

Nonthermal plasma for capturing CO₂ as a path to ecologically clean energy

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Abstract. One of the serious environmental problems of our time is the impact on global climate change of the atmospheric pollution processes with greenhouse gases. Carbon dioxide is the most significant component of the anthropogenic impact on the heat balance of the earth. Therefore, reducing the concentration of greenhouse gases in the atmosphere is becoming increasingly important. Non-thermal plasma technology is considered as an attractive alternative for converting greenhouse gases into syngas and other valuable chemicals at lower temperatures. Highly active species generated in such a plasma are favourable for both initiation and propagation of chemical reactions. The combined effect of plasma and heterogeneous catalysis for fuel production from CH₄ reforming has attracted increasing attention. The coupling between plasma and catalyst become complex when the catalyst is placed directly in the plasma. Both chemical and physical properties of the plasma and catalyst can be changed by the presence of each other. In this paper we studied recent progress in non-thermal plasma-catalysis research for CO₂ capturing application.

1 Introduction

When greenhouse gas emissions are under discussion, CO₂ is generally the gas which receives the most attention for its greenhouse effect. Although the radiative forcing of CO₂ is much less than other greenhouse gases (CH₄, N₂O, CFCs, etc.), CO₂ is emitted in large amounts into the atmosphere and has a rather long atmospheric lifetime. The CO₂ is estimated to contribute approximately 60% of the enhanced greenhouse gas effect.

The exponential growth of the global economy since 1860 has been based on fossil fuel consumption. During this period, mankind has collectively released approximately 950 billion tons of carbon dioxide (260 Gt of carbon) from the burning of oil, coal and natural gas. These fossil fuel emissions have been increasing at an average rate of 2% a year to a 1997 annual global output of around 23 billion tons of carbon dioxide (6.3 Gt of carbon). Roughly half of these emissions (3.5 Gt of carbon) remain in the atmosphere, the rest being adsorbed by natural processes. CO₂ concentrations have increased by 35% from the pre-

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industrial 280 parts per million by volume (ppmv) to the current 370 ppmv. At the same time that CO₂ levels have risen, there has been a substantial increase in the mean global temperature. [1-3].

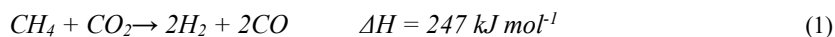
The link between elevated levels of CO₂ in the Earth's atmosphere and rising temperatures is well established. Most of the sun's radiation comprises photons with frequencies well above the infrared, and these passes unimpeded through the Earth's atmosphere. The Earth, however, by virtue of being much cooler than the sun, radiates much of its heat energy in the infrared band. This flux of infrared energy is subject to absorption and re-radiation by the greenhouse gases in the Earth's atmosphere, leading to an overall warming of the lower atmosphere. Indeed, the warming influence of natural greenhouse gases over Earth's history already accounts for global temperatures that are well above freezing. Without the greenhouse warming of water vapor and natural CO₂, the Earth's mean temperature would languish at 18°C below freezing, and we would not be here. The recent increases in anthropogenic CO₂ have led, over the last century, to a further rise in the mean global temperature of approximately 0.7°C [4-6].

About 30 billion tons of CO₂ is produced annually and released into the atmosphere as a result of human activity. Natural emissions of carbon dioxide into the atmosphere, mainly from volcanoes, represent approximately 1% of this figure. Anthropogenic CO₂ emissions over the last 2 centuries fully account for the 30% increase in atmospheric CO₂ that has occurred over the same period [6]. Currently, the main sources of greenhouse gases in the atmosphere are: transport (28%), electricity generation (25%), industry (23%), commercial and residential sector (13%), agriculture (11%). The transition to environmentally friendly and resource-saving energy is one of the priorities of the state energy policy of many countries. Two ways of this transition can be distinguished: quantitative (increasing the share of using environmentally friendly sources - nuclear energy, water, wind and solar energy) and qualitative (introducing new technologies to reduce the negative impact on the environment when using traditional hydrocarbon fuels). The use of renewable energy sources makes it possible to reduce the anthropogenic load on the environment and the negative impact on the climate, as well as reduce dependence on fossil fuels. A significant contribution to the reduction of carbon dioxide emissions into the atmosphere can be made by the development of a modern efficient technology for capturing and converting CO₂ into environmentally friendly products [7,8].

