

Emissions Control Catalysis

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1. Overview

Important advances have been achieved over the past years in agriculture, industrial technology, energy, and health, which have contributed to human well-being. However, some of these improvements in our lives were accompanied by a great threat to the environment and public health, with photochemical smog, stratospheric ozone depletion, acid rain, global warming, and finally climate change being the most well-known major issues, as a result of a variety of pollutants emitted through these human activities. The indications are that we are already at a tipping point that might lead to non-linear, sudden environmental change on a global scale.

Aiming to ensure that “we live well, within the planet’s ecological limits” the United Nation’s Sustainable Development Goals [1] and the EU’s Environmental Action Plan [2] include calls to action and priority objectives to protect life on land and water and tackling climate change. In a full harmony, scientists around the world are developing tools and techniques to understand, monitor, protect, and improve the environment, and to ensure that our achievements must not adversely affect our environment and at the same time we must mitigate any damage that has already occurred. In turn, new tools, technology, and advanced materials are continuously added to our quiver that enable us to effectively control emissions, either of mobile (e.g., cars) or stationary (industrial) sources, and to improve the quality of outdoor and indoor air, with catalysis to play a major role on these efforts, i.e., as a leading technology for improving quality of life, health, and environment.

Emissions Control Catalysis in the area of Environmental Catalysis [3,4] is continuously growing up, providing novel multifunctional, nano-structured materials with active metal species at sizes of the level of nanoparticles, nanoclusters or even single atoms [5–8]. These materials are also often promoted by several ways (i.e., by surface- or support-induced promotion [9–13] and by electrochemical promotion [14–16], among others) in order to be very active and selective for the abatement of a variety of pollutants and greenhouse gases. Regarding the latter, representative cases concern the abatement of CO, NO_x, N₂O, NH₃, CH₄, higher hydrocarbons, volatile organic compounds (VOCs), particulate matter (PM), and specific pollutants emitted by industry (e.g., SO_x, H₂S, dioxins, and aromatic hydrocarbons) or landfill and wastewater treatment plants (biogas).

The concept of Cyclic Economy is currently of growing attention in emission control catalysis strategies for the production of useful chemicals and fuels from the controlled pollutants. The CO or CO₂ hydrogenation for the production of CH₄ or liquid fuels, biogas or methane reforming for the production of syngas, and/or H₂, oxidative coupling of methane for the production of ethylene are a few examples of such efforts.

2. Special Issue Contributions and Highlights

The present “Emissions Control Catalysis” Special Issue was successful in collecting 21 high-quality contributions by several research groups around the world, which covers recent research progress in the field of the catalytic control of air pollutants emitted by mobile or stationary sources, not limited only to the abatement of pollutants but also including research dedicated to cyclic economy strategies. These papers among others are ranging from the synthesis and physicochemical-textural-structural characterization of the materials, activity–selectivity–durability evaluation under environmentally important reactions, fundamental understanding of structure–activity relationships or other metal–metal and metal–support interactions on the multifunctional materials involved. In particular, three comprehensive review articles covering several major topics and directions in emissions control catalysis subject were published in this special issue. The review of the guest editors (Yentekakis I., and Vernoux P.) and co-workers [17] concerns mainly the of CO, CHs, and NO_x emissions abatement from stoichiometric, lean burn, and diesel engines exhausts, addressing the literature that concerns the electropositive promotion by alkalis or alkaline earths of platinum group metals (PGMs) that have found to be extremely effective for the related three-way and lean-burn reactions and catalytic chemistry. The review of Smirniotis P. and co-workers [18] concerns the selective catalytic reduction of NO_x with NH₃ (NH₃-SCR of NO_x) focusing to low temperature applications that is a highly desirable perspective, and finally the review of Bogaerts A. and co-workers [19] covering a hot recent trend in emissions control implicating cyclic economy strategies, that is the conversion and utilization of CO₂ for the production of value-added chemicals. On the other hand, a major part of contributions (9/21) concerns original research on nitrogen oxides reduction processes [20–28], reflecting the fact that this topic still remains hot among the targets of environmental catalysis. Five out of 21 studies concern CO and hydrocarbons oxidation processes [29–33] while the remained 4/21 concern CO₂ capture/recycling processes under the view of cyclic economy [34–37].

