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Short communication

Catalytic oxidation of benzene using DBD corona discharges

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Abstract

Plasma oxidation of benzene (C_6H_6) in oxygen and nitrogen was investigated using a dielectric barrier discharge (DBD) reactor with or without MnO_2 or TiO_2 at atmospheric pressure and without external heating except plasma heating. An alternative current power supply was used to generate corona discharges for the plasma oxidation. The energy density was controlled under 200 J/L to keep an increase in gas temperature less than 167 K. C_6H_6 was oxidized to carbon monoxide (CO) and dioxide (CO_2). Typically, the energy efficiency at an energy density of 92 J/L was about 0.052, 0.039, and 0.024 mol/kWh with MnO_2, TiO_2, and without MnO_2 and TiO_2, respectively. Benzene oxidation mechanism was mentioned. A comparison on energy efficiency as a function of initial concentration of hydrocarbons, inorganic sulphur compounds, and chloro (fluoro and bromo) carbons was given.
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Keywords: Benzene oxidation; Catalytic oxidation; Corona discharges; DBD reactor; Energy efficiency

1. Introduction

Recently, the abatement technologies for controlling hazardous air pollutants, such as volatile organic compounds (VOCs) in indoor air [1–3], are becoming more and more important both for considering of human health and global warming. Especially, high concentration VOCs from some sources such as paints, chemical plants, and printing industries, are of high risk and their emission should be reduced. Plasma technologies have potential for reducing VOCs emission [4,5]. Vercammen et al. [4] reported that plasma discharge technologies are useful for reducing VOCs at gas flow rates less than $1000\,\mathrm{N\,m^3/h}$ and concentrations less than 10%. Many types of plasma discharges have been developed, in which corona discharges are of interest as this kind of plasma can be carried at ambient temperature and atmospheric pressure. However, plasma discharge technologies have encountered site-specific constraints (e.g., economic considerations) that have limited their commercial availability, in comparison with conventional methods, such as thermal incineration with or without catalysts, adsorption, condensation, biofiltration, membrane separation, ultra-violet (UV) oxidation [6].

Recently, Ayrault et al. [7] used platinum (Pt)-based catalyst supported on an alumina wash-coated honeycomb monolith by means of a high voltage bi-polar pulsed excitation. 2-Heptanone is removed at an energy efficiency of 0.14 mol/kWh at an energy density of 200 J/L. They also found that energy efficiency decreases to 0.029 mol/kWh using an uncoated monolith even at an energy density of 500 J/L. H_2O (3%) in gases strongly decreases the efficiency of 2-heptanone elimination and ozone formation. Futamura found that VOCs can be removed using plasma discharges at an energy density of up to 15 kJ/L with catalysts such as MnO_2 and TiO_2 [8]. In 2003, Sekiguchi et al. studied ozone-decomposition catalyst for degradation of toluene under UV irradiation [9]. They found that TiO_2 has a lower toluene removal ratio without UV irradiation and MnO_2-based catalyst has higher toluene removal ratio at a higher H_2O humidity. MnO_2 is a catalyst for the decomposition of ozone [10]. Plasma discharges at high energy density cause an increase in catalyst temperature, which promotes VOCs removal by catalysts at high temperatures. For example, an energy density of 200 J/L causes an increase in air temperature to 197 °C if the air temperature is 30 °C before plasma discharge; at 195 °C 78% of toluene is decomposed over a Pt-based catalyst [11]. In this study, benzene decomposition was investigated with a dielectric barrier discharge (DBD) reactor with or without TiO_2 or MnO_2 bed downstream of the discharge zone at an energy density lower than 200 J/L, the increase in catalyst temperature was estimated

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to be less than 167 K. The mechanisms of benzene oxidation in plasmas and on catalysts were suggested.

2. Materials and methods

Fig. 1 shows the experimental systems including three mass flow meters (MF1-3), a C_6H_6 bubbling bottle hold in a water bath at 25 °C, a DBD plasma reactor, and a power supply unit. A gas mixture of N_2, O_2, and C_6H_6 was used. N_2 was supplied at a rate of 200 ml/min, in which 0.56 ml/min was used for bubbling C_6H_6 (99.5%). O_2 was supplied at a rate of 50 ml/min. C_6H_6 concentration in the gas mixture was estimated to be in a range of 300–380 ppm. An alternative current (AC) power supply was used to generate corona discharges within the DBD reactor.

