Interaction of Nonthermal Plasma with Catalyst for the Air Pollution Control

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Abstract—Physical interaction of atmospheric-pressure nonthermal plasma with catalysts was studied at ambient temperature. Microscope-ICCD camera and IR camera were used to observe the discharge plasma and the temperature profile of the catalyst. Two different discharge modes were observed in the catalysts-packed plasma reactors; partial discharge and surface streamer. Packing material, applied voltage and the presence of oxygen were found to play important role in determining the discharge patterns in the catalyst-packed plasma reactor. Metal nanoparticles supported on zeolites enhanced the surface streamer propagation over the wide area of surface. On the other hand, only partial discharge mode was observed with the BaTiO$_3$ pellets ($\varepsilon = 10000$). The presence of oxygen decreased the plasma intensity, while increased the number of surface streamers.

Keywords—Nonthermal plasma, catalyst, ICCD camera, IR imaging, surface streamer, adsorption, VOC

I. INTRODUCTION

Complementary combination of nonthermal plasma (NTP) with catalyst offers various advantages for air pollution control in terms of energy efficiency, product selectivity and carbon balance. The combination of NTP with catalyst can be categorized as single-stage and two-stage process according to the position of catalyst. In the single-stage plasma-driven catalyst (PDC) process, catalysts located inside the plasma zone [1-5]. In two-stage configuration, plasma reactor and catalyst bed are connected in series [6, 7]. Ozone-assisted catalysis is another type of two-stage combination, where the role of NTP is limited to the formation of ozone. The combination with various adsorbent (mostly zeolites) was also explored as a possible way to increase the performance of plasma processing of VOCs [8-11]. The authors have been studied the single-stage PDC system and reported a strong influence of oxygen partial pressure on the oxidation of VOC [12, 13]. It should be noted that this unique dependence on the O$_2$ partial pressure can be observed only with the PDC system. The singularity of oxygen-dependent behavior has adapted to the cyclic system comprised of adsorption step without plasma and the decomposition of adsorbed VOC using oxygen plasma. Oxygen plasma is necessary to activate deep oxidation to CO$_2$ with high energy efficiency. Recently, Fan et al. also reported total oxidation of dilute benzene (4.7 ppmv) using cycled system packed with Ag/HZSM5 catalyst [14, 15]. The major advantages of the cycled system include high energy efficiency, high CO$_2$ selectivity, flexibility to the operational conditions, and free from the NOx formation [12, 16]. The moderate operation conditions (atmospheric-pressure and ambient temperature) also distinguish plasma-catalyst system from the conventional catalysis, which requires high temperature (from 200 to 600°C depending on the reaction) to activate catalysts. The generation of discharge plasma has some degree of freedom so that the configuration of combined system largely depends on the shape of catalysts; such as pellet, bead, foam and honeycomb. Most of lab-scale experiments have been done with bead or pellet type catalyst. There have also been trials on the direct plasma generation inside honeycomb catalyst [17] or porous ceramics [18, 19]. Recently, an interesting way to generate plasma inside honeycomb has been proposed by applying additional DC electric field across the capillaries positioned above γ-alumina packed-bed reactor [20, 21]. Negative DC voltage was found to be more effective than positive in extending the streamer up to 20 mm.

The physico-chemical behavior in the combination of NPT with catalyst contains many of complex mechanisms of adsorption, electrical circuit, material science, surface chemistry, plasma chemistry, plus additional complexities resulting from the interaction of plasma and catalyst. Recent researches on the plasma-induced adsorption of gas molecules/atoms revealed that N atoms [22] and oxygen molecules [23, 24] can be adsorbed on the surface during the plasma treatment. These surface species fixed during plasma application could survive certain period and decayed by subsequent chemical reactions. Several independent research works concluded that optimum catalysts differ according to the type of combination (single-stage vs. two-stage) [25-29]. Ozone decomposition catalysts, such as manganese oxide (MnO$_x$) and Ba-CuO-Cr$_2$O$_3$/Al$_2$O$_3$, favor the two-stage combination. Better understanding on the fundamentals behind the complementary combination of NTP and catalyst may lead to a smart design of the system and extended use in industries.

