Effect of catalyst properties on the electric discharge characteristics in plasma-catalyst hybrid reactors

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Abstract: Methanol decomposition using a catalytic reactor with electric discharges was investigated in the present study. The methanol conversion at 190 °C was 58.0%; however, the methanol conversion increased by 65.9% under the electric discharge. An electric discharge produces high energy electrons with sufficient energy to break a C-OH bond.

Keywords: Catalyst, Electric discharge, Plasma, Hybrid reactor

1. Introduction

Hydrogen is a promising energy carrier for future society that is not dependent on fossil fuel energy. There are various hydrogen sources such as hydrocarbon species and oxygenate hydrocarbons including alcohol. Methanol has merits of being liquid phase and having high hydrogen to carbon ratio.

Heterogeneous catalytic processes at high temperature have been used to produce hydrogen from hydrocarbons and alcohols such as methanol. High reforming temperature caused serious catalyst deteriorations; thus, the periodic catalyst replacement was required. In order to improve the stability and durability of the reforming catalyst [1], plasma-catalyst hybrid process was used. Plasma-catalyst hybrid process is expected to improve the catalytic performance at low temperature.

Recently, plasma-catalyst hybrid process has been attempted to reduce the reforming temperature [2-6]. Yu et al. [4] performed CO₂ reforming of propane in combination of non-thermal plasma and Ni/γ-Al₂O₃ catalyst. They showed that the temperature for activating the reaction was reduced, and the propane conversion was improved compared with using the plasma or the catalyst only. Sekine et al. [5] reported that at low temperature condition, where no reactivity was observed using catalyst only, methane was converted by introducing discharge in the volume of catalyst. They also disclosed that ZrO₂, which is not active on a catalytic reaction, improved the reactivity on methane reforming under the electric discharge because the reducibility of lattice oxygen on a catalyst support was improved.

The electric discharge was also used to initiate ethanol-steam reforming at low temperature [6]. The ethanol under the electric discharge was initiated to be decomposed at low temperature where the catalyst was not working. The effect of the electric discharge on water-gas shift reaction was higher than that of ethanol decomposition.

In our previous study [3], we used an electric discharge on the catalyst to improve the reactivity and selectivity for various reactions such as methanol steam reforming and methanol decomposition. The electric discharge improved the methanol conversion. The effect of the discharge condition such as the discharge voltage and frequency on the reaction was investigated at the various temperatures and feed rates.

Although many works regarding the plasma-catalyst hybrid reaction has been already reported, a study on electric properties of catalyst is still insufficient for understanding the plasma-catalyst hybrid reaction. Effect of catalyst properties on the electric discharge characteristics in plasma-catalyst hybrid reactions was investigated in the present study.

2. Experiments

The catalyst-bed porosity was controlled by packing the different size of catalyst pellets in a reactor. Fig. 1 shows a photograph of the catalyst pellets. A spherical γ-Al₂O₃ pellet (Alfar Aesar) was used. The Cu/ZnO was loaded in the γ-Al₂O₃ pellet using the wet impregnation method. A mixture containing a 0.7 M aqueous solution of Cu(NO₃)₂ and a 0.3 M aqueous solution of Zn(NO₃)₂ was prepared. The catalyst support, γ-Al₂O₃ pellet, was immersed in the mixture. The moisture was removed by drying the catalyst-loaded support in a convection oven at 70 °C for 12 hours.

Fig. 1 Catalyst pellets with the different size.
hours followed by calcination in a furnace at 350°C for 3 hours. In this step, CuO/ZnO/γ-Al₂O₃ catalyst was obtained. After the coating, the catalyst surface was activated by reduction in a hot hydrogen flow; Cu/ZnO/γ-Al₂O₃ catalyst was obtained. The electric discharge characteristics of Cu/ZnO/γ-Al₂O₃ and CuO/ZnO/γ-Al₂O₃ catalysts were compared. The Cu/ZnO loading was 5.0 wt.% of the total weight of the catalyst support. The catalysts were coated uniformly on the surface of the spherical pellet and the particle size of the catalyst was approximately 20 nm [7-9].

A quartz tube was used as the reactor, in which the catalyst pellet was packed as shown in Fig. 2. Two electrodes were used; one was inserted in the middle of reactor and the other was wrapped around the outer wall of the reactor. A flange, which is not electrically conducting, was installed at the lower part of reactor to fix the catalyst pellet. The flange was also used to fix the electrode precisely at the middle of the reactor because the electric discharge can be distorted if the gap between the two electrodes is not uniform. The gap between the two electrodes was 4.925 mm, between which 10 g catalyst pellets were packed. During the reaction, the reaction temperature was monitored with a K-type thermocouple, which was placed 1 cm away from the catalyst to avoid an electric discharge to the thermocouple. The electric discharge was generated only between the two electrodes due to the larger space between the catalyst and thermocouple than between the two electrodes [3].