The DBD reactor mainly consisted of a glass tube (10 mm outside diameter, 8 mm inside diameter, 20 cm length), a stainless steel rod (6 mm outside diameter, 13 cm length), and an electric conductive tape (width 1 mm). The stainless steel rod was inserted in the glass tube and was connected to the high voltage output of the AC power supply. The electric conductive tape was covered on the outside surface of the glass tube. The discharge zone was limited in the space between the inside surface of the glass tube covered with the electric conductive tape and the outside surface of the stainless steel rod.

TiO_2 (≥99.0%, Damao Chemical Reagent, Tianjin) and MnO_2 (≥85.0%, Bodi Chemicals, Tianjin) were used as catalysts. The specific surface areas of TiO_2 and MnO_2 by nitrogen adsorption were 50 and 74 m^2/g, respectively. The primary particle diameters of TiO_2 and MnO_2 were 15–60 and 10–40 nm, respectively. 0.3 g of TiO_2 or MnO_2 particles were pressed to 0.28–0.45 mm (40–60 mesh) particles and filled 16 mm beneath the stainless steel rod with a 6-mm bed height.

The discharge voltage and discharge current were measured with a voltage probe (V-P, P6015A, Tektronix) and a current transformer (CT, TCP202, Tektronix), respectively. The analogue signals from the voltage probe and current transformer were recorded with a digital phosphor oscilloscope (TDS3054B, Tektronix).

All experiments were carried out at atmospheric pressure and without external heating except plasma heating.

C_6H_6 and its gaseous oxidation products were analyzed online with a gas chromatograph (SP-3430, BFRL, Beijing) equipped with a 2-m Porapak-N and a methanizer prior to FID detector. The gaseous sample for analysis was taken at a time around 40 min after discharge started. C_6H_6 conversion was calculated using Eq. (1). Carbon dioxide (CO_2) and monoxide (CO) were found in this study. The carbon balance was >90%. The selectivity of CO_2 was calculated using Eq. (2).

$$\text{Bezene conversion} = \frac{C_0 - C}{C_0} \times 100\%, \tag{1}$$

where C_0 and C are C_6H_6 concentrations in ppm at inlet and outlet of the DBD reactor, respectively.

$$CO_2 \text{ selectivity} = \frac{\text{moles of } CO_2 \text{ formed}}{6 \times \text{moles of } C_6H_6 \text{ converted}} \times 100\%. \tag{2}$$

The energy injection density in J/L is defined as the energy injection to the DBD reactor (P) per unit gas volume treated over 1 s. The energy efficiency in mol-C_6H_6/kWh is defined as Eq. (3).

$$\eta_d = \frac{C_6H_6 \text{ conversion} \times C_0 \times F}{P \times 0.082 \times T} \times 3.6, \tag{3}$$

where F is the flow rate of the gas mixture (ml/min). T is the gas temperature (298 K) at the inlet of the DBD reactor. P was calculated from the average input voltage and current of the AC power.

3. Results and discussion

3.1. Typical waveforms of discharge voltage and current

The typical waveforms of discharge voltage and current are shown in Fig. 2 at average output voltage of 7.8 kV. Although there was not obvious drop in voltage on the sine waveform of voltage, there were multiple discharge current pulses that could be found from the waveform of discharge current. Those multiple discharge current pulses typically contribute the formation of corona discharges [12,13]. The energy injection was calculated to be 144 J/L at 7.8 kV.
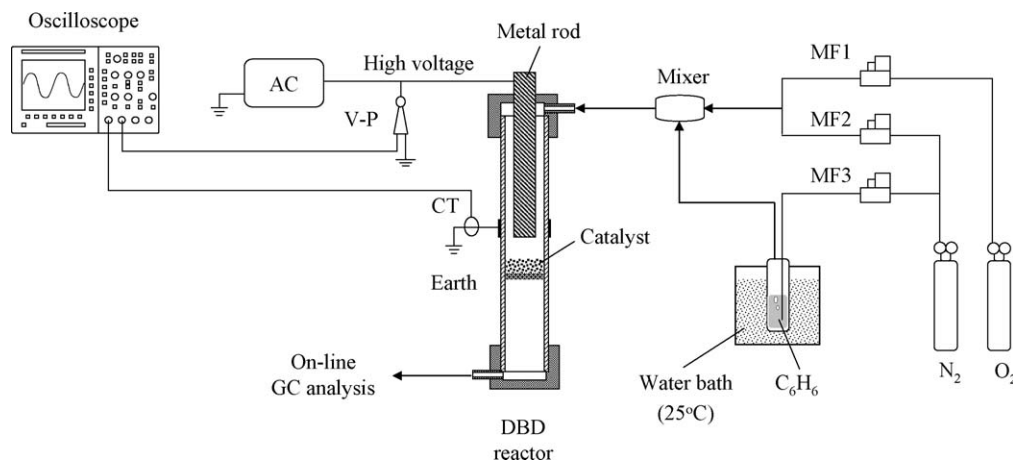

