On the performance and mechanisms of toluene removal by FeOx/SBA-15-assisted non-thermal plasma at atmospheric pressure and room temperature

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ABSTRACT

FeO_x/SBA-15 catalysts were prepared via impregnation and utilized for toluene removal in dielectric barrier discharge (DBD) plasma at atmospheric pressure and room temperature. Toluene removal was investigated in the environment of various mixed N_2/O_2 plasmas, showing that toluene removal efficiency and CO_x selectivity were greatly increased by FeO_x/SBA-15 and that the organic intermediates were greatly reduced by catalysts. In pure N_2 plasma, the bulk oxygen in the catalyst was involved in the toluene oxidation, and the 3%FeO_x/SBA-15 catalyst showed the optimal toluene oxidation activity. The catalysts were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), N_2 adsorption–desorption, X-ray photoelectron spectroscopy (XPS), H_2 temperature-programmed reduction (H_2-TPR) and O_2 temperature-programmed desorption (O_2-TPD), showing that toluene oxidation was closely related to the highly dispersed nature of iron on the SBA-15 surface, the reduction temperature of Fe^{2+} and the oxygen adsorption ability of the catalyst. The pathways of toluene decomposition in the combination of FeO_x/SBA-15 with a non-thermal plasma (NTP) system were proposed based on the identified intermediates.

1. Introduction

Volatile organic compounds (VOCs), as chief atmospheric pollution precursors, are harmful to humans and the environment [1]. The toluene is a typical VOC in that it is emitted in high levels and difficult to abate [2]. Consequently, considerable attention has been paid to the development of methods for its removal. Recently, NTP technology has emerged as a promising method [3–11]. However, it also suffers from high energy consumption and incomplete oxidization, and the process is difficult to control [12,13]. To overcome these problems, the used of a catalyst has been coupled with NTP [14–16], wherein the VOCs removal rate increases with the assistance of adsorption [17]. Considering the importance of adsorption, various porous materials, such as γ-Al_2O_3 and molecular sieves, have been studied [18–20]. The mesoporous material SBA-15 shows relatively high adsorption for toluene because of its special micropore structure [20]. Thus, the residence time of toluene can be further increased if SBA-15 is added into the plasma system. However, SBA-15 is chemically inert for various catalytic applications because of its lack of acid and redox sites [21]. The incorporation of metal is an efficient method to improve the catalysis properties of this material. Among the various metal oxides, iron oxide has received extensive attention due to its relatively low cost, high activity, and environmental friendliness [22,23] as well as the O_2 transportation via facile interconversion between Fe^{2+} and Fe^{3+} states [24]. Our previous work has also disclosed the outstanding performance of FeO_x for toluene degradation in DBD plasma [25]. Therefore, it is vital to incorporate iron into SBA-15 material for VOCs plasma-catalysis oxidation because of the contrasting characteristics of these two materials. However, at present, the application of NTP coupled with FeO_x/SBA-15 catalysis in toluene degradation is scarce in the literature.

Oxygen species serve as an oxidizing agent to scavenge the VOCs and form carbon oxides. Their two main sources are gas-phase oxygen in the feed gas stream and bulk-phase oxygen in the catalyst. The gas-phase oxygen can be dissociated into atomic oxygen by discharge [26], and can promote the decomposition of CF_4 into CO_x in air thermal plasmas [27]. Previous research shows

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that the decomposition efficiency of benzene increases with the O_2 partial pressures [28]. However, the catalysts, especially transition metal oxides, generally contain lattice oxygen, surface oxygen and adsorbed oxygen [29,30]. Regardless of type, all oxygen in the catalyst can be described as the bulk-phase oxygen of the catalyst, which can also oxidize VOCs into CO_x in the plasma [31,32]. Herein, gas-phase oxygen in the feed gas stream and bulk-phase oxygen in the catalyst are both expected to play important roles during VOC removal.

In this work, iron loaded on SBA-15 was selected as a catalyst to oxidize toluene (100 ppm) in various mixed N_2/O_2 plasmas at atmospheric pressure and room temperature. To better understand the structure and possible metal–support interaction of the iron oxide species and SBA-15 support, the catalysts were characterized by SEM, XRD, N_2 adsorption–desorption, XPS, H_2-TPR and O_2-TPD. The organic by-products of toluene oxidation were identified to provide a better understanding of the VOC oxidation mechanism over FeO_x/SBA-15 catalysts.

2. Experimental

2.1. Experimental setup

Fig. 1 shows a schematic diagram of the experimental arrangement designed for toluene removal via the combination of a catalyst with plasma. The toluene used was obtained by bubbling toluene with a N_2 gas stream in a bubbler. High-purity N_2 (99.999%) was divided into two streams. The first stream was allowed to pass through the pure toluene liquid (99.5%) (Guangzhou Chemical Reagent, China) kept in an ice and water bath (0 °C) to produce the toluene vapor. The second stream was mixed with high-purity O_2 (99.99%) in a mixing chamber. The combined stream was then mixed with vaporized toluene in another mixing chamber. The gas flow rates were adjusted and controlled using mass flow controllers (MFCs) (Seven Star Co., China). The mixture was introduced into the reactor at a flow rate of 300 mL/min, with an initial toluene concentration of 100 ppm and a gas residence time of 0.45 s. All of the gases used in this study were purchased from Guangzhou Jun Qi Gas Co., Ltd.

