Effect of the adsorbent/catalyst preparation method and plasma reactor configuration on the removal of dilute ethylene from air stream

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ABSTRACT

13X zeolite-supported Ag was employed as the dual-functional adsorbent/catalyst for the plasma-catalytic abatement of dilute ethylene. The adsorbent/catalyst prepared by ion exchange (Ag-EX/13X) exhibited better adsorption capability than the parent 13X and Ag-IM/13X prepared by the impregnation method. The oxidative transformation of the adsorbed ethylene was then performed by using three different reactor configurations such as one-stage (*i.e.*, adsorbent/catalyst in direct contact with plasma), two-stage (*i.e.*, adsorbent/catalyst located downstream of the plasma region), and the combination of the two (hybrid). The oxidation of the adsorbed ethylene to CO_2 in the two-stage configuration can be explained by the diffusion of ozone into zeolite micro-pores, which was, however, much slower than in the one-stage and hybrid configurations. When compared at an identical applied voltage of 20 kV (inlet ethylene: 200 ppm; adsorption time: 100 min; plasma oxidation time: 20 min), the mineralization efficiency of the hybrid reactor was greater than the sum of those of one- and two-stage reactors, *i.e.*, 63, 42, and 10%, respectively. Using the hybrid configuration, ozone and other reactive species were more effectively produced, thereby shortening the oxidation time of ethylene and therefore achieving a higher energy efficiency which was evaluated to be *ca.* 2.4 g $(kWh)^{-1}$.

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1. Introduction

Non-thermal plasma (NTP) chemical processing of hazardous air pollutants (HAPs) has been extensively investigated and appears to be a clean, efficient, and eco-friendly pollution control technology [1,2]. In NTP, the temperature of the bulk gas molecules and ions is close to ambient temperature, while the mean electron energy or temperature of the electrons is considerably higher (1–10 eV). The input electrical energy is mainly used to energize electrons for ionization and excitation of gas molecules, leading to the formation of active chemical species, such as ozone (O_3), oxygen atoms ($O(^1D)$ and $O(^3P)$), and hydroxyl radicals (OH) to destroy the hazardous gaseous pollutants [3]. Volatile organic compounds (VOCs) constitute a major class of air pollution, causing various adverse effects on human health and environment. Abatement of VOCs by using NTP-based technologies has also received much attention, so far [4–10]. However, it should be noted that the oxidation of dilute VOCs in air by NTP is non-selective, not

energy-efficient and usually leads to the formation of undesired byproducts, such as carbon monoxide (CO), formaldehyde (HCHO), ozone, nitric and nitrous oxides (NO, N_2O). The combination of NTP and catalysis may be a promising approach to solve such problems. The synergetic effects of plasma-catalysis have been proven to improve the selectivity toward carbon dioxide (CO_2), enhance the destruction and energy efficiencies, and suppress the formation of unwanted byproducts [11,12]. Depending on the position of the catalyst, the plasma-catalysis technique can be classified into two major systems—one-stage and two-stage systems. In the one-stage system, the catalyst is exposed to plasma, *i.e.*, plasma and the catalyst could directly interact with each other [13]; whereas, in the two-stage system, the catalyst is located downstream of the discharge zone.

In order to further improve the energy efficiency and minimize the emission of harmful byproducts through purification of the contaminated air, plasma-catalysis had also been combined with adsorption in a cyclic process. In this process, dilute VOCs were first concentrated on an adsorbent for a long time, and then plasma-catalytically oxidized to CO_2 in a relatively short time, leading to a reduction in both energy consumption and emission of toxic compounds [14–16]. The adsorbent and catalyst can be separated or integrated using a dual-functional material. The selection of a

proper adsorbent is crucial for achieving high energy efficiency, especially when dealing with highly volatile compounds, such as ethylene (C_2H_4). C_2H_4 is emitted from both industrial and agricultural activities. In agriculture, C_2H_4 plays an important role as a plant hormone that speeds up the ripening process, and thus, controlling C_2H_4 production after harvest helps to extend the lifetimes of agricultural commodities. Recently, attempts have been made to reduce the accumulation of C_2H_4 by using zeolite modified with cationic surfactants and group I metal ions as adsorbents [17–19]. The use of the adsorbent is possibly the simplest way to remove C_2H_4, but it requires periodic replacement of the saturated adsorbent.

In the current work, the removal of dilute ethylene from an air stream was studied by using silver-incorporated 13X zeolite as the dual-functional adsorbent/catalyst coupled with dielectric barrier discharge (DBD) plasma. The zeolite modification methods such as silver impregnation and ion exchange and their effect on the adsorption capacity for ethylene were investigated by dynamic adsorption at room temperature. Then, the ethylene-enriched adsorbent/catalyst was *in situ* regenerated by plasma-catalysis. Three different reactor configurations, namely, one-stage, two-stage, and hybrid, which is the combination of the former configurations, were compared and discussed. The adsorbent/catalyst in direct contact with plasma and located downstream the plasma region were referred to as the one-stage and the two-stage, respectively. The temporal evolutions of gaseous byproducts formed during the plasma-catalytic reactions were examined to clarify the roles of plasma-induced reactive species in the oxidative removal of the adsorbed ethylene and the regeneration of the adsorbent/catalyst.

