Green chemical pathway of N_2 fixation: Perspectives from plasma modelling

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Alternative sustainable N_2 fixation under ambient conditions that can be operated with renewable energy sources and feedstocks is globally sought to replace the conventional Haber–Bosch process. Plasma catalysis is receiving increasing attention as a green technology for the efficient synthesis of ammonia and also NOx. However, the current implementation of plasma catalysis of N_2 fixation application still faces challenges, especially the extensive energy usage for H_2 formation prior to NH_3 production, low energy efficiency and importantly the lack of understanding about the underpinned mechanism. In this study, we compare different green chemical pathway of plasma catalysis of ammonia and NOx and its effective storage in water using plasma chemistry modelling.

The zero-dimensional plasma chemistry modelling was performed using open source ZDPlaskin[1] combined with Boltzmann equation solver BOLSIG+[2] to understand different mechanisms of NH_3 and NOx production in N_2/H_2O and air plasma system with and without catalyst. The model provides the explanations about the important role of surface reactions to enhance the reactivity of the system at different plasma conditions.

Figure 1 shows the examples of plasma chemistry modelling for ammonia synthesis on SiO_2 surface in N_2/H_2O plasma based on activation energy calculation from DFT study.[3] The quenching effect of vibrationally excited $N_2(v_i)$ species by water molecules was considered to be the important difference to cause the limitations of ammonia synthesis in N_2/H_2O system not only the competing oxidation reactions. Therefore, the role of catalytic surface reactions becomes even more crucial to improve production rate and energy efficiency and as well as relatively high gas temperature condition enabled by high density electrons. As in a similar approach, NOx synthesis using Graphene oxide/TiO_2 catalyst was also investigated[4] by integrating accurate activation energies from DFT calculations for each oxidation and dissociation steps.

Further discussions will be presented regarding the important role of surface reactions to circumvent the current limitations of plasma catalysis in different N_2 fixation process.

References

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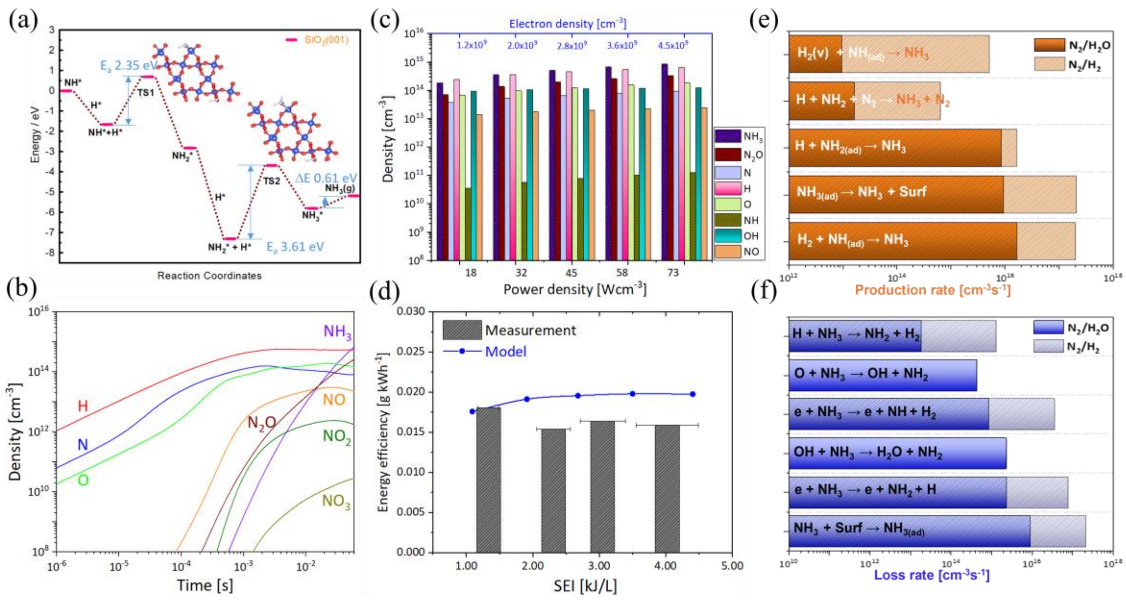

Figure 1 (a) Summary of DFT calculation results for SiO_2 surface, (b) density profile of important gas phase species in N_2/H_2O plasma system, comparison of (c) gas composition at different power density and (d) energy efficiency of model and the measurement, and important (e)production and (f)loss mechanism of NH_3 in N_2/H_2 and N_2/H_2O system