Editorial—Special Issue “Catalysis for Energy Production”

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Abstract: The rapid increase in anthropogenic greenhouse gas concentrations in the last several decades means that the effects of climate change are fast becoming the familiar horsemen of a planetary apocalypse. Catalysis, one of the pillars of the chemical and petrochemical industries, will play a critical role in the effort to reduce the flow of greenhouse gases into the atmosphere. This Special Issue is timely, as it provides a collection of high-quality manuscripts in a diverse range of topics, which include the production of green hydrogen via water electrolysis, the steam reforming of ethanol, propane or glycerol, the dry reforming of methane, and the autothermal reforming of diesel surrogate fuel. The topic of the transformation of biomass waste to chemicals is also well represented as is the tackling of CO₂ emissions via novel utilization technologies. The Editors are grateful to all authors for their valuable contributions and confident that this Special Issue will prove valuable to scholars, university professors and students alike.

Our dependency on fossil fuels and the rapid rise in greenhouse gas emissions are clearly unsustainable in the long term, due to the detrimental consequences on our planet’s climate and ecosystems. New and cleaner methods for sustainable energy production, such as water electrolysis using excess renewable energy to produce hydrogen, are thus urgent. Additionally, the utilization of lignocellulosic biomass and waste fats and oils, as well as CO₂ contained in flue gases, can also be of crucial importance towards the energy transition in order to obtain high value-added products. For example, biomass gasification and the reforming of biomass-derived products (e.g., biogas, bio-oil, crude glycerol) can lead to the production of synthesis gas, a crucial intermediate in the petrochemical industry, as well as hydrogen, which is a clean fuel that emits no greenhouse gases upon its combustion. All the while, CO₂ captured from flue gases can be hydrogenated into added-value products such as methane, methanol and higher hydrocarbons, reducing our carbon footprint. To realize such demanding processes, the development of appropriate catalysts is of paramount importance. These catalytic systems should exhibit high activity in order to accelerate the corresponding reactions, as well as sufficient stability towards deactivation (e.g., nanoparticle sintering and/or coke deposition) in order to be viable for industrial implementation. High-quality review articles and original research papers collected in this Special Issue contribute to tackling the above challenges and provide novel ideas and perspectives regarding catalysis for energy production.

As it is well known, the production of green hydrogen via water electrolysis results in a green fuel with zero carbon footprint. The development of electrocatalysts that can realize the individual reactions during water splitting is thus a very important topic for the research community. For this purpose, Zhang et al. [1] developed a multifunctional CoFe₂O₄ spinel via electrodeposition on Ni foam. The electrodeposited CoFe₂O₄ material had a higher conductivity than the dip-coated one, while the electrode material was highly durable during the water-splitting reaction. Finally, this material could also function as supercapacitor for energy storage. Zhao et al. [2] synthesized a nanoflower-shaped Fe-Ni sulfide (FeNiS) over a Ni foam substrate via a facile hydrothermal synthesis route. The
material exhibited high electrocatalytic activity for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) while also being quite durable, and it could rival the performance of a standard IrO$_2$-Pt/C system. This Special Issue also includes a review paper by Hu et al. [3], which highlights the nickel phosphide catalysts for the hydrogen evolution reaction. Nickel phosphides present the advantages of a high electrocatalytic performance and anti-corrosion properties; however, they still receive criticism for practical applications in electrolyzers due to their low activity. In their review [3], Hu et al. present the latest attempts to synthesize nickel phosphide catalysts, which have a high HER activity, required for practical implementation.

Besides water electrolysis, alternative hydrogen production technologies also need to be developed during the smooth energy transition from fossil fuels to a more sustainable energy carrier. Li et al. [4] prepared Ni- and Co-containing perovskites as catalysts for the chemical looping steam reforming of ethanol. The presence of Co alongside Ni provided a synergistic effect and led to an increase in the yield of produced H$_2$. Moreover, Co doping increased the number of oxygen vacancies and led to an improved self-regeneration of the catalyst. Do et al. [5] aimed to produce H$_2$ via propane steam reforming, and for this reason, they employed cerium-doped cobalt-alumina (Co$_x$Ce$_y$/Al$_2$O$_3$) catalysts. The addition of Ce promoted CO to CO$_2$ conversion and further enhanced the H$_2$ yield and low-temperature activity.

Reforming of hydrocarbons is a mainstream hydrogen production technology, while dry reforming provides the additional advantage of utilizing CO$_2$ as a reactant and thus rendering the overall process greener. Swirk et al. [6] prepared Ce- and Y-doped double-layered hydroxides for the dry reforming of methane. The introduction of promoters increased the dispersion of Ni particles, while Ce promotion also decreased the amount of basic sites and increased the reduction temperature of Ni. The promoted catalysts in turn showed an enhanced catalytic activity during the methane dry reforming reaction. Ju et al. [7] also developed Ni-Al$_2$O$_3$ catalysts and examined the effect of aromatic hydrocarbons during the autothermal reforming of diesel surrogate fuel. Promoting Ni-Al$_2$O$_3$ catalysts with Rh acted to hinder catalyst deactivation via coking and sulfur poisoning, while intermediate C$_2$H$_4$ was found to play a major role during the catalyst deactivation process via coke deposition.