2. Experimental

2.1. Apparatus and materials

The dynamic adsorption of dilute ethylene and plasma-catalytic oxidation of the adsorbed ethylene were performed in a packed-bed DBD reactor system, as shown in Fig. 1(a). The concentration of ethylene in air stream (21% O_2 and 79% N_2) was controlled at 200 ppm by mass flow controllers (MFCs). Dry synthetic air with a flow rate of 1 L min^{-1} at room temperature was used for all experiments.

Three different configurations of the packed-bed DBD reactor are depicted in Fig. 1(b). The reactor consisted of a quartz dielectric tube (inner diameter: 25.5 mm, thickness: 2 mm) concentric with a threaded steel rod (diameter: 5.5 mm), acting as the discharge electrode. A 50 mm long aluminum foil wrapped outside the quartz tube served as the ground electrode. In the one-stage reactor configuration, 15 g of the adsorbent/catalyst was packed in the plasma discharge region. On the other hand, in the two-stage configuration, the same amount of the packing material was placed downstream the plasma discharge region. The hybrid reactor was the combination of the one- and two-stage reactors, resulting in a 100 mm long discharge region in which the first half was left blank and the second half was filled with the adsorbent/catalyst. The reactor was energized by an alternating current (AC) power supply at a constant frequency of 400 Hz with a discharge gap of 10 mm. For one cycle of treatment, dilute ethylene was first adsorbed on the adsorbent/catalyst without plasma for a certain period of time. After that, the gas stream was switched from ethylene-contaminated air to pure air and plasma was ignited soon afterwards.

A commercially available pelleted 13X zeolite (diameter: 4.2 mm; Cosmo Fine Chemicals) was modified with silver by either ion exchange or the incipient wetness impregnation method using aqueous solution of silver nitrate (Sigma Aldrich, USA). The ion exchange was carried out with the silver nitrate solution (0.02 M) at 80 °C for 4 h under vigorous stirring. The Ag-exchanged zeolite was then filtered, washed several times with deionized water, then dried overnight in a dry oven at 110 °C and finally calcined at 500 °C for 3 h in ambient air. The content of silver in the zeolite was determined to be *ca.* 3.0 wt% using inductively coupled plasma optical emission spectrometry (Agilent Technologies, 700 series ICP-OES). For the impregnation method, the zeolite was impregnated by adding an appropriate amount of silver nitrate solution dropwise to obtain 3.0 wt% Ag loading, and then dried and calcined under the same conditions as were done in the ion exchange method. The adsorbent/catalysts prepared by the ion exchange and impregnation method were named as Ag-EX/13X and Ag-IM/13X, respectively. Each Ag-incorporated zeolite with a weight of 30 g was packed into a quartz tube (inner diameter: 25.5 mm) for investigating the ethylene adsorption capacity. In this test, ethylene concentration and gas flow rate were also kept at 200 ppm and 1 L min^{-1}, respectively.

2.2. Measurement methods

The voltage applied on the discharge electrode was recorded by a digital oscilloscope (Tektronix DPO3034) using a high-voltage probe with a DC attenuation ratio of 1000:1 (Tektronix P6015A). The dissipated charge was determined by measuring the voltage across a capacitor (capacitance: 1.0 μF) connected to the reactor in series using a 10:1 voltage probe (Tektronix P6139B). The power consumed by the plasma reactor was then evaluated from the so-called Lissajous voltage–charge figure.

The concentration of ethylene at the outlet of the reactor was monitored by a gas chromatograph (Bruker 450-GC) equipped with a flame ionization detector (FID). The products formed during the plasma-catalytic oxidation of the adsorbed ethylene were identified and quantified by a Fourier-transform infrared (FTIR) spectrometer (Bruker IFS 66/S) fitted with a 21 cm long gas cell. All samples were collected at a resolution of 0.5 cm^{-1} with 10 scans. The FTIR was calibrated with known concentrations of ethylene, carbon monoxide (CO), and carbon dioxide (CO_2). The concentration of ozone in the effluent was analyzed by a portable gas analyzer (PortaSens II, Analytical Technology, Inc.). The reactor temperature was measured at an interval of 5 min using an ethanol thermometer placed 5 mm downstream from the discharge region, as in Fig. 1(a).

The contribution of an individual carbon-containing product (A) detected at the outlet of the reactor to the carbon balance was evaluated as the percentage ratio of the atomic carbon contained in the product A (C_A) to the atomic carbon in the adsorbed ethylene (C_{tot}):

$$\%C_A = \frac{C_A}{C_{tot}} \times 100 \tag{1}$$

The mineralization efficiency is defined as the fraction of the adsorbed ethylene oxidized to carbon dioxide which corresponds to the contribution of CO_2 to the carbon balance.

The Brunauer–Emmett–Teller (BET) surface areas of the parent and silver-modified 13X zeolites were measured by N_2 adsorption at 77 K using a surface area analyzer (TriStar II 3020, Micromeritics). The crystalline phases of the investigated adsorbent/catalysts were characterized by an X-ray diffraction (XRD) system (SPD-2000, Scinco) equipped with Cu K$_\alpha$ radiation (40 kV, 30 mA).

3. Results and discussion

3.1. Characterization of adsorbent/catalysts

The BET surface areas of the parent and silver-modified 13X zeolites are presented in Table 1. As seen, the surface area was mainly contributed by the micropores (*ca.* 97%), and it decreased by 10.2