Review Contributions

Alkali metals as surface-promoters of platinum group metals (PGMs) have shown remarkable promotional effects on the vast majority of reactions related to the emissions control catalysis either they are applied by traditional routes (e.g., impregnation) or electrochemically, via the so called, concept of the electrochemical promotion of catalysis (EPOC) or non-faradaic electrochemical modification of catalytic activity (NEMCA effect) [14,15]. In the comprehensive review of Yentekakis et al. [17] published in this Special Issue, more than 120 papers on the subject were collected and discussed comparatively after classification in groups, on the basis of the specific reaction promoted, e.g., (CO, HCs, or H₂)-SCR of NO_x, and CO or hydrocarbons oxidation. The authors also present and analyze, by means of indirect (kinetics) and direct (spectroscopic) evidences, a mechanistic model for the mode of action of electropositive promoters, which consistently interprets all the observed promoting phenomena. Concluding, they claim that this very pronounced (in some cases extraordinarily) alkali-induced promotion in emissions control catalysis prompts to the development of novel catalyst formulations for a more efficient and cost-effective control of the emissions of automotives and stationary combustion processes.

Since the emission standards for NO_x are becoming more stringent to keep our atmosphere clean and severe pollution regulations being imposed around the world, the challenge of a cost-effective, i.e., low-temperature, selective catalytic reduction (LT-SCR) of NO_x by NH₃ with a combination of high NO_x activity and N₂ selectivity in a wide operation temperature window and good resistance to SO₂/H₂O have attracted paramount attention. Supported and mixed transition metal oxides have been widely investigated for LT-SCR technology. However, these catalytic materials have some drawbacks, especially in terms of catalyst poisoning by H₂O or/and SO₂. Hence, the development of catalysts for the LT-SCR process is still under active investigation throughout seeking better performance. Extensive research efforts have been made to develop new advanced materials for this technology. The comprehensive review of Smirniotis and co-workers [18] collected and comparatively analyses

more than 140 publications in the topic, covering the description of the influence of operating conditions, materials, and promoters on the LT-SCR performance, as well as active sites, reaction intermediates, and mechanistic implications evidenced by using isotopic labeling and in situ FT-IR studies.

Global climate change as a result of the greenhouse effects of the increasing emissions of the so-called greenhouse gases, with CO₂ to be the most representative one, is of major concern currently. CO₂ capture, conversion, and utilization is one of the possible solutions to reduce CO₂ concentration in the atmosphere. Among other methods, this can be accomplished by direct catalytic hydrogenation of CO₂, producing value-added products. In their comprehensive review, Bogaerts A. and co-workers [19], focused mainly in the last 5-years progress on the topic summarized the literature research (~125 papers) and the current priorities on CO₂ hydrogenation to CO, CH₄, CH₃OH, DME, olefins, and higher hydrocarbons value-added chemicals by heterogeneous catalysis and plasma catalysis. Although, its energy efficiency is still deterring for commercialization, plasma catalysis has currently attracted sufficient attention, due to its simple operating conditions (ambient temperature and atmospheric pressure) and unique advantages in activating inert molecules; its potential advantages and current limitations on CO₂ hydrogenation process have been accounted in the review.

3. Original Contributions

3.1. NO_x Abatement Related Results

A major part of the contributions (9/21) involves research on the selective catalytic reduction (SCR) of NO and/or its direct catalytic decomposition. In particular:

Shen D. and co-workers [20] investigated the deNO_x activity on a series of bimetallic Cu–Mn molecular sieve catalysts (Cu–Mn/SAPO-34) with different loadings of Cu and Mn components during the selective catalytic reduction (SCR) of NO with NH₃ at low temperatures (ca. 120–330 °C), including the effects of H₂O vapor and/or SO₂. Among the catalysts tested, the performance of 2 wt% Cu-6 wt% Mn/SAPO-34 one found to be superior, achieving 72% NO conversion at 120 °C and even better (90%) at 180–330 °C. The reversible negative effect of H₂O on NO conversion was attributed to the competitive adsorption of H₂O and NH₃ on Lewis acid sites; this poisoning was diminished upon increasing the reaction temperature to 300 °C. A permanent poisoning effect of SO₂ on deNO_x activity found is strongly dependent on the reaction temperature, becomes more pronounced at lower ones and is further enhanced by H₂O co-feed; this is assigned to the formation of (NH₄)₂SO₄, which results in the plug of active sites and a decrease of surface area.

