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Generation of non-thermal plasma combined with catalysts and their application in environmental technology

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ABSTRACT

Non-thermal plasma (NTP) promotes formation and reaction of radicals at low temperature condition. In order to use NTP, selectivity and energy efficiency should be improved. For this purpose combination of NTP and catalysts has been proposed for several industrial applications. Several systems are at first introduced in this review, and then generation of NTP suitable for combination with catalysts will be introduced. The first generation of NTP combined with catalysts was a pulsed streamer corona with a TiO_2 solid catalyst. This combination has been commercialized successfully as an indoor air cleaner attached to an air conditioner. However, this system cannot use honeycomb catalysts. A packed bed has therefore been used for testing the combination of NTP and pellet type catalysts. Packed bed uses a layer of ferroelectric pellets of a few mm in diameter. The pellet layer is sandwiched by the electrode energized with AC or pulsed voltages. Each contacting point of the pellets is ionized. The packed bed can be an important candidate for plasma-assisted combustion. An existing application for the packed bed is the volatile organic compounds (VOCs) decomposition. Recently, discharges in honeycomb catalysts have been developed. One end of a honeycomb catalyst is attached with a packed bed or a surface dielectric barrier discharge to generate NTP. This electrode serves as a plasma electrode. When a DC electric field is applied, ionization proceeds along the surface of fine channels of ceramic honeycomb. This honeycomb discharge could be used for various processes to combine NTP and catalysts. It could also be used for surface treatment of honeycomb catalysts by NTP.

1. Introduction

With positive pulsed voltage application to corona electrode system in atmospheric air, volume in the electrode spacing can be ionized even at atmospheric pressure [1]. With short pulsed high voltages, electrons migrate longer distance compared to ions having heavier mass, therefore, electrons are driven across larger voltage drop so that most of the input electrical energy is mainly used to energize electrons. This is the reason of better efficiency of pulse energization for plasma chemical processes. The plasma produced by a short-pulsed voltage is non-thermal plasma, defined as low temperature plasma having high-energy electrons. NTP in air produces reactive radicals such as O and OH. These radicals promote various chemical reactions [2–10]. For environmental remediation such as removal of odor/allergen and volatile organic compounds (VOCs) in air, NTP has been used and various products have been commercialized.

For environmental applications, plasma chemical processes should be energy efficient, cheap and small-sized, to be competitive with conventional methods. Recently, significant improvement of NTP processes for gas cleaning has been achieved by combining NTP with catalysts. In this review, several commercialized processes are introduced at first. Then several NTPs are introduced which are suitable for combining with catalysts.

2. Examples of NTP processes combined with catalysts

2.1. Indoor air cleaning system using a combination of plasma and catalysts

Contamination of indoor environments receives a great concern as it causes many health problems (for example: sick buildings). Plasma/catalyst combination has been applied for indoor air cleaner [11,12]. Fig. 1(a) shows a first mass-produced plasma reactor attached to a room air conditioner. The reactor consists of a wire-plate electrode system stressed by pulses superimposed on DC voltage as shown in Fig. 1(b). The DC voltage contributes to the collection of suspended particles. To enhance the removal performance of gaseous pollutants, TiO_2 catalyst was placed just after the electrode system to be exposed to the electric field, Fig. 1(a). The catalyst was prepared by coating an aluminum mesh with TiO_2 powder.

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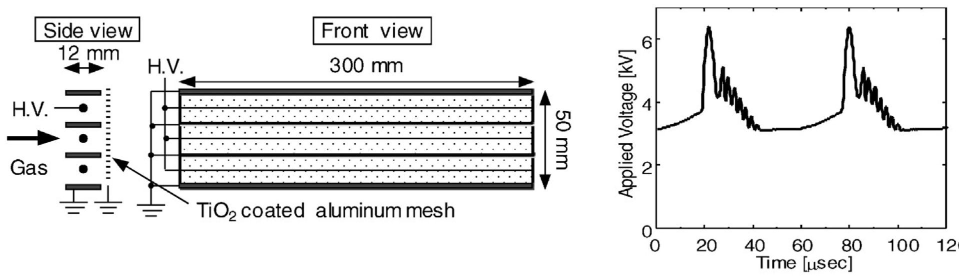


(a) Electrode and catalyst mesh (b) Applied voltage

Fig. 1. Indoor air cleaning system for air conditioner using plasma and catalyst combination [12]. (a) Electrode and catalyst mesh and (b) applied voltage.

Results of the one-pass test are given in Table 1. The measurement was carried out at room temperature and atmospheric pressure. The velocity of the airflow was 1.0 m/s, the gas residence time was 10 ms, and the pressure drop in the reactor was less than 1 mm-H_2O. Acetaldehyde (CH_3CHO) diluted with dry air (initial concentration: 1.0 ppm) was used as the sample gas. Without stressing the reactor, absorption-produced-acetaldehyde removal efficiency is about 0.5% and the particle collection efficiency is 12%. With stressing the reactor, 70% particle removal (0.5 μm size) and 27% acetaldehyde removal were achieved. The ozone generation during this operating condition was less than 0.1 ppm and the energy efficiency was 55.4 eV/molecule $-CH_3CHO$. With large air-circulation rate of the air conditioner, this one-pass efficiency would be practically effective.

