The increasing demand for fine and high-value-added chemicals has motivated the lasting exploration of high-performance catalysts with desirable activity, selectivity, and durability. Owing to its high natural abundance and low cost, copper, as well as its various derivatives, has been widely employed as a catalytically active component in a diversity of organic transformations. On the other hand, the accessible multiple oxidation states of reactive Cu elements (Cu^0, Cu^I, Cu^II, and Cu^III) within Cu-based catalysts can enable targeted catalytic reactions that proceed via both single- and multi-electron transfer. As a result, these Cu-based catalysts have also found many applications in redox reactions, such as CO oxidation, selective oxidation of organic compounds, selective catalytic reduction of NOₓ by CO (CO-SCR), electrochemical hydrogen evolution reaction (HER), electrochemical CO₂ reduction reaction (CO₂RR), etc. While great progress has been made, Cu-based catalysts must be delicately designed and their local electron structure of active sites must be regulated. Besides, the catalytic activity of real Cu-based catalysts can be only predicted to some extent by theoretical modeling and calculations. Therefore, it is of great significance to continue the exploration of novel and more efficient Cu-based catalysts that deliver enhanced performance. Some recent and key advances in Cu-based catalysts are included in this Special Issue, as summarized below.

Duan et al. [1], reported a CVD in situ catalytic method to prepare a layer of BCN/Gr two-dimensional composite that directly grew on the surface of copper foil. The anti-corrosion performance characterized via electrochemical and salt spray experiments revealed that the in situ grown BCN/Gr two-dimensional composite exhibited stronger adhesion to the substrate and superior grain boundary dislocation, thus showing an enhanced anti-corrosion capability with the corrosion rate reduced by 91.4% and 57.1% compared with bare Cu foil and BCN-Gr composite synthesized through the transfer method, respectively. This work proposed a new 2D material for researching corrosion prevention mechanisms.

Results obtained by Kaplin et al. [2] demonstrated a one-pot precipitation method employing sacrificial CTAB templates and complexing agents of citric acid to incorporate copper into Ce-Sn and comparative Ce-Zr oxide supports to produce CuCeSn and CuCeZr catalysts. Compared with the counterparts prepared by post-impregnating double CeSn/CEzr oxides with copper salt, the one-pot synthesized CuCeSn and CuCeZr catalysts exhibited improved catalytic performance toward the continuous-flow preferential oxidation of CO in hydrogen excess (CO-PROX). Moreover, a small number of tin dopants in cerium-based catalysts were shown to have better reducibility than that of zirconium, and the switch from Sn^4+ to Sn^2+ can provide an additional redox pair, thus positively affecting its activity. In addition, the one-pot technique contributed to the uniform element distribution in the 20CuCeSn catalysts and promoted their micro- and mesoporosity. Besides, modulating the copper content was beneficial for tuning the CO conversion/CO₂ selectivity ratio, which should be ascribed to predominantly distributed copper in the CeSn phase at low loading, while separate copper oxide phases appear at higher loadings, thus increasing the interfacial interaction between copper-containing and CeSn oxides.
Surface adsorption and dissociation processes can play a vital role in the catalytic performance of metal alloys. Wang et al. [3] performed first-principles calculations to study the adsorption and dissociation of O$_2$ on the Cu-skin Cu$_3$Au(111) surface. According to the calculated results, the most energetically favorable adsorption configuration on the Cu-skin Cu$_3$Au(111) surface is b-f(h)-b. Meanwhile, two thermodynamically feasible dissociation paths are available for O$_2$ dissociation. One path is from b-f to two O atoms in adjacent hcp sites, and the other path is from b-h-b to two O atoms in adjacent fcc sites. Compared with the Cu(111) surface, the Cu-skin Cu$_3$Au(111) surface showed higher stability of O$_2$ adsorption and a lower dissociation energy barrier of the adsorbed O$_2$. These theoretical findings can offer useful guidance for the practical application of Cu-Au alloys as high-efficiency CO oxidation catalysts.