Gao Y. and co-workers [21] synthesized Mn–Co/TiO₂ and Mn–Fe/TiO₂ nanocatalysts by a hydrothermal method which were characterized by a variety of methods including Brunner–Emmet–Teller (BET)/Barrett–Joyner–Halenda (BJH) analysis of N₂ adsorption/desorption isotherms at –196 °C, transmission electron microscope (TEM), X-ray diffraction (XRD), H₂-temperature-programmed reduction (TPR), NH₃-temperature-programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS) that enabled the authors for a comprehensive comparison of the catalysts nanostructure characteristics and their de-NO_x catalytic performance, gained insight into the structure-activity relationships. The Mn–Co/TiO₂ catalyst offered superior structure characteristics than Mn–Fe/TiO₂: higher surface area and active components distribution, diminished crystallinity, reduced nanoparticle size and also higher Mn⁴⁺/Mnⁿ⁺ ratio, confirming its better oxidation ability and larger amount of Lewis and Brønsted acid sites on the Mn–Co/TiO₂ surface. As a result, Mn–Co/TiO₂ nanocatalyst displayed superior SCR of NO with NH₃ on both activity and selectivity in the temperature range of 75–250 °C. Kinetics data revealed that both Eley–Rideal (E–R) and Langmuir–Hinshelwood (L–H) mechanisms were implicated in NH₃-SCR process over Mn–Fe/TiO₂ and Mn–Co/TiO₂ catalysts.

Han J. and co-workers [22] investigated the enhanced deNO_x performance and stability of sulfated sintered ore catalysts (SSOC) during the selective catalytic reduction of NO_x with NH₃. The maximum deNO_x efficiency found was about 92% at 300 °C, NH₃/NO = 1 and 5000 h^{–1} gas hourly space velocity (GHSV). A systematic characterization of the materials by means of X-ray

fluorescence spectrometry (XRF), Brunauer–Emmett–Teller (BET) analyzer, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and diffuse reflectance infrared spectroscopy (DRIFTS) was conducted to provide an in depth understanding of the NH_3 -SCR reaction mechanism and to explain the denitration performance and stability of SSOC. The existence of more Brønsted acid sites at the surface of SSOC found to be responsible for the improved adsorption capacity of NH_3 and NO over the SSOC surface that accomplished the formation of amide species ($-\text{NH}_2$), NH_4^+ species, NO_2 molecules in a gaseous or weakly adsorbed state, and nitrates. The reaction between $-\text{NH}_2$, NH_4^+ , and NO (E–R mechanism) and the reaction of the coordinated ammonia with the adsorbed NO_2 (L–H mechanism) were attributed to NO_x reduction.

Song C. and co-workers [23] studied the promotional effect of Ce and/or Zr incorporation by ion exchange on Cu/ZMS-5 catalysts for the NH_3 -SCR of NO. The cerium and zirconium addition promotes the activity of catalysts; the cerium-rich catalysts exhibiting superior SCR activities compared to the zirconium-rich ones. The improved low temperature activity of the $\text{CuCe}_x\text{Zr}_{1-x}\text{O}_y/\text{ZSM-5}$ catalysts in comparison to the unpromoted Cu/ZSM-5 (the former achieving >95% NO conversion at 175–468 °C, the later at 209–405 °C) was attributed to an increase of the reactive lattice oxygen content and reducibility of the catalysts via the $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple and its interaction with cooper species. Moreover, the presence of zirconium in the catalysts promotes surface copper enrichment, prevents copper crystallization and causes suppression of N_2O formation, increasing N_2 -selectivity of the system.

