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Toluene abatement through adsorption and plasma oxidation using ZSM-5 mixed with γ-Al_2O_3, TiO_2 or $BaTiO_3$

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ABSTRACT

Toluene abatement through adsorption and then plasma oxidation using ZSM-5, ZSM-5-γ-Al_2O_3 (Z-Al), ZSM-5-TiO_2 (Z-Ti), ZSM-5-$BaTiO_3$ (Z-Ba), and AgMn/ZSM-5-$BaTiO_3$ (AgMn/Z-Ba) as adsorbents/catalysts was investigated. The efficiency of toluene removal reached ~100% for all the tested adsorbents/catalysts. ZSM-5 had the lowest mineralization rate (MR) of ~43%, while Z-Ba had the highest MR (88%) with an S_{CO2} of ~80%. After loading AgMn onto Z-Ba, both the breakthrough capacity of toluene and S_{CO2} was increased, while the production of byproduct O_3 and MR was decreased. The mixed materials created a higher amount of active species capable of deeply oxidizing adsorbed toluene.

Introduction

Dielectric barrier discharge (DBD) plasma, which can create a large uniform area of plasma at atmospheric pressure, has been extensively studied for decomposition of air-borne volatile organic compounds (VOCs) [1,2]. However, DBD-based techniques are impractical due to their high energy costs, low CO_2 selectivity, undesirable byproducts and low tolerance of humidity [3,4]. To overcome these issues, catalyst packed-bed DBD reactors have been used to increase CO_2 selectivity and reduce the amount of byproducts [5,6]. Moreover, when catalyst packed-bed DBD reactors are operated using adsorption followed by plasma oxidation, the energy efficiency notably improved for low concentrations of VOCs removal [7,8]. The performance of the catalysts may be improved by plasma oxidation because plasma oxidation technique was used for catalysts preparation such as Cu_2O film growth [9,10] and the synthesis of supported nano-catalysts [11].

In sequential adsorption-plasma oxidation system, low concentrations of VOCs are first adsorbed, enriching on the packed adsorbent/catalyst (plasma off), and then the adsorbed VOCs are oxidized into CO_2 by plasma (plasma on). When optimizing DBD reactor performance, in addition to controlling different operating conditions, including discharge gap, applied voltage, and discharge gas, using an adsorbent/catalyst that is both highly adsorbent and a good plasma oxidation assistant is critical. As the adsorption capacity of the adsorbent/catalyst increases, more VOCs can be adsorbed in the discharge region, which lowers energy consumption [9]. In addition, the better the plasma oxidation, the more VOCs can be oxidized into CO_2 with fewer byproducts. Hydrophobic zeolites are highly adsorbent for most VOCs in the presence of humidity [12–14], and many studies have used zeolite loaded metals and/or metal oxides for plasma catalytic oxidation of VOCs [3,15,16]. However, the relatively small dielectric constant of zeolites (1.5–5) causes poor plasma catalytic oxidation performance [17]. Materials with a high dielectric constant, such as γ-Al_2O_3, TiO_2, or $BaTiO_3$, have better plasma oxidation performance [18–20]. A packed adsorbent/catalyst with a higher dielectric constant can decrease breakdown voltage and enhance the electric field, thus resulting in more active species for VOC oxidation [21]. However, the adsorption capacity of an adsorbent/catalyst with higher dielectric constant is lower than zeolites due to a smaller Brunauer–Emmett–Teller (BET) surface area. Dou et al. combined ZSM-5, TiO_2, and Al_2O_3 to increase plasma oxidation performance [22]. In our previous study, the zeolite HZSM-5 was mixed with γ-Al_2O_3 to serve as adsorbent/catalyst and used in adsorption followed by plasma oxidation system, resulting in a higher toluene mineralization rate compared to HZSM-5 or γ-Al_2O_3 alone [17]. To obtain an appropriate adsorbent/catalyst

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that has both high adsorption capacity and high plasma oxidation capability, adding materials with high dielectric constant into zeolite is required and needs to be further studied.

In the present study, the zeolite, ZSM-5 was mixed with γ-Al_2O_3, TiO_2, or $BaTiO_3$ used as adsorbent/catalyst for removal of toluene by adsorption followed by plasma oxidation system. The performance of each adsorbent/catalyst was assessed based on breakthrough capacity, mineralization rate, CO_2 selectivity, removal efficiency, and byproduct formation. Furthermore, the selected material was loaded with Ag and Mn, because Ag and Mn have been extensively studied and shown to improve CO_2 selectivity and reduce byproduct formation [16,23,24]. Finally, the reasons for the different levels of adsorption and plasma oxidation observed for the studied adsorbents/catalysts are discussed, where surface area and discharge characteristics are taken into account.

Experimental

Catalyst preparation and characterization

ZSM-5 (Nankai Catalyst Co., China), γ-Al_2O_3 (Shanghai Youxin Zeolite Co., Ltd., China), TiO_2 (Guangdong Guanghua Sci-Tech Co., Ltd., China), and $BaTiO_3$ (Shanghai Macklin Biochemical Co., Ltd., China) were dried at 393 K for 3 h prior to use. The ZSM-5 was composed of SiO_2 and γ-Al_2O_3 with molar ratio of 360:1. The individual components in ZSM-5-γ-Al_2O_3 (Z-Al), ZSM-5-TiO_2(Z-Ti), and ZSM-5-$BaTiO_3$ (Z-Ba) were bonded at mass ratio of 1:1 using a binder. For example, when synthesizing Z-Ba, ZSM-5, $BaTiO_3$, and binder powders were mixed at a mass ratio of 1:1:0.4. Then, deionized water (30% mass ratio of the total amount of powder) was mixed into the powder before tableting. Subsequently, samples were dried at 378 K for 2 h prior to calcination at 773 K for 2 h. Finally, the synthesized particles were crushed and sieved through 40–60 meshes.

