High-frequency spark discharge enabled efficient NO_x synthesis

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Abstract: High-frequency spark discharge showed much higher performance for NO_x synthis than conventional spark discharge operated at low frequencies. To get insight into the main factors for enhancing energy efficiency and understanding the underlying mechanism, the performance of the reactor was evaluated at different operating conditions. The results revealed that higher vibrational and rotational excitations at a higher frequency and a long electrode gap are critical factors in improving the efficiency of NO_x production.

Keywords: Sustainable NO_x formation, spark discharge, crucial factors,

1. Introduction

Recently, the interest in plasma technology for sustainable nitrogen fixation is increasing significantly due to its ability to operate using renewable energy as well as the desirable process-intensified and decentralization. A promising way for plasma-based nitrogen fixation is converting the inert N_2 molecules of the ambient air to NO_x through the reaction at atmospheric pressure. Hence, many plasma reactors are applied under different operating conditions to improve the energy efficiency of this process and many models as well as computational investigations were developed to understand the underlying mechanism [1,2]. However, still more efforts are required to reduce the energy cost of this process to make this promising technology commercially attractive.

Herein, we performed a thorough investigation of plasma NO_x synthesis under different operating conditions to determine the key factors and their role in improving the efficiency of this process. Moreover, the analysis of the results refined the reaction pathways for efficient NO_x formation in plasma reactors.

2. Experimental setup

In this work, a plate-to-plate spark discharge reactor is used, and its performance was compared with DBD in terms of NO_x yield, energy cost and selectivity of the produced species. The details of the experimental setup and reactors are described elsewhere [3]. To determine the key factors and get insight into the underlying mechanism, the investigation of NO_x formation in spark discharge was performed under different operating conditions, including different oxygen contents (0–80%), humidity levels (0.01–2%), gas flow rate (0.5–4 L/min), frequency (up to 40 kHz), and electrode gap (5–10 mm). Moreover, the OES measurements were conducted and analysed to determine the produced species and to estimate the $T_{vib.}$ and $T_{rot.}$

3. Results and discussion

It is found the spark discharge reactor was operated in a reduced electric field of 20–80 Td, which is preferable for NO_x formation, owing to higher $T_{vib.}$ with a desirable range of $T_{rot.}$ (3000–3500 K) for NO oxidation and N_2 thermal dissociation. The rate constant of NO-oxidation reactions is higher than the reduction and increased with temperature in this range of temperature range. In contrast, the vibrational excitation in cold plasma (DBD) was much lower than that of spark discharge, and NO_x formation was controlled by the electronically excited species and electron dissociation of N_2 molecules, which are energy costly. Furthermore, $T_{rot.}$ of the DBD was less than 1000 K, which is a favourite for NO reduction.

To efficiently utilize the produced vibrational excitation in the spark discharge reactor, we proposed to reduce the time interval between two constructive discharges (i.e., frequency of the applied voltage) by increasing the frequency.

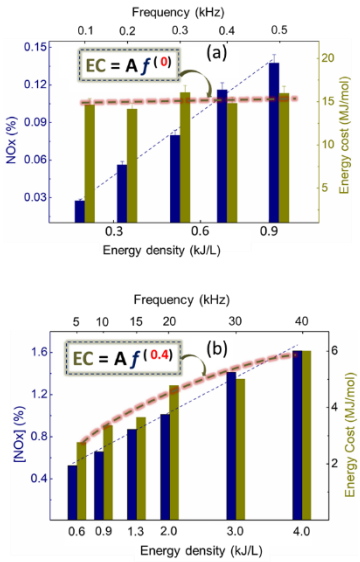

Fig. 1. NO_x concentration and corresponding energy cost at (a) f = 0.1–0.5 kHz and (b) f = 6 – 40 kHz.

Fig. 1 shows that the performance of the spark discharge at a higher frequency range (6–40 kHz) was much higher than that at a lower frequency range (0.1–0.5 kHz). The higher frequencies also lowered the possibility of V-T

relaxation which has a much longer time scale compared to the time interval between two consecutive discharges. More importantly, the spark discharge at higher frequencies led the $T_{rot.}$ of the reactor in the range of 3000–3500 K resulting in lowering the NO reduction and decomposition. Therefore, the common chemical loss process in plasma NO_x synthesis disappeared. On the other hand, higher frequencies were associated with higher loss in the deposited energy through electrode heating due to the increase in the conductivity of the plasma channel. However, the positive effects of the higher frequency overcome its negative effect resulting in a slow increase in the energy cost with the energy density. To reduce this energy loss pathway, an approach of increasing the electrode gap was effective to decrease the resistance of the plasma channel, and, subsequently, increased the part of energy utilized in the gas conversion. To overcome the limitation of the increasing the electrode gap, a floating electrode was inserted between the electrodes, and it resulted in improving the NO_x yield and reducing the energy cost. The discharge behaviour was monitored, and the observed phenomena were investigated in more detail to determine the favourite conditions for plasma-based NO_x formation, as summarized in Fig. 2.

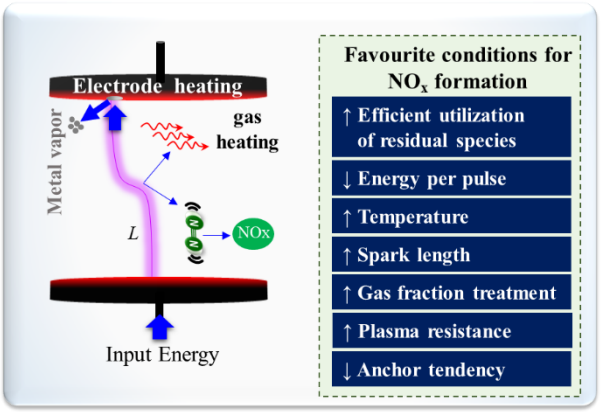

Fig. 2. Schematic shows the main process of spark discharge for NO_x synthesis and corresponding favourite conditions.

The gas flow rate didn't show a noticeable effect on the energy cost, but it has a remarkable effect on NO selectivity. The higher flow rate, the higher is the NO selectivity. This is because that the longer residence time of the formed NO oxidized to NO_2 in the plasma zone, owing to the increase its rate constant with temperature.

Adjusting the oxygen content in the feeding gas to 50% at lower humidity level showed also a great effect on the NO_x yield and its energy cost.

4. Conclusions

The deep investigation of NOx synthesis in spark discharge indicates the efficient utilization of vibrational excitation through reducing the time interval between two consecutive discharges is crucial for efficient plasma-based NOx formation. The desirable gas temperature for NOx oxidation provided in the reactor played also another important role. Therefore, high-frequency spark discharge showed a promising energy efficiency, which improved further by adjusting the operating conditions, particularly the electrode gap and oxygen content.

5. Acknowledgment

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6. References

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