He H. and co-workers [24] synthesized $\text{CeZr}_{0.5}\text{Ti}_a\text{O}_x$ (with $a = 0, 1, 2, 5$, and 10) catalysts by a stepwise precipitation approach, which were studied on the NH_3 -SCR of NO_x . In all contents, Ti addition was beneficial to the de NO_x catalytic performance. Superior behavior was obtained by the $\text{CeZr}_{0.5}\text{Ti}_2\text{O}_x$ particular catalyst composition. Controlling pH and precipitation time during the two steps involved in the preparation method enabled the authors to achieve a catalyst with enhanced acidity (favorable for NH_3 adsorption in NH_3 -SCR processes) and high dispersion of CeO_2 onto the surface of ZrO_2 - TiO_2 synthesized first. The as-prepared $\text{CeZr}_{0.5}\text{Ti}_2\text{O}_x$ catalyst was characterized by superior redox properties, enhanced adsorption and activation of NO_x and NH_3 and enhanced surface adsorbed oxygen such as O_2^{2-} and O^- belonging to defect-oxide or a hydroxyl-like group; all these factors positively affecting its SCR of NO_x with NH_3 performance.

Olson L. and co-workers [25] investigated the poisoning effect of a phosphorous containing atmosphere on the NO_x storage capacity of a Pt/Ba/ Al_2O_3 structured (i.e., washcoated on a ceramic monolith) catalyst. A significant loss of the NO_x storage capacity was caused by phosphorous exposure characterized by a progressively decreasing axial distribution of phosphorous concentration from the inlet to the outlet of the monolith. The values of the specific surface area and pore volume of phosphorous-poisoned monolithic catalysts followed an inverse order: lower at the inlet, higher at the outlet of the monolith. Additional features of the axial phosphorous accumulation detected were: a higher surface accumulation at the inlet of the monolith mostly appeared in the form of P_4O_{10} , the presence of more metaphosphate (PO_3^-) in the middle section of the monolith, and a less surface accumulation of phosphorous at the outlet of the monolith due to its extended diffusion into the washcoat. In respect to the poisoning effect of phosphorous on the SCR of NO_x it was revealed that the formations of N_2 and N_2O were decreased in favor of NH_3 production; the reaction is more influenced by the phosphorous poisoning than the ammonia formation from the stored nitrates.

The direct NO decomposition activity on PdO or PtO supported on Co_3O_4 spinel was studied by Reddy et al. [26] in an attempt to discover means of enhancing the activity of Co_3O_4 spinel, one of the most active single-element oxide catalysts for NO decomposition at high temperatures (typically > 650 °C). In fact, the authors demonstrated a four-fold higher promotion on the NO decomposition activity of PdO- rather than of PtO-modified Co_3O_4 at 650 °C, accompanied by superior selectivity towards N_2 as well. Structural and surface analysis measurements using a variety of methods (e.g., XRD, XPS, H_2 -TPR, and in situ FT-IR) showed an enhanced reducibility of PdO/ Co_3O_4 with an increased thermal stability of surface adsorbed NO_x species, both considered to contribute on

the promotion observed. In opposite, PtO enters into the Co_3O_4 structure, without notable influences on the redox and NO adsorption properties of Co_3O_4 , resulting in marginal promotion compared to PdO. The PdO promotion followed volcano behavior with an optimal PdO loading of 3 wt%.

Zhang et al. [27] investigated the NO_x storage capacity of a series of Pd/BEA catalysts with various Pd loadings for cold-start applications. In situ FTIR measurements using CO and NH_3 enable the authors to identify two isolated Pd^{2+} species, $\text{Z}^- - \text{Pd}^{2+} - \text{Z}^-$ and $\text{Z}^- - \text{Pd}(\text{OH})^+$, on exchanged sites of zeolites, as the main active sites for NO trapping. Among these active sites a superior NO_x storage capacity of $\text{Z}^- - \text{Pd}^{2+} - \text{Z}^-$ was demonstrated, which is caused by the different resistance to H_2O . Atom utilization of Pd can be improved by using lower Pd loading, with an optimum at 0.5 wt%, since this leads to a sharp decline of $\text{Z}^- - \text{Pd}(\text{OH})^+$ attributed to the 'exchange preference' for $\text{Z}^- - \text{Pd}^{2+} - \text{Z}^-$ in BEA.