In all cases where fossil fuels are used as an energy source, carbon dioxide is inevitably produced. Thus, humanity is interested in preventing CO₂ from entering the atmosphere, so the issue of the need to develop carbon capture technologies is currently the most acute.

2 Researches using nonthermal plasma for CO₂ capture

Dry reforming of methane has recently attracted significant interest due to simultaneous utilization and reduction of two abundant and undesirable greenhouse gases, CH₄ and CO₂.



This process generates syngas (H₂ + CO) with a low H₂/CO molar ratio close to 1, which is suitable for the synthesis of value-added oxygenated chemicals and long-chain hydrocarbons. Moreover, this reaction can be carried out with biogas from sources containing large amounts of CO₂ without the pre-separation of CO₂ from the feed. However, dry reforming of methane using conventional catalytic methods still faces two major challenges that limit the use of this process on a commercial scale: firstly, high reaction temperatures (>700 °C) are required to obtain reasonable yields of syngas due to the very endothermic reaction and the strength of the C-H bond in CH₄, incurring a high

energy cost; secondly, the formation of severe coke deposition and a subsequent blocking of active metal sites on the catalyst surface, causing rapid deactivation of the catalysts, especially for non-noble metal catalysts [9-11].

There are several methods that can be used to convert carbon dioxide, including catalytic conversion, photo-catalytic/photochemical processes, electro-catalytic/electrochemical processes, enzymatic/biochemical processes and plasma processes. Each of these methods result in a slight variation in the product created, with hydrocarbons, hydrogen and oxygenates forming via catalytic conversion whilst carbon monoxide, hydrocarbons, syngas and oxygenates are the main products of plasma processes. Along with the need for high temperatures in thermal-catalytic processes, issues can be encountered with catalyst deactivation due to coking. Electro-catalytic processes show promise for producing methanol, formic acid and a variety of other organic chemicals. However, these processes have low thermodynamic efficiency.

The least researched, yet predicted to be the most effective, is the plasma process. In comparison to the other processes, it is simple and fast: plasma has the potential to enable thermodynamically unfavourable chemical reactions (e.g. CO₂ dissociation) to occur at ambient conditions [12,13].

Non-thermal plasma technology provides an attractive alternative to the conventional catalytic route for converting greenhouse gases into syngas and other valuable chemicals because of its nonequilibrium properties, low power requirement and its unique capacity to induce physical and chemical reactions at low temperatures. In non-thermal plasma, the overall gas kinetic temperature remains low, while the electrons are highly energetic with a typical electron temperature of 10,000–100,000 K (1–10 eV), which is sufficient to breakdown inert molecules and produce highly reactive species: free radicals, excited atoms, ions and molecules. The non-equilibrium character of such plasma could overcome thermodynamic barriers in chemical reactions (e.g. dry reforming) and enable thermodynamically unfavourable reactions to occur at atmospheric pressure and low temperatures. Several different types of non-thermal plasmas have been investigated for dry reforming of methane including dielectric barrier discharges (DBDs), corona discharges, glow discharge and gliding arcs. The use of a plasma discharge alone has shown that syngas can be generated at low temperatures [14].

Non-thermal plasma therefore shows great potential in the production of an efficient CO₂ utilization process, as it can overcome the stability of CO₂ without the need for the high temperatures required in thermal catalytic processes. Plasma technology is also advantageous over thermal processes as reaction rates are high and steady state is quickly reached [15]. This facilitates quick start-up and shut-down; a promising feature that enables plasma technology powered by renewable energy to act as an efficient chemical energy storage localized or distributed system at peak grid times.

