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Editorial: Special issue on CO_2 utilization with plasma technology

Plasma technology has advanced significantly in recent years, with application ranging from chemical conversion, to surface treatment, material development and several other fields. Special attention has been paid to the development of possible novel approaches for the conversion of chemicals in a more sustainable way. Plasma technology offers advantages over thermochemical routes such as high process versatility, mild reaction condition, one-step synthesis, fast reaction and instant control. More importantly, it can be easily combined with electricity generated from various renewable sources and is suitable for energy storage via the conversion of intermittent renewable energy into carbon-neutral fuels or other chemicals. In recent years, there has been a growing interest in the development of plasma technology for CO_2 utilization. Investigation on different reactions such as CO_2 splitting, dry reforming of methane (DRM) and CO_2 hydrogenation with different types of plasma reactors and catalysts have been reported by researchers worldwide. Although technological maturity still needs to be increased, the potential of plasma has been well-recognized by the scientific community and industry. More research output in the future is expected as a result of intensive research activities and various kinds of investment. In this context, we present this special issue on CO_2 utilization with plasma technology, which collects 22 articles, covering topics in related areas such as plasma reactor design, plasma catalysis, plasma-material interaction, modeling and new ideas for possible applications.

1. The collection of papers

Two review articles are included in this special issue. Chen et al. reviewed the main theoretical aspects as well as the most recent achievements in the field of CO_2 conversion by non-thermal plasma [1]. With a special accent on the advantage of plasma catalysis, they systematically analyzed different plasma processes and catalyst materials. Discussion on further progress and potential application has also been made to provide directions for future research. Centi et al. conducted a concept review that analyzes the CO_2 splitting to carbon by possible technical solutions [2]. This “dream reaction” will be a good tool to address the issue of greenhouse gas emissions but realizing it in practical situations remains a big challenge. The authors discussed non-thermal plasma in combination with catalysts as a promising approach. By analyzing the current status of plasma-based CO_2 splitting and proposing conceptual ideas, this paper can stimulate research in this field and promote the generation of alternative possibilities.

The design of plasma reactors plays a crucial role in CO_2 conversion and is a key research direction at this moment. Depending on the reaction and the type of plasma discharge, different kinds of reactors have been reported in papers collected by this special issue. Mei et al. made a comparison between single-dielectric and double-dielectric DBD reactors through experiments on CO_2 reforming of CH_4 [3]. Measurements on the temperature, electrical and optical characteristics and related discussion were made to explain the difference in reactor performance regarding CO_2 conversion, selectivity of the liquid and gaseous products as well as carbon deposition. Martin-Del-Campo et al. developed a rotating gliding arc-spouted bed reactor for the DRM at atmospheric pressure [4]. Two Ni-based catalysts with different loadings were tested to investigate the plasma-catalyst interaction. Several interesting results have been observed, including increased selectivity towards H_2 and CO, as well as a significant decrease in carbon deposition on the electrode, indicating the potential of this type of reactor to be used for plasma-catalytic reactions. In the study by Chen et al., a fluidized-bed DBD reactor was developed and compared with the packed-bed DBD reactor [5]. It was found that the forward reaction was promoted by the generation of DBD in the fluidized bed reactor, but the reverse reaction was not influenced. Those two papers provide a different point of view than classical packed-bed DBD reactors for the coupling of plasma with catalyst.

It has been shown in many previous studies that microwave plasma has a good performance for the splitting of CO_2 at low-pressure conditions. Hecimovic et al. investigated the CO_2 conversion in a microwave plasma torch equipped with a nozzle in the pressure range of 100–900 mbar [6]. The obtained results showed that with the nozzle, it is possible to increase the conversion and energy efficiency at high pressure towards values achieved at low pressure. Such enhancement is highly beneficial, considering the industrial application of this technology.

Renninger et al. investigated CO_2 splitting in a DC atmospheric pressure discharge reactor [7]. An improved configuration, optimized gas flow and external magnetic field were applied to achieve high splitting efficiency and to study the scaling effect involved in the process. In the paper of Wanten et al., a confined atmospheric pressure glow discharge plasma reactor was used for DRM and good performance was achieved (conversion of 64% and 94% for CO_2 and CH_4 and energy cost of 3.5–4 eV/molecule) [8]. A quasi-1D chemical kinetics model was also developed to discuss the reaction pathways and formation of different products. Trenchev et al. reported their study of CO_2 splitting using atmospheric glow discharge reactors [9]. Three different reactor configurations were tested, and the plasma properties were also studied by using an advanced model.

