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Effect of Temperature and Water on the Selective Oxidation of H_2S to Elemental Sulfur on a Macroscopic Carbon Nanofiber Based Catalyst

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Abstract Carbon nanofibers were synthesized on graphite felt substrate by catalytic decomposition of ethane. The preshaped material was efficiently used as catalyst support for the active phase NiS_2 in the direct oxidation of H_2S into elemental sulfur. The catalyst was extremely active, selective, and stable at 60 °C in a fixed bed reactor due to the high resistance of carbon nanofiber based catalyst to the solid sulfur loading. This is explained by the specific mode of sulfur deposition, involving the role of water in the sulfur transport and the hydrophobic nature of the support.

Keywords Macroscopic support · Carbon nanofibers · H_2S oxidation · Modified claus

1 Introduction

The selective oxidation of H_2S to elemental sulfur is one of the most interesting and efficient ways of removing residual H_2S from waste gases generated by petrochemical refineries and natural gas plants [1]. This is an important reaction from the viewpoint of environmental protection due to the high toxicity of H_2S. Many methods have been developed to remove H_2S from waste emissions. A general trend is to transform H_2S into elemental sulfur by the modified Claus process. However, for a three-stage reactor, sulfur recovery efficiencies are typically only 96% due to the thermodynamic limitations of the Claus reaction [2]. Accordingly, additional removal of H_2S from tail gas is necessary to obtain an ultralow concentration.

Nowadays there are several methods available for Claus tail-gas treatments; however, they require relatively large investments and high operating costs [3]. The catalytic processes based on direct H_2S oxidation to elemental sulfur are more effective and require lower investments.

The drawbacks of the catalysts most frequently used in these processes are basically the high reactivation cost and the low selectivity for elemental sulfur. In addition, in the presence of sulfur and steam, oxide-based supports can be easily sulfated over time [4, 5].

The main advantages of carbon nanofibers over traditional catalyst supports are their high thermal conductivity, excellent chemical inertia, and absence of ink-bottle pores [6]. As a matter of fact, the nonstructural pores of these materials, formed of microvoids between the nanofibers, have the additional advantage of a higher sulfur uptake capacity [7]. On the other hand, the nanometric size of these materials can make them difficult to employ in a fixed bed, since they can induce detrimental pressure drops along the catalyst beds. In order to eliminate this disadvantage, a new material based on carbon nanofibers was developed; growing carbon nanofibers on a macroscopic precursor seems to optimally combine the structural and catalytic properties of this material [8], which will be investigated in this work during a selective H_2S oxidation to elemental sulfur.

Carbon nanofibers have no catalytic activity in hydrogen sulfide decomposition, but nickel sulfide has semiconductor properties and plays an important role as catalyst for

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this reaction. Delafosse et al. [9] proposed a catalytic mechanism for this reaction comprised of three steps assuming that there are free electrons available:

$$O_2\text{chemisorption: } {}^1\!/_2\, O_2(g) \ + e^- \rightarrow \ O^-(ads)$$

$$H_2S \text{ chemisorption: } H_2S(g) \ \rightarrow \ H_2S^+(ads) \ + e^-$$

$$O_2/H_2S \text{ interaction: } H_2S^+(ads) \ + \ O^-(ads) \rightarrow \ H_2O \ + \ S \ + e^-$$

The oxygen chemisorption is the rate-determining step, where the O_2 captures a free electron, decreasing the conductivity of the active phase.

Olivas et al. [10] observed that the chemisorption of sulfur on nickel single monocrystals at or close to a monolayer causes electron transfer from Ni to S. This rise in the electron density at the surface increases acidity and favors the binding of hydrogen atoms, creating acid S–H sites.

2 Experimental

The carbon nanofiber based catalyst support was prepared from a carbon felt precursor (Seecil Carbon Technologies) cut in a cylindrical shape, with a diameter exactly the same as the internal diameter of the catalytic test reactor. Felt disks were impregnated with 2 wt% nickel, employing a nickel nitrate (Acrōs) alcoholic solution (50% ethanol). After the incipient impregnation step, the material was dried for 12 h in a furnace at 120 °C.

The disks were placed in a quartz tube located in a horizontal oven under argon flow. The temperature was elevated from room temperature to 680 °C at a rate of 10 °C/min. At this temperature the argon was replaced by the reaction mixture containing hydrogen and ethane at a volumetric ratio of 4:1 (H_2:C_2H_6), amounting to 125 mL/min. The synthesis was carried out at 680 °C for 2 h and the carbon nanofiber yield amounted to about 100 wt% of the initial material weight. The felt surface was completely covered by a layer of carbon nanofiber, significantly increasing the specific surface area of the composite from 1 to 95 m^2/g.

