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Selective oxidation of H_2S in Claus tail-gas over SiC supported NiS_2 catalyst

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Abstract

Very high activity and selectivity could be achieved for the direct oxidation of H_2S into elemental sulfur at low reaction temperature (40–60°C), on nickel sulfide supported SiC catalyst. The heterogeneous nature of the support surface (hydrophilic and hydrophobic areas) could explain the important role played by water to maintain a high and stable H_2S conversion level. The formation of a very active superficial nickel oxysulfide phase was proposed in order to explain the activation period necessary at reaction temperatures $<60°C$. Total selectivity for sulfur was attributed to the very low reaction temperature and the absence of any microporosity in the support. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: SiC supported catalyst; H_2S; H_2S abatement

1. Introduction

Hydrogen sulfide, H_2S, contained in the acid gases generated by oil refineries or natural gas plants must be recovered before releasing the gases to the atmosphere, due to the high toxicity of H_2S. The general trend is to selectively transform H_2S into elemental sulfur which is a valuable product, by the modified Claus process. However, due to thermodynamic limitations of the Claus equilibrium reaction, typical sulfur recovery efficiencies are only 90–96% for a two stage reactor plant and 95–98% for a three stage reactor plant [1,2]. For this reason, new processes to deal with the Claus tail-gas were developed based on the direct oxidation of H_2S by oxygen and H_2S absorption/recycling technologies. All these processes were recently summarized in a series of reviews published in the literature covering a large temperature domain [2–4], i.e. discontinuous processes working under the sulfur dew point typically between 100 and 120°C [5,6] and continuous processes working over dew point (>200°C) [7,8].

All these processes are based on catalysts supported on different oxidic supports such as α-alumina, TiO_2, SiO_2 and to a lesser extent activated charcoal [9–14]. However, most of the oxidic supports used

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are very sensitive to the problem of sulfatation during the reaction in the presence of steam, sulfur, SO_2 and oxygen. At lower reaction temperature, high surface area activated charcoal allows to obtain high H_2S conversion. Deactivation rapidly occurs as a function of the sulfur deposition, due to pore plugging of the catalyst. In addition, regeneration in order to remove the sulfur deposit from the catalyst surface leads to a decrease in the sulfur storage capacity and in the initial desulfurization activity [13,14]. It is of interest to find new catalytic materials which could overcome these disadvantages. Among them silicon carbide seems to be a promising candidate due to its chemical inertness [15].

The aim of this work is to report the selective oxidation of H_2S into elemental sulfur in a discontinuous mode (reaction–regeneration) on a NiS_2/SiC catalyst at low reaction temperature (60°C) [16–18]. The catalyst after test was characterized by several techniques such as powder X-ray diffraction (XRD), surface area and pore size distribution measurements, and scanning electron microscopy (SEM). The influence of different reaction parameters on the catalytic behavior was also checked.

2. Experimental

2.1. Support and catalyst

Silicon carbide used as support was synthesized by the gas–solid reaction between SiO vapors and pre-shaped activated charcoal under dynamic vacuum at a temperature around 1200–1250°C [19,20]. The resulting silicon carbide obtained had a particle size ranging from 0.250 to 0.425 mm. A calcination was then performed at 700°C for 3 h in order to stabilize the textural characteristics and to burn off the remaining unreacted carbon. No microporosity was present in the SiC used as support.

The catalysts were prepared by incipient wetness impregnation of the support with an aqueous solution of $Ni(NO_3)_2\cdot H_2O$ (Merck). They were dried at 120°C for 14 h and then calcined at 350°C for 2 h in order to decompose the nitrate salt and to form nickel oxide. NiS_2/SiC was obtained by sulfidation of NiO/SiC by reaction with a H_2S/He flow at 300°C.

2.2. Selective oxidation of H_2S

The catalyst was placed on a silica wool in a Pyrex heated fixed-bed reactor (30 mm internal diameter and 600 mm height). The catalyst weight was varied between 2.5 and 3.5 g corresponding to a catalyst volume of $5.0\pm0.1\,cm^3$. The gas mixture was passed downwards through the catalyst bed. The reactor was vertically mounted in an electric furnace. The flow rate of gases (H_2S and O_2) was monitored by Tylan FC 280A flowmeters linked to a Tylan RC280 control unit. Steam was provided by a saturator kept at the required temperature allowing variations of the partial pressure of the water from 0 to 30 vol.%. The reactant mixture contained H_2S (2000 ppm vol.), O_2 (3200 ppm vol.), steam (0–30 vol.%) and balance helium. The volume hour space velocity was $1000\,h^{-1}$, a typical value used in industrial processes.

