Diagnostics of a pulsed microwave discharge used for nitrogen oxidation: Optical emission and infrared absorption studies

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Abstract

In this study, a low pressure surfaguide microwave discharge working in pulsed regime is characterized by optical spectroscopy method aiming at a better insight of N_2 oxidation process. The rotational and vibrational excitation were examined in the discharge zone. Infrared absorption spectroscopy is performed for ro-vibrational bands monitoring of the generated molecular species at post-discharge region. The effects of input power, gas pressure and duty ratio are investigated in order to optimize NO production in the pulsed microwave discharge.

Keywords: Nitrogen fixation, pulsed microwave discharge, absorption spectroscopy, vibrational excitation

1- Introduction

Abundant attempts have been made to artificially convert N_2 molecules into N-containing compounds, such as NO_x, NH_3, etc, in a process known as nitrogen fixation [1,2]. The majority of fertilizers are produced from non-sustainable fossil fuels via the Haber–Bosch (H-B) process. The H-B process, however, is quite inefficient due to the high temperature and extreme pressure conditions, resulting in a drastic perturbation to the worldwide geochemical N-cycle.

Nowadays, *plasma-assisted* nitrogen fixation is gaining more interest and is considered as a very promising alternative to the H–B process. Microwave (MW) discharges, in particular those based on surface wave launchers where plasma is sustained by surface electromagnetic waves [3,4] have recently attracted much attention for chemical synthesis. The vibrationally excited N_2 molecules can populate higher vibrational energy levels through a stepwise vibrational-vibrational (V-V) quanta exchange, sometimes called as "vibrational ladder climbing" [5,6]. This important property makes MW plasmas very interesting for energy-efficient vibrational excitation.

Although the strong efforts aiming in NO_x synthesis have been done in the high pressure discharges [7], the results in terms of NO_x yield and energy efficiency are rather low. Achieving a better NO_x yield with lower energy cost is of great interest in our case. In this study, we used a pulsed discharge based on surface wave launchers operating at 2.45 GHz. Particular attention is devoted to investigate the effects of input power, duty ratio and pressure by absorption and emission spectroscopies.

2- Experimental setup and methodology

2.1. The microwave plasma source. A scheme of the experimental setup of the pulsed MW plasma reactor used in this study is shown in Fig. 1. The reactor represents a surfaguide plasma source operating at 2.45 GHz and working in the pulsed regime triggered by an external delay generator. The discharge was sustained inside a quartz tube with a 14 mm inner diameter and about 31 cm length, surrounded by a polycarbonate tube. Silicone oil was circulated between these tubes to cool the surface down. The main parameters of the described microwave system are also listed in Table 1. The microwave was fed into the waveguide, connected to a manually tuned three-stub system and terminated by a movable plunger in order to minimize the reflected power. The MW power was also modulated by square pulses with duty cycle adjustment. N_2 and O_2 gases are used for NO_x production in this work.

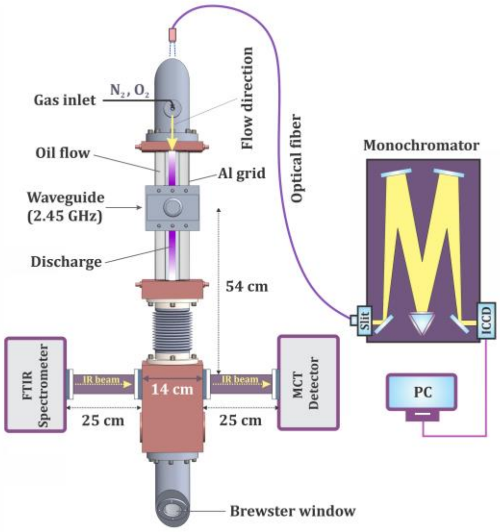

Fig. 1. Schematic view of the microwave plasma source with the spectroscopic tools used in this work.

Table 1. Main parameters of the microwave surfaguide discharges used in this study.

Microwave discharge	**Value**
MW frequency	2.45 GHz
Mean applied power	0.5-0.9 kW
Quartz tube inner diameter	14 mm
Polycarbonate tube inner diameter	32 mm
Pressure range	0.5-15 Torr
Gas flow rate range	100-5000 sccm

2.2. The diagnostic tools. For the discharge and post-discharge characterizations, optical emission spectroscopy (OES) as well as Fourier Transform infrared (FTIR) apparatus are used in this study. The main spectroscopic parameters are listed in Table 2. In FTIR study the spectral resolution of the measurements was set to 0.08 cm^{-1}, and 30 scans were averaged to create each spectrum. The interferometer was configured with a KBr beam-splitter and MCT detector to record the 1300–2500 cm^{-1} region [8] (in press), as shown in Fig. 2.

