Kinetic roles of vibrational excitation in non-equilibrium plasma assisted NH$_3$ synthesis

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Abstract: A combined experimental and simulational work was carried out in this report to investigate the kinetic effects of vibrational excitation on synthesis of NH$_3$ in a NSD dielectric barrier discharge. Special attention was placed on the vibrational chemistry of N$_2$ and H$_2$ in N$_2$/H$_2$ discharge. The path flux analysis revealed that the vibrationally excited molecules H$_2$(v) enhanced chain propagation reactions, such as NH+H$_2$(v)→NH$_2$+H, NH$_2$+H$_2$(v)→NH$_3$+H, further stimulating the production of active radicals and final product.

Keywords: Non-equilibrium, ammonia synthesis, vibrational excitation, path flux analysis

1. Introduction

Ammonia is of huge economic importance as a basic precursor of the production of chemicals used for many essential applications. The production of the required ammonia by the well-known Haber-Bosch process consumes 1-2% of total world energy consumption [1,2]. The traditional Haber-Bosch process typically operates at high temperature and pressure from 200 to 400 atm and 400-600 °C [3]. These intense temperature and pressure conditions are the main disadvantages of the Haber-Bosch process, which prevents it from lowering the capital cost and be accessible to small facilities and farms [4,5]. Therefore, it is necessary to explore the new opportunities and approaches for ammonia synthesis. In recent years, non-thermal plasma has been found to be a potential alternative to the high temperature and pressure method for the synthesis of ammonia [6,7]. However, the mechanism of the generation of the excited species in a plasma as well as their roles in exciting the overall NH$_3$ synthesis processes is still not well addressed, and more mechanisms studies are needed from both experimental measurements and theoretical modelling.

The plasma-chemistry system is complicated by the different types of excited species and the reactions involved with these excited species. Plasma generated excited species and their effects on ammonia synthesis have been studied by experiments and simulations in the past years [8,9]. Nevertheless, vibrational excitation effect on ammonia synthesis was not mentioned in the published results. Despite these detailed above and importance of the molecule excitation, quantitative characterization of the molecular excitation, especially the vibrational excitation during the overall ammonia synthesis process by low temperature have not been well studied.

In this report, we combined experiments and computations to study the kinetic processes involving vibrational and electronic excitations of gas molecules in a NSD plasma assisted ammonia synthesis system.

2. Method

A zero-dimensional reaction kinetics model incorporating a set of reactions involving neutral, charged, vibrationally and electronically excited molecules, was developed to simulate the kinetic processes of NH$_3$ synthesis in a N$_2$/H$_2$ mixture activated by nanosecond pulsed discharge. The plasma kinetics solver ZDPlasKin [10] was used to obtain steady-state or time-dependent densities of the species produced in the discharge. The residence time was consistent with the corresponding experimental conditions. The electron energy distribution function (EEDF) and the rate coefficients of the electron impact elementary reactions were calculated by a Boltzmann equation solver (BOLSIG+) [11] incorporated into ZDPlasKin. The Poisson equation for the electric field was not solved during the kinetic modelling and the charge separation and sheath formation near the electrodes was therefore neglected.

A set of elementary reactions was modelled for NH$_3$ synthesis in a NSD plasma. The gas-phase reactions considered in the model can be divided into 14 categories: (1) electron impact vibrational excitation, electronic excitation, dissociation and ionization. (2) electron-ions recombination reactions; (3) ion-molecule reactions; (4) vibrational-vibrational (V-V) interactions; (5) vibrational-translational (V-T) interactions; (6) electronic transitions and radiative transitions; (7) wall relaxation; (8) binary processes with nitrogen, hydrogen or NH$_x$. Besides, reactions involving vibrationally- and electronically-excited species were incorporated in this numerical model. The reaction rate constants between excited reagents and radicals were calculated by using Fridman-Macheret α-Model [12] and MMVT method [13] for vibrationally and electronically excited species, respectively. Accordingly, a total of 338 reactions with 42 species were given out for plasma assisted NH$_3$ synthesis in this study. The species contained in this model are listed in Table 1.

