

High Temperature Removal of H₂S over Iron Oxide Supported on SiC Sorbent

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Abstract.

A new material, Fe₂O₃ supported on high specific surface area SiC, is very efficient for the H₂S removal from hot exhaust gas. The specific properties of the silicon carbide allows a very large number of sulfidation/regeneration cycles.

1. INTRODUCTION

H₂S is produced in large amounts from the gasification of coal and also from many other industrial processes: pyrolysis, cracking, hydrocracking and hydrotreatment. The purification of the exit gas to remove H₂S is essential prior to subsequent utilization. The solid sorbents used for high temperature H₂S removal are widely investigated in the literature [1-3] which mainly deals with calcium oxide, zinc oxide, zinc ferrite or zinc titanate in an unsupported form. However, during the absorption and regeneration cycles a contraction (sulfidation) and an expansion (oxidative regeneration) occur and lead to sorbent deterioration and sintering. This is followed by a pressure drop across the bed due to the attrition of the material, reducing its H₂S removal capacity. These phenomena can be avoided by replacing the unsupported sorbent by a supported one [4,5]. Silicon carbide is well known to be an efficient heat conductor, with a high thermal resistance and a high mechanical strength, which can be efficient for the use of this material as a support for high temperature H₂S removal. In addition, silicon carbide is a chemically inert material which cannot interact with the active phase by destroying its sorbent capacity as is the case for alumina support [5].

The aim of this article is to report the preparation, the characterization and the performance of Fe₂O₃/SiC solid sorbent for high temperature H₂S removal and its stability as a function of absorption-regeneration cycles.

2. EXPERIMENTAL

The silicon carbide is synthesized by a gas-solid reaction, under dynamic vacuum, between a vapor of SiO, generated by a mixture Si + SiO₂, and a high surface area activated charcoal as described in detail elsewhere [6]. The SiC obtained by this method has a surface area of 25 m² g⁻¹. The sorbent is prepared by incipient wetness impregnation of the SiC with an aqueous solution of iron nitrate. After impregnation the sorbent is dried at room temperature for 12h and then calcinated at 400°C for 2h.

The H₂S removal experiment is performed in a flow micropilot working at atmospheric pressure and on a fixed bed. The composition of the reactant mixture is constant and contains H₂S (0.5 vol. %) and balance helium. The products from the reactor unit are analyzed on-line by gas chromatography, which allows the separation of H₂S, H₂O and SO₂. The regeneration is performed at 650°C in flowing air for 2h.

3. RESULTS AND DISCUSSION

The amount of iron oxide measured by atomic absorption spectroscopy is 15 wt. %. The surface area of the calcined sorbent (Fe₂O₃/SiC) measured by N₂ adsorption is 45 m² g⁻¹ with the pore size distribution centered between 4 and 10 nm. The iron oxide is finely and homogeneously dispersed on the support and no diffraction lines corresponding to iron oxide are observed. The presence of small iron oxide particles on the sorbent is also confirmed by magnetic measurements (Fig. 1) which show the presence of magnetic compounds and the lack of the magnetization saturation (existence of small magnetic particles).

The H_2S removal capacity obtained at 400°C on $\text{Fe}_2\text{O}_3/\text{SiC}$ is presented in Fig. 2. The H_2S removal is almost complete during the first 300 minutes of absorption and only water is detected at the exit of the reactor. At that point, the concentration of H_2S starts to rise rapidly to the inlet value of around 6200 ppmv of H_2S . The sulfur capacity breakthrough is around 90-95% of the theoretical capacity assuming the transformation $\text{Fe}_2\text{O}_3 \rightarrow \text{FeS}$.

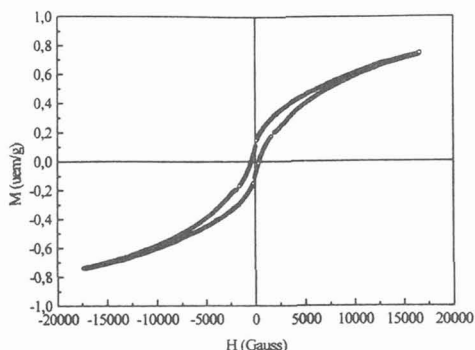


Figure 1: Magnetic measurement of the fresh sorbent after calcination at 400°C for 2h.

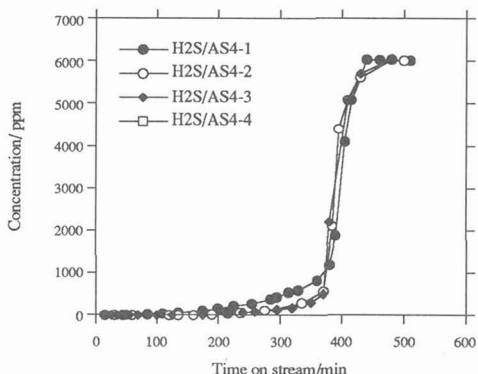


Figure 2: H_2S removal capacity as a function of the sulfidation-regeneration cycle on the $\text{Fe}_2\text{O}_3/\text{SiC}$ sorbent at 400°C and with a space velocity of 1200h^{-1} .

The high capacity for H_2S absorption is attributed to the high surface area of the sorbent which allows a high surface contact between H_2S and the iron oxide. The XRD pattern of the sorbent after absorption shows the presence of FeS_x and a small amount of FeS_2 which means that some sintering occurred during the absorption. This phenomenon is correlated by a concomitant decrease in the sorbent surface area from 45 to $27\text{ m}^2\text{ g}^{-1}$. The decrease of the surface area during sulfidation has already been reported by Groot [7] and is attributed to the structural alteration of the starting oxide. The sorbent is regenerated in air at 650°C for 2h. After regeneration all the iron sulfide is oxidized into iron oxide as observed by the XRD characterization and only SO_2 is detected at the exit of the reactor. The surface area decreased slightly from 27 to $24\text{ m}^2\text{ g}^{-1}$. The H_2S removal capacity obtained on the regenerated sorbent is identical to that obtained on the fresh one.

The stability of the sorbent as a function of the absorption and regeneration cycles is reported in Fig. 2. The reactor is flushed with helium between reactions. As shown from the results no change in the H_2S removal capacity occurred after four cycles. The surface area of the sorbent after the set of experiments decreased slightly to $17\text{ m}^2\text{ g}^{-1}$ after the second cycle and then remained unchanged for the rest of the experiments. The high stability of the sorbent is attributed to the high thermal conductivity of the silicon carbide support which prevents the formation of hot spots during the regeneration, hot spots which can be responsible for a drastic sintering of the active phase.

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