Ammonia synthesis mechanism by P/L reaction between water and atomic nitrogen in plasma by discharge

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Ammonia has a wide range of applications, including fertilizer, chemical feedstock, and denitrification reducing, carbon-free fuels, and energy carriers. Currently, the industrial production of ammonia is carried out by catalytic reduction of nitrogen (N_2) and hydrogen (H_2). In contrast, green ammonia synthesis, in particular a reaction system that does not use hydrogen as a row material, is significantly different from these existing synthesis systems. It is expected to be a new technology that will contribute to the development of a sustainable chemical industry. We have developed a plasma/liquid (P/L) reaction that can synthesize ammonia from nitrogen and water under ambient temperature, atmospheric pressure, and without catalyst.[1]

In the P/L reaction, nitrogen is reduced to synthesize ammonia through a two-step reaction: (1) activation of nitrogen by discharge (dissociation and excitation), and (2) a self-reduction reaction in which activated nitrogen abstracts hydrogen from water molecules. The activated nitrogen species can be roughly divided into three types of nitrogen: atomic nitrogen, excited nitrogen molecules, and nitrogen molecular ions. Of these, excited nitrogen molecules and nitrogen molecular ions are also called metastable nitrogen. We have already reported that atomic nitrogen (N_{atom}) is particularly highly reactive and exhibits high selectivity and speed in abstracting hydrogen from water molecules in P/L reaction.[2]

We have so far focused on N_{atom} and devoted our efforts to elucidating the reaction mechanism. Because water is used as the hydrogen source, nitrogen oxides are in principle synthesized in the liquid phase together with ammonia. However, when the P/L reaction is carried out under conditions where N_{atom} is abundant, the synthesis selectivity of ammonia accumulated in the liquid phase reaches nearly 100%, while oxygen derived from water molecules is released as NO in the gas phase.[3] Our previous research results have shown that filling the discharge locus with dielectric beads can increase the amount of N_{atom} produced (the N_{atom} ratio in active nitrogen). In this study, we quantitatively analyzed the amount of N_{atom} when beads with various dielectric constants were filled into the discharge locus, and analyzed the plasma by optical emission spectroscopy. We considered the electron energy in the plasma and the vibrational and rotational excitation of nitrogen molecules, and clarified the plasma conditions necessary for N_{atom} production.

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