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Adsorption-oxidation of hydrogen sulfide on Fe/walnut-shell activated carbon surface modified by NH_3-plasma

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ABSTRACT

Walnut-shell activated carbon (WSAC) supported ferric oxide was modified by non-thermal plasma (NTP), and the removal efficiency for hydrogen sulfide over Fe/WSAC modified by dielectric barrier discharge (DBD) was significantly promoted. The sample modified for 10 min and 6.8 kV output (30 V input voltage) maintained 100% H_2S conversion over a long reaction time of 390 min. The surface properties of adsorbents modified by NTP under different conditions were evaluated by the methods of X-ray photoelectron spectroscopy (XPS), Brunauer–Emmett–Teller (BET) analysis and *in-situ* Fourier transform infrared spectroscopy (FTIR), to help understand the effect of the NTP treatment. NTP treatment enhanced the adsorption capacity of Fe/WSAC, which could due to the formation of micro-pores with sizes of 0.4, 0.5 and 0.75 nm. XPS revealed that chemisorbed oxygen changed into lattice oxygen after NTP treatment, and lattice oxygen is beneficial for H_2S oxidation. From the *in-situ* FTIR result, transformation of the reaction path on Fe/WSAC was observed after NTP modification. The research results indicate that NTP is an effective method to improve the surface properties of the Fe/WSAC catalyst for H_2S adsorption-oxidation.

Introduction

Removal of sulfur-containing species is currently a strategic issue in the application of yellow phosphorus tail gas (Li et al., 2015; Ping et al., 2004). CO is the primary component (more than 90%) of yellow phosphorus tail gas, and is an important raw material of "one-carbon" chemical processes (Li et al., 2015). However, hydrogen sulfide (800–1100 mg/m^3) in the tail gas is obstructing the development of "one-carbon" processes. H_2S removal has important implications for the ability to obtain pure CO from yellow phosphorus tail gas. Usually, adsorption is the conventional and effective way for H_2S removal. It is well known that activated carbon is commonly used as an adsorbent in gas applications in industry (Chen et al., 2013b; Gupta and Saleh, 2013; Moreno-Castilla and Perez-Cadenas, 2010), and adsorption on activated carbon is considered to be a very effective method for removal of impurities (Bagreev and Bandosz, 2001; Bandosz, 2002).

Activated carbon (AC) can be obtained by carbonization of biomass (such as wood, bamboo, coconut shells, walnut shells), and has large surface area, huge pore volume and complex pore structure. Activated carbons with broad pore size distributions are applied for removal of large organic molecules, and microporous carbons are used for adsorption of light gases. The specific surface chemistry is also important in adsorption processes (Bagreev et al., 2002; Yan et al., 2002). However, compared to adsorbent metal oxides such as mesoporous-alumina, the components on the surface of AC are not sufficiently effective to

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improve the specific adsorption and catalytic processes for desulfurization (Wang et al., 2011; Xie et al., 2011). In order to enhance the adsorption and catalytic properties of activated carbon, various modification methods have been used, such as the heat treatment method (Kang et al., 2005), microwave method (Hesas et al., 2013), surface oxidation (El-Hendawy, 2003) and so on, among which the most effective is surface property modification.

In recent years, non-thermal plasma (NTP) has been increasingly used in the field of materials surface modification and new materials preparation. Compared with traditional surface modification technologies, NTP treatment is easy to operate and the process of modifying materials requires only a few minutes. It also does not produce any secondary pollution. NTP treatment can produce numerous non-equilibrium high activity particles or species. After NTP surface modification of catalyst materials, most loaded components exhibit amorphous forms, and research has found that modification has a significant impact on the size of the loaded component particles, resulting in higher metal dispersion (Di et al., 2013; Li et al., 2014; Rahemi et al., 2013b; Xu et al., 2014; Yan and Liu, 2013). Jin et al. (2014) prepared a Ni/γ-Al_2O_3 catalyst by NTP, in order to decompose the nickel nitrate into Ni oxides. Various researchers have reported on modification of surface properties by NTP. Estifaee et al. (2014) investigated the beneficial use of NTP in the synthesis of a Ni/Al_2O_3-MgO catalyst for CH_4/CO_2 reforming. The calculated surface area of the NTP-treated sample was 11% higher after treatment. In addition, Zhang et al., 2015b found that an AC sample modified by NTP had higher mercury removal efficiency, which could be due to the increase in the number of active sites after NTP modification, including carbonyl groups (C═O) and ester groups (C(O) – O – C).