In order to prepare the Claus tail-gas catalysts, the macroscopic support was loaded with 15 wt% nickel by incipient impregnation, using the same alcoholic solution employed previously. Sequentially, the material was placed in a Pirex® fixed-bed tubular reactor. Ten cylindrical catalyst disks (approximately 3.5 g) 22 mm in diameter and 0.5 mm thick were inserted into the reactor in such a way as to fit the reactor wall tightly. The reactor was positioned vertically in a Carbolite electric tubular oven in order to facilitate removal of elemental sulfur. Then the catalysts were calcined in situ at 350 °C during 2 h under He atmosphere, followed by sulfuring at 300 °C for 2 h under H_2S flow to form the NiS_2 active phase [11]. The H_2S oxidation reaction was carried out under atmospheric pressure and in the isothermal mode. The gas flow was set at 70 mL/min, an H_2S concentration of 1,000 ppm, an O_2 concentration of 2,000 ppm, and consequently a space velocity of 1,500 h^{-1} and a contact time of 2 s. The flows of reactional gases (H_2S and O_2) and the diluting gas (He) were monitored by mass flow controllers (Aalborg), whereas steam was provided by a saturator kept at the required temperature, allowing maintenance of the partial pressure of the water at 30 vol%. The analysis of outlet gases was performed on-line using a Perkin Elmer Clarus 500 Gas Chromatograph equipped with a thermal conductivity detector. A Chromosorb® 102 packed column and a sulfur detection limit of approximately 5 ppm were used in this analysis.

3 Results and Discussion

Wu et al. [12] studied the influence of the O_2/H_2S ratio on the performance of activated carbon catalyst in H_2S oxidation to elemental sulfur conducted at 150 °C. According to the authors, ratios between 0.5 and 1 are high enough to achieve a complete H_2S conversion. However, low ratios can cause the formation of COS. For this reason the authors chose a 2:1 ratio. Thus, we decided to set the O_2/H_2S ratio at 2 and the metal loading at 15 wt% Ni in this work. Under these conditions, the effects of reaction temperature (60, 120, and 180 °C) on catalyst activity and selectivity were studied with and without water. The table shows the conditions used in the tests as well as their respective results. The response labeled t_{100} was defined as the length of time the reaction maintained a 100% conversion (Fig. 1; Table 1).

The figure shows only the reaction without the addition of water (Experiments 1, 3, and 5), since the others showed higher activity, maintaining 100% conversion for at least 30 h of reaction. Analyzing the curves obtained, an increase in maximum conversion time was observed as a function of increasing the temperature from 60 to 180 °C. However, for the reaction at 120 °C, where the deactivation started earlier than that obtained for the reaction at 60 °C, this was not observed. These results show the fundamental role of water in this reaction.

Primavera et al. [13] also studied the effect of water on this reaction, employing activated carbon as catalytic support and reaction temperatures varying from 25 to 70 °C. The authors noted that the amount of sulfur that could be stored in the catalyst during the reaction was positively influenced by the presence of water. In the presence of water, the water film acted as a conveyor belt

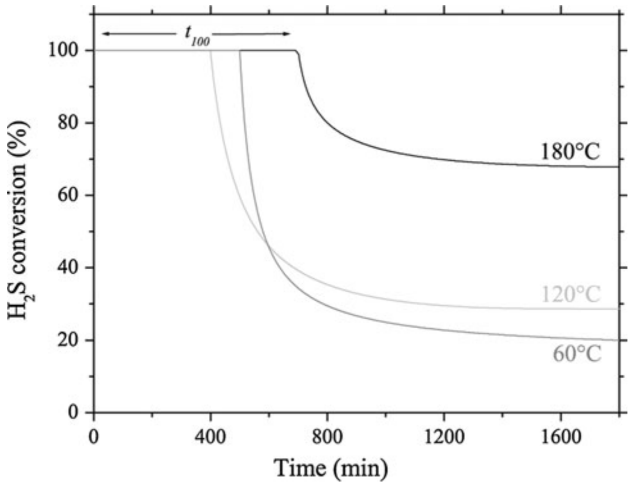

Fig. 1 H_2S conversion as a function of the time on stream at different temperatures without addition of water

Table 1 Experimental conditions adopted and H_2S conversion, where t_{100} means the length of time with a 100% conversion. The Ni content was maintained at 15% and the O_2/H_2S ratio was set at 2

Experiment	T(°C)	H_2O	t_{100} (min)
1	60	No	480
2	60	Yes	>1,800
3	120	No	390
4	120	Yes	>1,800
5	180	No	700
6	180	Yes	>1,800

to transport the sulfur particles out of the catalyst pores. In the absence of water, the solid sulfur particles were directly deposited on the active sites in the pores of the catalyst.

