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Selective oxidation of hydrogen sulfide to sulfur over activated carbon-supported metal oxides

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ABSTRACT

The selective oxidation of hydrogen sulfide (H_2S) to sulfur on activated carbon-supported metal oxide sorbents (M/AC) was investigated for hot fuel gas desulfurization. Various M/AC sorbents loaded with 1 wt.% metal oxide were separately prepared by pore volume impregnation and their breakthrough capacity was examined. The results showed that the breakthrough capacity of different sorbents can be placed in the following order: Mn/AC > Cu/AC > Fe/AC > Ce/AC > Co/AC > V/AC. The metal oxides loaded on the M/AC surface catalyze the reaction between hydrogen sulfide and oxygen to form element sulfur; the activated carbon, as an adsorbent, can adsorb and store the element sulfur in its pore passage. The DTG analysis and determination of forms of sulfur confirmed that the main product of the catalytic oxidation of hydrogen sulfide was elemental sulfur. The regeneration of exhausted sorbents was carried out using hot gas N_2 and H_2O desorption methods at temperature 500 °C. The breakthrough capacity of the sorbent was mostly recovered after regeneration. The mechanism of the catalytic oxidation of H_2S on M/AC sorbent was also discussed.

1. Introduction

Gasification-based clean coal technology (CCT) is considered to be one of the most efficient and environmentally acceptable technologies for comprehensive utilization of coal. Hydrogen sulfide (H_2S), the main sulfur-containing pollutant from coal-derived fuel gas, may result in equipment corrosion, catalyst poisoning and environmental pollution. Therefore, the key part in the CCT processes is the removal of hydrogen sulfide from the coal-derived fuel gas.

For the large-scale coal chemistry processes, ambient or low temperature desulfurization technologies have been successfully used for gas purification, such as rectisol process, but there are still problems, such as high investment cost, high energy consumption and high operating cost. Especially in advanced poly-generation systems for combined electricity and chemicals production, extremely low temperature gas cleanup causes the abundant heat loss. Hot gas desulfurization (>400 °C) using metal oxide absorbents, is the current gas desulfurization technology frontier and the development direction [1,2]. However, because of the stringent requirements for sorbent mechanical strength and complex sulfur recovery process, especially the upstream process bottlenecks of high-temperature dust removal technology, it still needs to be improved for the industrial applications. At present, in advanced pressurized gasification technologies (Shell, Texaco), the water scrubbing is still an essential step. The fuel gas temperature is normally about 200 °C after the water scrubbing for raw gas. Therefore, the development of desulfurization technology at the mild temperature is more promising [3].

Activated carbon, which has large surface area, huge pore volume and complex pore structure, fulfils a dual role as a catalyst for the direct oxidation of hydrogen sulfide to sulfur and as an adsorbent for removing sulfur and its oxides from the gas stream [4,5]. Activated carbon has been used in an industrial application, but its breakthrough capacity becomes low as temperature increasing [5–9], because the higher temperature results in the poor efficiency and selectivity to produce COS and SO_2. The selectivity of activated carbon for oxidation of H_2S to sulfur is dependent on process conditions and textural, structural, and surface chemical characteristics of the carbon catalyst. The oak ridge national laboratory [5,7] reported a laboratory-synthesized carbon “WSC”, which was superior to the other carbon sorbents, can effectively remove H_2S at the temperature more than 150 °C. However, its breakthrough capacity was slightly lower than other carbons. Metal oxides are also developed as catalyst to promote the reaction between hydrogen sulfide and oxygen to form element sulfur, such as Fe_2O_3, CuO, V_2O_5, Al_2O_3, TiO_2, and Mn_2O_3 [10]. Therefore, it is possible to improve the ability of activated carbon to selectively oxidize hydrogen sulfide to sulfur by modifying it with metal

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oxides. The metal oxides can catalytically oxidize hydrogen sulfide to element sulfur; the activated carbon, as an adsorbent, can store the element sulfur in its pore passage by the adsorption. However, developing this method for catalytic oxidation removal of hydrogen sulfide in the temperature range 150–250 °C has never been reported.

In the present work, we reported on the ability of activated carbon supported metal oxide for the direct oxidation of hydrogen sulfide to elemental sulfur. Mn/AC, Fe/AC, Cu/AC, Ce/AC, Co/AC and V/AC were prepared for hot gas desulfurization and their breakthrough capacity was examined. The products of the catalytic oxidation of hydrogen sulfide on the sorbents were determined using different methods. Regeneration of the exhausted sorbent was carried out at high temperature in H_2O/N_2 atmosphere.

