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Influence of discharge characteristics on methane decomposition in dielectric barrier discharge reactor

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ABSTRACT

The conversion rate of methane is measured in a planar-type dielectric barrier discharge reactor with three different discharge gases, He, Ne, and Ar. The empirical result indicates that these discharge 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 effect of packing alumina inside a discharge reactor is also investigated and the empirical result is discussed. As a result, the methane conversion shows different value according to the packing condition and it is observed that the condition of packed-bed with Al_2O_3 bead is favorable to activate methane.

1. INTRODUCTION

Recently, many researchers have been interested in methane as an alternative energy source (Makogon *et al*. 2007). For the conversion of methane to useful species such as H_2, CO, and oxygenates, various methods have been studied based on partial oxidation, dry reforming, and steam reforming (Lee *et al*. 2010, Tao *et al*. 2011, Cormier and Rusu 2001). 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, catalysts have been employed. However, a further drop in the reaction temperature is still needed.

Plasma comprises diverse types of chemically active species such as high-energy electrons, ions, and excited gas molecules, and is expected to achieve chemical activation even at room temperature (Fridman 2008). Therefore, plasma-catalyst hybrid systems for methane activation and after-treatment of exhaust gases have been widely studied (Pietruszka and Heintze 2004, Nozaki *et al*. 2004, Mlotek *et al*. 2009). Although many studies report valuable facts and suggest how to use plasma and catalyst optimally, additional studies are still needed. The effects of discharge gas and packing materials are necessary to study plasma-catalyst interactions. In this study, three

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different discharge gas (He, Ne, and Ar) and alumina packing conditions inside a planar-type dielectric barrier discharge (DBD) reactor are selected and methane activation with the different conditions is tested to investigate the influences of discharge characteristics.

2. EXPERIMENTS

The DBD reactor used in this study has a planar-type configuration having a discharge gap of 3.0 mm and a chamber volume of 4.0 cm^3. 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 1.0 mm. A schematic diagram of the reactor and the electrical circuit used in this study are shown in Fig. 1.

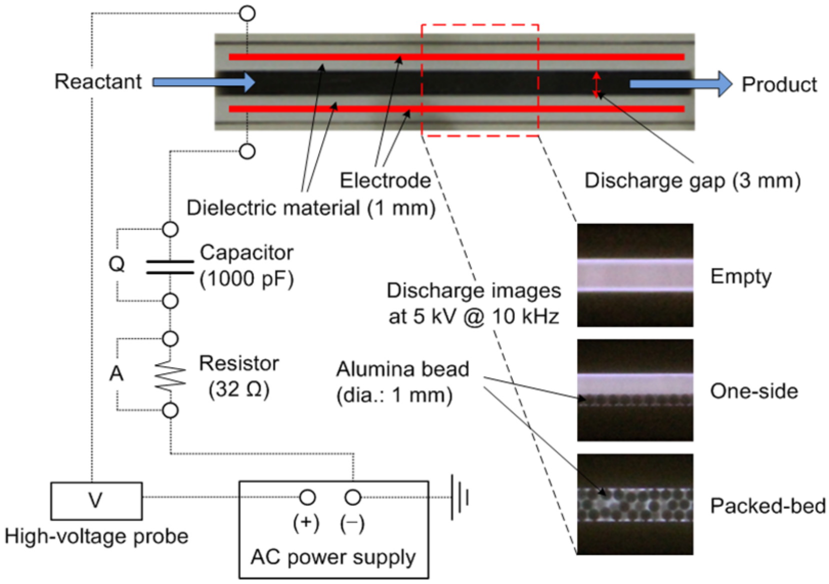

Fig. 1 Experimental setup and discharge image inside DBD reactor

The reactant is prepared by mixing methane of 10 vol.% and Ar gas of 90 vol.%. In all these experiments, the total flow rate is fixed at 336.0 cm^3/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. Electrical signals such as voltage, current, and electric charge 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 (Kim *et al*. 2004) 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 4.5 to 6.0 kV. The product gases passing through discharge space are analyzed by gas chromatography. The methane conversion rate is defined by Eq. (1).

$$Conversion\ (CH_4) = \frac{mole\ (converted\ CH_4)}{mole\ (supplied\ CH_4)} \times 100\ [\%], \tag{1}$$

As packing materials, alumina (Al_2O_3) which is commonly used as catalytic support is selected. The Al_2O_3 is sphere having diameter of 1.0 mm and γ–type alumina.

