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Editorial

New Trends in Catalysis for Sustainable CO_2 Conversion

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Over the past few decades, there have been many advances in the world, leading to improvements in quality of life. Due to demographic and industrial growth, consumption has increased, as well as the amount of waste and pollution. Today, global warming and climate change are mainly attributed to the emission of anthropogenic greenhouse gases, with carbon dioxide (CO_2) being the most relevant one, due to the huge emissions of this gas into the atmosphere (mainly derived from the consumption of fossil fuels).

Carbon capture and storage (CCS) is a physical process consisting of separating the CO_2 (emitted by industry and the combustion processes for energy generation) and transporting it to geological storage to isolate it from the atmosphere in the long term. However, the most promising routes for CO_2 mitigation are those pursuing its catalytic valorization. By applying specific catalysts and suitable operating conditions, CO_2 molecules react with other components to form longer chains (i.e., hydrocarbons). Accordingly, effort should be made to catalytically valorize CO_2 (alone or co-fed with syngas) as an alternative way for reducing greenhouse gas emissions and obtaining high-value fuels and chemicals.

Carbon capture and utilization (CCU) is a developing field with significant demand for research in the following aspects:

- The development of new catalysts, catalytic routes, and technologies for CO_2 conversion;
- The study of new processes for obtaining fuels and chemicals from CO_2;
- Optimization of the catalysts and the reaction conditions for these processes;
- Further steps in advanced processes using CO_2-rich feeds (H_2 + CO_2 or CO_2 mixed with syngas), increasing product yields.

This Special Issue on "New Trends in Catalysis for Sustainable CO_2 Conversion" shows new research on the development of catalysts and catalytic routes for CO_2 valorization, and the optimization of the reaction conditions for the process.

This Special Issue includes ten articles and three reviews. In the paper by Amin et al., waste biomass is converted into activated carbon, and then a carbon-supported iron-based catalyst is prepared (Fe–C) [1]. The catalyst is used to assess the influence of temperature on the subsequent transformation of syngas to liquid fuels. Potassium is used as a structural promoter in the iron carbon-supported catalyst to boost catalyst activity and structural stability. Potassium promoter increases gasoline conversion from 36.4% (Fe–C) to 72.5% (Fe–C–K), and diesel conversion from 60.8% (Fe–C) to 80.0% (Fe–C–K). The influence of copper content and particle morphology on the performance of Cu/FeO_x catalysts in the hydrogenation of CO_2 is analyzed by Simkovičová et al. [2]. All the catalysts, with a copper content between 0 and 5 wt%, are found to be highly efficient, with CO_2 conversion reaching 36.8%. Their selectivity towards C_1 (versus C_2–C_4, C_2–$C_{4=}$, and C_{5+} products) is dependent on the catalyst's composition, and morphology, and on the temperature. The results indicate new potential methods of altering the morphology and composition of iron-oxide-based particles. The electrolysis of CO_2 in molten carbonate as an alternative mechanism to synthesize carbon nanomaterials is introduced in the paper by Liu et al. [3]. This study focuses on controlled electrochemical conditions in molten lithium carbonate to split CO_2 absorbed from the atmosphere into carbon nanotubes (CNT), and into various

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Citation: Ereña, J.; Ateka, A. New Trends in Catalysis for Sustainable CO_2 Conversion. *Catalysts* **2022**, *12*, 1300. https://doi.org/10.3390/catal12111300