It is quite clear that hydrogen production using waste organic matter is an environmentally friendlier process compared to fossil fuel use for its production. The steam reforming of crude glycerol, which is obtained as a by-product during the transesterification of biomass, can potentially yield 7 moles of hydrogen per mole of glycerol converted [8]. Ni catalysts supported on cost-effective natural clay attapulgite were used in the glycerol steam reforming process by Charisiou et al. [8]. The attapulgite support improved the dispersion and reducibility of Ni, while it also enhanced the conversion of glycerol into gaseous products, compared to a reference Ni/Al$_2$O$_3$ catalyst. The production of H$_2$ and CO$_2$ was also favored over CO and CH$_4$, while coke deposition in the form of a filamentous carbon that encapsulated the Ni species was the main factor leading to catalyst deactivation. Another pillar of the so-called H$_2$ economy is hydrogen storage. Towards this front, the storage of the produced hydrogen discussed thus far can be aided by the use of storage materials such as ammonia borane [9]. Zhang et al. [9] prepared graphite carbon nitride-supported NiPt alloy nanoparticles as catalysts for the hydrogen evolution reaction from ammonia borane. The charge interaction between the nanoparticles and support greatly accelerated the corresponding reaction, while 100% conversion and H$_2$ selectivity were attained at 10 °C.

Waste-to-chemicals transformation through an energy-efficient process can also contribute to sustainability. Besides hydrogen, biomass-derived organics can lead to the production of other value-added products. Adsuar-Garcia et al. [10] used Ru catalysts supported on carbon black for the hydrolysis and hydrogenation of cellulose to higher-value products. The treatment of carbon black with sulfuric acid modified the porous structure and surface chemistry of the support while aiding the production of sorbitol. Wu et al. [11]
prepared Zn-Mn-Co/Al$_2$O$_3$ catalysts for the conversion of 1-butanol (which can be derived from sugars contained in biomass) into butanes, which can act as jet fuel. The catalyst modified with Zn-Mn-Co $\gamma$-Al$_2$O$_3$ presented a high stability and long lifetime, and the reaction conditions to achieve a maximum yield for butanes were also examined. Moreover, Dominguez-Baroso et al. [12] studied the acetalization of glycerol into solketal, which acts as a fuel additive component. The acid carbon-based structured catalyst employed was found to be active and stable for the glycerol conversion into solketal, and the operational parameters for the reaction process were optimized.

Bio-oil and biogas are also typical products derived from waste lignocellulosic biomass. Kuan et al. [13] studied the hydrolysis of microalgae oil from Schizochytrium sp. to produce free fatty acids. A higher hydrolysis degree could be obtained via the use of sulfuric acid and a 3:1 water-to-oil ratio. Moreover, the conversion of these free fatty acids to biodiesel via lipase Novozzym435-mediated methanolysis was also examined. The utilization of biogas, on the other hand, was studied by Dong et al. [14]. A Re-promoted Ni catalyst supported on H$_2$O$_2$-modified manganese sand was employed for the methanation of the CO content of biogas, which was then coupled with a water–gas shift. The effect of gas internal and external diffusion was examined, and three kinetic models were proposed, with the empirical model providing the best fit.

The utilization of ambient sunlight for solar energy conversion is another crucial topic nowadays. Ziems et al. [15] provided insight into the function of a meso-mesityl-2,6-iodine-substituted boron dipyrromethene (BODIPY) dye as a photosensitizer for the scope of solar light-driven hydrogen evolution. For this purpose, they employed novel quantum chemical methods such as time-dependent density functional theory (TDDFT) and multi-state restricted active space perturbation theory through the second order (MS-RASPT2).

Finally, this Special Issue addresses the major concern of tackling CO$_2$ emissions via CO$_2$ utilization technologies. Manzoor et al. [16] prepared ZnFe$_2$O$_4$ coupled with TiO$_2$ for the photocatalytic conversion of CO$_2$ into methanol. The resulting photocatalyst produced methanol as a sole hydrogenation product, while its recycling ability was also tested over five cycles. This Special Issue also contains two review papers on the subject of CO$_2$ utilization. In the first one, Tabish et al. [17] dealt with the use of a particularly important and versatile class of materials, i.e., perovskite oxides, for CO$_2$ conversion into value-added products. The review emphasized, among others, the structure of the catalysts, as well as defect engineering and interface tuning at the nanoscale. In the second review, Tsiotias et al. [18] provided an overview of the effect of alkaline and alkaline earth metal additives during the CO$_2$ methanation reaction, which is a core reaction in the power-to-gas and power-to-methane processes. The basic elements typically act as promoters in this reaction by enhancing the catalyst surface alkalinity and thus providing more active sites for the initial CO$_2$ chemisorption and activation. Moreover, the recent developments in dual-function materials (DFMs), that is, materials that can realize both CO$_2$ sorption and methanation functions, were also addressed in this review paper.

In conclusion, the publications collected in this Special Issue well represent progresses and recent trends, as well as novel ideas, in the constantly evolving field of catalysis for energy production. We would like to greatly thank all the authors for their valuable contributions. We hope that this Special Issue will be inspiring for many scholars, university professors and students alike, whose research interests lie in this emerging field of catalysis.

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