For OES measurements (to realize the discharge area) an Andor SR750 monochromator with either 1800 g/mm (for T_{vibr} determination) or 3600 g/mm (for T_{rot} determination) diffraction gratings has been used. An Andor iStar740 ICCD camera working in accumulative mode was used for detection. The details parameters related to the OES are also listed in Table 2. A typical wide emission spectrum from the discharge active zone in N_2:O_2 gas mixture is shown in Fig. 3(a). Spectral lines of a second positive system (SPS) of N_2 $C^3\Pi_u \rightarrow B^3\Pi_g$ transition are used to determine the vibrational (T_{vibr}) and rotational (T_{rot}) temperatures [9] (see Fig. 3(b,c)). MassiveOES software [10] is used to fit N_2 SPS experimental and theoretical spectra, providing T_{rot} and T_{vibr} as a result of the fitting process. The gas temperature is assumed equal to T_{rot} in our case.

Table 2: Main spectroscopic parameters (FTIR and OES diagnostics).

FTIR diagnostics	**Specification**
IR Source	Mid-IR
Detector	MCT mid band
Spectral resolution	0.08 cm^{-1}
Aperture	1.5 mm
Detector cooling	Liquid nitrogen
Optical emission diagnostics	**Specification**
Spectrometer	Andor SR750
Grating	1800 g/mm, 3600 g/mm
Spectral resolution	20 pm (with 3600 g/mm)
Optical detector	Andor ICCD iStar 740

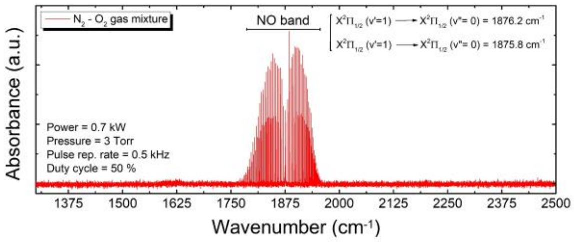

Fig. 2. A typical FTIR spectrum for N_2:O_2 gas mixture detected in the post-discharge region. Two sets of fundamental vibrational transition of NO in ground electronic states are also specified in the legend.

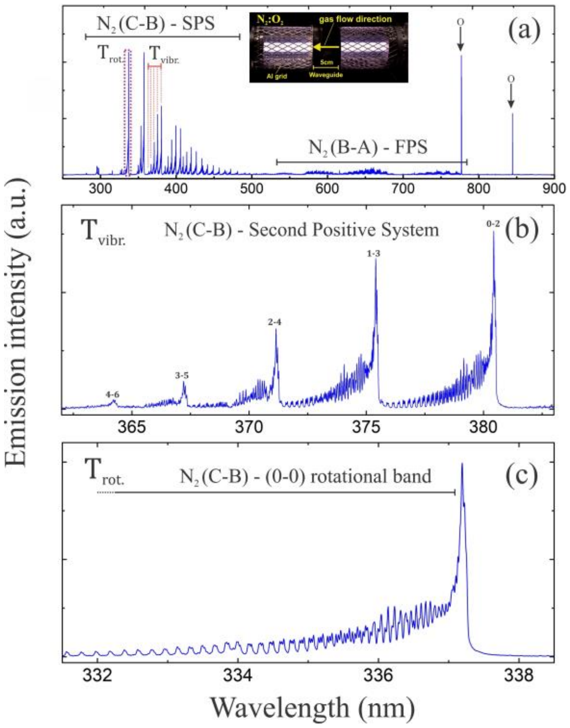

Fig. 3. (a) The wide emission spectrum taken in the pulsed MW discharge for N_2:O_2 gas mixture, (b) magnified view of the vibrational band sequences from N_2 SPS (C,v-2 - B,v) used for T_{vibr} determination in the N_2 (C) state, and (c) enlarged view of N_2 C-B (0-0) at 337.2 nm used for T_{rot} determination acquired with 23 pm resolution.

3. Results and discussions

3.1. Power effect. The evolution of the T_{vibr} and T_{rot} was examined as a function of applied power taken at different pressures. A higher energy input results in the enhanced production of N- and O-reactive species, primarily as a result of electron impact excitation as well as vibrational excitation of N_2 and O_2 (see Fig. 4(a)). Those reactive species could then combine via reactions: N_2+O→NO+N and N+O_2→NO+O, resulting in a higher NO concentration. These pathways are known as the Zeldovich mechanism stimulated by a non-equilibrium N_2 vibrational excitation. A higher applied power, however, facilitates the vibrational-translational (V–T) relaxation processes when the vibrational energy is transferred to gas heating, as shown in Fig. 4(b).