Ceria-based catalysts are highly efficient in the selective catalytic hydrogenation of CO$_2$ to methanol. However, the intrinsic reaction mechanism concerning the formation of active H species remains obscure. Gong et al. [4], performed DFT + U calculations to systematically investigate the impact of pristine and Cu-doped CeO$_2$(111) surfaces on the catalytic dissociation of H$_2$ to produce hydride species. The obtained results showed that doping a single Cu atom on the CeO$_2$(111) surface resulted in the creation of an oxygen vacancy, which played a decisive role in promoting the heterolytic dissociation of H$_2$ to produce H$^+$ species. Moreover, the Cu dopant can also facilitate the adsorption of CO$_2$ and the subsequent hydrogenation of CO$_2$ to produce HCOO*, thus leading to the improved catalytic activity and selectivity of methanol. It is expected that this work can provide valuable guidance for rationally designing high-performance ceria and Cu-based catalysts toward CO$_2$ catalytic reduction reactions.

The hydrogen evolution reaction (HER), which is derived from electrochemical water splitting, is one of the most economical and environmentally benign avenues to produce green hydrogen. Dang et al. [5] synthesized self-supported Cu/Cu$_3$P nanoarrays through a low-temperature phosphidation process, which were directly grown on the surfaces of Cu nanosheets from Cu/CuO nanoarrays precursor. Typically, Cu/Cu$_3$P nanoarray-270 electrocatalysts show superior electrocatalytic activity and long-term stability for HER in an acidic electrolyte solution, accompanied by an onset overpotential of 96 mV and a small Tafel slope of 131 mV per decade. The unique nanoarray architecture of Cu/Cu$_3$P rendered abundant active sites and promoted diffusion of the products, contributing to a faster electron transfer rate and good electrical conductivity, thus resulting in enhanced electrocatalytic efficiency toward the HER. This novel strategy offers unique opportunities in HER and can be extended to more metal phosphides and metal-related nanostructures.

Selective catalytic reduction of NO with CO (CO-SCR) is regarded as a valid and economical denitrification technology to simultaneously eliminate NO and CO from flue gas. Spinel structural manganese–copper spinels are considered potential CO-SCR materials due to their excellent stability and redox properties. Thus, Liu et al. [6], synthesized foam-like Cu$_x$Mn$_{3-x}$O$_4$ spinel (x = 0, 1, 1.5, 2, 3) with varying CuO/MnO$_x$ contents via a citrate-based pechini method. Meaningfully, the redox balance that occurred on the Cu$_x$Mn$_{3-x}$O$_4$ catalyst (Cu$^{2+}$ + Mn$^{3+}$ = Mn$^{4+}$ + Cu$^+$) was shifted to improve the redox property and CO-SCR catalytic performance because of the doped Cu species, which promoted the generation of grain and growth of the spinel structural Cu$_{1.5}$Mn$_{1.5}$O$_4$ with increased surface area and particle size. Therefore, compared with pure Mn$_2$O$_3$, a higher content of Mn$^{4+}$/Mn and more highly active oxygen-containing species were created on the surface of Cu$_{1.5}$Mn$_{1.5}$O$_4$ spinels, which is favorable for the adsorption of oxygen molecules, thus improving the adsorption capacity of CO and NO. Consequently, Cu$_{1.5}$Mn$_{1.5}$O$_4$ catalysts are capable of reaching 100% NO conversion together with 53.3% CO conversion at a low temperature of 200 °C, and this study provided a practicable method for the rational design and synthesis of reactive Mn-based catalysts toward CO-SCR.