In previous studies other authors suggested that O_2 and H_2S dissolve in the water film and therefore the catalytic reaction takes place more quickly in the aqueous phase than in the dry catalyst [14]. Bineesh et al. [15] noted that the effect of water could be positive or negative depending on its concentration. The authors suggested that when there were very high levels of water it could compete with H_2S for the catalyst's active sites; furthermore, the yield of the reverse Claus reaction could be increased by excess water.

Keller et al. [16] described the high stability of the NiS_2/SiC catalytic system as a function of time and solid sulfur loading in the presence of water by a peculiar mode of sulfur deposition involving the role of water and the hydrophilic/hydrophobic duality of the SiC support surface. Water acts as a conveyor belt, continuously cleaning the active phase particles located on the hydrophilic oxygen-containing surfaces of the support. Therefore, hydrophobic SiC surfaces located outside the mesopores and free of active phase remain available for the storage of large amounts of solid sulfur.

In the present work, the hydrophobicity of the carbon nanofibers confirms the suggestions made by Keller et al. [16], i.e., when the water added to the gaseous flow penetrates the material, it is expelled from the tangles of carbon nanofibers carrying particles of sulfur with it, maintaining the actives sites exposed for an extra period of time. This behavior explains perfectly why the same reaction at 60 °C had 100% conversion (t_{100}) during 30 h of reaction with water, and without water the maximum conversion was maintained for only 8 h. These results show that the carbon nanofiber based catalyst has long-term stability, mainly due to the hydrophobicity of the catalytic support, but also due to its high specific surface area, large external void volume among nanofibers, and the absence of ink-bottle pores.

The role of condensed water, acting as a conveyor belt on the catalyst surface, could be seen more clearly when observing the reactions without water at 60, 120, and 180 °C (Fig. 1). In this case, an increase in temperature increased reactivity and consequently the reaction conversion. However, this was not observed for reactions at 60 °C in relation to 120 °C, for which t_{100} decreased from 480 to 390 min. This phenomenon could be explained by the fact that the direct reaction of H_2S oxidation to elemental sulfur produces water and at 120 °C water is a gas and therefore its mechanical role in removing sulfur is not carried out. For the reaction at 180 °C, extension of t_{100} over that for the reaction at 120 °C is not related to the presence of water, since in both reactions water is gaseous. This could be explained by the fact that sulfur is a gas at 180 °C and can move away from the active sites without water, leaving the catalyst 100% active for longer. In all of the tests, including at 180 °C, no sulfated products (COS, SO_2, or CS_2) other than H_2S were detected.

Finally a test was carried out to observe the activity of the catalytic system over time under the following conditions: a 15% metal content, a 60 °C reaction temperature, a 70 mL/min total gas flow, a 30% water vapor molar percentage, a 3,000 ppm H_2S concentration, a 6,000 ppm O_2 concentration, an approximately 1,500 h^{-1} spatial velocity, and a contact time of around 2 s. Under these conditions, the reaction conversion was 100% during 288 h of the test, leading to the conclusion that the presence of water is a primordial factor for maintaining catalyst activity for a prolonged period of time. At the end of the test the catalyst had a sulfur load of approximately two-thirds of its initial mass, i.e., 4.5 g of elemental sulfur were trapped for each gram of nickel.

Carbon nanofiber composites have a bimodal pore distribution. The pores in the CNF are formed of microvoids of tangled nanofibers and have a pore volume, measured by the BET method, of 0.09 mL/g with pore diameters between 3 and 5 nm. The total pore volume of the composite, obtained by helium picnometry, however, is 6.58 mL/g. This high nonstructural porosity is a great advantage for reactions with high sulfur loadings, thus making carbon nanofiber based composites an interesting alternative to traditional catalysts supports. In a preliminary study, Nhut et al. [17] showed that the desulfurization activity and resistance of the catalyst to high sulfur loading in the feed are higher than those of a traditional SiC grain based catalyst.

4 Conclusions

A catalytic support made by covering the surface of carbon felt with carbon nanofibers was successfully used in the selective reaction of H_2S oxidation to elemental sulfur, mainly due to its large nonstructural pore area and high hydrophobicity. The peculiar morphology of this new macroscopic support allowed a high sulfur load capacity of up to 150 times that of traditional catalysts. The sulfur particles resulting in the desulfurization reaction were also seen to be brought out of the nanofiber tangles by condensed water, thus leaving the active sites exposed for longer and increasing the activity and stability of the catalyst independent of the amount of sulfur stored. Thus, due to the ease with which it can be manipulated and regenerated, this material is highly recommended for industrial use as a filter to capture sulfur at low temperatures.

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