Catalysis Communications 113 (2018) 36–40

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Plasma-assisted oxidation of toluene over Fe/zeolite catalyst in DBD reactor using adsorption/desorption system

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ARTICLE INFO

Keywords:
Plasma-catalyst hybrid system
DBD plasma
Fe/zeolite
Toluene oxidation
Adsorption/desorption process

ABSTRACT

Fe/ZSM-5 and Fe/Beta catalysts were applied to the oxidation of toluene in the DBD plasma-catalyst hybrid system using two-step adsorption/desorption process. Desorption and oxidation activity of the adsorbed toluene was affected significantly by both catalyst properties and process variables. Pore volume, Fe content, and Si/Al ratio of the catalyst influenced the formation of products by changing the interaction between the catalyst and the plasma species. The desorption process time was also controlled by varying the concentration of O_3 and the air flow rate. Consequently, these results could contribute to advance the plasma-catalyst system with an optimal VOCs oxidation efficiency.

1. Introduction

Volatile organic compounds (VOCs) are being produced through various industrial processes including semi-conductor manufacturing process and many chemical processes which involve organic solvents [1]. VOCs are categorized as hazardous air pollutants for causing various health problems and having harmful effects on the ecosystem [2–4]. Additionally, VOCs undergo photochemical reactions in atmosphere which produce secondary pollutant species such as ozone [5,6]. Hence, it is essential to remove the VOCs in industrial exhaust gases before emission to atmosphere.

Among many modern VOC removal methods, non-thermal plasma (NTP) has attracted much attention as a promising process for VOC removal [7–10]. The NTP method is known to be cost-efficient and easy to adopt because it can be operated at a room temperature and atmospheric pressure. However, production of undesirable byproducts such as O_3 and NO_x still needs to be overcome [11,12]. As a promising solution to this problem, integration of various metal oxide and noble catalysts such as MnO [13–16] and Ag [17] into the NTP system is under active research. It has been reported that reduction in byproducts and improvement in CO_2 selectivity along with enhanced energy efficiency could be achieved through the integrated NTP-catalyst system. Furthermore, zeolites are known to be able to oxidize VOCs by ozone [18,19]. Several studies investigated the VOC removal method using Fe/zeolite catalyst [20–23]. It has been reported that Fe/zeolite catalyst showed high effectiveness for the oxidation of the adsorbed ethylene [21].

In general, the exhaust gas stream in industries contains ppm level of VOCs concentration. Hence, the exhaust gas treatment is commonly composed of two sequential steps [7,24]. First step is the VOCs concentration where VOCs get selectively adsorbed onto adsorbents. Second step is the combustion where the adsorbed VOCs are oxidatively removed and the adsorbents are regenerated. However, this two-step VOCs removal process suffers from low energy efficiency because the second step particularly requires a significant amount of heat supply to maintain a high temperature for desorption and complete oxidation of VOCs [7]. Alternative VOCs removal process has been proposed to overcome this problem. It has been reported that a continuous removal system with dielectric barrier discharge (DBD) plasma which is one type of NTP could enhance the energy efficiency but the DBD plasma system still has a low carbon balance problem [8–10,24]. Therefore, a two-step adsorption/desorption DBD system is conceived in an effort to overcome both limitations of the low energy efficiency and low carbon balance. In the study by Xiaoxin Xu et al. [24], a continuous DBD system and a two-step adsorption/desorption DBD system were directly compared for toluene removal. The authors found that the two-step adsorption/desorption DBD system resulted in the less amount of byproducts with carbon balance as high as 80%.

In this work, with insight from the prior findings, we examined the effect of catalyst properties and reaction process variables to find an optimal oxidative VOCs removal system with improved energy efficiency, CO_2 selectivity, and carbon balance. We used a two-step

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https://doi.org/10.1016/j.catcom.2018.05.013
Received 20 March 2018; Received in revised form 17 May 2018; Accepted 22 May 2018
Available online 23 May 2018

Table 1
Physicochemical properties of the catalyst.

	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)	H_2 consumption (mmol/g)	Fe contents (wt%)
H-ZSM-5	345.8	0.15	17.6	–	–
2 wt% Fe/ZSM-5	372.0	0.17	18.4	0.196	2.14
5 wt% Fe/ZSM-5	362.3	0.17	19.6	0.947	5.16
2 wt% Fe/Beta	596.6	0.87	57.7	0.228	2.12
5 wt% Fe/Beta	587.8	0.90	60.4	0.957	5.01

adsorption/desorption DBD plasma-catalyst system for high energy efficiency and applied Fe/zeolite catalyst to utilize ozone and NO_x generated by plasma for effective oxidation.

2. Experimental

2.1. Catalyst preparation

Fe/ZSM-5 and Fe/Beta catalysts were prepared by an impregnation method. Fe content was controlled to be 2 wt% and 5 wt%. A proper amount of $FeCl_3{\cdot}6H_2O$ (Osaka) was dissolved in a distilled water. Then, NH_4ZSM-5 (Albemarle, SiO_2/Al_2O_3 = 29) was added into the solution and aged for 1 h. After aging, the solution was dried in a dry oven at 120 °C for 12 h. Finally, the dried powder was heated with a ramping rate of 5 °C/min up to 550 °C and calcined at 550 °C for 3 h in an air atmosphere. Likewise, Fe was impregnated on NH_4Beta (CP814E, Zeolyst, SiO_2/Al_2O_3 = 25). The prepared powder catalyst was then pelletized with a pelletizer and, granulized and sieved with a 1 mm mesh.

