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Interaction of Plasma and Catalyst; Current Status and Road to Industrial Use
プラズマと触媒の相互作用の現状と実用化への課題

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Combination of NTP with catalyst is gathering attention due to its various synergistic effects. In the decomposition of volatile organic compounds (VOCs), for example, the combined system can achieve deep oxidation of VOC to benign CO_2 without forming unwanted byproducts (CO, NOx, and aerosols). We report here some experimental evidence on the interaction of NTP with the active metal nanoparticles supported catalysts using various measurement techniques, such as a microscope-ICCD camera system, OES, chemical probe using isotope-labelled oxygen ($^{18}O_2$), and electron-spin resonance ESR and catalyst characterization (BET surface area, TEM, ICP). Current status of the technology will be presented together with the future challenges in this field.

1. General

The combination of nonthermal plasma (NTP) and catalyst is gathering attentions in various applications such as decomposition of volatile organic compounds (VOCs), NOx and PM removal in vehicles, and fuel reforming [1]. One of smart ways to remove VOCs at moderate operating conditions (room temperature and atmospheric pressure) is combined system of adsorption and oxygen plasma, which is referred to as cycled system. The how and why of the cycled system will be presented. Adsorption and subsequent O_2 plasma oxidation can oxidize VOC into CO_2 without forming unwanted byproducts such as CO, NOx, and aerosols. It is necessary to investigate the physical and chemical interactions of NTP and catalyst which can provide important insights into the understanding of fundamental aspects in plasma-catalyst process. These interactions were studied using isotope oxygen ($^{18}O_2$), ICCD camera, ESR, XRD, XPS, and online FTIR.

We report here some recent progress in experimental evidence for the better understanding of the interaction between NTP and catalyst.

2. Experimental

Plasma was generated using barrier-type reactor consisting of coil electrode (corona electrode), quartz tube (barrier) and silver paste (ground electrode). The plasma reactor was energized with an AC high voltage (Trek 20/20B). Discharge power of the PDC reactor was measured using the automated V-Q Lissajous program (Insight Co. ver 1.71). A condenser (about 100 nF) was connected in series to the ground line of the plasma reactor. The charge Q (i.e. time-integrated current) was measured with a 10:1 voltage probe. Zeolite pellets (1.6 mm in diameter) were packed in the plasma zone, which is also referred to as single-stage plasma-catalyst reactor. The specific surface areas of zeolites tested in this work were in the order of HSY ((high-silica Y zeolite, 690 m^2/g), MS-13X (540 m^2/g), HY (520 m^2/g) and MOR (380 m^2/g). The HSY zeolite is known to have hydrophobic nature, which provides stable property at humid condition. Various metal nanoparticles were impregnated on the zeolites using various precursors such as $AgNO_3$ and $Cu(NO_2)_2$. The size and the shape of the loaded metals were measured by transmission electron microscopy (TEM, Topcon Co., Model EM002B).

3. Results and Discussion

Catalyst materials packed in plasma reactors can change the electrical properties and so does the plasma generation. The authors have been studied the plasma generation on the surface of various catalysts using optical lens and ICCD camera system. Figure 1 shows one example of the plasma generation on the Ag/HSY zeolite [2]. The ICCD camera observation provided an important insight into the understanding of interaction between discharge plasma and catalyst. Two different modes have been confirmed in the catalysts packed plasma reactors. One is partial discharge, which is usually observed vicinity of contact points between catalysts. As increasing the applied voltage, plasma was observed not only at the contact points (partial discharge) but also on the surface of the catalysts.

Voltage-current characteristics of $BaTiO_3$ pellet packed reactor showed similar patterns compared to Ag/HSY zeolite packed plasma reactor. However, the plasma expansion was not observed on the surface of $BaTiO_3$. These results clearly indicate that multidisciplinary analysis is necessary to get a better understanding on the plasma properties in the catalyst packed reactor. 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) [3]. The presence of oxygen decreased the luminescence of surface discharge plasma [4], which is consistent with the work reported by Hensel et al for the discharge on porous ceramic [5]. A positive correlation was found between the plasma generation pattern and the catalytic activity in the combined process. The area of discharge plasma expanded over a wide range by the metal nanoparticles. We also have reported that the plasma-induced fixation of oxygen on the surface of catalysts and their contribution in subsequent chemical reaction using isotope-labelled oxygen ($^{18}O_2$) [6]

Figure 2 summarizes the current understanding of synergy effects in the complementary combination of plasma with catalyst. The most common finding in the study of synergistic effects is the better CO_2 selectivity (i.e. low CO formation). It is now believed that surface activation by UV is negligible in the PDC process due to the low UV flux from the discharge plasma in an air-like mixture. The packing of catalytic materials within plasma reactors also changes the physical-/ electrical characteristics of plasma generation in the following ways; 1) Decrease in the plasma onset voltage, 2) Increase in the number of microdischarges, 3) Extension of the plasma area by loading metal nanoparticles on the surface. To make catalysts being active under plasma activation, it is important to form the plasma just near the surface of catalyst. Recently, the fluorescence from the plasma-excited Ag clusters on the surface of zeolites has been observed [7-8], which provides good evidence for the direct interaction of plasma with surface.

4. Conclusions

The interaction of plasma and catalyst is interesting hot topics in the field of plasma chemistry. Ongoing progress for the fundamental aspects can accelerate the application of plasma-catalyst process in various fields in the near future.

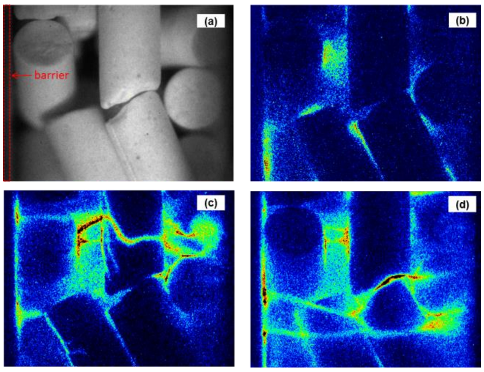

Figure 1. ICCD camera images of plasma over Ag/HSY catalyst (in N_2): (a) without discharge, (b) 16 kV, (c) 19 kV, (d) 21 kV. Discharge power was in the range of 0.36~1.2 W for the tested applied voltages.

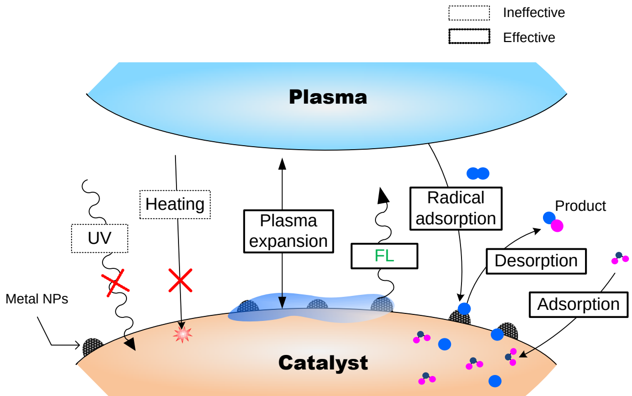

Figure 2. Overview of interaction of plasma and catalyst

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