Mn-Ag/ZSM-5-$BaTiO_3$ (Mn-Ag/Z-Ba) catalysts were prepared by using the wetness impregnation method. Detailed synthesis information for Mn-Ag/Z-Ba was as follows: Firstly, ZSM-5 was impregnated with an $Mn(NO_3)_2$ solution and then incubated for 24 h at room temperature. Water was removed at 353 K by vigorously stirring in a thermostatic water bath. The obtained sample was calcinated for 3 h at 773 K after dried for 6 h at 393 K. Subsequently, Ag was loaded as previously described for Mn using an $AgNO_3$ solution. Mn and Ag were loaded onto ZSM-5 at ~5 wt%, respectively. Finally, the Mn–Ag/Z-Ba was obtained when AgMn/ZSM-5 was mixed with $BaTiO_3$ using a binder as described for Z-Ba preparation.

The specific surface areas of the adsorbents/catalysts were determined by measuring N_2 adsorption–desorption at 77 K using the BET method (V-Sorb X800, China). Briefly, ~0.1 g of sample was placed in the degas port of an adsorption apparatus and degassed at 353 K for 1 h and then at 473 K for 4 h. The X-ray diffraction (XRD) patterns of the adsorbent/catalyst were collected with an XRD analyzer (D/MAX-2400, Japan) using radiation from Cu-Kα and a scanning speed of 0.02°/s. The XRD patterns of each material remained unchanged after combing the materials.

Experimental system

The experimental system is presented in Fig. 1. Compressed air was passed through a drying tube to remove water vapor and other impurities from the air. Pure liquid toluene was injected into the system at a constant rate using an injection pump and volatilized using a temperature controlled bath (353 K). The inlet concentration of toluene (C_{in}) was fixed by controlling the airflow rate through a mass flow controller and injected rate of toluene. Sequential adsorption and plasma oxidation experiments were carried out in a fixed-bed reactor loaded with adsorbent/catalyst (40–60 mesh) in the discharge gap. The coaxial cylindrical reactor was made of quartz glass (10 mm inner diameter, 12 mm outer diameter, and 150 mm length) that was wrapped with copper sheet (50 mm length) to serve as a ground electrode and had a stainless steel rod (0.8 mm diameter) placed in the center to serve as a high voltage electrode. High voltage alternating current (0–23 kV, 50 Hz) was used to generate non-thermal plasma. The adsorption and plasma oxidation experiments were conducted under dynamic conditions at room temperature and atmospheric pressure. An oscilloscope with a 1000:1 voltage probe (TektronixDPO3054, TektronixP6015A) was used to measure the voltage and current of discharge as shown in the circuit diagram in Fig. 2. The C_7H_8, CO_2,

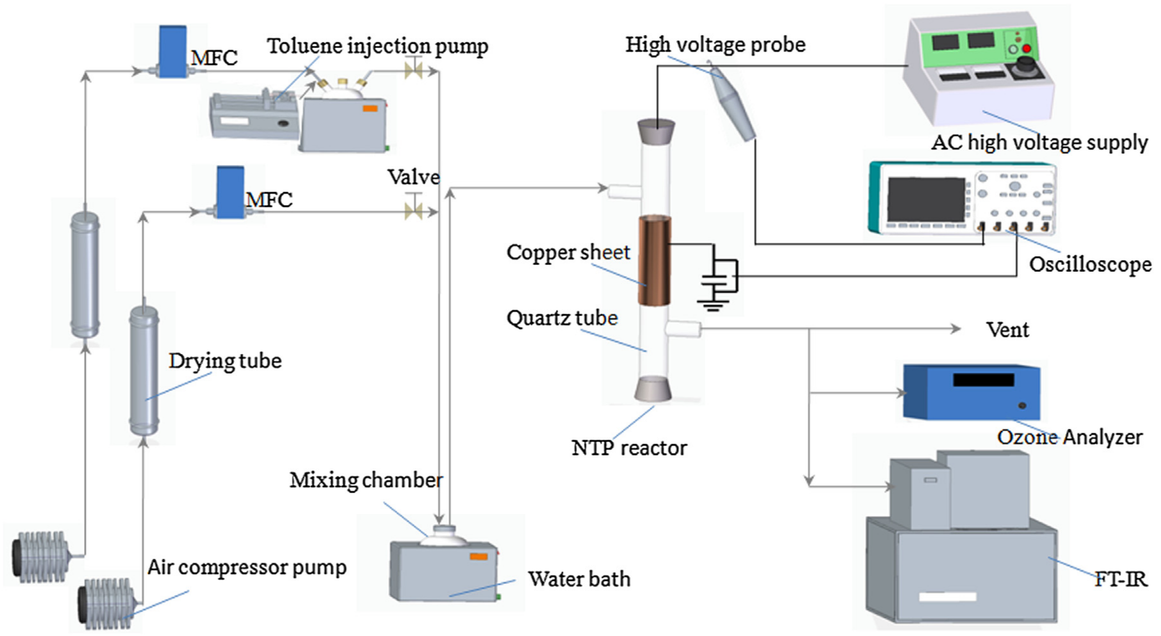

Fig. 1. Schematic of the experimental system.

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