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Investigation of hybrid plasma-catalytic removal of acetone over CuO/γ-Al_2O_3 catalysts using response surface method

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HIGHLIGHTS

- Acetone removal was improved using CuO/γ-Al_2O_3 catalysts in a plasma reactor.
- 5 wt% CuO/γ-Al_2O_3 exhibited the best plasma-catalytic performance for the removal of acetone.
- Response surface method was used to evaluate the importance of different operating parameters.
- The gas flow rate was the most significant factor to determine the removal efficiency of acetone.
- The initial concentration of acetone played the most important role in the energy efficiency.

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ABSTRACT

In this work, plasma-catalytic removal of low concentrations of acetone over CuO/γ-Al_2O_3 catalysts was carried out in a cylindrical dielectric barrier discharge (DBD) reactor. The combination of plasma and the CuO/γ-Al_2O_3 catalysts significantly enhanced the removal efficiency of acetone compared to the plasma process using the pure γ-Al_2O_3 support, with the 5.0 wt% CuO/γ-Al_2O_3 catalyst exhibiting the best acetone removal efficiency of 67.9%. Catalyst characterization was carried out to understand the effect the catalyst properties had on the activity of the CuO/γ-Al_2O_3 catalysts in the plasma-catalytic reaction. The results indicated that the formation of surface oxygen species on the surface of the catalysts was crucial for the oxidation of acetone in the plasma-catalytic reaction. The effects that various operating parameters (discharge power, flow rate and initial concentration of acetone) and the interactions between these parameters had on the performance of the plasma-catalytic removal of acetone over the 5.0 wt% CuO/γ-Al_2O_3 catalyst were investigated using central composite design (CCD). The significance of the independent variables and their interactions were evaluated by means of the Analysis of Variance (ANOVA). The results showed that the gas flow rate was the most significant factor affecting the removal efficiency of acetone, whilst the initial concentration of acetone played the most important role in determining the energy efficiency of the plasma-catalytic process.

1. Introduction

Acetone, one of the most abundant oxygenates in air, has been widely used as paint thinner, solvent and raw material in chemical industry. The emission of acetone has negative effects on both the global environment and human health (Koppmann, 2008). Exposure to acetone can cause dizziness, unconsciousness and nausea (Flowers et al., 2003). Great efforts have been devoted to technology research and development to meet the stringent regulations for air pollution control. However, conventional technologies including catalytic combustion, regenerative oxidation, photo-catalytic oxidation, adsorption and condensation are not cost-effective for the removal of low concentrations of acetone in high volume waste gas streams (Schnelle Jr. and Brown, 2001).

For the last two decades, non-thermal plasma (NTP) has been regarded as a promising gas cleaning technology for the abatement of low concentration volatile organic compounds (VOCs) in high

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volume waste gas streams (Chen et al., 2009; Tu and Whitehead, 2012). Using air as a carrier gas, energetic electrons and a large number of highly reactive species including O, O_3, N and metastable N_2 can be generated in the plasma even at room temperature. Both high energy electrons and reactive species are capable of initiating a cascade of physical and chemical reactions, which contribute to the removal of gas pollutants. The main challenges in the industrial application of NTP for waste gas clean-up are the formation of unwanted by-products and the low energy efficiency of the plasma process (Kogelschatz, 2003; Kim, 2004). CO, CH_4, HCOOH and HCHO were found to be the major organic by-products in plasma decomposition of acetone (Lyulyukin et al., 2010; Narengerile and Watanabe, 2012; Zheng et al., 2014).

Recently, the combination of plasma and heterogeneous catalysis, namely plasma-catalysis, has been considered as a promising solution for waste gas clean-up. The presence of a catalyst in the plasma has great potential to generate a synergistic effect, which can reduce the activation energy of the reaction, enhance the removal of the gas pollutant and the selectivity of the desired final products, and minimize the formation of unwanted by-products. All of these contribute in different ways to increasing the energy efficiency of the plasma-catalytic process (Van Durme et al., 2008; Chen et al., 2009; Vandenbroucke et al., 2011). Chang and Lin (2005) reported the acetone decomposition efficiency of a plasma process to be 25% higher in the presence of TiO_2 compared to that using NTP alone. Trinh and Mok (2014) found that placing ceramic supported MnO_2 catalysts in a dielectric barrier discharge (DBD) significantly improved the removal efficiency of acetone, by 37%, at a specific energy density (SED) of 600 J L^{-1}. In our previous work, we showed that the energy yield of acetone removal (3.72 g kWh^{-1}) was 51.0% higher in the presence of γ-Al_2O_3 than when using plasma alone (Zheng et al., 2014).

