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Editorial

CO_2 Capture, Utilization and Storage: Catalysts Design

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Today, the problem of CO_2 emission into the atmosphere is one of the most urgent and complex challenges facing humanity. CO_2 is a greenhouse gas that contributes to global warming and climate change, which have serious implications for the environment, health, economy and security of people around the world. Reducing CO_2 emission requires coordinated actions from governments, businesses, civil society and individuals, as well as innovative solutions in various sectors such as energy, transport, industry and agriculture [1,2]. However, there are many barriers and trade-offs that hinder the transition to a low-carbon society, such as economic costs, social inequalities, political resistance and technological limitations.

The role of scientific research in the transition to a low-carbon society is crucial and multifaceted. Scientific research can provide evidence-based insights into the causes and consequences of climate change, as well as the potential solutions and trade-offs involved in mitigating and adapting to it. Scientific research can also foster the innovation and development of low-carbon technologies, practices and policies that can reduce greenhouse gas emissions and enhance resilience in light of the climate impacts [3]. In recent years, new technologies such as CO_2 capture and store (CCS) and CO_2 capture and use (CCU) have become increasingly important [4,5]. CCS is the main way to reduce the amount of CO_2 in the atmosphere, while CCU is the most promising way to convert CO_2 into valuable products, such as organic compounds [6,7] and polymers [8,9].

In this scenario, catalysis can facilitate the capture and utilization of carbon dioxide, turning it into a valuable resource rather than a waste product. By developing novel catalysts and catalytic systems, we can accelerate the transition to a low-carbon society that is sustainable, resilient and prosperous.

This Special Issue contains six articles focusing on different catalytic approaches for CO_2 transformation and valorization, such as the Dry Reforming of Methane [10] and Coal Char Gasification with CO_2 [11], as well as Direct Dimethyl Ether Synthesis from CO_2-Rich Syngas [12], CO_2 Fixation into Cyclic Carbonates [13], the Epoxide Ring-opening in CO_2 [14] and the N-Formylation of Amine and CO_2 [15].

In recent years, the methane dry reforming reaction ($CH_4 + CO_2 \rightarrow 2H_2 + 2CO$) has gained particular attention. This is because it can effectively transform two major greenhouse gases, carbon dioxide (CO_2) and methane (CH_4), into hydrogen (H_2) and carbon monoxide (CO) with high yields. Noble metal catalysts (Rh, Ru, Pd, Pt and Ir) are commonly used for this reaction as they exhibit high catalytic activity and stability [16]. However, transition metal-based catalysts, especially Ni, have also become popular in methane dry reforming due to their availability and lower cost [17]. Furthermore, the support plays a crucial role in the catalytic performances of the deposited metal catalysts, as it provides the necessary surface area for active sites' dispersion, and basic oxides favor CO_2 adsorption and activation [18,19].

In the first article of this Special Issue, Wang et al. [10] used the urea hydrolysis method to prepare NiO–ZrOm and NiO–ZrOm–YOn catalysts that were characterized by several

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techniques (BET, TPR-H_2, CO_2-TPD, XRD, TEM and XPS) and investigated them in terms of the dry reforming of methane. The presence of yttrium in NiO-ZrOm led to a strong interaction between the metal and the support, which prevented the growth of nickel particles and kept them small even after the reaction. On the other hand, the NiO–ZrOm catalyst without yttrium showed an aggregation of Ni particles and carbon deposition. Furthermore, yttrium enhanced the creation of weak and medium-strong basic sites on the NiO–ZrOm–YOn catalyst, which improved the ability to remove carbon.

The Boudouard reaction represents a way to convert char into CO_2. This reaction requires high heat and only works well when the temperature is above 700 °C. To make the process more efficient and cheaper, it would be better to use catalysts that can speed up the reaction and lower the temperature [20,21]. This could help overcome the challenges and costs of using gasifiers. The gasification reactions of different chars have been studied extensively using catalysts based on alkali and alkali–earth metals (AAEMs) and transition metal salts that, however, have some drawbacks, such as high costs, environmental hazards from acid radicals and sintering problems. Therefore, there is a need for a more affordable and effective catalyst. Recently, metal chlorides have emerged as promising candidates for catalytic gasification, because they have relatively high reactivities and low costs. The second article addresses the Kinetics and Mechanisms of Metal Chlorides Catalysis for Coal Char Gasification with CO_2 [11]. Using a thermal gravimetric analyzer (TGA), the authors performed isothermal gasification experiments of coal chars with CO_2 and different chloride catalysts (K, Ca, Ni and Zn) from 800 to 1100 °C. The volumetric model (VM), the grain model (GM) and the random pore model (PRM) were used to analyze the kinetic characteristic of the samples. K, Ca and Ni chlorides enhanced the gasification rate and char reactivities, while $ZnCl_2$ had a negative effect. The catalysis ability followed the order: Ca > K > Ni > Zn. The PRM model fit the data best and was used to calculate the kinetics parameters. Regarding the catalytic mechanism, it was suggested that K metals formed intermediate complexes and interacted with coal char repeatedly, Ca species underwent oxidation–reduction reactions and Ni metals facilitated the gasification process.