Toluene oxidation was carried out in a fixed-bed flow reactor that containing 0.2 g of the catalyst (40–60 mesh) and 1.6 g of silica sand (40–60 mesh). All of the experiments in the discharge stages were conducted at atmospheric pressure and room temperature. The gas leaving the reactor was analyzed using an online gas chromatograph (GC2014C, Shimadzu) equipped with two FID detectors: one for organic compounds, featuring a TG-BOND Q column (30 m, 0.32 mm) (60 °C), and one, equipped with a methanizer, for carbon monoxide and carbon dioxide analysis using a 5 A molecular sieve (2 m, 2 mm) and Poraplot Q column (4 m, 2 mm) (60 °C).

The organic by-products (gas phase) were preconcentrated by active carbon placed downstream of the NTP reactor, and then the active carbon was dispersed into the CS_2 solution (Chromatographic Grade) under ultrasonic vibration for 120 min. The supernatant was filtered with a 0.22-μL filter membrane and analyzed by a GC–MS (QP2010, Shimadzu) using an Rtx-5MS capillary column. The column temperature was 40 °C for the first 2 min and was then increased to 220 °C at 6 °C/min, where it was maintained for 5 min. The MS detector was run in scan mode with a mass range of 45–450 amu. The electron ionization (EI) method was used. MS identification was conducted using the NIST 08 databank (NIST/EPA/NIH Mass Spectral Library). The organic by-products on the catalyst surface were analyzed using the same procedure.

The toluene removal was expressed as follows:

$$\text{toluene removal efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100\%$$

$$\text{CO}_2 \text{ selectivity (\%)} = \frac{C_{\text{CO}_2}}{7(C_0 - C)} \times 100\%$$

$$\text{CO}_x \text{ selectivity (\%)} = \frac{C_{\text{CO}_x}}{7(C_0 - C)} \times 100\%$$

where C_0 and C are the initial and final concentrations of toluene, C_{CO_2} is the outlet concentration of CO_2 and C_{CO_x} is the sum of the outlet concentrations of CO and CO_2. All concentrations are units of ppm and the data were recorded by an online gas chromatograph after the plasma starting for 30 min, which was a stabilized state for toluene removal.

2.2. Plasma system

The cylinder reactor was made of quartz glass, with a length of 180 mm, inner diameter of 10 mm and wall thickness of 1 mm. The quartz cylinder was wrapped by copper wire as the ground electrode, delimiting the length of the discharge zone to 30 mm. A stainless-steel rod with a diameter of 2 mm was used as the inner electrode and was connected to an AC high-voltage power supply that varied from 0 to 15 kV at a frequency of 50 Hz, resulting in a discharge gap of 4 mm. The applied voltage and current of the reactor were measured by a high-voltage probe and a digital power meter. The discharge power was the product of the applied voltage and the current [14,33–35]. The SED was calculated from the following expression:

$$\text{SED (J/L)} = \frac{\text{discharge power (W)}}{\text{gas flow rate (L/s)}}$$

All of the experimental results were compared based on specific energy density (SED) in this investigation.

2.3. Catalyst preparation

Catalysts were prepared via impregnation using SBA-15 (Nanjing XFNANO Materials Tech Co., Ltd.) as the support and iron nitrate ethanol solution of the desired concentration as the precursor. The support was stirred in the iron solution for 24 h at room temperature, and the solvent was then removed by evaporation at 60 °C. The residue was dried at 120 °C for 12 h, and calcined at 500 °C for 4 h. The resulting catalysts contained 1%, 3% and 5% (wt.%) iron loading and were denoted as 1%FeO_x/SBA-15, 3%FeO_x/SBA-15 and 5%FeO_x/SBA-15, respectively.

2.4. Catalyst characterization

SEM microphotographs were obtained with an S-3700N electron microscope (Hitachi, Japan) operating at 5.0 kV.

XRD patterns were collected using a D8 ADVANCE X-ray diffractometer (Bruker, Germany) with Ni-filtered Cu $K\alpha$ radiation ($k = 0.15418$ nm) in the 2θ range of 0.6 to 5° and 5 to 90° at a scanning rate of 4° min^{-1}. The X-ray tube was operated at 40 kV and 40 mA.

N_2 adsorption–desorption isotherms were measured at −196 °C using a Micromeritics ASAP 2020 system. The sample (0.1 g) was pretreated for 6 h at 300 °C in a vacuum system, and the Brunauer–Emmett–Teller (BET) equation (relative pressure between 0.06 and 0.20) was employed to calculate the specific surface areas. The pore size and pore volume were calculated from the adsorption branches of N_2 physisorption isotherms and the Barrett–Joyner–Halenda (BJH) model.

The composition of elements and their valences on the catalyst surface were analyzed by XPS using an ESCALAB 250 spectrometer (Thermo Fisher Scientific, USA) equipped with a hemispherical