Removal of NO by Microwave Discharge with the Addition of CH_4

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Removal of NO by a continuous microwave discharge at atmospheric pressure with the addition of CH_4 is reported. The conversion of NO to N_2 is approximately 80%, and the energy efficiency is up to 0.55 g-NO/kWh. The effects of CH_4 addition and three discharge modes on NO conversion and energy efficiency are investigated. The dependence of NO conversion on experimental time is also observed.

Activation of small molecules such as CH_4, CO_2 and NO has been the focus of many researchers in the areas of catalysis, energy conversion, environmental monitoring, as well as other areas.[1] Discharge can be used to activate gaseous species, and in certain cases, non-thermodynamic equilibria can be obtain to selectively activate stable small molecules.[2] Various types of energy and radiation, such as microwave,[3–5] radio frequency,[6] and electrity,[7,8] can be used to generate discharge. Suib et al. have reported the activation of CH_4, CO_2 in the high-voltage ac discharge or microwave discharge.[7,9] However, they did not investigate the conversion of NO using the methods. Compared with the other discharge, microwave discharge is energy efficient because a large amount of energy goes into the production of energetic electrons rather than into heating of gas, and the performance is good due to the large ionization region.

However, due to the difficulties in generating the discharge and in controlling its quality under atmospheric condition, the application of microwave discharge has been limited to a vacuum condition. We reported that the continuous microwave discharge (CMD) was realized at atmospheric pressure and it was used to decompose NO.[5] By the addition of the additive to reaction gas, the energy requirement for NO removal can be largely reduced without production of any harmful byproducts in a pulsed corona discharge.[10] As a readily available commodity chemical, CH_4 offers a rich source of hydrogen atoms which are beneficial for the reduction of NO. Given the plentiful supply of CH_4 in the world, the use of CH_4 as an attractive additive would be desirable in the removal of NO.[11]

In this work, an experimental investigation has been conducted for the removal of NO with the addition of CH_4 under microwave discharge, and the effects of CH_4 additive and different gas discharge modes on NO removal and energy efficiencies are also illustrated.

The microwave reaction system was described elsewhere.[5] For the experiments, a Y-type reactor was designed to enable the CMD at atmospheric pressure and activation of different gases. The quartz reactor is shown in Figure 1. The angle between the two arms is about 5°, and the i.d. of each arm is 4 mm. The reactor was aligned vertically at the center of the single mode resonant cavity, so that the discharge region was located in the microwave field of maximum intensity. The microwave discharge was induced in one arm by the cooperation of a mass of quartz wool and quartz reactor wall. The quartz wool was about 3 mL. The formed discharge had a bright red color with a weak sound. The distance between the quartz wool and the junction of the reactor ranged from 40 to 50 mm according to the discharge mode. This arm was named the D arm (discharge arm). Another arm of the Y-type reactor was denoted as the G arm (gas arm). The concentrations of reactants and products were determined by an on-line NO_x analyzer (FGA 4000/4005) and a gas chromatograph (GC-8800, thermal conductivity detector with 13x and PQ columns)

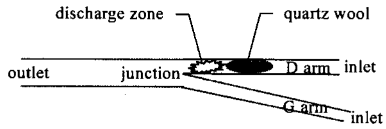

Figure 1. The diagram of a Y-type reactor.

The effects of various discharge modes on NO conversion are shown in Figure 2. The total gas flow rate is 60 mL/min. First, the mixture gas, comprised of 2000 ppm NO, 1600 ppm CH_4, 2% O_2 and He balance gas, was introduced into the D arm to discharge, while the G arm was sealed. The results of NO conversion to N_2 are represented by the curve of circles in Figure 2. This process was nominated as CH_4 and NO discharge. Second, the mixture gas, made up of 2000 ppm NO, 2% O_2 and He balance gas, was introduced into the D arm to discharge. The discharge zone was controlled out of the junction by moving the quartz wool. 1600 ppm of CH_4 was introduced along the G arm to the junction to react with the discharge gas from the D arm. The results are also shown in the Figure 2 by the curve of triangles, and this process was nominated as NO discharge. Finally, the path of CH_4 and that of the mixture gas were exchanged, such that CH_4 was used to discharge along the D arm, while the mixture gas was introduced along the G arm, and the results are shown by the curve of squares in Figure 2. This process was nominated as CH_4 discharge.

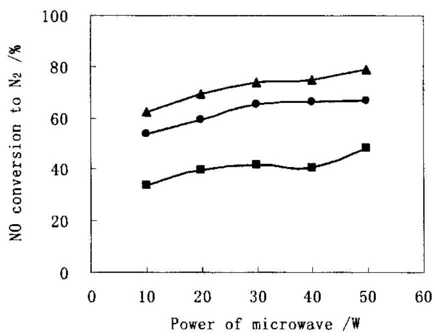

Figure 2. The effect of different discharge modes on NO conversion to N_2 in CMD, NO discharge mode (triangles), NO and CH_4 discharge mode (circles), CH_4 discharge mode (squares). Reaction conditions, 2000 ppm NO, 1600 ppm CH_4, 2% O_2, He balance gas, flow rate 60 mL/min.