Table 1. Species considered in plasma kinetic model.

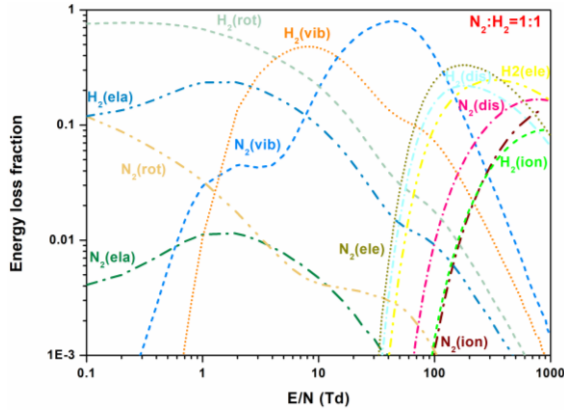|	
Molecules	N$_2$, H$_2$, NH$_3$
Atoms	N, H, N(2D), N(2P)
Radicals	NH, NH$_2$
Charged species	e, N$^+$, N$_2^+$, N$_3^+$, N$_4^+$, H$^+$, H$_2^+$, H$_3^+$, H$^-$, NH$^+$, NH$_2^+$, NH$_3^+$, NH$_4^+$, N$_2$H$^+$
Vibrationally-excited molecules	N$_2$(v1), N$_2$(v2), N$_2$(v3), N$_2$(v4), N$_2$(v5), N$_2$(v6), N$_2$(v7), N$_2$(v8), H$_2$(v1), H$_2$(v2), H$_2$(v3)
Electronically-excited molecules	N$_2$(A3), N$_2$(B3), N$_2$(a'1), N$_2$(C3), H$_2$(B3), H$_2$(B1), H$_2$(C3), H$_2$(A3)

3. Results and Discussion

Fig. 1. Energy loss by electron into different molecular degrees of freedom as a function of *E/N*.

The reduced electric field *E/N* is a key parameter in plasma discharge, which dominates the direction of electron energy transferring to the different molecular degrees of freedom and the composition of active particles. Fig.1 presents the energy branching at different values of *E/N* between 0 and 1000 Td in a 0.5 N_2/0.5 H_2 discharge mixture. As depicted in Fig.1, the most efficient mechanism of energy deposition is the rotational excitation of H_2 below an *E/N* value of 10 Td. Moreover, energy loss fraction for elastic collision of H_2 shows significant at this relatively lower *E/N* value region. However, there is still a considerable percentage of plasma energy going to the vibrational excitation of H_2. At *E/N* value between 10 and 100 Td, the majority of electron energy transfers to the vibrational excitation of H_2 and N_2, the vibrational excitation processes can effectively compete with the electronic excitation, dissociation and ionization processes of gas molecules in this value range. When the *E/N* value above 100 Td, most of the discharge power is localized within electronic excitation and dissociation, however, the efficiency of further vibrational excitation. By lowering the energy barrier especially for the endothermic processes, the vibrational states of reagents can significantly accelerate the chemical reactions involving vibrationally excited molecules and thus have a significant role effect on the production of radicals and NH_3 [12]. It is therefore necessary to consider the kinetic roles of the vibrationally excited molecules in the energy branching as well as the chemistry reaction calculation.

Vibrationally excited molecules are considered to play significant roles in plasma-chemical kinetics due to an effective decrease of activation energy compared to the ground state counterparts under conditions of incomplete vibrational relaxation, especially for endothermic processes. The elementary reactions between vibrationally excited molecules and radicals are such focused in Fig.2. The Fridman-Macheret α-model was proposed to calculate the rate coefficients of vibrationally excited molecules involving reactions. The core of the model is to consider the decreased reaction activation energy by $\alpha Evib$, where the coefficient α donates the efficiency of vibrational energy usage, and can be estimated based on the

