Effect of noble gas for methane decomposition in DBD reactor

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Abstract: The conversion rate of methane is measured in a planar-type dielectric barrier discharge reactor with three different noble gases, He, Ne, and Ar. The empirical result indicates that these noble gases considerably affect the methane conversion rate. From the comparison between discharge characteristics and experimental results, it is found that the electron temperature is an important factor for realizing high methane conversion. The experimental results are interpreted based on the energy and charge transfer reactions. In addition, based on the calculations, all the noble gases, including Kr and Xe gases, are compared and discussed for their effectiveness in methane conversion.

Keywords: discharge, methane activation, noble gas, electron temperature

1. Introduction
Recently, many researchers have been interested in methane as an alternative energy source [1]. For the conversion of methane to useful species such as H2, CO, and oxygenates, various methods have been studied based on partial oxidation, dry reforming, and steam reforming [2-4]. However, methane is one of the stable species, and a temperature above 1000 °C is required to thermally decompose it. To reduce the temperature of the methane activation and to enhance performances of reforming processes, plasma and plasma-catalyst hybrid techniques have been studied over a decade. Although many studies have been performed to effectively use plasma techniques in methane conversion, the conversion rate, compared to the energy cost of plasma generation, remains impractical. Therefore, additional efforts are needed to develop more efficient methods for methane conversion. This study investigates the control of discharge as a possible means for the modulation of electron temperature, excitation level, and energy transfer to reactant molecules, which would thereby influence the effectiveness of methane activation. Different discharge characteristics by different noble gases in a planar-type dielectric barrier discharge (DBD) reactor have been analyzed. Mixtures of 10 vol.% methane with various noble gases are introduced inside the reactor as reactants, and the noble gases selected in this study are helium (He), neon (Ne), and argon (Ar). The conversion rate of methane is measured with varying applied voltages ranging from 3 to 6 kV. Both the experimental results and calculation on electron temperature and electron density are analyzed.

2. Experiment
The experimental setup consists of a DBD reactor, system for gas flow control, power supply, and an electrical data measurement system. The DBD reactor used in this study has a planar-type configuration having a discharge gap of 3 mm and a chamber volume of 4 cm³. As an electrode, silver is used, and is covered with alumina as the dielectric material. The thickness of dielectric material between electrode and discharge region is 1 mm. A schematic diagram of the planar-type DBD reactor and the electrical circuit used in this study are shown in Fig. 1.

![Schematic diagram of the DBD reactor including the electrical circuit for measuring plasma power, and the discharge images with three different noble gases at 5 kV.](image-url)

The reactant is prepared by mixing methane of 10 vol.% and one of the selected noble gases from among He, Ne, and Ar. In all these experiments, the total flow rate is fixed at 336.0 cm³/min, corresponding to a space velocity of 5000 h⁻¹. In order to generate plasma inside the DBD reactor, a function generator and a high voltage power amplifier are used. As shown in Fig. 1, electrical signals such as voltage (V), current (A), and electric charge (Q) are measured by using a 1000:1 high voltage probe, a
resistor for high voltage, and a capacitor, respectively. The electrical power delivered to the reactor is calculated by the Lissajous method [5], from the measurement data of voltage and electric charge. All experiments are carried out under an identical condition of AC power supply with a 10 kHz sinusoidal wave, except that the amplitude of the applied voltage is different in each case. As a variable, the applied voltage is varied from 3 to 6 kV. The discharge images with different noble gases at 5 kV are also shown in Fig. 1. The product gases passing through the reactor are analyzed by gas chromatography (GC). The methane conversion rate is defined by Eqn. (1).

\[
\text{Conversion (CH}_4) = \frac{\text{mole (converted CH}_4)}{\text{mole (supplied CH}_4)} \times 100 \text{ [%]} \quad (1)
\]

3. Result
For each noble gas, the conversion rate of methane with applied voltage is measured, and the results are plotted in Fig. 2. When Ar is used, discharge does not occur at 3 kV. When Ne is used, arcs occur inside the reactor at 6 kV. Both these conditions are excluded in the plot. In all the experimental conditions used, the methane conversion rate increases with an increasing applied voltage. This is because the increase in the applied voltage induces a stronger electric field inside the reactor and this stronger electric field generates electrons that have higher electron temperature than before. In addition to the electron temperature, the electric power delivered to the reactor is generally increased with an increasing applied voltage. Therefore, the methane conversion is proportional to applied voltage. An important result in this study is that the methane conversion rate is considerably affected by the use of noble gas. Our experiments confirmed that the conversion rate of methane is significantly different for each noble gas, and it increases in the order He, Ne, and Ar. The increment in the conversion rate from Ne to Ar is relatively high compared to that from He to Ne.

![Fig. 2 Conversion rate of methane with applied voltage.](image_url)

The methane conversion rate with discharge power is shown in Fig. 3. The result shows a similar trend compared to that of the applied voltage. The conversion rate increases with the discharge power. The difference in the conversion rate for each noble gas is noticeable. Based on the experimental results, Ar as a noble gas gives the highest methane conversion rate, which is 13.2% at an applied voltage of 6.0 kV, corresponding to a discharge power of 14.3 W.