One way to store chemical energy and enable a green transportation system that relies on renewable sources and non-fossil carbon materials, such as biomass or captured CO_2, is to use power-to-liquid (PtL) methods [22]. Dimethyl ether (DME) represents a key intermediate in PtL processes. There are two ways to produce DME from syngas: a direct process and an indirect process. The direct process converts syngas to DME in a single step, while the indirect process involves two steps: first, syngas is converted to MeOH, and then MeOH is dehydrated to DME [23].

In the article by Polierer and coworkers [12], the authors tested the continuous co-precipitation method in comparison to conventional semi-batch precipitation for the preparation of catalysts with the composition $Cu/ZnO/ZrO_2$ (CZZ) used in the direct DME synthesis from CO_2/CO syngas. They based their approach on the assumption that the process parameters of the initial precipitation significantly influenced the distribution and the particulate structure of the metal oxide phases formed after calcination. The CZZ catalysts were investigated in comparison with a commercial CZA catalyst, $Cu/ZnO/Al_2O_3$ with very similar chemical composition in terms of Cu and Zn content.

The superior performance in converting CO_2/CO mixtures to DME by CZZ catalysts prepared by continuous co-precipitation was ascribed to the large surface areas and to the easy accessibility to the Cu sites. For catalyst production technology in general, the continuous co-precipitation method should enable easy scaling-up to the industrial level by using multiple mixing units in parallel. This would ensure a high level of control over material properties.

In addition to what has been so far reported, the synthesis of cyclic carbonates is another important application of CO_2. Cyclic carbonates are widely used for various purposes, such as polar aprotic solvents [24], lithium-ion battery electrolytes [25,26], chemical intermediates and polymer monomers [27,28]. Therefore, in recent years, they have attracted a lot of attention. To synthesize cyclic carbonates with high conversion and yield, different catalytic systems are needed. Various catalysts have been developed for this purpose; they mainly include organometallic complexes [29,30] and organocatalysts [31,32] that have high efficiency. Among them, aluminum complexes are of interest because aluminum is very abundant in nature and suitable for large-scale production.

In the fourth article, Mesías-Salazar and coworkers [13] synthesized new tetranuclear alkyl aluminum complexes with benzodiimidazole–diylidene ligands, based on their previous investigations [33] and tested their ability to convert CO_2 into cyclic carbonates. These complexes showed outstanding performance in the synthesis of monosubstituted cyclic carbonates (3a–o) from terminal epoxides (2a–o) and CO_2, using tetrabutylammonium iodide as a nucleophile without any solvent. The reactions were performed at 70 °C and 1 bar CO_2 pressure for 24 h, and the best catalyst was found to be adduct 1, which gave excellent conversions and yields for a wide range of cyclic carbonates.

The fifth contribution is a work by Wang and coworkers [14] focusing on a highly efficient heterogeneous catalyst based on Pd for the N-formylation reaction of amine and CO_2 under mild conditions and represents another example of the transformation of CO_2 into value-added chemicals. They reported the synthesis of a Pd catalyst on porous organic polymers (POPs) synthesized by the solvothermal polymerization of 3v-PPh_3, $Pd(OAc)_2$ was used as a palladium precursor. The authors demonstrated that the POP was able to immobilize Pd active species, with the uniform dispersion of active species due to the formation of strong Pd–P coordination bonds. This system showed high catalytic efficiency in the N-formylation reaction and excellent stability.

The synthesis of polycarbonates from CO_2 and epoxides is a relevant and challenging area of research, which has gained increasing interest in the last years [27,34]. These reactions could offer a viable method to produce durable materials for commercial use. Moreover, since the CO_2/epoxide coupling occurs in a liquid epoxide, which acts as both a reactant and a solvent, it could reduce the generation of chemical waste. Furthermore, these processes could potentially contribute to the use of CO_2 as a renewable source of C1 carbon in chemical synthesis and help to mitigate the emission of greenhouse gases. The sixth article published in this Special Issue, by Dyduch et al. [15], deals with a theoretical study of epoxide ring-opening in CO_2/epoxide copolymerization catalyzed by bifunctional salen-type cobalt(III) complexes. Cobalt(III) systems with tetradentate salen-type ligands (such as salen = N,N′-bis(salicylidene)ethylene-diamine, salcy = N,N′-bis(3-methylsalicylidene)-1,2-trans-diaminocyclohexane, etc.) are widely known among various CO_2/epoxide copolymerization catalysts based on both early-and late-transition-metal complexes [35–37]. In their article, Dyduch et al. [15] examined how propylene oxide binds in the bifunctional Co(III)-salcy catalyst with two quaternary ammonium salts with n-butyl substituents. They also studied the epoxide ring-opening by methyl carbonate, which is a key step in the copolymerization process. Finally, the various possible reaction pathways from different epoxide-complex local minima were analyzed.

In conclusion, in terms of all the articles published in this Special Issue it is worth noting that they highlight different aspects and catalytic approaches for the use and valorization of CO_2, an abundant, low-cost, and nontoxic raw material that can be useful converted into valuable products and useful chemicals. Such methodologies can help to mitigate global warming by reducing into the atmosphere the amount of CO_2 that is a major contributor to climate change, being a greenhouse gas.

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