Modeling of plasma and plasma catalysis for CO_2 conversion

Annemie Bogaerts[1], Antonin Berthelot[1], Stijn Heijkers[1], Stanimir Kolev[2], Ramses Snoeckx[1], Surong Sun[1], Georgi Trenchev[1], Koen Van Laer[1], Weizong Wang[1], Yu-Ru Zhang[1], and Erik Neyts[1]

[1] *University of Antwerp* [2] *Sofia University*

Plasma-based CO_2 conversion is gaining increasing interest. To improve this application in terms of conversion, energy efficiency and product formation, a good insight in the underlying mechanisms is desirable. We try to obtain this by computer modeling. We used 0D chemical kinetics modelling to describe the plasma chemistry, and 2D or 3D fluid models to describe the plasma behavior in the three types of plasma reactors most commonly used for CO_2 conversion, i.e., dielectric barrier discharges (DBDs), microwave (MW) plasmas and gliding arc (GA) discharges, as well as to investigate whether plasma can be formed inside catalyst pores.

When studying the plasma chemistry in pure CO_2, we focus especially on the the role of vibrationally excited CO_2 levels, which are the key species for enhanced energy efficiency of the CO_2 conversion [1]. Our model reveals the relative importance of various processes, responsible for the CO_2 conversion, in a range of different conditions, and this is linked to the energy efficiency in the various types of plasma reactors. We have also studied the plasma chemistry in CO_2/CH_4 [2,3] and in CO_2/H_2O [4] mixtures in a DBD reactor, with the purpose of producing value-added chemicals. The main products formed are a mixture of H_2 and CO, or syngas, with a tuneable H_2/CO ratio depending on the gas mixing ratio. The production of oxygenated compounds, such as methanol, formaldehyde, etc, is very limited. On the other hand, in the CO_2/H_2O mixture, significant amounts of H_2O2 could be produced. A detailed chemical kinetics analysis allows to elucidate the different pathways leading to the observed results, and to propose solutions on how to further improve the formation of value-added products.

Finally, we also studied the plasma chemistry in a CO_2/N_2 mixture, both in a DBD [5] and in a MW [6] plasma reactor, to investigate the effect of this important impurity in effluent gases on the CO_2 conversion, energy efficiency and product formation. The presence of N_2 up to 50 % in the mixture barely influences the effective (or overall) CO_2 conversion and energy efficiency, because the N_2 metastable molecules enhance the absolute CO_2 conversion, and this compensates for the lower CO_2 fraction in the mixture. Higher N_2 fractions, however, cause a drop in the CO_2 conversion and energy efficiency. Moreover, in the entire CO_2/N_2 mixing ratio, several harmful compounds, i.e., N_2O and NO_x compounds, are produced in the range of several 100 ppm. The reaction pathways for the formation of these compounds are again explained based on a kinetic analysis, which allows proposing solutions on how to prevent the formation of these harmful compounds.

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