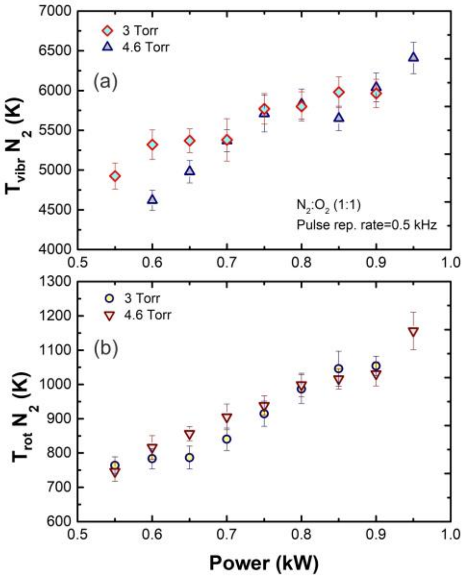

Fig. 4. (a) T_{vibr} and (b) T_{rot} determined as a function of the applied power. The measurements are taken at a pulse repetition rate of 0.5 kHz with duty ratio of 50%.

3.2. Duty ratio effect. A proper-tuning of the pulse repetition rate and duty ratio could play a major role to improve NO production. A stable growth for both T_{vibr} and NO yield have been observed by increasing the pulse duration (see Fig. 5(a)). The T_{rot} behavior is barely sensitive to the pulse duty ratio, as shown in Fig. 5(b).

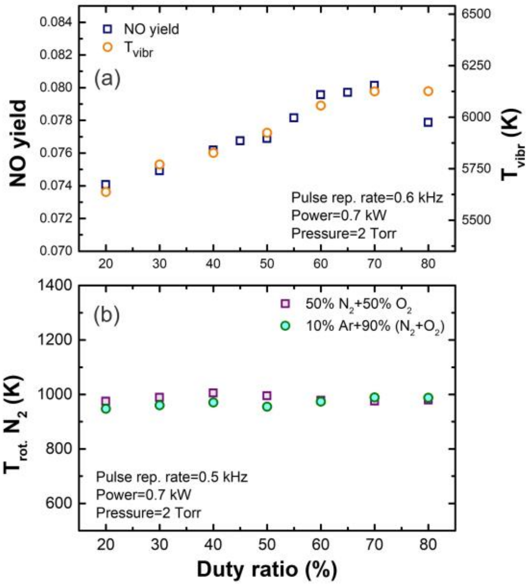

Fig. 5. (a) Evolutions of the NO yield and T_{vibr} as a function of duty ratio measured in a N_2:O_2 gas mixture; (b) T_{rot} determined in N_2 SPS C-B (0-0) at 337.2 nm.

3.3. Pressure effect. The dependency of T_{vibr} and T_{rot} on pressure is depicted in Fig. 6. Higher collision rates between electrons and heavy particles at high pressures, resulting in a certain drop in electron temperature as well as elevating in V-T relaxation processes by transferring vibrational energy to gas heating leading to rise in T_{rot}. Thus, it seems a non-equilibrium is better exploited in relatively low pressures when the gas temperature remains low.

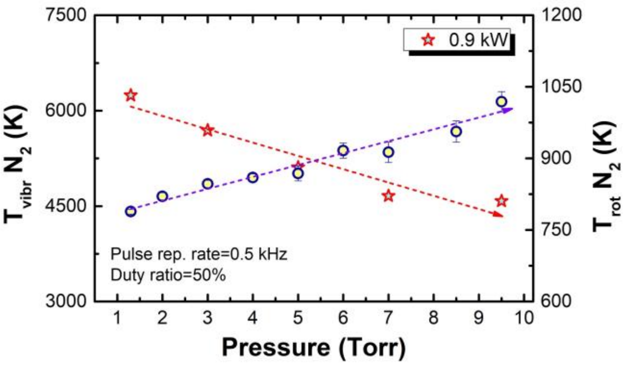

Fig. 6. Vibrational and rotational temperature measurements as a function of the total gas pressure.

4. Conclusions

In this study an attempt to clarify the capabilities of a pulsed MW discharge for NO formation have been undertaken by infrared absorption and emission spectroscopy. Typical values for the NO yield of about 7% were obtained, after calibration. At the same time the energy cost for NO production is estimated as 8 MJ/mol in an optimum discharge condition.

We have shown the vibrationally excited N_2 molecules could populate higher vibrational energy levels by ladder climbing at high input powers leading to enhanced N_2 dissociation. The measurements reveal that working at high pressures have a negative effect on NO formation, while a lower pressure is beneficial, as it supports vibrational excitation of the involved molecules. The results also show that the NO yield can be further improved by a proper-tuning of the pulse duration.

Acknowledgments

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