This work reports how catalyst influences the discharge mode in single-stage PDC system. Microscope-ICCD camera was used to observe the discharge plasmas on the surface of packing materials such as BaTiO$_3$ and high-silica Y zeolite (HSY). Infrared (IR) camera was used to measure temperature gradient on the catalyst during the plasma turned on. We also focused on physical interaction of NTP with the active metal
nanoparticles supported zeolites. The discharge patterns were also compared with different oxygen content. Especially we focused on the interaction between the supported metal catalyst and the expansion of plasma (surface streamer) over the zeolites.

II. EXPERIMENTAL

Experimental setup for observing the plasma generation on the surface of various packing materials is illustrated in Figure 1. A plate-type dielectric barrier discharge (DBD) reactor with a 6 mm gap distance was used for the observation of plasma generation. An aluminum tape (60 mm × 50 mm) was attached to the outer sides of the glass plates as electrodes. The upper part was covered by a quartz plate, which is mounted just below the microscope (Mitutoyo, M Plan Apo objective lens). Various catalysts were packed in the plate-type DBD plasma reactor. Gas was fed to the reactor with a flow rate of 1 L/min at standard condition (273 K, 0.1 MPa). Gas flow was set with mass flow controllers (KOFLOC, FCC-3000). The microscopic observation system consists of an XY stage, optical microscope, and an intensified charge coupled device (ICCD) camera (Hamamatsu Photonics). The observation area can be adjusted by changing the optical lens. For example, the observation area of the M plan Apo 5X objective was 2.0 mm × 2.6 mm, which corresponds to the size of single pellet. This observation system provides rapid and simple means of visualizing the interaction of plasma with catalyst. The images were recorded with a HiPic software (Ver 8.1). Temperature profile near the catalyst was monitored using IR camera (NEC/Avio, TVS-500EX with TVS-25 μm lens) capable of measuring up to 60 frames per second (fps). The plate-type DBD reactor (4 mm gap with electrode area of 10 mm × 30 mm) used for IR camera where its top-side was open to room air. In this works, temperature was measured at 20 fps for 5 minute after plasma turned on. The DBD reactor was energized with a Trek 20/20B power supply. The frequency of AC high voltage was changed in the range of 50-1000 Hz. Applied voltage and discharge current were determined using a digital oscilloscope (Tektronix, Model TDS 3034B) with high-voltage probe (Tektronix, Model 6101A) and current transformer (Pearson Electronics, Model 2877). Discharge power dissipated in the reactor was measured by the automated V-Q Lissajous program (Insight Co, Ver. 1.72) [1]. The waveforms of the charge (i.e. integrated discharge current) and the applied voltage were monitored with a digital oscilloscope (Tektronix, TDS3032B). Tektronix P6139A probe (10:1) and capacitor of 95 nF were used for the charge (Q) measurement.

The specific surface areas of HSY (high-silica Y zeolite), and MOR (mordenite) were 690 m$^2$/g and 380 m$^2$/g, respectively. The HSY zeolite (Si/Al ratio = 12) is known to have hydrophobic nature, which provides stable property at humid condition. Silver (Ag) was supported on the zeolites by impregnation method.

Ag(NO$_3$)$_2$ was used as precursors. The resistivity of zeolite pellet was measured with a Keithley 6514 electrometer. The size and the shape of the loaded metals were measured by transmission electron microscopy (TEM, Topcon Co., Model EM002B). BaTiO$_3$ and TiO$_2$ beads were also tested as reference materials.

