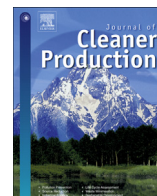




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Methyl mercaptan removal from gas streams using metal-modified activated carbon

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ABSTRACT

In this paper, removal characteristics of methyl mercaptan (CH_3SH) on virgin activated carbon and the metal-modified activated carbons (M-AC) prepared by sol-gel method were studied by using a dynamic method in a fixed bed. The detailed characterization of the catalyst has been done using Scanning electron microscope (SEM), Energy-dispersive X-ray spectrometry (EDS), X-ray photoelectron spectroscopy (XPS), and N_2 adsorption/desorption techniques. The results showed that impregnation of metal oxides on the AC significantly enhanced the removal capacity of methyl mercaptan, despite a notable decrease in microporosity. The catalytic activity of different kinds of metal-containing catalysts decrease in the following sequence: $\text{Cu-AC} \approx \text{Ni-AC} > \text{Al-AC} > \text{Fe-AC} > \text{Zn-AC}$. Moreover, calcinations temperature can influence the catalytic activity of the catalyst greatly. XPS results showed that the methyl mercaptan were oxidized by the catalyst. Sulfate species and methyl thiolate accumulated on the catalyst surface, which can block the pores and reduce the active sites.

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1. Introduction

Methyl mercaptan (methanethiol, CH_3SH , MM), a colorless gas that has an odor of rotten or cooked cabbage, is a kind of typical volatile organic sulfur in natural gas, petroleum gas, and water gas (Tangerman and Winkel, 2013; Iliuta and Larachi, 2007; Ding et al., 2014). Methyl mercaptan has a very low olfactory threshold of approximately 0.002 ppm, but at high concentrations methyl mercaptan is significantly toxic. Methyl mercaptan can poison the catalyst in synthesis of methanol and ammonia. As little as 4 mg of sulfur per gram of catalyst on the surface of the Fe-Cu-K catalyst decreases the activity by ca.50% in the Fischer-Tropsch process (Zhao-Tie et al., 1994). Thus it must be strictly removed from the feed gas. Furthermore, not only does methyl mercaptan provide economic problems, but also affect the environment. Methyl mercaptan are ultimately oxidized via sulfur dioxide to sulfuric acid in the troposphere and/or stratosphere. The formed sulfate particles alter the radiative properties of the Earth's atmosphere, potentially leading to the climate change. It can also contribute to the acid rains (Wu et al., 2010; Brühl et al., 2012; Whelan et al.,

2013). Over the past few decades, considerable efforts have sought the deep removal of methyl mercaptan in gas streams because of their potent role in the industrial catalysis and the global atmospheric chemistry.

Removal of methyl mercaptan from gas stream has been investigated by adsorption (Ryzhikov et al., 2011; Cammarano et al., 2014; Jung et al., 2014), photocatalytic oxidation (Cai et al., 2012; Li et al., 2006; Liu et al., 2008), catalytic incineration (Chu et al., 2001), decomposition ($\text{CH}_3\text{SH} \rightarrow \text{Hydrocarbons} + \text{H}_2\text{S}$) (Huguet et al., 2013), biological degradation (Liu et al., 2010; van den Bosch et al., 2009a,b; van Leerdam et al., 2011), and catalytic oxidation (Conti-Ramsden et al., 2013). However, there are a variety of advantages and disadvantages of these techniques, and they showed different degrees of cost effectiveness. Catalytic oxidation is regarded as a kind of effective method for methyl mercaptan deep-removal from natural gas due to the high desulfurization rate, moderate conditions, and low cost.

Activated carbons (AC) are well known for their exceptional ability to remove some acidic gases because of its porosity, large internal surface area and surface chemistry. The application of AC to remove methyl mercaptan is widely described in literature. T.J. Bandoz et al. (Bagreev et al., 2005; Bashkova et al., 2003, 2005) reported that methyl mercaptan adsorbed at room temperature on AC is easily oxidized to dimethyl disulfide (DMDS), which remains

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strongly adsorbed on the carbon surface. The capacity of AC is largely influenced by pore characteristics such as pore size, morphology and surface property. It has reported that the functional groups of the carbon surface can be modified either by the chemical and thermal treatments or by the impregnation method (Lee et al., 2010). In addition, alkali metals, alkaline earth metals, transition metal oxides, and rare earth metal oxides are proved to be excellent active component (Fan et al., 2013; Laosiripojana and Assabumrungrat, 2011; Park and Novak, 2013; Viviers et al., 2013; Vega et al., 2013; Laosiripojana et al., 2014).

The sol–gel deposition method renders a good distribution of the active species on the substrate (He et al., 2012; Yi et al., 2012; Habibi and Sheibani, 2013). In the present work, a series of coal–based active carbon (AC) catalysts, combined with metal oxides, were prepared by sol–gel method for methyl mercaptan removal. The aim of this work is to achieve high desulfurization effect by modified AC and understand the cause of catalyst deactivation. With that purpose, the activity of the catalyst which prepared by different modified metals and calcination temperatures was tested. Meanwhile, the chemical and physical properties of the catalyst was characterized by SEM–EDS, XPS, and N₂ adsorption/desorption. In Section 2, we have reported the details of the experiment. The preparation method of the catalyst, characterization method, and measurement of the catalytic activity were introduced. In Section 3, we have reported and discussed the experiment results. Effect of the loaded metal and calcinations temperature was investigated. In order to study the reaction mechanism, the properties of the deactivated catalyst was also studied. At the end of this paper, a possible reaction pathway was proposed.