Finally, Ingel et al. [28] in a different approach for controlling N_2O emissions in ammonia oxidation process at high temperature, proposed the design of experiments and response surface methodology to study this process. The reactor's load, the temperature of reaction and the number of catalytic gauzes were selected as independent variables, whereas ammonia oxidation efficiency and N_2O concentration in nitrous gases were assumed as dependent variables (response). Statistically significant mathematical models were developed from the achieved results, which describe the effect of independent variables on the analyzed responses. The ammonia oxidation efficiency value depends on the reactor's load and the number of catalytic gauzes but not on the temperature in the studied range (870–910 °C). The concentration of N_2O in nitrous gases depends on all three parameters. The developed models were used for the multi-criteria optimization with the application of desirability function. Sets of parameters were achieved for which optimization assumptions were met: maximization of ammonia oxidation efficiency and minimization of the N_2O amount being formed in the reaction. As authors claim, the presented methodology can be used to minimize the primary N_2O emission at high ammonia oxidation efficiency. It can be applied for optimization of operating parameters of ammonia oxidation reactor with two types of catalysts: catalytic gauzes and catalyst for high temperature of N_2O decomposition. As a result, it is possible to obtain the set of independent variables ensuring low N_2O emission and to meet the binding environmental regulations.

3.2. CO, CH_4 , and Other Hydrocarbons Oxidation Reactions

Avgouropoulos and co-workers [29] synthesized a series of atomically dispersed copper-ceria nanocatalysts via appropriate tuning of a novel hydrothermal method and investigated their activity on CO oxidation, which was found to be strongly dependent on the nanostructured morphology, oxygen vacancy concentration, and nature of atomically dispersed Cu^{2+} clusters. A number of techniques including electron paramagnetic resonance (EPR) spectroscopy, X-ray diffraction (XRD), N_2 adsorption, scanning electron microscopy (SEM), Raman spectroscopy, and ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS) were employed in the characterization of the synthesized materials. The aim was to find the key factors that govern the physicochemical properties of the synthesized materials during preparation and then to provide convincing structure-activity correlations. Elevated temperatures and low concentrations of NaOH (≤ 0.1 M) during preparation have led to more active ceria-based catalysts in CO oxidation. This was explained with the obtained morphology, the nature of oxygen vacancies and dispersed copper species, and to a lesser extent, with the specific surface area of the materials and the concentration of defects.

Briois and co-workers [30] in an attempt to provide means of replacing expensive platinum group metals with cost-effective perovskite type materials for catalytic oxidation reactions, prepared thin catalytic coatings of Sr and Ag doped lanthanum perovskites, $\text{La}_{1-x-y}\text{Sr}_x\text{Ag}_y\text{CoO}_{3-\alpha}$ ($x = 0.13\text{--}0.28$, and $y = 0.14\text{--}0.48$), on alumina substrates by using the cathodic co-sputtering magnetron method in reactive condition. Such thin porous catalytic film arrangements can optimize the surface/bulk ratio by combining a large gas exposure surface area with an extremely low loading, thus saving raw materials. The sputtering method was optimized to generate crystallized and thin perovskite

films. The authors found that high Ag contents has a strong impact on the morphology of the coatings, favoring the growth of covering films with a porous wire-like morphology that showed a good catalytic activity for CO oxidation. Interestingly, the optimal composition ($\text{La}_{0.40}\text{Sr}_{0.1}\text{Ag}_{0.48}\text{Co}_{0.93}\text{O}_3$) displayed similar catalytic performance than this of a Pt film, and was also efficient for CO and NO abatement in a simulated Diesel exhaust gas mixture, demonstrating the promising catalytic properties of such nanostructured thin sputtered perovskite films.