Besides the reactor design, it is also worth looking into the plasma operation schemes and conditions. Soldatov et al. reported their work on ultrafast microwave pulsing of a plasma torch [10]. The pulsation parameter was scanned along with plasma diagnostics to analyze the mechanism that limits the CO yield, and models were built to give

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insights into the gas flow dynamics. Silva et al. studied the time evolution of CO_2 dissociation in a pulsed discharge through kinetic modeling [11]. They used their model to analyze the effect of pulse configurations and revealed the importance of electronically excited states in the CO_2 dissociation process. In the paper of Van Alphen et al., the effect of N_2 on CO_2-CH_4 conversion in a gliding arc plasmatron was reported, and a combination of four computational models was used to discuss the benefits of N_2 addition [12]. Considering the practical application of plasma, this research finding is important since N_2 exists in most industrial gas emissions.

In the plasma-catalytic conversion of CO_2, the performance of catalysts is of great importance and the effect of material properties needs to be understood. This was the goal of the research conducted by Kaliyappan et al. who investigated the properties of core-shell SiO_2@TiO_2 spheres in a packed-bed DBD reactor [13]. The preparation condition of the shell and the morphology of the core-shell introduced surface changes that influenced the CO_2 dissociation. Cheng et al. developed a novel plasma catalysis model by coupling CO_2 plasma and surface reactions on Ni/γ-Al_2O_3 [14]. Their model suggested that vibrationally excited CO_2 molecules can be efficiently dissociated on the surface of the catalyst, and increasing the population of the vibrational levels would improve the plasma-catalytic efficiency. In the paper from Li et al., plasma-catalytic conversion of CO_2/CH_4 into oxygenates was investigated by using a series of nickel foam supported Ni catalysts [15]. The authors showed that surface microstructure and valence state can efficiently modulate the distribution of oxygenates produced. The role of catalysts in plasma-catalytic hydrogenation of CO_2 was studied by Ashford with the target of C_2H_6 production [16]. Several alumina-supported catalysts, including Ru, Cu, Ni and Fe, were tested and the highest selectivity was obtained with the Ru catalyst. In the paper from Gorky et al., metal organic framework (MOF)-177 was used in the plasma reactor as CO_2 and CH_4 adsorbent and plasma-induced desorption was reported [17]. In addition, plasma-catalytic methanol synthesis from CH_4 oxidation with O_2 and CO_2 has also been investigated.

Besides CO_2 conversion through plasma-induced chemical reactions, there are also other indirect ways in which plasma can be applied. As a novel tool for catalyst preparation, the plasma process could be used to synthesize or modify catalysts for the conversion of CO_2, and an improvement in catalyst performance is often achieved. Woldu et al. reported their study of Ar-plasma treatment on Au film for electrocatalytic conversion of CO_2 to CO [18]. This treatment method is capable of creating new active sites of under-coordinated facet with open structure, Au (311), lower surface work function and increased electrochemical surface area. In the research conducted by Dai et al., DBD plasma was used to prepare ceria-zirconia solid solution supported Ni catalyst via decomposition of nickel precursor, and a comparison was made with catalysts prepared by conventional thermal decomposition method [19]. Several advantages of plasma-prepared catalysts were observed, including smaller Ni particle size, higher reducibility, more basic sites and oxygen vacancies which promote CO_2 activation. In addition, highly reactive carbon can be formed on the surface of the plasma-prepared catalyst during the DRM process, leading to better coke resistance.

Moreover, other possibilities can be generated in the area of material synthesis and modification. Ekanayake et al. proposed a plasma-assisted approach to synthesize carbon-MgO nanohybrids for CO_2 capture [20]. In this method, the carbon source was provided by biomass and the MgO was derived from plasma-electrified seawater. Considering the plasma is powered by renewable electricity, this material recovery process demonstrates the potential of plasma for application in a “power-to-decarbonization” scenario.

Another important application is to use CO_2 as the gaseous medium for the plasma treatment of materials. Lin et al. used CO_2/N_2 DBD plasma to modify the surface of polytetrafluoroethylene (PTFE) membranes and investigated the effect of different CO_2 concentrations and exposure time [21]. Their study provided useful insight for CO_2 plasma treatment to induce the formation of carboxylic groups on treated polymer surfaces. Another study by Kang et al. used CO_2 and low-density polyethylene powder as the reactants in a rotating gliding arc plasma reactor [22]. The reduction of CO_2 and upcycling of plastic powder were achieved in this process, demonstrating a new area of possible application.

Acknowledgment

Overall, plasma technology has great potential in CO_2 utilization and progress in research has been made during the past few years. We hope this special issue, with the topics and depth it covered, could serve as a stepstone to the next step development of this technology. With the continuous efforts of researchers around the world, higher energy efficiency in CO_2 conversion, a better understanding of the mechanisms and a wider range of applications can be expected in the future. At last, we would like to thank all the authors, reviewers and editors who participated in the publication of this special issue.

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