2. Experimental

2.1. Catalyst preparation

The commercial coconut shell based AC is from the WEISHIMEI science and Technology Ltd. The AC was ground into small particles and then sieved to 40–60 mesh size. The AC was washed four times with distilled water. The catalyst was prepared with sol–gel method. Five kinds of metal–sols were prepared in this study, including Zn, Ni, Fe, Cu and Al. The preparation process is as follows. Firstly, the commercial AC was dipped in a solution of 1 M caustic potash (KOH) and boiled for 1.5 h, then washed with distilled water till there was no further change in pH, and then filtered and dried for 3–4 h at 120 °C in a drying oven. For Fe and Al, 5 ml 2 M ferric nitrate or aluminum nitrate and 5 ml 2 M sodium carbonate were mixed together and stirred. For Zn, Ni and Cu, 5 ml 2 M zinc nitrate or nickel nitrate or copper nitrate and 5 ml 0.667 M sodium carbonate were mixed together and stirred. And thus 10 ml metal–sol was prepared. Then it is mixed with 10 g AC. Therefore, 1 g AC adsorbed 1 mmol metal, denoted by 1 mmol/g. Similarly, 0.25 mmol/g, 0.50 mmol/g and 0.75 mmol/g materials can be prepared. The mixture was treated under ultrasonic wave for 30 min, followed by drying for 4 h at 110 °C. The samples were then calcinated under air flow for 3 h at 450 °C. In order to evaluate the effect of metal on the removal of methyl mercaptan, a control experiment where AC was also calcinated under air flow for 3 h at 450 °C, was established. The obtained catalysts are denoted Fe–AC, Al–AC, Zn–AC, Ni–AC, and Cu–AC, respectively.

2.2. Characterization

2.2.1. SEM–EDS

XL30ESEM–TMP (Poland) type scanning electron microscope (SEM) was used to obtain high–resolution images of the catalysts, which was used for microstructure observation of the surface. An

energy–dispersive X–ray spectrometry (EDS) was used, which was attached to the SEM system, to examine the distribution of the elements on the surface.

2.2.2. Surface area and pore size distribution

Physisorption of N₂ was performed at 77 K using a NOVA2000e (Quanta chrome instruments) surface area analyzer after the samples were degassed for 2 h at 298 K. The surface area and pore size distribution were calculated by the Brunauer–Emmett–Teller (BET) method and Barrett–Joyner–Hallender (BJH) method, respectively.

2.2.3. XPS

X–ray photoelectron spectroscopy (XPS) was performed on ESCALab220i–XL electron spectrometer from VG Scientific using Al K α radiation. The power was 300 W, with a pass energy of 50.0 eV and a step size of 0.1 eV. The data were analyzed with Xpspeak 4.1 software.

2.3. Evaluation of catalytic activity

Desulphurization tests were performed in a fixed–bed quartz reactor (10 mm i.d \times 100 mm length) under atmospheric pressure. For Methyl mercaptan removal, methyl mercaptan from the gas cylinder (1% methyl mercaptan in N₂) was diluted with N₂ to the concentration of 500 ppm. The overall flow rate was controlled using calibrated mass flow controllers. The temperature of the reactor was controlled to 50 °C over its entire length by water–bath with circulating pump, with accuracy ± 1 °C. Chemical analysis of the gas effluent stream of the reactor during desulfurizing process was done by an on line mass spectrometer (MAX 300–LG, Extrel CMS, LLC).

3. Results and discussion

3.1. Catalytic activity of different kinds of metal-containing catalysts

Fig. 1 shows the conversion of methyl mercaptan on different kinds of catalysts. After calcinations for 3 h at 450 °C, most of the metallic compounds (mainly hydroxide and nitrate) are broken down into oxides, which constitute the active sites for the adsorption and oxidation of methyl mercaptan. It is indicated that the Free–AC performs worst in the adsorption process. This is likely

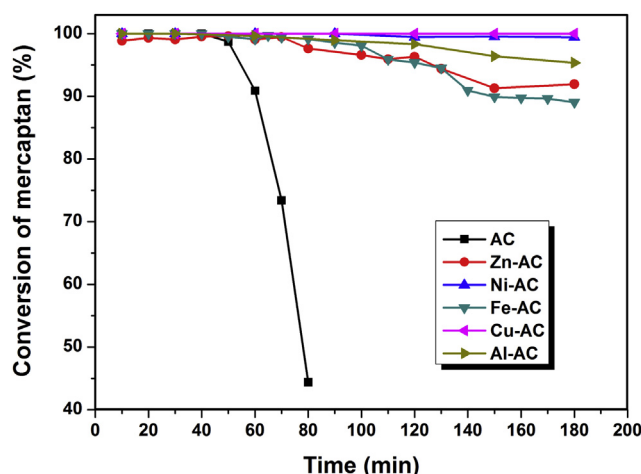


Fig. 1. Removal of the methyl mercaptan over all the prepared catalysts.

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