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Plasma and Plasma Catalysis for Sustainable Chemistry

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Plasma is an ionized gas, which is created by applying energy to a gas. This can be done by heating or by applying electricity. Plasma is often called the "fourth state of matter", next to solid, liquid and gas. Gas discharge plasmas are created by applying electricity to a gas, and they are used for many technological applications. One emerging application is in sustainable chemistry, for the electrification of chemical reactions (in chemical industry), also called power-to-X applications.

When an electric field is applied to a gas (e.g., due a potential difference between two electrodes), this causes electrical breakdown of the gas, creating positive ions and electrons. The electrons are easily accelerated by this electric field, due to their small mass, and they collide with the gas molecules, causing ionization, excitation and dissociation of the molecules, thereby creating new ions, as well as excited molecules and radicals, respectively. These reactive species easily react with each other, making plasma a highly reactive chemical cocktail. This is particularly interesting for the conversion of stable molecules, such as carbon dioxide, CO_2, nitrogen, N_2 and methane, CH_4, into value-added compounds. Indeed, the conversion of these molecules typically requires a lot of energy, which otherwise would be reached by heating of the gas. In plasma, however, the gas must not be heated as a whole, but it is activated by the energetic electrons. Hence, this makes it potentially more energy-efficient than classical chemical reactions.

In addition, because plasma operates by applying electricity, and it can be switched on/off quasi-immediately, it is very suitable for storage of peak powers in renewable electricity and for grid stabilization. Therefore, it can use fluctuating renewable electricity for the conversion of CO_2, N_2 and CH_4 into value-added compounds (chemicals or fuels), hence the name "power-to-X".

Plasma-chemical conversion has several other advantages as well, such as flexibility in terms of feed gas. It can be used (i) for CO_2 splitting into CO and O_2 (where the CO is a useful base chemical for the chemical industry), (ii) for CH_4 conversion into higher hydrocarbons (e.g., acetylene (C_2H_2) and ethylene (C_2H_4; also very interesting for the chemical industry)) or into H_2 and valuable carbon (e.g., carbon-black or carbon nanotubes), or (iii) for the combined conversion of CO_2 and CH_4 (so-called dry reforming of methane (DRM)), for producing syngas (i.e., synthesis gas, a mixture of CO and H_2, which is very useful for the further conversion into hydrocarbons and oxygenates; i.e., fuel additives that contain oxygen, such as alcohols). In addition, (iv) H_2 or H_2O can also be used as H-sources for the production of oxygenates from CO_2; and (v) the same can be achieved by a mixture of CH_4 and O_2, i.e., so-called partial oxidation of methane. Next to CO_2 and CH_4 conversion, plasmas are also very interesting (vi) for nitrogen fixation into either NH_3 (ammonia) or NOx (nitrates), for e.g., fertilizer production.

Other advantages of plasma for sustainable chemistry applications are the low CAPEX costs (Capital Expenditure), as plasma reactors are typically low cost (in comparison to other technologies, that for instance make use of rare-earth metals). Figure 1 shows a microwave (MW) plasma reactor, which simply consists of a quartz tube and a waveguide.

Finally, plasma reactors can be scaled up, needed for larger scale production of chemicals in industry, simply by placing a large number of reactors in parallel, as demonstrated already many years ago for commercial-scale ozone production. On the other hand, plasma reactors can also operate at small scale, in contrast to some well-established chemical processes in industry, such as the Haber-Bosch process for NH_3 synthesis. This is very convenient for the storage of peak powers, even from a few wind turbines or solar panels, hence for the distributed production of value-added compounds

Figure 1: Picture of a microwave (MW) plasma reactor used for nitrate production from air, for fertilizer production. Air (or an N_2/O_2 mixture) is inserted at one end, it flows through the reactor towards the other end, where it is (partially) converted into a mixture of NO/NO_2. After the reactor, NO is further oxidized into NO_2, which is captured in H_2O, forming nitric acid (HNO_3).

(e.g., fertilizer production by local farmers in underdeveloped countries).

Plasma, however, also has some disadvantages for the application of sustainable chemistry. It is very reactive, and therefore, it typically creates a plethora of different products. That makes product separation not straightforward. To increase the selectivity towards specific compounds, the plasma can be combined with heterogeneous catalysts, in so-called plasma catalysis. The catalyst can be placed inside the plasma reactor (so-called single-stage or in-plasma catalysis) or after the plasma reactor (so-called two-stage or post-plasma catalysis). In the first case, the short-lived reactive plasma species can directly come in contact with the catalyst surface, creating more possibilities for plasma catalysis synergy. The latter means that the performance (in terms of conversion, energy efficiency, product yields,…) of plasma catalysis is better than the sum of the individual processes (i.e., plasma and catalysis alone). Synergy in plasma catalysis is not always demonstrated yet, and more research is needed to find optimal catalysts, tailored to the plasma environment. Indeed, plasma catalysis is quite complicated, and there exist many different plasma-catalyst surface interaction mechanisms (see figure 2). Hence, the optimal catalysts in plasma catalysis are not necessarily the same as in thermal (classical) catalysis.

Various types of plasma reactors can be used for these gas conversion applications, but the most common are dielectric barrier discharges (DBDs), microwave (MW) plasmas, and gliding arc (GA) plasmas, although radio-frequency (RF)

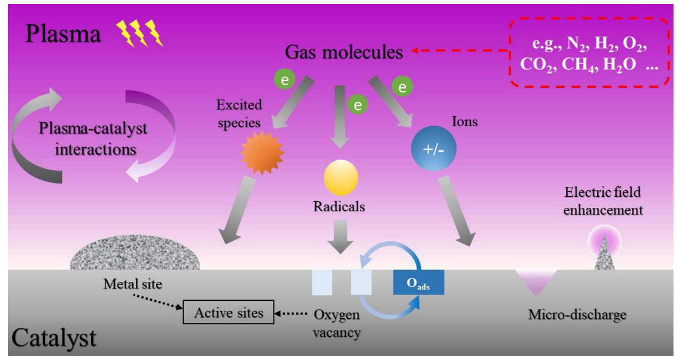

Figure 2: Schematic picture of the various processes occurring in plasma catalysis.

plasmas, corona discharges, nanosecond-pulsed plasmas, spark discharges and atmospheric pressure glow discharges (APGDs) are also being investigated. Each of these plasma reactors has its own characteristics, strengths and limitations. In general, DBD plasmas exhibit a lower energy efficiency (and higher energy cost), but as they operate near room temperature, they are more suitable for catalyst integration inside the plasma, i.e., single-stage plasma catalysis, for the selective production of value-added compounds, such as oxygenates or higher hydrocarbons , or for NH_3 synthesis, which requires a low-temperature plasma (due to its exothermic reaction). At the other end of the spectrum, low-pressure MW plasmas exhibit a high energy efficiency, due to efficient dissociation of the molecules, but are less convenient for practical application. Finally, in atmospheric pressure MW plasmas, as well as in GA plasmas and APGDs, the conversion mainly proceeds by thermal reactions, but these so-called warm plasmas also exhibit a relatively high energy efficiency, and it is believed they are very promising for later commercial exploitation. Due to their high temperature, they are however less suitable for in-plasma catalysis, but post-plasma catalysis should be explored, especially because the hot gas flowing out of the reactor can be used to thermally activate the catalyst materials.

In summary, sustainable chemistry is one of the emerging applications of plasma technology, and will even gain in importance, because of the need for electrification of the chemical industry. However, more research is needed to further improve the performance, in terms of (i) conversion, (ii) energy efficiency, and (iii) product selectivities, by smart reactor design and catalyst selection tailored to the plasma environment.

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