N₂O Decomposition by Catalyst-Assisted Cold Plasma

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Abstract: Nitrous oxide (N₂O) has been recognized as a relatively strong greenhouse gas. Heterogeneous catalytic processes have been mainly used to decompose N₂O at high temperature. Characteristics of N₂O decomposition by catalyst-assisted cold plasma were investigated in the present study. Tubular quartz reactor with annular-shaped electrodes was prepared and ruthenium catalysts supported on alumina pellets were packed in the reactor. We investigated the effects of space velocity, temperature, discharge voltage, and reactant compositions on the N₂O decomposition. Ar plasmas broke strong bonds of N₂O into NO, N, and O radicals. It was discovered that the radicals were more reactive on the active sites of the catalyst at low temperature.

Keywords: Nitrous oxide; Decomposition; Cold plasma; Catalyst-assisted plasma; Greenhouse gas control

1. Introduction

Nitrous oxide (N₂O) is a contributor to the ozone destruction in the stratosphere and a strong greenhouse gas. The N₂O sources include adipic acid production, nitric acid manufacture, nylon polymer manufacture, fossil fuels and biomass combustion, and land cultivation.

N₂O emission can be reduced in two ways either by lowering N₂O formation or by after-treatment. N₂O control techniques will depend on the conditions of N₂O abatement in the local industrial infrastructure [1].

Until now, heterogeneous catalytic processes have been mainly used to decompose N₂O emission at high temperature [2]. The high temperature reaction causes the serious catalyst deterioration during the N₂O decomposition [3]. Therefore, the periodic catalyst replacement is required, which increase the total process expense.

Plasma technology was used for N₂O decomposition in the present study. Catalyst-assisted cold plasma has two advantages; one is the low temperature requirement for N₂O decomposition and the other is the low power consumption comparing to the thermal plasma. In the present study, characteristics of N₂O decomposition by catalyst-assisted cold plasma were investigated.

2. N₂O decomposition reaction

N₂O molecule is quite stable at room temperature. In the asymmetric N-N-O molecule, the N-N bond is stronger than the N-O bond; thus the N-O bond is the most probable to be first broken. The activation energy for N-O bond break is 250-270 kJ/mol. The temperature above 900 K is required to initiate the N₂O decomposition given below:

\[ \text{N}_2\text{O} \rightarrow \text{N}_2 + 0.5\text{O}_2 \quad \Delta H = -163 \text{ kJ/mol} \quad (1) \]

Several mechanisms of N₂O decomposition have been reported. The N₂O decomposition reaction can be simply described as the followings: (a) absorption of N₂O at the active site, (b) decomposition resulting in the formation of N₂ and surface oxygen, (c) desorption of surface oxygen by combination with another oxygen atom, and (d) direct reaction of surface oxygen with another N₂O.

\[ \text{N}_2\text{O} + \ast \leftrightarrow \text{N}_2\text{O}^\ast \quad (2) \]
\[ \text{N}_2\text{O}^\ast \rightarrow \text{N}_2 + \text{O}^\ast \quad (3) \]
\[ 2\text{O}^\ast \leftrightarrow \text{O}_2 + 2\ast \quad (4) \]
\[ \text{N}_2\text{O} + \text{O}^\ast \rightarrow \text{N}_2 + \text{O}_2 + \ast \quad (5) \]

It is expected that the plasma formation in the N₂O reaction process will make the other radicals such as NO, N, and O, which are more reactive on the active sites of the catalyst at low temperature.
3. Experiments

Experimental apparatus was prepared to investigate characteristics of N₂O decomposition by catalyst-assisted cold plasma as shown in Fig. 1.

The tubular quartz reactor with annular-shaped electrodes was prepared and then ruthenium catalysts supported on alumina pellets were packed in the reactor. High voltage power supply (HPS1200) was used to supply power for plasma formation in the reactor. The supply voltage and current were measured to calculate the power consumption using oscilloscope.

The N₂O and Ar gases were mixed and supplied to the reactor in the controlled flow rate using mass flow controller (BRONKHORST). The composition of products was analyzed in the gas chromatography (YONGLIN) to calculate the N₂O conversion. A thermocouple was inserted in the middle of the reactor to measure the reaction temperature.