information of the activation energies of the corresponding direct and reverse reactions. The reaction rate coefficient of N + H_2(v1)→NH + H, is about two orders of magnitude higher than the reaction N + H_2=NH+H in the temperature region of 373 K-473 K, which demonstrates the influence of vibrational excitation of molecules on their reaction rate coefficients. Other vibrationally excited species generated in a discharge, such as H_2(v1), H_2(v2) and N_2(v=1-8) also have the ability to accelerate the reactions if the thermal equilibrium reaction path has a significant activation barrier.
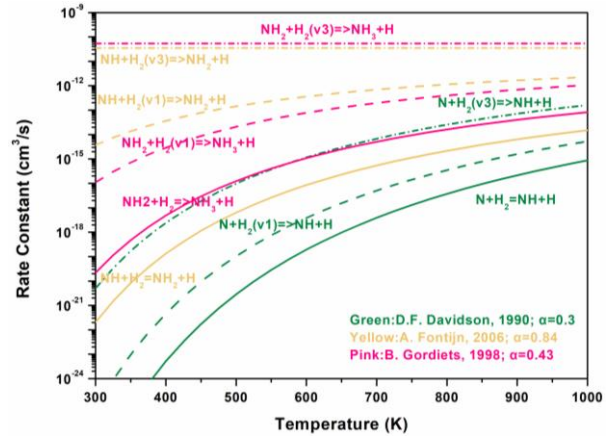

Fig. 2. Reaction rate constants for typical chain branching reactions stimulated by vibrationally excited molecules.
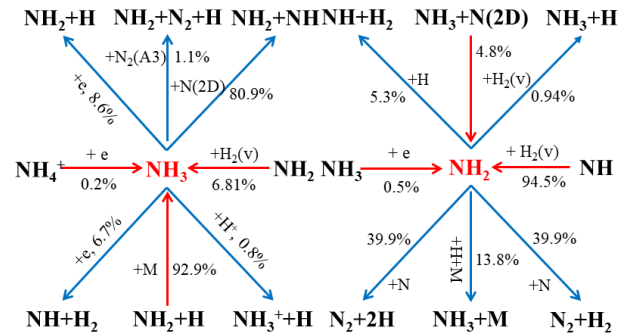

Fig. 3. Path flux analysis for NH_3 and NH_2 in a 0.5 N_2/0.5 H_2 mixture under the pressure of 40 kPa.

In order to elucidate the importance of vibrationally excited molecules to the information of primary intermediate species and final product, a detailed flux analysis is conducted. Fig. 3 shows the dominant production and consumption pathways for NH_2 and NH_3 at steady state temperature as predicted by the model (473 K). It is seen that the three-body reaction NH_2+H+M→NH_3+M, is responsible for 92.9% formation of NH_3. For the vibrational states, the energy of excitation is sufficient to reduce the activation energy barrier and further to affect NH_3 formation, as shown in Fig. 3. Specifically, reaction NH_2+H_2(v)→NH_3+H accounts for 6.81% of NH_3 formation. As Fig. 3 presented, the NH_2 radical plays more of a significant role in NH_3 formation, suggesting that this radical is the blocks for NH_3. From the perspective of NH_2

formation, the predicted pathway shows that reaction of NH with $H_2(v)$, is the most significant pathway for NH_2 radical formation, accounting for 94.5% of NH_2 formation.

4. Conclusion

The kinetic effects of vibrationally excited molecules activated by NSD plasmas on NH_3 synthesis was investigated experimentally in a DBD flow reactor in a N_2/H_2 mixture at pressure of 40 kPa and controlled temperature of 473 K. A detailed kinetic mechanism including a set of electron impact reactions, dissociative recombination reactions, reactions involving vibrationally- and electronically-excited species was assembled to simulate the kinetic processes of NH_3 synthesis using ZDPlasKin. The modelling results showed that the vibrationally excited reagents can accelerate the formation of active radicals and NH_3 significantly through chain branching reactions. The path flux analysis further demonstrated the significant roles of the vibrationally excited molecules, in stimulating the formation of active radicals and NH_3. It was found that reaction $NH+H_2(v) \rightarrow NH_2+H$ is responsible for 94.5% of NH_2 radical formation and $NH_2+H_2(v) \rightarrow NH_3+H$ accounts for 6.81% of total NH_3 synthesis.

5. References

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