III. RESULTS

Most of materials used as catalyst are electrically insulator. TiO$_2$ is known as n-type semiconductor. When these materials (catalysts) are packed in a plasma reactor, their electrical properties may affect the plasma generation. The equivalent electric circuit of catalyst-packed plasma reactor is shown in Figure 2. It is basically close to that of BaTiO$_3$ pellet packed bed reactor [30]. Since the dielectric constants of packing materials (ε$_d$ 10-10000) are much larger than that of air gap, applied voltage is mostly distributed to the air gap between the packing materials. The larger the dielectric constant the lower the plasma onset voltage. Voltage-current characteristics are also influenced by the dielectric constant [31]. Electric field augmented by the packing of dielectric material can be given as follows [32].

$$E = \frac{\sqrt{3e_0}}{d} \frac{3e_p}{2e_p + e_g}$$  \hspace{1cm} (1)
The $\varepsilon_p$ and $\varepsilon_g$ indicate dielectric constants of beads and gas, respectively. For example, the electric field can be augmented by a factor of 1.5 when BaTiO$_3$ pellets with a dielectric constant ($\varepsilon_p$) of 5000 are packed in the plasma reactor. This field modification was confirmed by the low plasma onset voltage compared to the DBD reactor without any packing materials. Figure 3 shows the influence of catalyst packing on the plasma onset voltage. The DBD reactor of 6 mm gap was energized with AC high voltage at fixed frequency of 200 Hz. In the case of the DBD reactor (i.e. without catalyst packing), plasma onset voltage was about 18 kV. The packing of Ag/HSY decreased the onset voltage down to about 10 kV. The decrease in plasma onset voltage is one physical aspect brought by catalyst packing in the single-stage PDC system.

Figure 4 shows the ICCD camera images of discharge plasma for BaTiO$_3$-pellet ($\varepsilon_p = 10,000$), (a)-(c), and Ag/HSY zeolite (d)-(f) packed plasma reactor. BaTiO$_3$ pellet has been used over the years for VOC removal [33-36]. In the case of BaTiO$_3$ beads, discharge plasma was first appeared with several plasma spots at the contact points of BaTiO$_3$ pellets, which is also referred to as partial discharge [31, 37]. The number and size of plasma spots became large as the applied voltage increased. Luminescence of the discharge increased with the applied voltage. However, surface streamer did not appear on the surface of BaTiO$_3$ beads even for long exposure time of 500 ms. Arai et al. indicated that the BaTiO$_3$ beads with low dielectric constant produces larger plasma area compared to those with larger dielectric constant [17]. The Ag/HSY zeolite packed reactor exhibited similar discharge pattern to BaTiO$_3$ at near corona onset voltage. As increasing the applied voltage, plasma was observed not only at the contact points (partial discharge) but also on the surface of the Ag/HSY zeolite (surface streamer). The behavior of surface streamer generation on the Ag/HSY is consistent with those observed on the other zeolites, such as MS-13X, HY and MOR, where nanoparticles of Ag or Cu were impregnated [38].

The resistivity of bulk zeolite pellets (MS-13X, MOR, HSY) was measured to clarify whether the impregnation of Ag nanoparticle changes the resistivity. Although the measured values changes with temperature and humidity, the resistivity was in the range of $10^5$-$10^6$ $\Omega$-cm. The significant modification of resistivity by the Ag nanoparticles was not confirmed in this study. One plausible explanation about the role of Ag in surface streamer is that Ag nanoparticles act as floating electrode on the surface of catalyst. Electric-field can be enhanced near the Ag nanoparticles, resulting in the augmentation of plasma propagation on the surface. Levchenko et al. reported the linear carbon growth between Ag nanoparticle on the Si(100) surface in atmospheric pressure Ar/CH$_4$ microplasma [39]. Electric field
calculation revealed that Ag nanoparticles enhance electric field resulting in the higher flux of carbon precursors.

The channel size of surface streamer, estimated for the ICCD camera images, ranged from 150 to 180 μm. These values are quite close to those with the gas-phase streamers in DBD reactor (100-200 μm) [38, 40-42]. Despite the large difference in plasma generation area, as one can see from Figure 5, no apparent difference can be seen in I-V characteristics between the BaTiO₃ beads and the Ag/HSY pellets. In both cases, plasma consisted of a number of current pulses. Each current pulse had FWHM of about 40 ns. These current pulses are usually referred to as microdischarges. Similar I-V characteristics does not assure the similar plasma generation, especially in the catalyst-packed plasma reactor. In other words, it is necessary to pay attention to draw plasma property from I-V characteristics alone. Considering the small volume of plasma area in the case of BaTiO₃ beads, relatively dense plasma is produced at a fixed area (at contact point of pellets) which result in high plasma density. This dense current flow in a small volume may increase the local gas temperature. This trend may rationalized by the low ozone formation and high NOx formation in the case of BaTiO₃-packed reactor [43].