The selective oxidation of styrene to benzaldehyde with highly efficient and environmentally friendly catalysts is significant in fine chemical industries. An advanced core–shell structural Cu$_2$O@Cu-BDC-NH$_2$ heterogeneous catalyst with a tunable Cu$^+$/Cu$^{2+}$ interface
and variable MOF loadings and Cu$_2$O crystal phases was prepared by Zhang et al. [7] via a facile in situ self-assembly method. Importantly, the alkaline properties of Cu$_2$O and the introduced –NH$_2$ group can dramatically prevent the excessive oxidation of target products, thus allowing the selective oxidation of styrene to proceed without a base condition. Meanwhile, the well-designed combination of Cu$_2$O and Cu-BDC-NH$_2$ further produced an appropriate Cu$^+$/Cu$^{2+}$ active interface and porous MOF shells, thus simultaneously facilitating the mass transfer and protecting the active Cu$_2$O component. Hence, the optimal Cu$_2$O@Cu-BDC-NH$_2$-8h exhibited a high styrene conversion of 85% and benzaldehyde selectivity of 76% with H$_2$O$_2$ as a non-polluting oxidant under an ambient condition of 40 °C. This work demonstrated a new perspective for developing cost-efficient and eco-friendly catalysts with moderate basicity toward the selective catalytic oxidation of styrene under base-free conditions.

At the beginning of the 21st century, the fast development of the copper-catalyzed amination of aryl halides provided an efficient approach to constructing the C(sp$^2$)-N bond, which competed against the classic Buchwald–Hartwig amination reaction. Averin et al. [8] reviewed recent progress in the copper-catalyzed arylation and heteroarylation of adamantane-containing amines, diamines, and polyamines. With the primary purpose of classifying the dimension and limitation of the copper catalysis involved in the arylation and heteroarylation of the as-mentioned amines, this review addressed the following issues: the dependence of the most suitable catalytic systems on the property of reagents, the chance of N,N$'$-di(hetero) arylation of the diamines, oxadiamines, and polyamines, the utilization of unsupported copper nanoparticles, and the feather of the Chan–Lam amination using adamantane-containing amines, diamines, and oxadiamines.

Sulfur-containing heterocyclic compounds have attracted significant research interest in recent years owing to their abundant biological activities and universal use in biopharmaceuticals, pesticides, and material science fields. Guo et al. [9] provided a brief review of recent achievements involved in the preparation of a crucial series of sulfur-heterocycles-2-alkylthiochroman-4-ones and thioflavanones through Cu-catalyzed conjugate introduction of Grignard reagents to thiochromones. Moreover, the latest advance in the production of 2-alkynyl thiochroman-4-ones by the alkynylation and alkenylation of thiochromones with the aid of copper catalysts was also summarized. The recent progress comprises introducing alkyl, aryl, and alkenyl to thiochromones via 1,4-conjugate addition of Grignard reagents together with the formal conjugate addition of alkynyl groups to thiochromones catalyzed by Cu(I) salts. This work comprehensively reviewed the above-mentioned, providing a rapid understanding of 2-substituted thiochroman-4-ones.

Cost-effective Cu-based catalysts exhibit fascinating catalytic activity in CO-SCR; however, some technical problems including high reaction temperature and poor resistance to O$_2$, H$_2$O, and SO$_2$ still hinder their industrial implementation. Ji et al. [10] comprehensively reviewed Cu-catalyzed CO-SCR under O$_2$-containing conditions, including the catalytic performance of non-supported, supported mono-metallic, supported bimetallic, and supported multi-metallic Cu-based catalysts. Besides, the impact of O$_2$ concentration, reaction temperature, and the existence of H$_2$O and SO$_2$ on the CO-SCR performance was briefly summarized. The reaction mechanism, future challenges, and perspectives regarding CO-SCR were discussed as well. This review can be beneficial in offering guidance for designing effective Cu-based catalysts for the CO-SCR.

In summary, this Special Issue on “Synthesis and Applications of Copper-Based Catalysts” provided an overview of the recent progress in the synthesis and application of Cu-based materials, with particular emphasis on the latest advanced synthetic approaches, the structure modulation strategies, and catalytic performance of copper-based catalysts in heterogeneous and homogeneous catalysis, which can contribute to the development of efficient Cu-based catalysts. We hope that our compilation of this meaningful research progress can help to provide researchers with new inspiration in this field.

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