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Journal of Hazardous Materials 143 (2007) 409–414
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Reducing nitric oxide into nitrogen via a radio-frequency discharge

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Received 4 May 2006; received in revised form 15 September 2006; accepted 16 September 2006

Abstract

$NO/N_2/O_2/H_2O$ mixtures are usually converted into HNO_3 and/or NO_2 using different discharge approaches. In this study, a radio-frequency discharge was successfully used to reduce NO mainly into N_2 at a low pressure (4 kPa). The influences of experimental parameters, including carrier gas, inlet concentration of NO, O_2, steam, and applied power, are discussed. At least 95.7% of the total N atoms converted from NO into N_2. Other traces of byproducts were N_2O and HNO_2, but neither HNO_3 nor NO_2 were detected. In addition, conversion of NO apparently increased with elevated applied power or decreased inlet concentration of O_2, reaching 92.8% and 74.2% for the $NO/N_2/O_2$ (2%) and $NO/N_2/O_2$ (6%)/H_2O (10%) mixtures, respectively, at 120 W. In addition, from the optical emission spectra, a large amount of N_2 (first positive band and second positive band) and NO (γ system) were observed, and the important reactions for NO removal and N_2 formation are proposed.

Keywords: Nitric oxide; rf discharge; Reduction; Nitrogen

1. Introduction

NOx, the precursor of photochemistry products and acid smog, is mainly emitted from industrial processes or mobile sources. NOx is harmful to the human health and the ecosystem, damages vegetation and degrades or corrodes materials through acid deposition [1]. Many emissions control strategies have been implemented, such as selective catalytic reduction, selective noncatalytic reduction, and direct thermal decomposition. However, the typical operating temperature of these is relatively high, ranging between 300 and 1000 °C [2,3].

Hence, nonthermal plasma approaches, which can be free of high temperature control and avoid the problems of catalyst poisons and deactivities, have been developed to remove NO. Several kinds of plasma technologies have been demonstrated that can be operated at room temperature and be proceeded in dry or wet process, such as dielectric barrier discharge, corona discharge, and microwave discharge [4–8].

However, higher oxidized nitrogen compounds, such as NO_2 and/or HNO_3, are commonly formed when converting the $NO/N_2/O_2/H_2O$ mixtures [6,9–11]. Although NO_2 and HNO_3 are water soluble and can be removal with scrubbers, to reduce NO into N_2 seems a better choice because it does not need further treatment of acidic wastewater and sludge. Hence, a dry, single-stage, noncatalytic radio-frequency (rf) discharge approach, which has previously not been tried to remove NO, is successfully demonstrated to reduce NO mainly into N_2 in this study. The 13.56 MHz rf plasma is commonly used in industry for IC manufacture and surface modification, as well as being used to recover sulfur from SO_2 and convert methane into syngas [12,13].

In addition, high concentrations of NOx are yielded from nitric acid plants, the high ovens of heat treating automotive catalysts, and automobile exhaust gases. The NOx can reach a concentration of 2000 or up to 10,000 ppm [3,14], which is fed into the rf discharge reactor in this study.

In the discharge zone, electrons interact with N_2, NO, and O_2 to generate initiating species for the overall reaction chains [15]. In addition to electron-impact dissociation and ionization reactions, Penning ionization and charge-transfer processes take

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doi:10.1016/j.jhazmat.2006.09.042

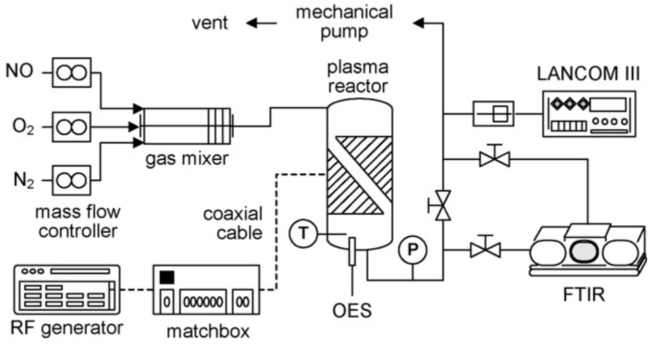

Fig. 1. Sketch of the rf discharge system.