The effects of space velocity, temperature, discharge voltage, and reactant compositions on the N₂O decomposition were investigated.

4. Results and discussion

Figure 2 shows the effect of N₂O/Ar ratio to the N₂O conversion. The Ar flow rate was 10 sccm and the reaction temperature was 245 °C. The N₂O conversion was decreased as the N₂O/Ar ratio was increased.

This result means that the Ar played an important role to break the chemical bond of N₂O molecules. When the N₂O was 3 times greater than Ar, the N₂O conversion was decreased to 23.8%.

The effect of space velocity to the N₂O conversion is shown in Fig. 3. SV* is defined as a normalized space velocity. The N₂O conversion was decreased as the space velocity was increased. From the result it can be seen that the catalyst-assisted plasma depends on the space velocity of the reactor during the N₂O decomposition. That is because the radicals formed by plasma are reacted on the surface of catalyst.
Figure 4. Effect of the supply voltage to the N\textsubscript{2}O conversion at the reaction temperature of 245°C.

Figure 5. Effect of reaction temperature to N\textsubscript{2}O conversion at the reaction temperature of 245°C.

The N\textsubscript{2}O conversion was increased with the reaction temperature. The N\textsubscript{2}O conversion result consists of two regions; one is from 60 to 190 °C (Region I) and the other is from 190 to 245 °C (Region II). At the Region I the N\textsubscript{2}O conversion would be zero if no plasma interaction because the catalyst has no activity on the N\textsubscript{2}O decomposition. However, the N\textsubscript{2}O conversion was increased slowly at Region I. It means that the Ar plasma accelerates the destruction of N\textsubscript{2}O bonds. The N\textsubscript{2}O conversion was sharply increased at the Region II. In this temperature range the N\textsubscript{2}O conversion has a high reactivity on the catalyst.

Figure 6 shows the N\textsubscript{2}O conversion with the space velocity (SV*) of 0.43 at the reaction temperature of 60°C.

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Figure 4 shows the effect of supply voltage to the N\textsubscript{2}O conversion at the reaction temperature of 245 °C. The N\textsubscript{2}O conversion was increased with the supply voltage. The highly excited Ar plasma at the high voltage seems to enhance the surface reaction of radicals on the catalyst.

The effect of reaction temperature to the N\textsubscript{2}O conversion at the reaction temperature of 245 °C is shown in Fig. 5. The catalytic reaction depends strongly in the temperature of the active site on the catalyst surface. It is expected that the catalyst-assisted plasma reaction has also the same property on the N\textsubscript{2}O decomposition reaction.

In this situation Ar plasmas broke strong bonds of N\textsubscript{2}O into NO, N, and O radicals. It was discovered that the radicals were more reactive on the active sites of the catalyst at low temperature.

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Figure 6 shows the N\textsubscript{2}O conversion with the space velocity (SV*) of 0.43 at the reaction temperature of 60°C. The Ar* is defined by the normalized Ar flow rate. At the temperature of 60 °C there is no catalytic activity on the N\textsubscript{2}O decomposition under any reaction conditions. However, the N\textsubscript{2}O bond could be broken by the catalyst-assisted plasma. The N\textsubscript{2}O conversion was linearly increased with the Ar flow rate. It seems that the sufficient amount of excited Ar ions is required to achieve the measurable N\textsubscript{2}O conversion.

In this situation Ar plasmas broke strong bonds of N\textsubscript{2}O into NO, N, and O radicals. It was discovered that the radicals were more reactive on the active sites of the catalyst at low temperature.
5. Conclusion

Characteristics of N₂O decomposition by catalyst-assisted cold plasma were investigated in the present study. Tubular quartz reactor with annular-shaped electrodes was prepared, in which the ruthenium catalysts supported on alumina pellets were packed. The effects of space velocity, temperature, discharge voltage, and reactant compositions on the N₂O decomposition were investigated. The N₂O bond was broken by the catalyst-assisted plasma at the low temperature, because the radicals were more reactive on the active sites of the catalyst at low temperature.

References