Fig. 1. Schematic diagram of a plasma system for the plasma oxidation of benzene.
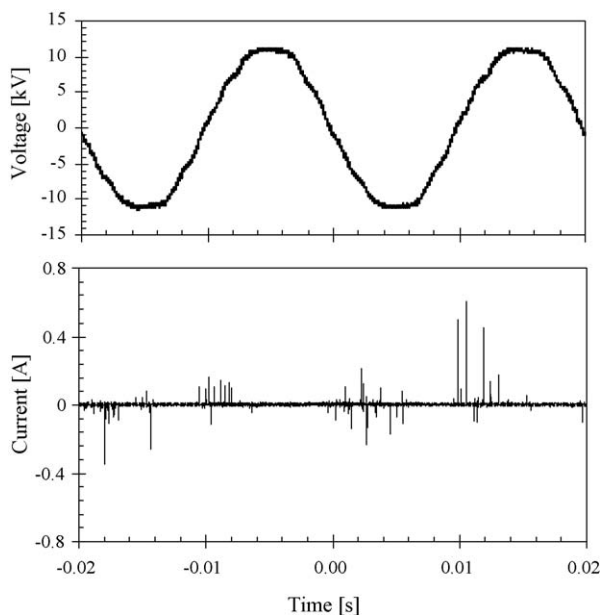
Fig. 2. Waveforms of discharge voltage and current using the DBD reactor.

Fig. 4. CO$_2$ selectivity at various energy densities.

3.2. Mechanism of benzene oxidation

Benzene conversion is shown in Fig. 3 as a function of energy density with or without TiO$_2$ or MnO$_2$. Benzene conversion increased with increasing energy density linearly. Benzene conversion had an order of MnO$_2$ > TiO$_2$ > none (without catalyst) at the same energy density. This finding implied that benzene could be decomposed using the corona discharge and MnO$_2$ and TiO$_2$ have catalytic activity in benzene oxidation.

Sekiguchi et al. reported that oxidation of toluene with ozone strongly depends on the water concentration in air [9]. If water concentration is low, the effect of catalyst (such as MnO$_2$) is not obvious even in the presence of UV onto the catalyst. In this study, MnO$_2$ and TiO$_2$ could obviously improve benzene conversion without water addition into the gas mixture, this
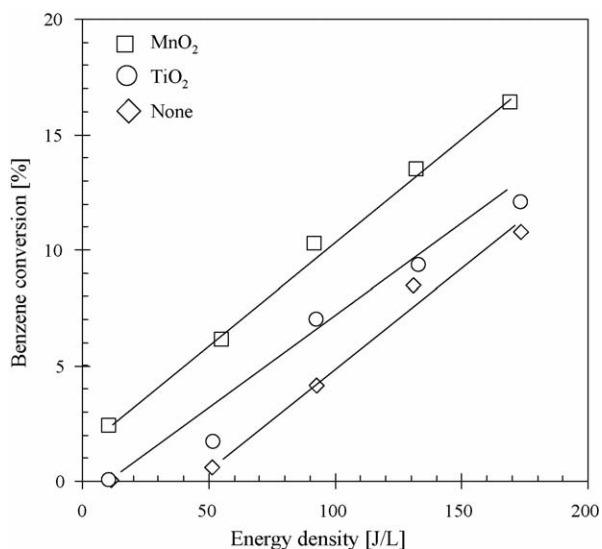
fact suggested that benzene oxidation in plasma discharges with MnO$_2$ and TiO$_2$ differs from that with ozone and MnO$_2$ reported by Sekiguchi et al. [9]. H$_2$O promotes benzene decomposition on MnO$_2$ in the presence of UV and ozone, but H$_2$O is not necessary in a DBD reactor as benzene can be decomposed by such as reactive O atoms and OH radicals generated in the discharge zone (Reactions (4) and (5)). The intermediate products of benzene oxidation may improve benzene oxidation by [O] such as ozone on MnO$_2$ or TiO$_2$ downstream of the discharge zone.