2. Experimental

2.1. Preparation of sorbents

Activated carbon (30–60 mesh, surface area 876 m^2/g), analytical grade $Ce(NO_3)_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2$, NH_4VO_3, $H_2C_2O_4$ were used as raw materials to prepare sorbents in this study. Various M/AC sorbents loaded with 1 wt.% metal oxide were separately prepared by pore volume impregnation of the activated carbon with aqueous solutions of nitrate salts, $Ce(NO_3)_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2$, respectively. For V/AC, the aqueous solution was made by mixing ammonium vanadate in a 0.1 N oxalic acid solution. The mixture was dried by evaporation at 60 °C for 10 h, then dried at 110 °C for 10 h, and finally calcined at corresponding temperature for 4 h in nitrogen. The conditions of the samples preparation used in this study are shown in Table 1. The activated carbon supported metal (include Fe, V, Ce, Mn, Cu, Co) oxides sorbents were denoted as M(*x*)/AC. M denotes the transition metal of the loaded oxide.

2.2. Experimental apparatus and procedure

The test was performed in a vertical fixed-bed reactor, which was composed of quartz with an inner diameter of 1.4 cm. The reactor was placed vertically in an electric furnace equipped with a PID controller. The 6 ml sorbent was placed on the fritted quartz disk in the center of the quartz reactor. The influent H_2S concentration was 3000 ppm, and was balanced by N_2. Air was introduced into the influent gas stream to keep a certain O_2/H_2S ratio as 1:1. The experiments were conducted at atmospheric pressure with a gas hourly space velocity (GHSV) of 3000 h^{-1} and a total gas flow rate of 300 ml/min. The temperature of the breakthrough tests was 180 °C. Before the experiment, pure nitrogen gas (purity 99.99%) was fed into the reactor for 30 min at experimental temperature to remove any adsorbed water and impure gaseous molecules coated on the surface of the sorbents. The inlet concentration of H_2S and the outlet concentration of H_2S, COS and SO_2 were analyzed through a gas chromatograph (GC 7890) equipped with a flame photometry detector. The breakthrough desulfurization efficiency (DE) was calculated using the following equation:

$$\mathrm{DE}(\%) = \frac{\int_0^t (C_{H_2S,in} - C_{H_2S,out} - C_{COS,out} - C_{SO_2,out})dt}{C_{H_2S,in}t} \times 100\%$$

where $C_{H_2S,in}$ is the initial concentration of H_2S of 3000 ppm, $C_{H_2S,out}$, $C_{COS,out}$, and $C_{SO_2,out}$ are the concentrations of H_2S, COS and SO_2, respectively, at the exit of the reactor.

Regeneration of exhausted sorbents was performed in the same fixed-bed reactor. The heating temperature was set at 500 °C. The regeneration mixed gas was 50% gaseous H_2O in N_2 with a total gas flow rate of 450 ml/min.

2.3. Sorption of nitrogen

Nitrogen isotherms were measured using a Tristar 3000 (Micromeritics) at −196 °C. Before the experiment the samples were heated at 120 °C and then outgassed at this temperature under a vacuum of 1.33×10^{-3} Pa to constant pressure. The isotherms were used to calculate the specific surface area, S_{BET}; micropore volume, V_{mic}; total pore volume, V_t; average pore diameter, *D*.

2.4. Thermal analysis, total sulfur and forms of sulfur analysis

Thermal analysis was carried out using Netzsch Sta 409 PC/PG Thermal Analyzer. The instrument settings were that heating rate 10 K/min and nitrogen atmosphere with a 40 ml/min flow rate. The analysis of total sulfur was carried out according to ISO 334:1992 (Solid material fuels determination of total sulfur-Eschka method, NEQ) and ISO 351:1996 (Solid material fuels determination of total sulfur – High temperature combustion method, NEQ). The analysis of the forms of sulfur was carried out according to ISO 157:1996 (coal-determination of forms of sulfur, MOD).

2.5. SEM with EDX

To study the surface morphology and chemical elements presented on the surface of AC, Mn/AC, Mn/AC exhausted, and Mn/AC regenerated, scanning electron microscope (SEM) measurements were performed using Nova Nano SEM430 (FEI, USA) with an energy dispersive X-ray (EDX) detector INCA (Oxford, British).

3. Results and discussion

3.1. Catalytic performance of the sorbents

The breakthrough curves for the sorbents are presented in Fig. 1. The breakthrough time is defined here as the elapsed time from the beginning of the H_2S concentration until the exit total sulfur concentration in the effluent gas had reached 100 ppm. There

Table 1
Preparation conditions of the sorbents.

Sorbents	Metal salts used	Loading amount (as metal per g of AC)		Calcination temperature (°C)	Calcination time (h)
		(mmol)	(wt.%)		
Fe/AC	$Fe(NO_3)_3 \cdot 9H_2O$	1.79×10^{-2}	1	300	4
Mn/AC	$Mn(NO_3)_2$	1.82×10^{-2}	1	400	4
Co/AC	$Co(NO_3)_2 \cdot 6H_2O$	1.70×10^{-2}	1	300	4
Ce/AC	$Ce(NO_3)_3 \cdot 6H_2O$	7.13×10^{-3}	1	400	4
V/AC	NH_4VO_3, $H_2C_2O_4$	1.96×10^{-2}	1	450	4
Cu/AC	$Cu(NO_3)_2 \cdot 3H_2O$	1.57×10^{-2}	1	300	4