4. Discussion
Methane is one of the most stable species and has a high energy of dehydrogenation, in the range of 9–12 eV, consistent with Eqns. (2–6) [6]. Therefore, a discussion including the discharge characteristics is desirable to understand the relation between the use of a noble gas and methane decomposition.

\[
e + CH_4 \rightarrow e + CH_3 + H \quad (2)
\]
\[
e + CH_4 \rightarrow e + CH_2 + 2H \quad (3)
\]
\[
e + CH_4 \rightarrow e + CH_2 + H_2 \quad (4)
\]
\[
e + CH_4 \rightarrow e + CH + H_2 + H \quad (5)
\]
\[
e + CH_4 \rightarrow e + C + H_2 + H_2 \quad (6)
\]

To estimate bulk characteristics of electron temperature, \(T_e\), simple calculation is performed. The bulk electric field can be obtained by the plasma voltage divided by the discharge gap. By using the bulk electric field thus calculated, the diffusion coefficient, \(D_e\), mobility, \(\mu_e\), and drift velocity, \(v_e\), can be determined as the functions of the reduced electric field, \(E/n\), by solving the Boltzmann equation with a Boltzmann equation solver BOLSIG+ [7]. From the calculated data, the temporal variations of the spatially averaged electron density and spatially averaged electron temperature are estimated using the discharge current density, \(j(t)\), and Einstein’s relation, respectively, as shown by Eqns. (7–8),

\[
n_e(t) = j(t)/e\nu_e(t) \quad (7)
\]
\[ T_e(t) = \frac{e}{D_e(t)/k_b\mu_e(t)} \]  

where \( e \) is the electron charge (1.6 \times 10^{-19} \text{ C}) and \( k_b \) is Boltzmann’s constant (1.38 \times 10^{-23} \text{ J/K}).

The temporal variations in the electron density and electron temperature are calculated, and the results at the applied voltage of 5 kV are plotted in Fig. 4. The electron temperature obtained for each noble gas shows increasing magnitude in the order He, Ne, and Ar. The maximum values at the applied voltage of 5 kV are 4.5, 5.9, and 7.5 eV for He, Ne, and Ar, respectively. Although the maximum values do not exceed the activation energy of the reactions in Eqns. 2–6, the reactions can be activated by high-energy electrons at the tail of a Maxwellian distribution function. Moreover, an increase in the mean electron temperature implies that there is an increase in the number of electrons that have sufficiently high energies to activate the decomposition reactions of methane. Therefore, the experimental results for the conversion rate are in accordance with the order of electron temperatures for each noble gas.

In addition to the different electron excitations discussed above, the experimental results could also be attributed to an energy-transfer process, i.e., the Penning effect, or charge transfer from excited and ionic states of noble gases [8]. Energy is transferred to the methane molecules from the excited noble gas atoms, and the dissociation of methane occurs subsequently (Eqn. 9).

Charge transfer as an ionic process could also be expected (Eqn. 10) because methane has an ionization potential of 13.02 eV, which is lower than those of He, Ne, and Ar. The energy transfer and the charge transfer are represented by the following equations:

\[ R^* + CH_4 \rightarrow R + CH_4^* \rightarrow R + CH_3 + H \]  

Both the energy and charge transfer mechanisms are proportional to the numbers of excited and ionized noble gas atoms, respectively. Since Ar shows high electron temperature and electron density from the calculation results, the numbers of excited and ionized atoms are expected to be higher than those of He and Ne. Moreover, the difference in the density of active atoms is expected to additionally increase, because the energies of the excitation and ionization of Ar are lower than those of He and Ne. Consequently, Ar can be expected to generate a large number of excited and ionized atoms compared to He and Ne, and the experimental result is interpreted using both energy and charge transfer mechanisms.

To compare noble gases including Kr and Xe as well as He, Ne, and Ar, the electron temperatures for each gas are calculated as a function of the reduced electric field. The calculated results are shown in Fig. 5. As the magnitude of the reduced electric field increases, electron temperatures generally increase with different gradients; however, Kr and Xe show saturated values. In other words, optimal ranges should be identified for each noble gas to obtain a high electron temperature.

5. Conclusion
The effect of each noble gas on methane decomposition is investigated in a planar-type DBD reactor. The conversion rate of methane is experimentally measured with different noble gases. The results indicate that methane decomposition is considerably affected by the use of a noble gas. First, the discharge characteristics are compared with the experimental results, and it is found that electron temperature is a crucial factor to estimate the conversion rate of methane. Second, the energy and charge transfer mechanisms are discussed with the analysis of the results. Finally, the electron temperatures with...
respect to reduced electric field are compared among noble gases including Kr and Xe. With the results, the optimal strategy for effective methane conversion can be identified, including the selection of the noble gas and the discharge condition.

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7. References