$$O + C_6H_6 \rightarrow C_6H_5 + OH, \tag{4}$$

$$C_6H_5 + [O] \rightarrow \text{products}. \tag{5}$$

Nunez et al. suggested that benzene radical reacts as follows from their plasma destruction study of toluene [13]:

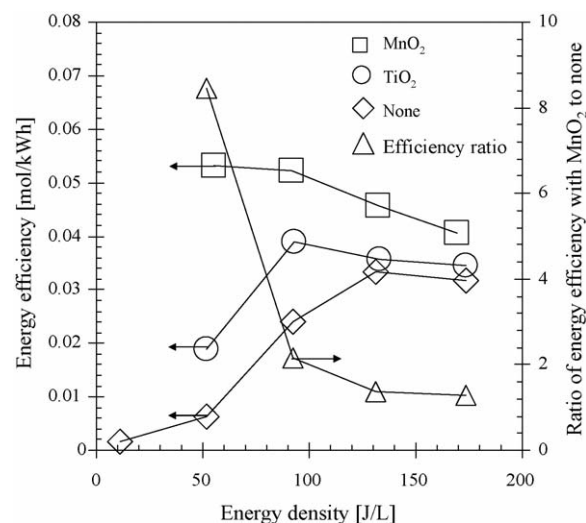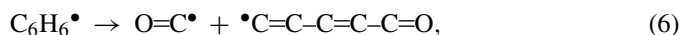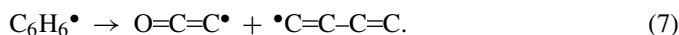$$C_6H_6^\bullet \rightarrow O{=}C^\bullet + {}^\bullet C{=}C{-}C{=}C{-}C{=}O, \tag{6}$$

Fig. 3. Benzene conversion as a function of energy density.

Fig. 5. Energy efficiencies as a function of energy density.

or

$$C_6H_6{}^\bullet \; \rightarrow \; O{=}C{=}C^\bullet + {}^\bullet C{=}C{-}C{=}C. \qquad (7)$$

The $O{=}C^\bullet$ or $O{=}C{=}C^\bullet$ radical reacts with oxygen to form CO_2. The radical oxidizes rapidly to CHO and then to CO_2. According to their suggestion, benzene oxidation products would be CO and CO_2, and the selectivity of each product would be 50%, while the ratio of CO_2 and CO is 2:1 in case of toluene plasma destruction. From a kinetic study result reported by Naydenov and Mehandjiev [14], the conversion of ozone on MnO_2 in complete oxidation of benzene is 11%, higher than 0.5% in incomplete oxidation to carbon monoxide at 25 °C. These reports implied that from the benzene oxidation product selectivity, the mechanism could be estimated.

We then measured concentrations of the gaseous products from benzene oxidation using gas chromatograph. Only CO and CO_2 were found with or without MnO_2 and TiO_2. CO_2 selectivity increased with increasing energy density (Fig. 4). The order of CO_2 selectivity is $MnO_2 > TiO_2 >$ none (without catalyst) at the same energy density. The level of CO_2 selectivity without MnO_2 or TiO_2 is less than 50%, suggested that the mechanism of benzene oxidation in such a plasma discharges is not the case suggested by Nunez et al. [13] but both of Reactions (6) and (7) happened.

3.3. Energy efficiency of benzene oxidation

The energy efficiencies of benzene oxidation at various energy densities are illustrated in Fig. 5. The energy efficiency with MnO_2 was highest and had a level of 0.05 mol/kWh. At the energy density of 51 J/L, the energy efficiency with MnO_2 was 7.4 times higher than that without catalysts (none). The energy efficiency with TiO_2 increased with increasing energy density and trended to a certain level of 0.035 mol/kWh, about 0.002 mol/kWh higher than those without catalysts (none).