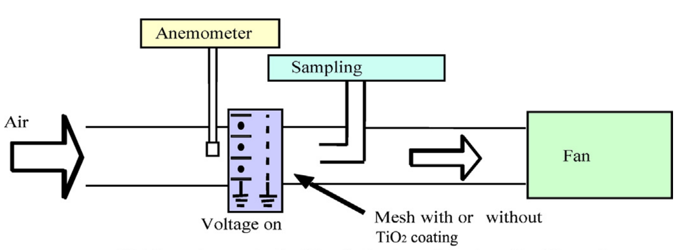
Synergetic effect of the combination of pulsed streamer corona and TiO_2 was studied. TiO_2 is known as a photo-catalyst and the oxidation ability of TiO_2 coated mesh stained by indigo-carmine dye was investigated. When oxidized, the dye becomes clear. Fig. 2 shows the TiO_2 coated mesh and the comparison of decolorization before and after oxidation. A color meter was used for quantitative measurement of the dye's color. Table 2 compares the color change under different operating conditions. Combination of plasma and the catalyst was effective to oxidize the dye with air flow from plasma electrode-system to mesh. At air flow velocity of 1.0 m/s, ozone concentration was less than 0.05 ppm. Ozone might affect for the oxidation, therefore, the direction of the air flow was reversed. Thus, the air passes at first through the catalyst mesh, and then arrives in the plasma zone ensuring that ozone does not reach the surface of the TiO_2 mesh. This is in addition to the increase of flow velocity to 2.5 m/s. The dye on the mesh was still oxidized. For comparison purpose, the effect of 2.5 ppm ozone supplied by an ozonizer was tested. The dye was oxidized at the same level as that with the plasma. Also, the effect of UV from the plasma was checked. The UV did not activate the catalyst. These results suggest that O_3 ions (in this case, positive ions) may activate TiO_2 surface exposed to plasma.

Kim and Ogata reported on the mechanism of activation of TiO_2 surface by being exposed to plasma in argon. Oxygen atom on lattice of TiO_2 and H_2O trapped on the surface could be activated to become oxygen radicals [13]. Generation of O radicals from O_3 on various surfaces has been studied [14]. Further understanding of surface chemistry coupled with plasma will contribute in improving energy efficiency of surface plasma chemical reactions.

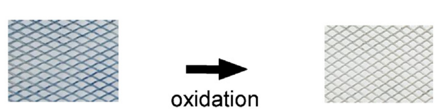
Indoor air cleaners for homes and offices have been widely used and a combination of plasma and catalyst has been adopted in these appliances [15].

Table 1
Performance of the indoor air cleaning system with plasma/catalyst combination.

Voltage (kV)	Particle collection efficiency (%) (for 0.5 μm diameter)	Acetaldehyde removal efficiency (%) (inlet concentration: 1.0 ppm)
0	12	0.5
3.0 (DC) + 2.6 (pulse)	70	27 (15%; without the catalyst mesh)



(a) Measuring method of decolorization of titanium dioxide catalyst



(b) Catalyst mesh before and after oxidation

Fig. 2. Oxidation of indigo-carmine dye on TiO_2 catalyst surface [12]. (a) Measuring method of decolorization of titanium dioxide catalyst and (b) catalyst mesh before and after oxidation.

2.2. Plasma-assisted catalytic combustion system for VOC removal

Volatile organic compounds are one of major pollutants in factories and other working places. NTP is an effective methodology for decomposition of VOC. For industrial applications, however, the decomposition process using NTP alone requires high energy. AC discharge in packed bed reactors has been investigated for VOC decomposition and a gamma-alumina or zeolite-base catalyst was found to improve efficiency of the decomposition [16–20]. Various by-products can possibly be generated if the plasma decomposition is incomplete. In order to deal with these shortcomings, the plasma-assisted catalytic combustion process has been developed and commercialized [21].

Fig. 3(a) is a commercialized VOC removal system of 60 m^3/min gas flow rate. A rotating zeolite disc having honeycomb geometry is used to condense VOCs in air. VOCs are desorbed using hot air of about 200 °C. The hot air is supplied through a heat exchanger having efficiency of about 40%. Typically, toluene can be condensed up to 2000 ppm by the rotating zeolite disc. The condensed VOCs are introduced to the plasma section as shown in Fig. 3(b). The reactor consists of a quartz cylinder of 20 mm diameter with a discharge electrode of 10 mm diameter extending along the cylinder axis. Length of the plasma section is 32 mm. The used dielectric pellets are Platinum catalyst for catalytic combustion. AC voltage of 22 kHz, 7 kV effective value is applied between the electrodes. The maximum discharge power per reactor is 34 W with a gas flow rate of 34 L/min, or specific input energy (SIE) of 55 J/L. At the downstream