In the NO discharge mode, CO_x was observed in the products. This suggested that inert CH_4 reacted with activated species containing O. A similar process occurred in the CH_4 discharge mode. All of these results indicated that some radical species with enough long lifetimes were produced in CMD, and they could reach the junction to react with other molecules. By moving the location of quartz wool, it could be controlled to allow different species and reaction intermediates to be obtained in the junction. In the present work, we have controlled the quartz wool to realize a high conversion of NO to N_2. From these results, it can be seen that the conversion of NO to N_2 increased with increasing of the microwave power in any discharge mode. By comparing the conversion of NO to N_2 in all discharge modes, the conversion in the NO discharge mode was the highest, while that in CH_4 discharge was the lowest. The conversion of NO to N_2 in the case of CH_4 and NO discharge together was in the middle level, which corresponds approximately to the results we have reported on NO discharge without any additives.[5] This indicated that CH_4 had little contribution to the conversion of NO to N_2 when it was discharged together with NO. In the NO discharge mode, the conversion of NO to N_2 was approximately 80%, which was almost 15% higher than that without the addition of CH_4 and 45% higher than that of CH_4 discharge. So it is suggested that different discharge modes affected greatly the conversion of NO to N_2.

The energy efficiencies of NO conversion to N_2 were calculated by Equation [1] for the three discharge modes. The dependence of energy efficiency on input power is shown in Figure 3. The

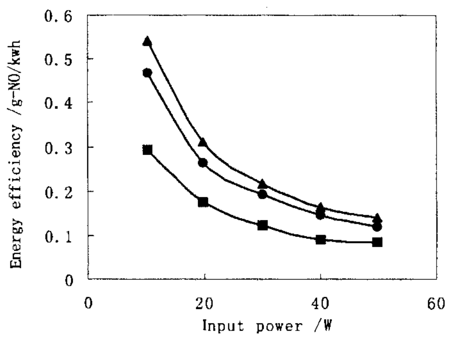

Figure 3. The effect of different discharge modes on energy efficiencies in CMD, NO discharge mode (triangles), NO and CH_4 discharge mode (circles), CH_4 discharge mode (squares). Reaction conditions, 2000 ppm NO, 1600 ppm CH_4, 2% O_2, He balance gas, flow rate 60 mL/min.

energy efficiencies of the three discharge modes decreased with the increasing of the input power, especially in the power range of 10–30 W. When the input power was 10 W, the energy efficiency in the NO discharge mode was 17% higher than that in the NO and CH_4 discharge mode, and 90% higher than that in the CH_4 discharge mode. The highest energy efficiency was 0.55 g-NO/kWh, which was realized in the NO discharge mode.

$$E_{N_2} = \frac{\nu \times [NO] \times X_N \% \times 60 \times 1000 \times 30}{P_{in} \times 24500} \quad [1]$$

where E_{N_2} is the energy efficiency (g-NO/kWh), ν is the total gas flow rate (mL/min), [NO] is the concentration of NO in the reactants, X_N% is the conversion of NO to N_2, P_{in} is the input power of microwave (W), 24500 is the volume (mL) of 1 mole of gas at room temperature, 30 is the molecular weight of NO.

In the NO discharge mode, we observed the dependence of NO conversion to N_2 on experimental time in 50 W power, and the results are shown in Figure 4. The conversion of NO to N_2 was about 80%, invariable with the delay of the time.

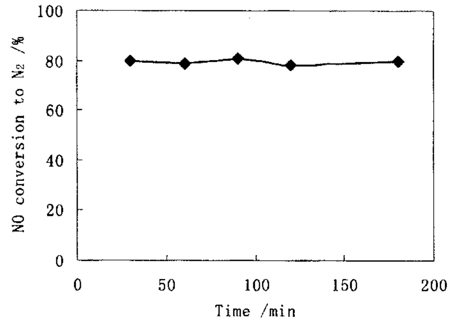

Figure 4. The dependence of NO conversion to N_2 on experimental time in the NO discharge mode. Reaction conditions, 50 W input power of microwave, 2000 ppm NO, 1600 ppm CH_4, 2% O_2, He balance gas, flow rate 60 mL/min.

Although the reaction mechanism of NO reacting with CH_4 under different CMD modes is still vague, the following reactions are proposed:

$$NO \xrightarrow{e^*} N \xrightarrow{NO} N_2 \quad (1)$$

$$NO \xrightarrow{CH_3} HCN \xrightarrow{OH} NCO \xrightarrow{NO} N_2O \xrightarrow{H,\, OH} N_2 \quad (2)$$

$$NO \xrightarrow{H} N \xrightarrow{NO} N_2 \quad (3)$$

Where the high-energy electrons (e^*) are provided by He which suffers the microwave irradiation. The CH_3 and H radicals are from CH_4.

Among reactions (1)–(3), reaction (1) is the easiest to be realized,[12,13] then reaction (2), and lastly reaction (3).[14] In the NO discharge mode, reaction (1) is mainly induced. Then, activated O species formed by the pyrolysis of NO excited CH_4 to form active CH_x, H and other radicals, these radicals could induce NO removal by reactions (2) and (3). In the CH_4 discharge mode, only reactions (2) and (3) are induced. In the NO and CH_4 discharge mode, only reaction (1) is induced to reduce NO, while excited CH_4 mainly reacts with excess O_2. Therefore, in this mode, the conversion of NO to N_2 is affected little by CH_4.

In conclusion, CH_4 addition affects the conversion of NO to N_2, and different discharge modes also affect greatly the NO reduction and energy efficiency.

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