



Innovative Catalytic Materials for Environmental Remediation and Energy Applications

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1. Introduction

The need for low-cost and environmentally friendly energy is greater than ever nowadays due to the global population growth as well as the modern lifestyle. Considering this, research has focused on the development of novel cost-effective, eco-friendly technologies with high performance for power production and energy storage in addition to conventional technology. The reforming processes for hydrogen or syn-gas production [1,2], fuel cells producing electrical power [3–5] or chemical energy (H₂, CH₄, etc.) [6,7], various types of batteries [8,9] and supercapacitors [10-12] are listed among them. Environmental remediation technologies have also experienced tremendous growth over the last few decades in order to effectively remove organic contaminants from wastewater [13–15]. The activation of persulfate [16,17] and a Fenton-like process [18,19] are some indicatively advanced oxidation processes (AOPs) typically applied for the degradation of organic contaminants. The common ground for most of the abovementioned technologies, considering both energy production and storage and environmental management, is that they are based on catalytic processes. Therefore, the design and synthesis of innovative and economically affordable catalytic materials for various catalytic processes are of particular importance for their potential application. The present Special Issue includes ten research articles and one review article highlighting new perspectives on the design and implementation of innovative catalytic materials for a series of processes. The materials studied in the presented works are related to both catalytic and electrocatalytic processes, thus applying to a wide range of researchers.

2. Overview of Published Articles

Investigating the development of electrocatalytic materials, Zhu and Kamali (contribution 1) introduced the synthesis of the α -MoO₃ nanoribbon structure, which is incorporated into MoS₂ and graphene nanosheets derived from natural graphite and MoS₂ minerals. They implement a rapid preparation method in order to harvest its storage properties as potential electrode material for Li-ion batteries. The proposed preparation method resulted in the formation of a molybdenum oxycarbide layer in the electrode/electrolyte interface, which can facilitate the charge and ion transfer and significantly reduces the electrochemical resistance of the electrode, thus favoring the Li-ion storage capacity (773.5 mAh g⁻¹) compared to that obtained from the bare MoS₂ (176.8 mAh g⁻¹). Next, the unique significance of the hydrogen production from the acetic acid (AA) process is underscored by Alshammari et al. (contribution 2) since it provides clean hydrogen fuel compared to reforming processes while also contributing to agricultural waste management. For this purpose, they studied the hydrogen evolution reaction (HER) over glassy carbon decorated with Au (Au/GCE) using a neutral KCl electrolyte solution in the presence of AA in a three-compartment cell, implementing the rotating disk electrode (RDE) technique. The



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). proton reduction was observed at a lower overpotential (-0.2 V vs. RHE), exhibiting higher current values in employed Au/GCE electrodes compared to the bare GCE electrode.

Kokkinou et al. investigated the electrochemical promotion of CO₂ hydrogenation over Rh-based catalysts deposited on an O^{2–}-conducting Y₂O₃-stabilized ZrO₂ (YSZ) solid electrolyte (contribution 3). This exceptionally detailed study is among the few works related to the CO₂ hydrogenation reaction for CH₄ production over Rh/YSZ at the laboratory scale in such narrow CO₂/H₂ ratios. It was found that applying a positive or negative potential or current to the electrode acted beneficially on the electrocatalytic performance towards the CH₄ production rate, thus confirming the electrochemical promotion of the catalysis (EPOC) theory.

The dry reforming of methane (DRM) towards syngas (CO and H₂) was studied over $Nd_{2-x}Sr_xNiO_{4\pm\delta}$ ($0 \le x \le 1.4$) solid solutions with a K₂NiF₄ structure synthesized via a freeze-drying method by Shlyakhtin et al. (contribution 4). Enhanced DRM activity was exhibited by samples with x = 0 and x > 1. These two peaks observed in the DRM performance were attributed to the contribution of Nd₂O₃ and SrCO₃, respectively. Hydrogen production was also investigated through the decomposition of H₂S, employing Co₃O₄/CeO₂ catalytic systems (contribution 5). Kraia et al. studied the hydrogen disulfide decomposition under water in an effort to simulate the concentration of H₂S in deep water layers of the Black Sea. The significance of this work is two-fold since it combines the production of chemical energy with the environmental management of the topical ecosystem, producing multiple benefits for coastal countries. The 30 wt.% Co₃O₄/CeO₂ catalyst exhibited the highest performance, which was attributed to the in situ sulfidation of cobalt species forming stable phases (Co₃S₄, CoS).

