Insight into nitrogen fixation kinetics in a pulsed microwave discharge

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Ongoing efforts to transform chemically inert N_2 into reactive species such as NH_3 or NO_x, used as a feedstock for the production of fertilizers, in a process known as nitrogen fixation (NF) are gaining more and more interests [1]. The industrial NF for NH_3 production via Haber-Bosch (H-B) process dominating artificial fertilizer manufacturing is associated with high energy cost and high CO_2 emissions causing a dramatic environmental impact. Therefore, the development and integration of alternative processes for NF are of key importance.

Plasma-assisted NF is a highly promising cost-effective approach when considering the utilization of intermittent renewable energy sources. Low-temperature discharges provide an opportunity for N-compounds production due to the high chemical reactivity of the plasma occurring as a result of a non-equilibrium between the electrons and heavy particles. Numerous efforts have been made to maximize the production yield and to minimize the corresponding energy cost in the fixation process. Among the plasma technologies, the low-pressure pulsed microwave (MW) discharges [2,3] are found to suit well for plasma-assisted NF due to the significant molecular vibrational excitation they allow. MW discharges, however, remain still barely explored in the field of NF.

Here we report the recent results obtained on NO formation in a surfaguide-type pulsed MW 2.45 GHz discharge working at a 0.5-12 Torr pressure range in N_2-O_2 gas mixtures. The aim of this work is primarily to give an insight into the kinetics of NF, namely ro-vibrational dynamics of NO and N_2 revealed during the pulse, using optical emission spectroscopy (OES). The effects of applied power, gas pressure and pulse duration have been studied elucidating their possibilities for optimization of pulsed MW discharges used for NF. The degree of vibrational non-equilibrium is gradually disappeared when the discharge pressure increases. The correlation between gas residence time, pulse duration and characteristic times estimated for different energy transfer channels are investigated in a N_2-O_2 discharge. The evaluation of the NO density is realized by using Fourier Transform Infrared (FTIR) calibrated spectroscopy [4]. Particular attention is given to estimate the evolutions of the NO yield and energy cost at different discharge conditions. Minimum energy cost of about 8 MJ mol^{-1} corresponding to the yield of about 7% are found for NO formation.

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