3. RESULTS

For each discharge gas, the conversion rate of methane with applied voltage is measured, and the results are plotted in Fig. 2. 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

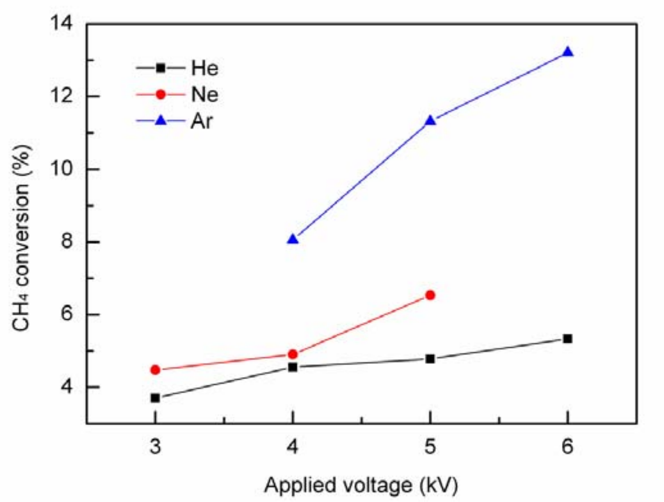

Fig. 2 Conversion rate of methane as function of applied voltage with different discharge gases

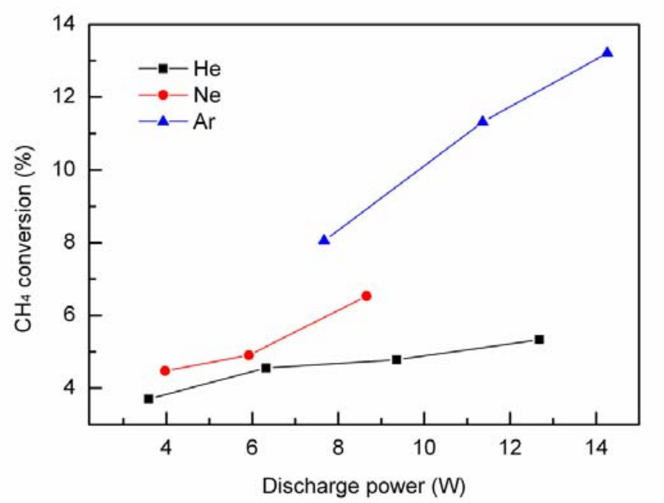

Fig. 3 Conversion rate of methane as a function of discharge power with different discharge gases

temperature than before. An important result in this study is that the methane conversion is considerably affected by the use of discharge gas. Our experiments confirmed that the conversion rate of methane is significantly different for each discharge 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.

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 discharge gas is noticeable. Based on the experimental results, Ar as a discharge 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.

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, μ_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+ (Hagelaar and Pitchford 2005). 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 Eqs. (2) and (3),

$$n_e(t) = j(t) / e v_e(t) , \quad (2)$$

$$T_e(t) = e D_e(t) / k_b \mu_e(t) , \quad (3)$$

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

The temporal variations in the electron density and electron temperature are

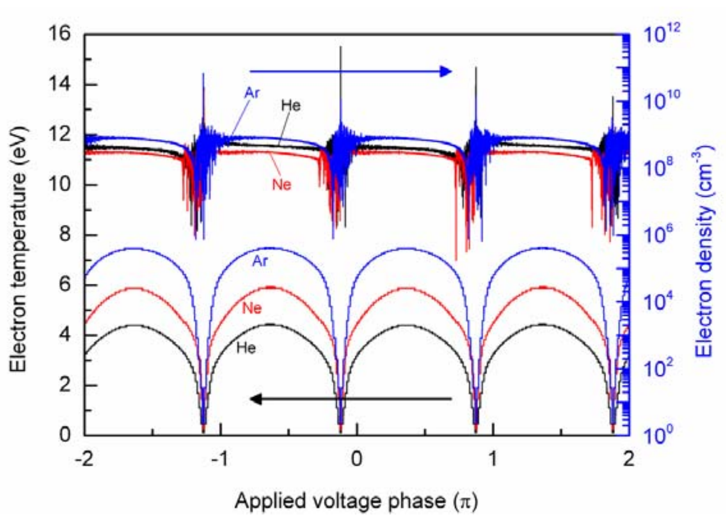

Fig. 4 Calculated results of the discharge characteristics for electron temperature and electron density at the applied voltage of 5 kV