The energy efficiency strongly correlates with the initial concentration of the compounds required to be removed. Fig. 6 summarizes the energy efficiencies of the removals of toluene, benzene, sulphur compounds, and chloro (fluoro and bromo) carbons using nonthermal plasma discharges with or without catalysts, those data from some other references [15–21]. In order to give a comparison with UV/TiO_2 benzene decomposition, two data reported by Wang et al. [22] are also illustrated in Fig. 6. The energy efficiency for the decomposition of inorganic sulphur compounds, hydrocarbons, chloro (fluoro and bromo) carbons are in range of 6×10^{-4} to 4×10^{-3}, 0.003–0.3, and 0.009–3 mol/kWh, respectively. The energy efficiency for the decomposition of benzene using UV/TiO_2 process is around 1.5×10^{-3} to 3×10^{-3} mol/kWh, about 18 times lower than that with this study using MnO_2. The removal of hydrocarbons is easier than inorganic sulphur compounds, but more difficult than chloro (fluoro and bromo) carbons. The use of catalysts can improve hydrocarbon decomposition by about three times as reported by Futamura [8] at an energy density of 125 J/L and by 7.4 times at 51 J/L in this study. Generally, the energy efficiency tends to increase with the increase in initial concentration of the compounds. From our previous results [21], the energy efficiency for methanol oxidation using a plasma reactor at an initial concentration of 1.8% is 0.22 mol/kWh without using catalysts; this fact implied that there may be a limit of the energy efficiency using the plasma discharges. Therefore, in order to improve the energy efficiency further, a high initial concentration would be desired. This means that additional adsorption/desorption and catalysis decomposition processes that can concentrate the VOCs into a high concentration
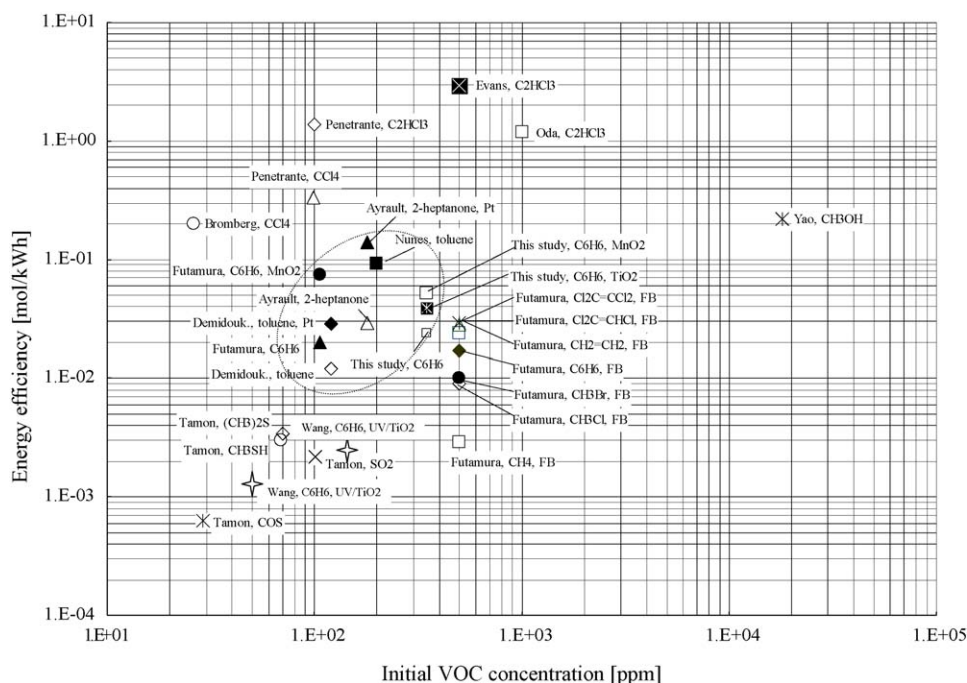

Fig. 6. Summary of energy efficiencies as a function of initial concentration of VOCs, sulphur compounds, chloro (fluoro and bromo) carbons in air.

level improve the energy efficiency of the plasma discharges process.

4. Conclusions

C_6H_6 oxidation using a DBD plasma discharges with or without MnO_2 and TiO_2 was investigated. The main conclusions are summarized as follows:

(1) The gaseous products of benzene plasma oxidation were CO and CO_2.
(2) MnO_2 and TiO_2 could promote benzene oxidation. MnO_2 was more active than TiO_2.
(3) The energy efficiency at an energy density of 92 J/L was 0.052 mol/kWh with MnO_2 and 0.039 mol/kWh with TiO_2, and 0.024 mol/kWh without catalyst. The energy efficiency level was improved by 7.4 times and 1 time when using MnO_2 at 51 and 92 J/L, respectively.
(4) The energy efficiency of VOC decomposition using plasma and catalysts is in a range of 0.01–0.1 mol/kWh, and tends to increase with the increase in initial concentration of VOCs. This tendency suggested additional adsorption/desorption processes that can concentrate the VOCs into a high concentration level contribute the improvement of energy efficiency of the plasma/catalysis process given in this study.

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