Post-plasma-catalytic removal of toluene using MnO_2–Co_3O_4 catalysts and their synergistic mechanism

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HIGHLIGHTS

- Toluene was broken in the post-plasma-catalytic system over MnO_2–Co_3O_4 catalysts.
- The Mn/Co molar ratio affected the characteristics of MnO_2–Co_3O_4 catalysts.
- The catalysts addition could improve the reaction performance significantly.
- A possible toluene degradation pathway in the hybrid system was proposed.

GRAPHICAL ABSTRACT
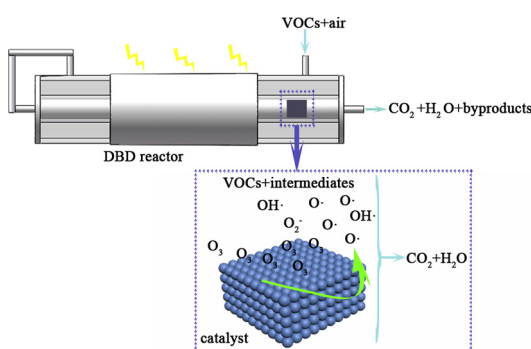
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ABSTRACT

To improve toluene removal efficiency and reduce unnecessary reaction products, a system combining a dielectric barrier discharge reactor with MnO_2–Co_3O_4 catalysts was developed. The addition of a catalyst enhanced the toluene removal efficiency, energy yield (EY), CO_x yield and CO_2 yield, and markedly suppressed O_3 and NO_2 generation compared with the non-thermal plasma (NTP) alone system. The Mn/Co molar ratio could alter the physicochemical properties of the catalysts and further influence their catalytic activity. The Mn1Co1 catalyst demonstrated the highest catalytic activity, which might be ascribed to the interactions of Mn and Co species (such as crystal structure, oxygen mobility and redox pairs of Mn^{4+}/Mn^{3+} and Co^{2+}/Co^{3+}). In the post-NTP-catalytic system over Mn1Co1 catalyst, the toluene removal efficiency, EY, CO_x yield and CO_2 yield were increased by 26.77%, 1.76 g kWh^{-1}, 25.65% and 21.07%, respectively, compared with that in the NTP alone system at specific energy densities of 423.58 J L^{-1}, 92.59 J L^{-1}, 456.76 J L^{-1} and 456.76 J L^{-1}, respectively. The pathway of toluene degradation in the post-NTP-catalytic system over Mn1Co1 catalyst was also investigated to further understand the synergistic effect of the hybrid system.

1. Introduction

Volatile organic compounds (VOCs) are mainly emitted from various industrial sources and are responsible for numerous human health and environmental problems [1–3]. Relevant environmental policies have been revised and implemented to limit atmospheric VOC emissions [4–6]. To date, numerous technologies (such as condensation, adsorption, catalytic combustion and membrane separation) have been
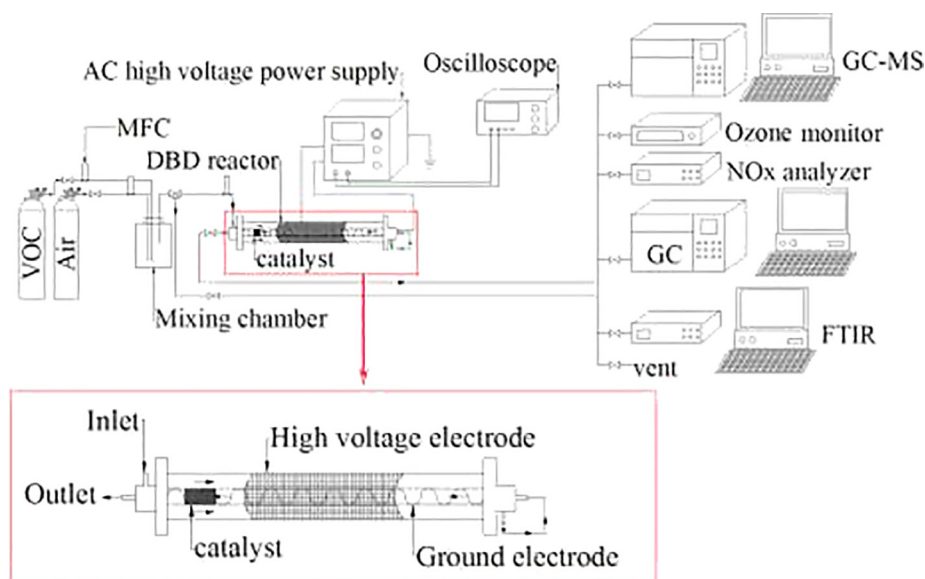

Fig. 1. Schematic diagram of the experiment.

employed to treat high concentrations of VOCs, but these technologies have been limited by their high cost and inefficiency [7,8].

