alkanes with emphasis on the design and preparation of novel heterogeneous catalysts in the recent 10 years. Three essential issues, C–H bond activation, product over-oxidation, and coke deposition are highly relevant to the activity, selectivity, and stability of catalytic processes, respectively. The catalytic conversion of shale gas not only provides an alternative way for chemicals synthesis but also can be employed as a facile method for the fabrication of nano-carbon materials, such as graphene, carbon nanofibers, and carbon nanotubes. Zhang et al. summarized the growth mechanism, kinetics, growth factors of vertically aligned carbon nanotubes arrays by light alkanes, and the strategies for how to improve their array lengths.

The photo/electro-catalysis of N$_2$ looping hold great potential to achieve sustainable and efficient utilization of N$_2$ because of its huge reserves on the Earth. Liang et al. provided a timely review on the recent progress, achievements, and essential challenges for the artificial nitrogen looping process. Especially, the photo/electro-catalysts involved in nitrogen looping, including nitrogen reduction reaction, nitrogen oxidation reaction, ammonia oxidation reaction, and so forth, are systematically introduced. There are still a series of key challenges remaining unsolved, such as low efficiency, high cost, poor stability, and absence of in-depth theoretical understanding. Thus, more efforts should be made on some key points in order to further promote the development of these catalysts, and finally, achieve the practical application.

Transition-metal/carbon hybrid catalysts show excellent potentials in O$_2$ electro-catalysis. Xia et al. summarized the recent achievements in transition metal/carbon hybrids for oxygen electro-catalysis. Their attention has been focused on the relationship between structure and performance with their synthesis strategies. Their application in rechargeable zinc-air batteries has been also comprehensively discussed. Halide perovskites have already received extraordinary attention from the research community due to their unique photo-physical properties, making them promising candidates for application in various fields like photovoltaic, photoelectric devices. Li et al. focused their attention on the energy-related applications of halide perovskites including light emission and artificial photosynthesis.

In addition to the above-mentioned review works for the development of functional materials for small molecules conversion, two exciting research papers have also been devoted to our special issue. We expect that these works can provide some inspiration for readers as well. Mintova et al. fabricated a stable protection TiO$_2$ layer on the surface of Al$_2$O$_3$ to inhibit the formation of unstable spinel phase. The introduction of TiO$_2$ significantly improved the stability of the adsorbents during cyclic hydrothermal treatments, while the sulfur capacity slightly dropped. Huang et al. proposed a redox mediation strategy to accelerate the electron transfer processes in working Li–S batteries with sulfurized polycrylonitrile as cathodes. The redox mediator-assisted sulfurized polycrylonitrile cathodes exhibit higher specific capacity, improved rate performance, reduced polarization, and longer cycling lifespan with both ether-based and carbonate-based electrolytes.

In summary, tremendous achievements for the rational design of functional materials for eco-catalysis have been made. Meanwhile, novel reaction pathways based on the functional materials and eco-catalysis processes have also been established for value-added chemicals synthesis. As the guest editors, we hope that this special issue can inspire the readers to explore the novel functional materials and reaction pathways for the highly efficient conversion of small molecules into value-added chemicals. Furthermore, the great contributions made by the authors, referees, and the EcoMat editorial team deserved to be greatly appreciated.

CONFLICT OF INTEREST
The authors declare no conflict of interest.
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