Currently, many technologies are available for the capture of CO₂ from flue gas. Such technologies include gas absorption into chemical solvents, permeation through membranes, cryogenic distillation, and gas adsorption onto a solid sorbent.

Non-thermal plasma technology is considered as an attractive alternative for converting greenhouse gases into syngas and other valuable chemicals at lower temperatures. Highly active species generated in such a plasma are favourable for both initiation and propagation of chemical reactions. Liu et al. [16] experimentally conformed that the CO₂ plasmas can generate a plentiful of active oxygen species and other active plasma species for further reaction with other reactants, like methane, low alkanes and others. These reactions lead to a formation of more valuable chemicals, like ethylene, propylene and oxygenates. The experiment has shown that the CO₂ plasma is an excellent “catalyst” for the conversion of low alkanes to alkenes (esp., ethylene and propylene).

A group of scientists from Europe [17] carried out an experimental study of the dissociation of carbon dioxide in dielectric barrier discharge. The results showed that the reactor geometry is not the most important parameter for CO₂ dissociation in a dielectric barrier discharge. During the study, it was found that the number of filaments per half-cycle obeys a power law depending on the injected power and does not depend on pressure, flow or other process parameters. Using quantum cascade laser absorption spectroscopy, the absolute number of CO molecules produced per filament was measured and found to be in the range of 5.1011 to 2.1012. The degree of CO₂ conversion to CO was estimated to be below 0.1% within a single filament and increased with increasing specific energy consumption. Thus, the specific energy input can act as a universal scalable parameter down to very low values.

Recent innovations in photocatalysis technology have made CO₂ conversion a potentially promising application. This process utilizes ultraviolet (UV) and/or visible light as the excitation source for semiconductor catalysts, and the photoexcited electrons reduce CO₂ with H₂O on the catalyst surface and form energy-bearing products such as carbon monoxide (CO), methane (CH₄), methanol (CH₃OH), formaldehyde (HCHO), and formic acid (HCOOH). A variety of photocatalysts such as TiO₂, CdS, ZnO, and MgO have been studied, and among them, wide band-gap TiO₂ catalysts (~3.2 eV) are considered the most convenient candidates in terms of cost and stability. Li et al. [18] used silica supported Cu/TiO₂ nanocomposites for photoreduction experiments, which were carried out in a continuous-flow reactor using CO₂ and water vapor as the reactants under the irradiation of a Xe lamp. The high surface area mesoporous silica substrate (>300m²/g) greatly enhanced CO₂ photoreduction, possibly due to improved TiO₂ dispersion and increased adsorption of CO₂ and H₂O on the catalyst.

Recently, the combination of plasma and heterogeneous catalysis for fuel production from CH₄ reforming has attracted increasing interest. The interactions between plasma and catalyst become complex when the catalyst is placed directly in the plasma (Aziznia et al. [19], Gallon et al. [20], Mok et al. [21], Yu et al. [22], Ashford et al. [23]). Both chemical and physical properties of the plasma and catalyst can be modified by the presence of each other. Jwa et al. [18] investigated methanation of carbon oxides (CO₂ and CO) in dielectric barrier discharge (DBD) – catalytic system. They used DBD plasma reactor packed with catalyst (Ni/β-zeolite, Ni/Al₂O₃ or Ru/TiO₂/Al₂O₃) to examine the effect of non-thermal plasma on methanation of carbon oxides in a temperature range of 180-360 °C. Dzhva et al. [24] studied the methanation of carbon oxides (CO₂ and CO) in a system combining a dielectric barrier discharge (DBD) and a catalyst. They used a DBD plasma reactor filled with a catalyst (Ni/β-zeolite, Ni/Al₂O₃ or Ru/TiO₂/Al₂O₃) to study the effect of low-temperature plasma on methanation of carbon oxides in the temperature range of 180-360 °C.