Although a number of studies have reported on NTP surface modification of catalyst materials, research on surface modification of carbon materials by NTP for H_2S removal has been rarely reported. The mechanism of NTP modification also needs further study.

There are many methods to generate NTP, such as glow discharge, corona discharge, RF microwave discharge, and dielectric barrier discharge (DBD). Among these methods, DBD has been frequently used for the surface modification of carbon-based catalysts (Kodama et al., 2002; Kodama and Sekiguchi, 2006; Zhang et al., 2015a). NTP can introduce different functional groups by transformation of the discharge gas (Chen et al., 2013a; Estifaee et al., 2014; Rahemi et al., 2013a). Previous research (Li et al., 2016) showed that NH_3-plasma could introduce amino-functional groups, which could enhance desulfurization performance. In this work, NH_3-plasma generated by DBD was used to improve the adsorption/oxidation capacity of AC. We studied the influence of treatment conditions on the catalyst structure and physicochemical properties. Samples were characterized by the methods of X-ray photoelectron spectroscopy (XPS), Brunauer–Emmett–Teller (BET) analysis and *in-situ* FTIR.

1. Experimental

1.1. Materials

Walnut shell-based activated carbon was used in this study. Walnut shells were calcined under nitrogen at 973.15 K for 1 hr with the heating rate of 278.15 K/min. Then the sample was sieved to 40–60 mesh size, mixed with KOH at the ratio of 2:1, calcined in nitrogen at 973.15 K for 1 hr and washed with distilled water to a constant pH, and lastly dried at 383.15 K for 3–4 hr. The material was designated as WSAC. In our previous study, microwave-treated coal-based AC catalysts combined with metal oxides were prepared by a sol–gel method for removal of carbon disulfide (COS) and carbonyl sulfide (CS_2) (Ning et al., 2012). In the present work, WSAC loaded with 5 wt% Fe oxide was prepared by a coprecipitation method where the activated carbon was mixed with a colloid solution (analytical grade $Fe(NO_3)_3{\cdot}9H_2O$ solution and Na_2CO_3 solution were used as the colloid solution) under ultrasonication for 30 min, dried at 100°C in a blast drying oven, and calcined at 573.15 K for 3 hr in nitrogen. Finally, in order to introduce alkaline species on the activated carbon surface, which are beneficial for H_2S removal (Meljac et al., 2004; Yan et al., 2004), the catalyst was immersed in KOH at the KOH:WSAC ratio of 13%, kept under ultrasonication for 30 min, and then dried for 3 hr at 373.15 K. The catalyst was designated as Fe/WSAC.

1.2. Non-thermal plasma treatment

In this study, a coaxial cylinder type dielectric barrier discharge (DBD) non-thermal plasma reactor was used for surface modification. As Fig. 1a shows the coaxial cylinder-type reactor, consisting of the dielectric barrier (glass tube: inner diameter 14 mm, outer diameter 17 mm) and the discharge electrode. The dielectric barrier is located between the inner high voltage electrode (stainless steel tube, diameter 3 mm) and a grounded electrode wrapped on the outer wall. The reactor controls the size of the discharge gap by changing the diameter of the high voltage electrode. The width of the grounded electrode can also be changed to control the length of the discharge area.

A schematic diagram of the NTP treatment is shown in Fig. 1b. The power source used for DBD is a high-frequency plasma generator (CTP-2000P, Nanjing Suman Plasma Co., China) with adjustable frequency (5–25 kHz) and adjustable output amplitude (0–30 kV). The plasma was generated with a discharge output voltage (kV) of 2.4–8.0 kV (input voltage (V) of 10–40 V). The frequency was 7.8 kHz, and a 0.1 g sample was placed in the reactor under NH_3 for each experiment. In this paper, Fe/WSAC-10 min-5.6 kV means a sample modified for 10 min with output voltage of 5.6 kV.

1.3. Adsorbent characterization

The *in-situ* Fourier transform infrared spectra (*in-situ* FTIR) were recorded on a Thermo Fisher IS50 (IS50, Thermo Fisher Scientific, USA) spectrometer equipped with a temperature-controllable diffuse reflection chamber and a high sensitivity mercury cadmium telluride (MCT) detector. The sample was placed in a micro sample holder. All the spectra were determined by accumulating 32 scans at a resolution of 4/cm. A background spectrum was taken at 333.15 K before each measurement. After this, a gas mixture containing 500 ppm H_2S was fed at a flow rate of 60 mL/min.

X-ray photoelectron spectroscopy (XPS) (PHI Quantera II, PHYCHEMI, China) was performed using Al $K\alpha$ radiation with

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