Methane, a substantially more potent greenhouse gas than CO_2 , is the main compound of natural gas, which is lately used with a continuous increased rate in various industrial processes and as an alternative fuel for heavy-duty transportation not excluding light-duty tracks. As a consequence, control of CH_4 emissions via catalytic deep oxidation has attracted considerable renewed attention, given that methane appears the lowest reactivity among alkanes. Under this view, Iliopoulou and co-workers [31] synthesized a series of novel Co–Ce mixed oxide catalysts in an effort to enhance synergistic effects that could improve their redox and oxygen storage properties and, thus, their activity in methane deep oxidation. The effect of the synthesis method (hydrothermal or precipitation) and Co loading (0, 2, 5, and 15 wt%) on the catalytic efficiency and stability was investigated. Hydrothermally synthesized $\text{Co}_3\text{O}_4/\text{CeO}_2$ catalysts appeared superior performance due to their improved physicochemical properties (smaller crystallite size, larger surface area, and enhanced reducibility). In respect to Co loading, the optimum performance was observed over a 15 wt% Co/ CeO_2 catalyst, which also presented sufficient tolerance to water presence.

Based on the fact that Pd is one of the most active catalysts for complete methane oxidation Baranova and coworkers [32] used the concept of electrochemical promotion of catalysis (EPOC) to further promote the reaction over palladium nano-structured catalysts deposited on yttria-stabilized zirconia (YSZ) solid electrolyte. Anodic polarization (O^{2-} supply to the catalyst) resulted to a rate enhancement up to ~ 3 at 450°C with an apparent Faradaic efficiency as high as 3000 (for a current application as low as $1\ \mu\text{A}$). Electrochemical promotion on this catalytic system showed persistent behavior the catalyst remained under promotion for a long period of time after interruption of the external bias induced EPOC. Increasing polarization time resulted in a longer-lasting persistent promotion (p-EPOC); more time was required for the reaction rate to reach its initial un-promoted value. The phenomenon was attributed to the continuing promotion by the stored oxygen in palladium oxide formed during the anodic polarization.

Taking into account that sulfur poisoning is one of the most important factors deteriorating the efficiency of diesel exhaust after-treatment systems and that bare TiO_2 appears high sulfur resistivity, Zhang et al. [33] prepared TiO_2 – CeO_2 composites by co-precipitation and studied their sulfur resistance and catalytic activity in the oxidation of diesel soluble organic fraction (SOF). They found that TiO_2 -modification of CeO_2 significantly improves the catalytic SOF purification efficiency of CeO_2 besides the fact that this ceria doping does not downgrade the excellent sulfur resistance of bare TiO_2 ; the prepared TiO_2 – CeO_2 exhibited superior sulfur resistance than e CeO_2 and commercial CeO_2 – ZrO_2 – Al_2O_3 . TiO_2 – CeO_2 characterization by X-ray diffraction (XRD) and Raman spectroscopy indicate that cerium ions can enter into the TiO_2 lattice, without forming complete CeO_2 crystals. Moreover, as confirmed by XPS and H_2 -TPR, the synthesized TiO_2 – CeO_2 composites appeared enhanced oxygen storage capacities (OSC) that considered responsible for their better SOF oxidation activity.

3.3. CO_2 Capture/Recycling: Combining Emissions Control with Added-Value Chemical Production (Cyclic Economy)

De Lucas-Consuegra and co-workers [34] developed a low-temperature (below 90°C) proton exchange membrane (Sterion) electrochemical cell for the electrocatalytic conversion of gaseous CO_2 to liquid fuels. This novel system achieved gas-phase electrocatalytic reduction of CO_2 over a Cu-based cathode by using water electrolysis-derived protons generated in-situ on an IrO_2 anode. Three Cu-activated carbon cathodes with varying Cu loading (10, 20, and 50 wt% Cu–AC), and thus particle size, were tested. Products distribution was a function of the Cu loading and particle size

of the Cu-AC cathode; methyl formate, acetaldehyde, and methanol were being the main reaction products, respectively, over 50, 20, and 10 wt% Cu-AC. The membrane electrode assembly (MEA) containing the cathode with the largest Cu loading and particle size (50 wt% Cu-AC, 40 nm) showed the highest CO₂ electrocatalytic activity per mole of Cu (and the lowest energy consumption values for the conversion of CO₂, 119 kW·h·mol⁻¹), which was attributed to the lower Cu-CO bonding strength over large Cu particles.