2.2. Catalyst characterization

The surface area and pore volume of the catalyst were measured by N_2 adsorption-desorption analysis at 77 K with an ASAP 2420 (Micromeritics, USA). The surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The pore volume and pore size were determined according to the Barrett-Joyner-Hallender (BJH) model. Temperature programmed reduction (H_2-TPR) measurement was carried out using an AutoChem II (Micromeritics, USA) instrument. The sample was pretreated at 800 °C for 30 min under air flow and then cooled down to 50 °C under He flow. For the TPR study, the temperature increased from 50 °C to 800 °C at a heating rate of 10 °C/min under a flow of 10% H_2 in Ar mixed gas (50 mL/min). The H_2 consumption was determined using a thermal conductivity detector. Fe content of the catalyst was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis (SHIMADZU, Japan).

2.3. Toluene oxidation in DBD plasma-catalyst hybrid system

DBD plasma was generated by an AC continuous power supply (TTI, TGA 1244) with 2 kHz frequency sinusoidal AC input. A high voltage amplifier (Trek, Model 20/20C) was used to supply 9 kV to maintain 1.5–2.5 W power consumption. A high voltage probe (Tekrtonix, P6015A) and an oscilloscope (Tektronix, DPO 5054) were utilized to measure discharge voltage, to monitor current pattern, and to obtain Lissajous plot subsequently to calculate the energy supplied into the plasma system.

A cylindrical alumina reactor was used and reactor wall acted as a dielectric barrier for generating DBD plasma. Then a stainless steel rod as a high voltage electrode was inserted into the reactor so that it is located at the center of reactor axially. The axial distance from the electrode rod surface to the reactor wall was 0.5 cm. The outer surface of the reactor was wrapped with a stainless steel plate which acted as an outer ground electrode to form a plasma zone. Volume of the plasma zone was 4 mL and a proper amount of catalyst filled the plasma zone.

A mixed gas of 1000 ppm toluene in air was used as a reactant gas. The reactant gas was introduced for 2 h with a flow rate of 200 mL/min in order to make toluene adsorb onto catalyst. Once toluene is concentrated on the catalyst, synthetic air was flowed at a rate of 50 mL/min to induce desorption of toluene and DBD plasma was discharged to oxidize the desorbed toluene for 3 h. Gas composition was analyzed by a micro gas chromatograph (Agilent, 490 Micro GC) and an ozone detector (Ozonetech, OM-1500B) attached on-line to the reactor outlet stream. CO_x and other products selectivity, and carbon balance are calculated by following equations.

$$\text{Selectivity for } CO_x(\%) = \frac{\textit{moles of } CO_x \textit{ formed}}{\textit{total moles of products}} \times 100 \quad (1)$$

$$\text{Selectivity for } C_xH_y(\%) = \frac{\textit{moles of } C_xH_y \textit{ formed}}{\textit{total moles of products}} \times 100 \quad (2)$$

$$\text{C} - \text{Balance}(\%) = \frac{\textit{total number of C in products}}{\textit{number of C in toluene adsorbed}} \times 100 \quad (3)$$

3. Results and discussion

3.1. Effect of catalyst properties on toluene oxidation in the DBD plasma-catalyst hybrid system

Fe/ZSM-5 and Fe/Beta catalysts were prepared to examine the effect of pore properties of the catalyst on the oxidation of toluene in the DBD-catalyst hybrid system. Particle size of the catalyst was controlled to be 1 mm and packing density of the catalyst was then calculated by measuring weight and volume of the packed catalyst. All the catalysts showed the similar packing density (ca. 0.40 g/mL). Fe/ZSM-5 showed lower pore volume and surface area than Fe/Beta, as listed in Table 1. Fig. 1 shows the catalytic performance of Fe/ZSM-5 and Fe/Beta in the toluene oxidation using DBD plasma-catalyst hybrid system. It has been reported that the greater the surface area, the greater the catalytic

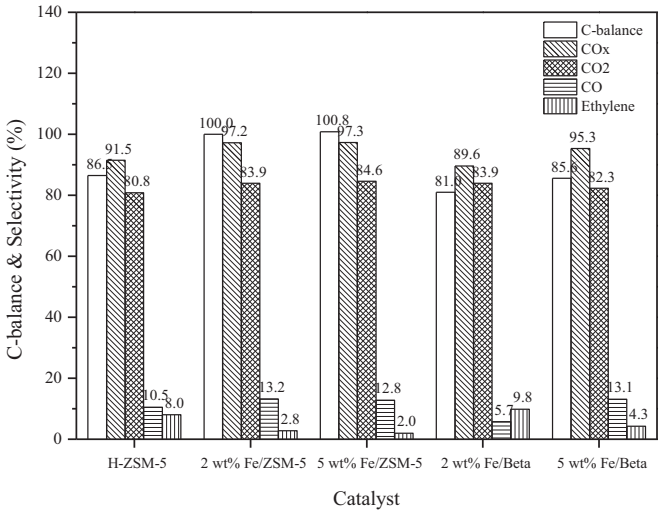

Fig. 1. Catalytic performance of Fe/ZSM-5 and Fe/Beta in toluene oxidation using DBD plasma-catalyst hybrid system.