Fig. 2 shows a schematic diagram of the experimental apparatus. High-purity helium gas was fed as a plasma medium. The electric discharge was generated with the various discharge conditions such as the discharge voltage and waveforms. A high-voltage amplifier (Trek 20/20C) was used to generate a high-voltage electric discharge on the catalyst. The voltage, frequency and waveform were controlled using a function generator (Agilent 33220A). The discharge voltage, frequency and waveform were monitored using an oscilloscope (WaveSurfer 424, LeCroy).

The discharge power was measured using the Lissajous method [10]. A 1,000 pF capacitor was connected between the reactor electrode and ground junction. The discharge energy charged the capacitor when the electric discharge was initiated. The discharge power can be calculated indirectly from the level of capacitor charging by integrating the area of the Q-V plot as Eq. (1).

\[ P_{\text{Discharge}} = \int QdV \]  

where \( P_{\text{Discharge}} \), \( f \), \( Q \) and \( V \) are the discharge power, frequency, capacitor charge and voltage, respectively.

3. Results and discussion

The discharge power and onset voltage of the plasma were measured as the catalyst-bed porosity was varied. The effect of discharge voltage, frequency and voltage waveforms such as the sine, pulse and square was investigated. In addition, the dielectric permeability of the catalyst was measured as the temperature was varied.

We found that the electric discharge was maximized at the optimal porosity of the catalyst-bed as shown in Fig. 3. At a low porosity, the electric discharge was not sustained stably because the space between catalysts got narrow nearly close to the sheath region. On the other hand, at a
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The discharge power increased as the discharge voltage and frequency increased as shown in Fig. 4. The square voltage wave was more efficient than the sine and pulse. At a high porosity, however, the effect of the voltage waveform was not considerable because the space between catalysts was too large for plasma to interact with the catalyst surface.

Fig. 5 shows the discharge power as a function of the pellet size at the different voltage waveforms. The discharge power was maximized when using the square voltage waveform, while the sine voltage waveform generated the minimum discharge power. Aforementioned before, the discharge power decreased as the pellet size increased. However, the decrease of the discharge power was the largest at the square voltage waveform.

Fig. 6 shows the Lissajous plots of CuO/ZnO/Al$_2$O$_3$ and Cu/ZnO/Al$_2$O$_3$ catalysts. The breakdown voltages of CuO/ZnO/Al$_2$O$_3$ and Cu/ZnO/Al$_2$O$_3$ catalysts were 1.3 kV and 3.6 kV, respectively. The breakdown voltage of CuO/ZnO/Al$_2$O$_3$ catalyst was much larger than that of Cu/ZnO/Al$_2$O$_3$ catalyst because the dielectric constant of CuO/ZnO/Al$_2$O$_3$ is much higher than that of Cu/ZnO/Al$_2$O$_3$ catalyst. On the other hand, the charge amount of Cu/ZnO/Al$_2$O$_3$ catalyst was twice greater than that of CuO/ZnO/Al$_2$O$_3$ catalyst. For example, the Cu/ZnO/Al$_2$O$_3$ catalyst was charged with 210 nC at 5.0 kV, whereas the CuO/ZnO/Al$_2$O$_3$ catalyst was charged with 100 nV at 7.0 kV. The onset voltages of the discharge of CuO/ZnO/Al$_2$O$_3$ and Cu/ZnO/Al$_2$O$_3$ catalyst were 7.0 kV and 3.6 kV, respectively.

Fig. 7 shows a photograph of the catalyst pellets when the plasma was applied. The characteristics of the electric discharge can be changed by the presence of the catalyst and gases between the electrodes. In addition, the presence of the catalyst can modify the electric conductivity between the electrodes. The catalyst has a content of metal, for example, in the Cu/ZnO/Al$_2$O$_3$ catalyst, Cu is exist as a metal so that the electrons that are generated by the discharge can jump onto the surface of the catalyst. Subsequently, the electrons on the catalyst can jump onto another metal on the surface of the catalyst. Consequently, the electric discharge can be generated between the surfaces of the catalysts.

4. Conclusion

Effect of catalyst properties on the electric discharge characteristics in plasma-catalyst hybrid reactions was investigated in the present study. The catalyst-bed porosity was controlled by packing the different size of catalyst pellets in a reactor. The discharge power and onset voltage of the plasma were measured as the catalyst-bed porosity was varied. The effect of discharge voltage, frequency and voltage waveforms such as the sine, pulse and square was investigated. In addition, the dielectric permeability of the catalyst was measured as the temperature was varied. We found that the electric discharge was maximized at the optimal porosity of the catalyst-bed. At
a low porosity, the electric discharge was not sustained stably because the space between catalysts got narrow nearly close to the sheath region. On the other hand, at a high porosity, the electric discharge became weak because the plasma was not interacted sufficiently with the catalyst surface. The discharge power increased as the discharge voltage and frequency increased. The square voltage wave was more efficient than the sine and pulse. At a high porosity, however, the effect of the voltage waveform was not considerable because the space between catalysts was too large for plasma to interact with the catalyst surface.

5. Acknowledgement

The authors appreciate the financial support from "Hybrid technology of nano catalyst-plasma for low carbon/emission" of MKE (Ministry of Knowledge Economy) and ISTK (Korea Research Council for Industrial Science and Technology) of Republic of Korea.

6. References