Non-thermal plasma (NTP) is a developing technology that has several potential applications. Studies have highlighted its unique advantages [9–11], such as its high-efficiency treatment of low concentrations of VOCs, rapid reaction time, wide range and distinctive ability to initiate physicochemical reactions at room temperature and ambient pressure [12,13]. This technology proceeds by high-energy electrons and highly reactive species that are generated in the NTP system [14]. However, its industrial applications are restricted by incomplete oxidation and undesirable byproducts (such as O_3 and NO_x) [7]. To overcome these limitations, a new method that combines NTP with heterogeneous catalysis has been proposed, where the catalyst is placed either in or downstream from the NTP discharge region [15,16]. The major strength of this method lies in the synergistic effect generated by the two technologies, which can encourage the mineralization of VOCs and reduce the formation of undesired byproducts. The unwanted byproducts may be more harmful than the original pollutants, thus, identifying and to determining the formation pathway of such byproducts is imperative to ensure that their formation can be reduced.

A post-NTP-catalytic system can take advantage of the O_3 emitted from an NTP system to form active oxygen species, which can strengthen VOCs oxidation [17]. Therefore, when using such a system, selecting a desirable catalyst is crucial to the effective decomposition of O_3. Manganese oxides have been introduced into the NTP-catalytic system as environmentally friendly catalysts owing to their polymorphism, polyvalence and high oxygen storage capacity [18,19]. Multi-metal combination oxides can improve the structure and enhance the catalytic activity more than monometallic oxides owing to the potential complementary advantages of different metals. Zhu et al. [20] reported that the introduction of Mn–Ce oxide catalyst could improve the methanol removal efficiency and inhibit the formation of major byproducts. The acetaldehyde removal efficiency and the carbon-dioxide selectivity were enhanced significantly in the post plasma-catalytic system over MnO_2/Al_2O_3 catalysts [21]. Li et al. [22] pointed out that the Co–OMS–2/Al_2O_3 exhibited the most favorable catalytic activity among the M-OMS-2/Al_2O_3 catalysts (M = Co, Ce, Cu) in the post-catalytic system in terms of aldehyde decomposition. Recently, the Mn–Co oxide catalyst has been investigated because of its higher active site and superior oxygen storage capacity compared with single metal oxides [23]. However, limited thorough and systematic studies have been conducted to investigate NTP combined with Mn–Co oxide

catalyst to degrade VOCs. The synergistic effect between NTP and Mn–Co oxide catalyst in the oxidation of VOCs is unclear, and studies to identify and eliminate multiple byproducts and intermediates are limited. The reaction mechanism of VOCs degradation in a post-NTP-catalytic system could be conductive to a deeper understanding of the synergistic interactions between NTP and catalysts. Furthermore, this could guide an improved application of the NTP-catalytic system.

In the present study, toluene was chosen as a representative VOC because it is employed extensively as a solvent and high-octane gasoline additive and as a crucial raw material for organic chemicals. A post-NTP-catalytic system was developed for toluene decomposition using a dielectric barrier discharge (DBD) reactor with MnO_2–Co_3O_4 catalysts with different Mn/Co molar ratios. The removal efficiency of toluene, energy yield (EY), carbon dioxide and carbon monoxide yield (CO_x yield), CO_2 yield and byproducts (O_3 and NO_2) generation as a function of specific energy density (SED) were selected as indexes. The reaction performances of the NTP system with and without catalysts were compared. The gas products of toluene degradation in the NTP and post-NTP-catalytic system were analyzed to explore the viable synergistic mechanism of the reaction, which provided insights into toluene destruction in the post-NTP-catalytic system.

2. Material and method

2.1. Experimental setup

Fig. 1 illustrated the three parts of the experimental setup: the gas-supply system, the post-NTP-catalytic system, and the gas-analysis system. The DBD reactor (Nanjing Suman Electronic Co., China) comprised a high-voltage electrode (150-mm long stainless-steel mesh) and a ground electrode (stainless-steel wire, 1-mm outer diameter). The high-voltage electrode was wrapped around a quartz tube (30 mm × 300 mm) and the ground electrode was coiled around the inner surface of the quartz tube with an external diameter of 14 mm. The discharge gap was filled with 5 mm of glass beads. The DBD reactor was powered by an alternating-current high-voltage power supply (CTP-2000 K, Nanjing Suman Electronic Co., China). All electrical signals were detected using an oscilloscope (Tektronix MDO3012). The classical V-Q Lissajous method was used to calculate the input discharge power of the DBD reactor.