The important chemical role of oxygen in the single-stage PDC system has been reported previously [12, 13]. The oxidation of VOC increases with increasing oxygen content even under a fixed specific input energy. Plasma-induced fixation of oxygen species on the surface of catalyst and their contribution in subsequent chemical reaction was demonstrated with isotope oxygen (¹⁸O₂) [24]. Figure 6 shows physical influence of oxygen on the plasma generation with Ag/HSY zeolites. The presence of oxygen decreased the luminescence of surface discharge plasma, which is consistent with the work reported by Hensel et al. for discharge on porous ceramic [18]. On the other hand, the number of surface streamer increased in the presence of oxygen. For example, the number of surface streamer on single zeolite pellet was 1-2 in N₂ at average, while that increased up to 3-4 streamers in air (i.e. the presence of oxygen). It is also interesting to note that the propagation of surface streamer is not always straight along the electric field. Some of the surface streamers propagated obliquely and even bending and curving shape. The bending of streamer channel was more significant in N₂ than air. In
the case of gas-phase DBD, microdischarges are usually propagated in a straight line from one electrode to the other. In the case of (c) and (f) two surface streamers merged together and vice versa. Furthermore, in some cases surface streamers jumped from one pellet to another. Basically the partial mode of discharge was always present in all voltage range. As one can see in many cases (Figs. 6 (c), (d), (f), (h), (k)), these partial discharges helped surface streamers jump from one pellet to the other pellets. Basically, the two modes of partial discharge and surface streamer were detected as current pulses.

Temperature inside plasma channel can be measured from rotational temperature of molecules (such as N₂ and OH) using optical emission spectroscopy [44, 45]. Temperature in the plasma channel increases up to 600-1000 K according to the input power and the type of discharge reactor. Several previous works indicated that the contribution of plasma heating on catalytic decomposition of VOC is negligible under typical operation condition [46]. To obtain a direct evidence on the role of temperature in activating the catalyst, IR camera was used. Figure 7 shows the temperature profile for the three different packing materials measured at 20 fps. The typical operation temperature of PDC system is below about 100°C, so the contribution of thermal heating has been considered negligible. However, instantaneous local heating of catalyst near the plasma channel may provide a thermal driving force for catalysis. In order to verify the instantaneous contribution of local heating by the plasma, time-resolved (in the order of 10⁻³ sec) temperature profile of the packing material was measured under typical operation voltage and frequency.

Although the discharge power was low at about 0.29 watt due to the, small area of electrode, power density was 0.1 W/cm², which is comparable for the normal discharge conditions in ozonizer. The surface temperature of packing material increased just after the plasma turned on, and reached a steady state within 3 min. Plasma-induced temperature increase of catalyst was about 10-12 K, which is far from the necessary temperature for thermal activation. Although the time-resolution is not sufficient to track the local heating by the impact of molecules with rotational- and kinetic energies, contribution of thermal factor in PDC system seems to be negligible.

IV. CONCLUSION

The physical interaction of nonthermal plasma and catalyst was studied using microscope objective lens and ICCD camera system. The ICCD camera observation of the discharge plasma on the surface of catalyst provided an important insight into the understanding of discharge plasma and catalyst. The area of discharge plasma expanded over a wide range by the metal nanoparticles. Two important features of plasma propagation were observed on the surface of catalyst. Plasma in the catalyst-packed bed reactor appeared in a mixed modes of partial discharge and surface streamer. Plasma initiates in a partial discharge mode for all test materials, and surface streamer started to appear together with the partial discharges as voltage increased. The presence of oxygen decreased the luminescence of the discharge. The temperature measured by the IR camera supported that the plasma-induced heating of catalyst play a minor role in the activation of catalyst.

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REFERENCES