Catalysts are of great significance in a plasma-catalysis system. Various catalysts have been reported for plasma-catalytic oxidation of VOCs, among which Cu-based catalysts showed their advantages over other transition metal oxide catalysts due to their low cost and comparative reaction performance (Guo et al., 2007; An et al., 2011; Wu et al., 2013; Zhu et al., 2015a). Our previous work showed that the addition of 10 wt% transition metal oxides (Ce, Co, Cu, Mn and Ni) on γ-Al_2O_3 support enhanced the removal of acetone, with the supported copper oxide catalyst exhibiting the best performance among the tested transition metals (Zhu et al., 2015b).

Although plasma-catalytic removal of acetone has been reported before, far less has been done for the optimization of the plasma-catalytic process since its reaction performance is largely affected by various operation parameters (Vandenbroucke et al., 2011; Samukawa et al., 2012). The optimization of plasma-catalytic systems in previous work has been mostly carried out via experimental approaches. The traditional univariate method fails to consider and represent the interactions between different input variables. Moreover, this method requires a large amount of experimental data to obtain the favorable sets of operating parameters for the optimization of the plasma process, which makes it time consuming and labor intensive (Aerts et al., 2013; Thevenet et al., 2014; Xu et al., 2014). Recently, response surface methodology (RSM) has drawn attention for the investigation and optimization of processes. RSM is a statistical model considering the nonlinear relationships between the multiple input and output variables based on design of experiments (DoE), which aims to predict and optimize the performance of complex systems via experiment design, model building, and evaluation of the significance of independent variables and the interactions between them. Until now, only limited work has been focused on the investigation of plasma processes using the DoE method (Butron-Garcia et al., 2015; Mei et al., 2015), while the use of DoE for the optimization of plasma-catalytic gas clean-up has not been reported before.

In this work, the effect of discharge power, gas flow rate, initial acetone concentration and Cu loading amount on the performance of the plasma-catalytic removal of acetone were investigated. Initial experiments were carried out to find an optimal Cu loading amount for the highest removal efficiency of acetone. A series of catalyst characterization techniques were performed to establish the relationships between catalyst properties and reaction performance. A central composite design (CCD) method was applied to investigate the interactions between the main process variables and to optimize the plasma-catalytic process in terms of removal efficiency and energy efficiency.

2. Experimental

2.1. Catalyst preparation and characterization

The x wt% CuO/γ-Al_2O_3 catalysts (x = 2.5, 5.0, 7.5 and 10.0) were prepared by incipient wetness impregnation using copper nitrate (Alfa Aesar, 99.5%) as the precursor. The appropriate weight of support (γ-Al_2O_3) was added to the copper nitrate solution with a concentration of 0.1 M and continuously stirred at 80 °C for 4 h. The resulting slurry was dried in an oven at 110 °C overnight, followed by calcination at 500 °C for 5 h. Pure γ-Al_2O_3 support was treated in the same way for comparison in this study. All the catalysts were sieved to 40–60 meshes prior to use.

The structural properties of the CuO/γ-Al_2O_3 catalysts, including specific surface area, average pore size and pore volume, were acquired via N_2 adsorption-desorption experiments using a Quantachrome Autosorb-1 instrument at −196 °C. The X-ray diffraction (XRD) patterns of the catalyst samples were analyzed by a Rikagu D/max-2000 X-ray diffractometer. The instrument was equipped with a Cu-Kα radiation source, with the scan conducted in the 2θ range from 10° to 80° with a scanning rate of 4° min^{-1} and a step size of 0.02°. The reducibility of the CuO/γ-Al_2O_3 catalysts was evaluated by temperature-programmed reduction with hydrogen (H_2-TPR) using a gas chromatograph (GC-1690). Each catalyst (50 mg) was pre-treated at 200 °C in a N_2 flow for 1 h before the test. The samples were then heated from room temperature to 800 °C at a heating rate of 10 °C min^{-1}. A 5% H_2/Ar flow with a flow rate of 40 mL min^{-1} was used. The amount of consumed H_2 was calculated by the integration of the H_2-TPR signals.

2.2. Experimental set-up

The schematic diagram of the experimental set-up is shown in Fig. 1. A 60 mm-long aluminum foil (ground electrode) was

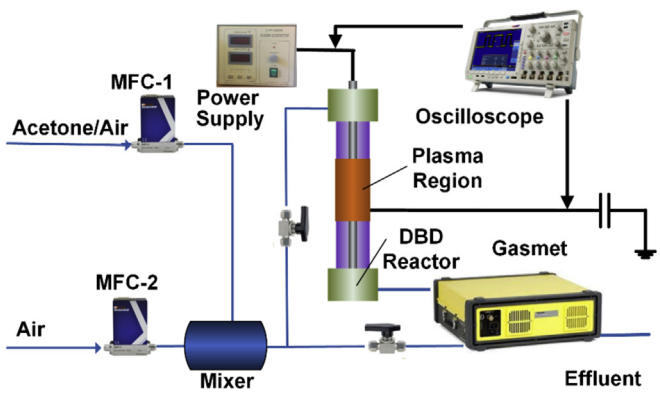

Fig. 1. Schematic diagram of the experimental setup.