Wang H., Lu J.-X. and co-workers [35] fabricated an electrocatalytic cell consisting of a 0.5 M KHCO₃ aqueous solution as electrolyte saturated with CO₂ by bubbling, a CuO/TiO₂-Nafion as working electrode, and Pt as counter and reference electrodes in order to study the electroreduction of CO₂ to added-value multi-carbon oxygenate products (ethanol, acetone, and n-propanol). The non-noble metal electrocatalyst CuO/TiO₂ was in situ reduced to Cu/TiO₂, which efficiently catalyzed CO₂ reduction, offering a maximum overall faradaic efficiency of 47.4% at a potential of -0.85 V vs. reversible hydrogen electrode (RHE). The catalytic activity for CO₂ electroreduction was strongly dependent on the CuO contents of the catalysts as-prepared, resulting in different electroactive surface areas. The significantly improved CO₂ reduction activity of CuO/TiO₂ was attributed to the high CO₂ adsorption ability of TiO₂ component of the working electrode.

Since hydrogen is currently considered as an efficient and environmentally benign energy carrier, among others, considerable attention is played by scientists worldwide for its sufficient production from hydrocarbon feedstocks (natural gas (NG), liquefied petroleum gas (LPG), etc.), biogas and bio-alcohols. To this end, Tang D. and co-workers [36] applied chemical looping reforming (CLR) as a prospective alternative for hydrogen production via ethanol steam reforming, which is characterized by energy efficiency and inherent CO₂ capture. Taking into account that oxygen carriers (OCs) with sufficient oxygen mobility and sintering resistance still remain the main challenges for the development of high-performance materials in the CLR process, the authors explore the performance of Ni/CeO₂ nanorod (NR) synthesized by a hydrothermal method as an OC in the CLR of ethanol. Using a variety of characterization techniques, they showed that the as-prepared Ni/CeO₂-NR possesses the desired properties for CLR, i.e., high Ni dispersion, abundant oxygen vacancies, and strong metal-support interaction, all factors improving catalytic activity. Testing the material in CLR process successfully offered a H₂ selectivity of 80% in 10-cycle stability test. The authors concluded that the small particle size and abundant oxygen vacancies contributed to improve water gas shift reaction, the high oxygen mobility of CeO₂-NR effectively eliminated surface coke on the Ni particle, and the covered interfacial Ni atoms closely anchored on the underlying surface oxygen vacancies on the (111) facets of CeO₂-NR enhance the anti-sintering capability.

Ioannidou et al. [37] contributed with a detailed and comparative catalytic-kinetic study of the performance of modified X-Ni/GDC electrodes (where X = Au, Mo, and Fe), in the form of half-electrolyte supported cells, in the reverse water gas shift reaction (RWGS). The importance of the RWGS reaction ($H_2 + CO_2 \rightarrow H_2O + CO$) is well known, since it takes place in most of the hydrocarbon processing reactions (e.g., hydrocarbons reforming processes) as well as in co-electrolysis of H₂O and CO₂ (CO₂ utilization) in solid oxide electrolysis cells (SOECs) yielding synthesis gas (CO + H₂), as considered in the present study. Solid oxide electrolysis is a contemporary process for CO₂ capture/recycling, which is proven as an attractive method to provide CO₂ neutral synthetic hydrocarbon fuels. The X-Ni/GDC catalysts were tested at open circuit conditions in order to elucidate their catalytic activity towards the production of CO; one of the products of the H₂O/CO₂ co-electrolysis reaction. The CO production rate increases by increasing the operating temperature and the partial pressure of H₂ in the reaction mixture. Fe and Mo modification enhances CO production, and 2 wt% Fe-Ni/GDC and 3 wt% Mo-Ni/GDC electrodes were superior compared to the other samples, in the whole studied temperature range (800–900 °C) reaching thermodynamic equilibrium. No carbon formation was detected.

Conflicts of Interest: The authors declare no conflict of interest.

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