Tu et al. [25] worked on plasma-catalytic dry reforming of methane. They examine chemical and physical effects on reaction performance for the addition of quartz wool, γ-Al₂O₃ and zeolite 3A, in order to gain a better understanding with plasma interactions with materials during CH₄ reforming reactions. Also they introduced three different packing methods into the single-stage plasma-catalysis system, using Ni/γ-Al₂O₃ as a catalyst.

The team of D. May [26] used a cylindrical DBD reactor for the conversion of undiluted CO₂ into CO and O₂, the discharge gap of which was filled with glass beads or BaTiO₃ granules. It was found that the use of BaTiO₃ and glass beads in the discharge gap makes the DBD reactor more efficient for CO₂ conversion, even though the residence time of CO₂ under the action of the discharge is reduced due to volume reduction at the same gas flow rate. This is due to the fact that high-energy electrons (>3.0 eV) generated by the discharge can activate the photocatalyst (BaTiO₃) with the formation of electron-hole pairs on the surface of BaTiO₃, which also contributes to the enhancement of CO₂ conversion.

Li et al. [27] studied plasma-based CO₂ capture and splitting by using the plasma generated in a DBD reactor packed with hydrotalcite as the solid sorbent. Results showed, that CO was produced during the plasma treatment and the average conversion of CO₂ during the detectable CO production period is 41.14%. Based on the technological advantages it can provide, the discussion has been made on the potential application as syngas production within the framework of “power to gas/liquid”, and CO₂ emission reduction from power plants.

Xu et al. [28] reviewed recent development of non-thermal plasma catalysis of CO₂ conversion, including CO₂ splitting and CO₂ hydrogenation and reforming, with the focus on mechanistic insights developed for catalytic CO₂ conversion. shown that the intrinsic properties of the catalysts, including the active metal species, metal particle size and the dispersion and location of active sites, and catalyst supports are the dominant factors in the performance of non-thermal plasma catalysis. The development of bespoke non-thermal plasma catalysts with highly dispersed metal active sites (e.g. single-atom catalysts) and hierarchical porous structures (e.g. modified metal-organic frameworks and zeolite) are beneficial for maximizing the plasma catalytic CO₂ conversion processes. Nevertheless, a fundamental understanding of the correlation on the structure, composition and activity is still needed to provide guidance on the rational design of cost-effective, highly selective and efficient catalysts specified for non-thermal plasma catalysis.

3 Conclusion

Plasma-based technologies for the conversion of CO₂ into value added fuels and chemicals show great potential due to the ability of non-thermal plasma to break bonds in the highly stable CO₂ molecule whilst operating at room temperature and pressure. Plasma systems therefore have an advantage over thermal processes, which require high temperature inputs; hence plasma conversion of CO₂ could prove much more feasible on an industrial scale.

However, a trade-off between energy efficiency and CO₂ conversion currently exists in the plasma process as conversion increases when energy input is raised, which also causes a decrease in energy efficiency. Several researches have shown that this problem can be overcome by modifying the plasma system, such as by combining the plasma discharge with a catalyst; however, further research is required to promote the simultaneous increase of energy efficiency and conversion. Once plasma processes can concurrently operate at high conversion and energy efficiency, they will become a front runner in green technologies for the conversion of carbon dioxide.

The scope and potential of plasma processes for application in the field of energy are therefore vast. These processes reduce the concentration of CO₂ in our atmosphere. In addition to fuel production, valuable chemicals can also be produced. A deeper understanding of plasma chemistry, both through plasma modelling and in combination with other methods such as catalysis, as well as further understanding of catalyst synthesis that will create synergy when combined with plasma, will expand this area. Along with this, further studies of CO₂ capture in feed gases mixed with other gases from industrial waste streams may also be useful for creating large-scale plasma processes.

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