The purification of the H₂-rich gas stream obtained from the various reforming processes (mostly steam reforming of hydrocarbons) was conducted via a series of processes, including water gas shift (WGS) reaction, methanation reaction, CO oxidation, etc.. Kouroumlidis et al. investigated the WGS reaction at high (HT) and low temperatures (LT) over a series of modified particulates and structure Pt/TiO₂ catalytic systems (contribution 6). The modification of the TiO₂ support was performed with alkali- or alkaline earth metals (Na, Cs, Ca, Sr), whereas, in another series, the metal phase of Pt (0.5 wt.%) was enriched with another metal (namely Ru, Cr, Fe, Cu). Among all the tested samples, 0.5 wt.% Pt/TiO₂(Ca) exhibited the best performance and was tested further in the form of pellets and monoliths. Its high WGS activity was attributed to metal support interaction effects.

Innovative $La_{0.8}Sr_{0.2}Co_xFe_{1-x}O_{3-\delta}$ perovskite oxides, with a varying Co to Fe ratio (x = 0, 0.1, 0.2, 0.4, 0.6, 0.8, 0.9, 1), were synthesized in the form of powders via the in situ combustion synthesis method and were tested via CO and propane combustion for CO_2 production by Safakas et al. (contribution 7). Increasing the Co/Fe ratio resulted in an increase in the catalytic performance of both reactions, which was attributed to the occurrence of the interfacial redox mechanism. The latter was due to the enhancement of the number of catalytically active sites, strongly related to oxygen-vacant sites neighboring the Co sites, as well as to the lower redox stability of Co cations compared to Fe ones. CO oxidation was also studied over a series of transition metal oxides—this was performed on CuO-based catalytic systems, which were supported on an α -MnO₂ nanowire structure employing the precipitation synthesis method (contribution 8). Specifically, in this detailed work, Zhang et al. examined the effect on the catalytic performance of the type of transition metal oxide used (Fe_2O_3, Co_3O_4, NiO) , the loading wt.% of the oxide and the calcination temperature. The highest performance in terms of CO conversion was found for the 3 wt.% Co₃O₄—10 wt.% CuO/α -MnO₂ catalytic system which was calcined at 400 °C. This enhanced catalytic activity was related to its high specific surface area, which resulted in an increase in oxygen vacancies, thus favoring the CO oxidation on the basis of the Mars–van Krevelen mechanism.

The beneficial effect of the combination of Ni-based catalytic systems with molten salt on the olive kernel– CO_2 gasification was thoroughly studied by Lampropoulos et al. (contribution 9). The gasification of biomass feedstock is a process of high significance since it enhances the total amount of renewable energy, whereas the exploitation of olive kernel as

feedstock is a step towards the energy independence of Mediterranean countries. The presence of molten salt improved the mass and heat transport properties, thus favoring catalytic activity.

The production of α , β -unsaturated compounds via condensation between an aldehyde or a ketone with an active hydrogen compound (Knoevenagel reaction) employing a basic catalytic system is a very important process towards the synthesis of various chemical compounds. Chowdhury et al. investigated Knoevenagel condensation over a porous magnesium–aluminum mixed-metal phosphate, which was prepared via a hydrothermal method (contribution 10). The basic sites of the synthesized catalyst were found to enhance its efficiency towards the condensation reaction, whereas its remarkable recyclability highlighted its potential application as a catalytic system for similar reactions.

Syngas conversion reactions are very important for the production of various chemicals. The recent trends of the unique role of magnetic nanomaterials as catalytic systems for syngas production and conversion were discussed in the review article authored by Chidhambaram et al. (contribution 11). Various synthesis methods and experimental parameters are discussed in detail in this very informative review paper, highlighting the role of the applied magnetic field and the beneficial effect of the addition of various modifiers.

3. Conclusions

Considering the published works in the current Special Issue, it is concluded that various technologies based on catalytic processes were investigated. New insights concerning both novel synthesis methods and innovative materials are revealed, paving the way for further developing power-producing and storage technologies as well as purification processes.

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