part in the NO decomposition [16]. The previous studies indicated that the major removal channels of NO were through reduction reaction (Eq. (1)) and/or oxidation reaction (Eq. (2)) [17–19]. However, long-lived excited N_2 in plasma jets did not play an important role in NO destruction via reaction of $NO + N_2 \rightarrow N_2 + N + O$ [20]:

$$NO + N \rightarrow N_2 + O \quad (k = 3.1 \times 10^{-11}\,cm^3\,s^{-1},\ at\,300\,K) \tag{1}$$

$$NO + O \rightarrow NO_2 \quad (k = 2.5 \times 10^{-12}\,cm^3\,s^{-1},\ at\,300\,K) \tag{2}$$

In addition, the decomposition of NO via electron impact dissociation ($e + NO \rightarrow N + O + e$) also yields a large amount of N and O. However, the rate of electron impact rate is dependent on discharge types owing to their different electron mean energy and plasma density. In order to infer the important mechanisms, plasma diagnostic technology, like optical emission spectroscopy, is often used [19] to examine the major active species in this rf discharge process.

2. Experimental section

A laboratory-scale rf discharge system is shown in Fig. 1. NO (4.8%, N_2 balanced), and high purity O_2 (99.95%) and N_2 (99.995%) were supplied from compressed gas cylinders and their flow rate was adjusted with a calibrated mass flow controller. The reactants were introduced into a gas mixer, and then entered a vertical, cylindrical glass reactor. A 13.56 MHz rf generator (PFG 600, Fritz Huttinger Elektronik Gmbh) coupled with a matching network (Matchbox PFM) was used to apply the power. The power was delivered to the plasma reactor that wrapped two outer copper electrodes, as well as to generate an inductively coupled glow discharge. The net power to the discharge was determined by obtaining an optimum match via reading the difference between the forward and reflected power. However, the reflected power is usually zero via the matchbox auto-matching the capacitance and inductance. Before the experiment, a mechanical vacuum pump was used to exhaust the effluents and to remove contaminants. For each experimental run the system was kept at working pressure until the effluents had been measured.

The qualitative and quantitative analyses of reactants and effluents were performed by an on-line Fourier transform infrared (FTIR) spectrometer (Nicolet, Avator 370, with a gas cell of 2.3 L and light path length of 9.6 m). Calibration of gaseous reactants and products was made by withdrawing unreacted gases and by going directly through the sampling line connected to the FTIR. Furthermore, the accuracy of the concentration of NOx was also checked by a commercially available analyzer (Land, Lancom III). Studies of optical emission spectra were carried out by using an optical spectrometer (Ocean Optics, Model HR 4000CG). The emission light was collected through an optical fiber, which was put in the rear part of the plasma and analyzed via a scanning monochromator.

The gas sampling lines, including the gas cell of FTIR are heated and keep at about 330 K by wrapping a heated belt coupling with a temperature controller in order to measure HNO_2 and HNO_3. Moreover, the boiling point decreases apparently with the decreased operating pressure, such as the boiling point of HNO_3 is about 315 K, hence, HNO_2 and HNO_3 can vapor in the overall close system (reactor, sampling lines, and gas cell are at the same pressure) until pumping out.

The main operational parameters and conditions were as follows: applied rf power = 30–120 W, inlet concentration of NO ($[NO]_{in}$) = 2400 or 10,000 ppm, inlet oxygen concentration ($[O_2]$) = 0–10%, inlet H_2O concentration = 0 or 10 vol.%, carrier gas = N_2, and total flow rate = 200 sccm (standard ml min^{-1}). In addition, the feeds were at room temperature and the pressure was operated at 4 kPa in order to start the discharge easily and keep the discharge was in a stable state. The gas temperature of effluents was measured by a thermocouple that was put at the rear of discharge zone in the reactor.

The temperature was in the range of 420–800 K and the gas mean residence times in the physical discharge zone was ranged between 0.2 and 0.4 s for all runs. Part of the forward power that supplied by the rf generator was consumed by the reflected power, heating electrodes, and the electron temperature, hence, the gas temperature was not very high.

3. Results and discussion

The conversion of NO (η_{NO}) and the fraction of total N atoms converted from NO into N_2 (F_{N_2}) are calculated by the following equations:

$$\eta_{NO} = \frac{\text{NO converted}}{\text{NO fed to the reactor}} \times 100\%,$$

$$F_{N_2} = \frac{2 \times N_2 \text{ yielded from decomposed NO}}{\text{NO converted}} \times 100\%$$

where NO and N_2 are the moles of compounds NO and N_2, respectively. The amounts of N_2 converted from inlet NO were calculated based on the mass balance of N atoms by quantifying all N-species detected, including NO, NO_2, N_2O, HNO_2, and HNO_3.