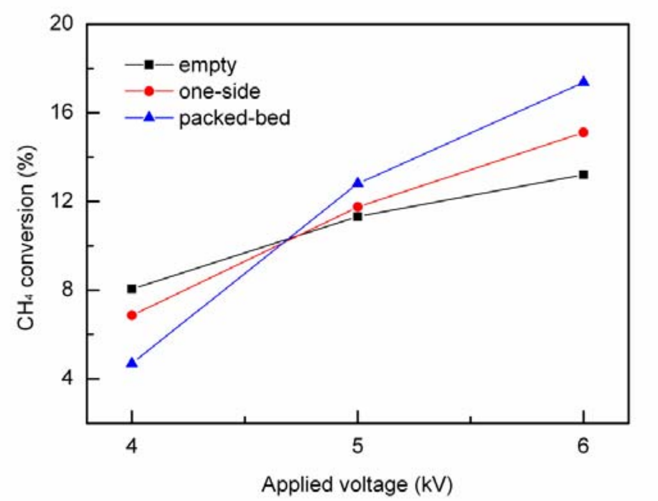

Fig. 5 Conversion rate of methane as function of applied voltage with different Al_2O_3 packing conditions

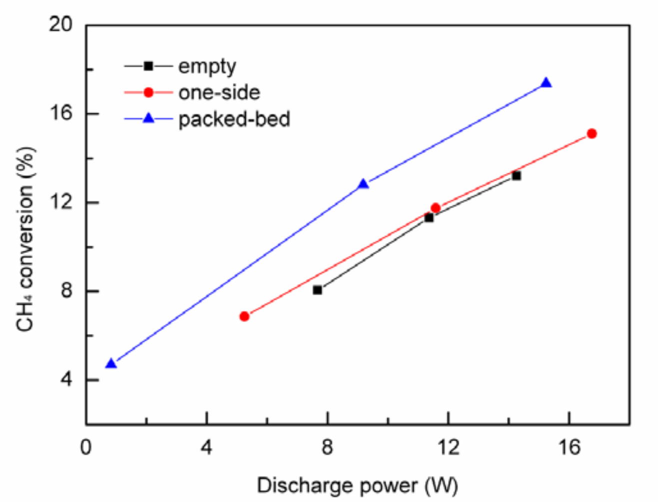

Fig. 6 Conversion rate of methane as a function of discharge power with different Al_2O_3 packing conditions

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. 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.

For an additional investigation of the effect of Al_2O_3 packing condition, three different packing conditions are considered in this study. For each packing configuration, the conversion rate of methane with applied voltage is measured, and the results are plotted in Fig. 5. In all the experimental conditions used, the methane conversion rate increases with an increasing applied voltage. And, the packed-bed condition shows much higher methane conversion rate than those of other conditions. This is because the condition of packed-bed with Al_2O_3 induces a stronger electric field around contact points between Al_2O_3 beads and this stronger electric field generates electrons that have higher electron temperature than empty case. This result was estimated using simulation by Kang *et al*. (2003). The calculation results can support our experimental result showing the condition of packed-bed is favorable to activate methane.

The methane conversion rate as a function of discharge power with different Al_2O_3 packing conditions is shown in Fig. 6. In addition to the effect of changing discharge gas, Al_2O_3 packing conditions can make additional enhancement of methane conversion. The difference in the conversion rate for each packing condition is noticeable according to the packing conditions. Based on the experimental results, the condition of packed-bed with γ-Al_2O_3 as a packing material gives the highest methane conversion rate, which is 17.4% at an applied voltage of 6.0 kV, corresponding to a discharge power of 15.2 W.

3. CONCLUSIONS

The effect of each discharge gas on methane activation is investigated in a planar-type DBD reactor. The conversion rate of methane is experimentally measured with different discharge gases. The results indicate that methane activation is considerably affected by the use of a discharge gas. 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. The effect of each packing condition on methane activation is also investigated and the conversion rate of methane is experimentally measured with different packing conditions. The methane conversion shows different value according to the packing condition and it is observed that the condition of packed-bed with Al_2O_3 bead is favorable to activate methane.

From overall experiments in this study, it is found that discharge gas and packed-bed type reactor can make the plasma characteristics and affect methane activation. Therefore, the effects of gas composition and packing condition should be considered when plasma-catalyst hybrid systems are studied.

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