Received: 19 October 2022
Accepted: 19 October 2022
Published: 23 October 2022

macroscopic assemblies of CNT, which may be useful for nano-filtration. Different CNT morphologies are prepared electrochemically by varying the anode's and cathode's composition and architecture, varying the electrolyte's composition pre-electrolysis processing, and varying the application and density of currents. The paper by Liu et al. shows that CO_2 can be transformed into distinct nano-bamboo, nano-pearl, nano-dragon, solid and hollow nano-onion, nano-tree, nano-rod, nano-belt, and nano-flower morphologies [4]. The capability to produce these unusual nanocarbon allotropes at high purity by a straightforward electrolysis process opens an array of inexpensive unique materials with high strength, electrical and thermal conductivity, flexibility, charge storage, lubricant, and robustness properties. A new photocatalyst for CO_2 reduction is presented by Morawski et al. [5]. The photocatalyst is prepared from a combination of a commercial TiO_2 with a mesopore structure and carbon spheres with a microporous structure with high CO_2 adsorption capacity. The combined TiO_2–carbon spheres/silica cloth photocatalysts show higher efficiency in the two-electron CO_2 reduction towards CO than in the eight-electron reaction to methane. The 0.5 g graphitic carbon spheres combined with 1 g of TiO_2 results in almost 100% selectivity to CO. In the article by Li et al., a series of Ni-xSi/ZrO_2 catalysts (x = 0, 0.1, 0.5, 1 wt% of Si) are prepared by co-impregnation with ZrO_2 as support and Si as a promoter [6]. The effect of different amounts of Si on the catalytic performance is investigated for CO_2 methanation. It is found that adding the appropriate amount of Si improves the catalytic performance of the Ni/ZrO_2 catalyst at a low reaction temperature (250 °C). It is observed that Si enhances the interaction between Ni and ZrO_2 and increases Ni dispersion, the number of active sites (including surface Ni^0), the number of oxygen vacancies, and the number of strong basic sites on the catalyst surface. Sim et al. report efficient CO_2 decomposition results using a nonperovskite metal oxide, $SrFeCo_{0.5}O_x$, in a continuous-flow system [7]. In this study, the authors obtain enhanced efficiency, reliability under isothermal conditions, and catalytic reproducibility through cyclic tests using $SrFeO_{3-\delta}$. Activated oxygen-deficient $SrFeO_{3-\delta}$ decomposes CO_2 into carbon monoxide (CO) and carbon (C). In the work by Ju et al., a new type of electrolyte solution constituted by ionic liquids and propylene carbonate is used as the cathodic solution to study the conversion of CO_2 on an Ag electrode [8]. Linear sweep voltammetry and Tafel characterization indicate that the chain length of 1-alkyl-3-methyl imidazolium cation has strong influences on the catalytic performance for CO_2 conversion. Electrochemical impedance spectroscopy shows that the imidazolium cation absorbed on the Ag electrode surface stabilizes the anion radical ($CO_2^{\bullet -}$), leading to the enhanced efficiency of CO_2 conversion. The synthesis and characterization of both binary (Cu_2O, Fe_2O_3, and In_2O_3) and ternary (Cu_2O–Fe_2O_3 and Cu_2O–In_2O_3) transition metal mixed-oxides as photocatalysts for solar-driven CO_2 conversion into energy-rich species is reported by Marcolongo et al. [9]. Two different preparation techniques (high-energy milling and coprecipitation) are compared. The composition and synthetic methodologies of mixed-oxides, the reactor geometry, and the method of dispersing the photocatalyst sample play key roles in the light-driven reaction of CO_2–H_2O. Willauer et al. study the behavior on CO_2 hydrogenation of an iron-based catalyst in a commercial-scale fixed-bed reactor under different feed rates and product recycling conditions [10]. CO_2 conversion increases from 26% to as high as 69% by recycling a portion of the product stream, and CO selectivity is greatly reduced from 45% to 9% in favor of hydrocarbon production. In addition, the catalyst is successfully regenerated for optimum performance. The review by Weidlich and Kamenická summarizes new developments in the ring opening of epoxides with a subsequent CO_2-based formation of cyclic carbonates [11]. The review highlights recent and major developments for sustainable CO_2 conversion from 2000 to the end of 2021. The syntheses of epoxides, especially from bio-based raw materials, are described, such as the types of raw materials used (vegetable oils or their esters) and the reaction conditions. The aim of this review is also to compare the types of homogeneous non-metallic catalysts. Weber et al. review recent advances in the mitigation of catalyst deactivation of CO_2 hydrogenation to light olefins [12]. The authors provide a brief summary of the two dominant reaction pathways (CO_2–Fischer–Tropsch and methanol-mediated path-

ways), mechanistic insights, and catalytic materials for CO_2 hydrogenation to light olefins. Then, they describe the main deactivation mechanisms caused by carbon deposition, water formation, phase transformation, and metal sintering/agglomeration. The main focus of this review is to provide a useful resource for researchers to correlate catalyst deactivation and the recent research effort on catalyst development for enhanced olefin yields and catalyst stability. CO_2 oxidative dehydrogenation is a greener alternative to the classical dehydrogenation method. The availability, cost, safety, and soft oxidizing properties of CO_2, with the assistance of appropriate catalysts at an industrial scale, can lead to breakthroughs in the pharmaceutical, polymer, and fuel industries. The review by Rahman et al. focuses on several applications of CO_2 in oxidation and oxidative dehydrogenation systems [13]. These processes and catalytic technologies reduce the cost of utilizing CO_2 in chemical and fuel production, which may lead to commercial applications in the imminent future.

In summary, these manuscripts clearly show the relevance of CO_2 conversion for the production of fuels and raw materials, avoiding CO_2 emission into the atmosphere and reducing global warming. Nowadays, efforts are being made on the co-feeding of CO_2 with syngas and on the use of new catalytic processes for CO_2 conversion under mild reaction conditions.

We would like to thank all the authors for their works and the reviewers for improving the quality of the papers with their comments. We are honored to be the Guest Editors of this Special Issue. We are also grateful to all the staff of the *Catalysts* Editorial Office.

Author Contributions: Conceptualization, J.E. and A.A.; writing—original draft preparation, J.E. and A.A.; writing—review and editing, J.E. and A.A.; visualization, J.E. and A.A.; supervision, J.E. and A.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Science, Innovation and Universities of the Spanish Government (PID2019-108448RB-100), the Basque Government (Project IT1645-22), the European Regional Development Funds (ERDF) and the European Commission (HORIZON H2020-MSCA RISE-2018. Contract No. 823745).

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

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