The analysis of the inlet and outlet gases were performed on-line using a Varian CX-3400 gas chromatograph equipped with a Chrompack JSQ capillary column able to separate O_2, H_2S, H_2O and SO_2, a catharometer detector and a calibrated six port loop (500 μl). Regeneration was carried out in flowing helium at 300°C for 2 h in order to vaporize the sulfur deposited on the catalyst during the test.

2.3. Characterization techniques

The metal loading, analyzed by atomic absorption spectroscopy (AAS) performed at the Service Central d'Analyse of the CNRS (Vernaison, France), was 5 wt.%.

Structural characterization of the samples was performed by powder XRD. XRD measurements were carried out with a Siemens Diffractometer Model D-5000, using a Cu Kα monochromatic radiation (λ= 1.5406 Å) operating at 40 kV and 20 mA. The pore size and surface area measurements were performed on a Coulter SA-3100 porosimeter using N_2 adsorption at 77 K. Before the N_2 adsorption, samples were not heated under dynamic vacuum in order to avoid any modification of the different phases on the surface. The morphology of the material was observed by SEM using a JEOL Model JSM-840 operating at 20 kV. The sample was supported on a stainless steel holder using double face tape, and coated with a carbon film prior to observation in order to avoid the charge effect phenomenon.

3. Results and discussion

3.1. Time on stream behavior

In Fig. 1, the desulfurization activity (expressed in terms of conversion) obtained on the NiS_2-5%/SiC catalyst in the presence of different steam concentrations at 60°C as a function of time on stream is reported. The catalyst exhibited high performances and was totally efficient (100% selective for a conversion of 100%) during a day on stream and seemed not to be affected by the solid sulfur deposition on the catalyst surface. Such high and stable activity was quite surprising in the sense that at low reaction temperatures the literature [13,14] reports that catalytic activity was a direct function of the sulfur deposition, continuously decreasing as the amount of sulfur on the catalyst increased. The long efficiency observed on SiC was attributed to the presence of steam which played a determinant role in the maintenance of the desulfurization activity. Decreasing the steam concentration in the feed led to a rapid deactivation of the catalyst with time on stream as shown in Fig. 1.

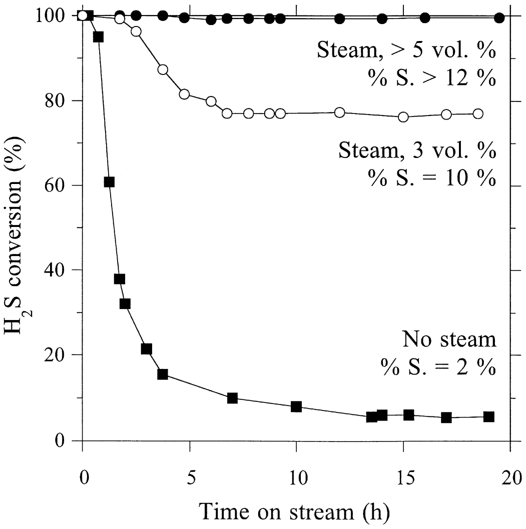

Fig. 1. H_2S conversion obtained on the NiS_2-5%/SiC catalyst as a function of time on stream at 60°C in the presence of different steam concentrations. The selectivity into sulfur remained total and no trace of SO_2 was ever detected at the exit of the reactor. The sulfur loading of the catalyst at the end of the test is reported. For steam concentrations above 5 vol.% sulfur loadings up to 60 wt.% could be achieved without any deactivation of the catalyst.

The water film formation on the catalyst surface allowed the evacuation of sulfur from the active sites thus keeping them free and accessible for the reactants. A quite similar role on the maintenance of the desulfurization activity was attributed to liquid water at higher reaction temperatures, i.e. 100°C [21]. Some authors also reported that water condensation on the catalyst surface was necessary for performing the oxidation of H_2S in the liquid phase [14,22,23]. The role of water on the SiC support is relatively easy to understand. Previous studies have shown that the surface of SiC prepared according to the gas–solid reaction is heterogeneous [19,20]: a large fraction of the surface contains oxygen (as Si oxycarbide or pseudosilica in the outermost layers), this surface being hydrophilic, while the remaining surface is mainly pure SiC, by nature hydrophobic. There are good reasons (mainly the density of defects) to think that the hydrophilic part is located inside the pores while the hydrophobic part is on the outside of these pores on the flat, low Miller index stable planes. As Ni was impregnated with a water solution by pore filling, it is rational to imagine that the particles of the active phase are localized on

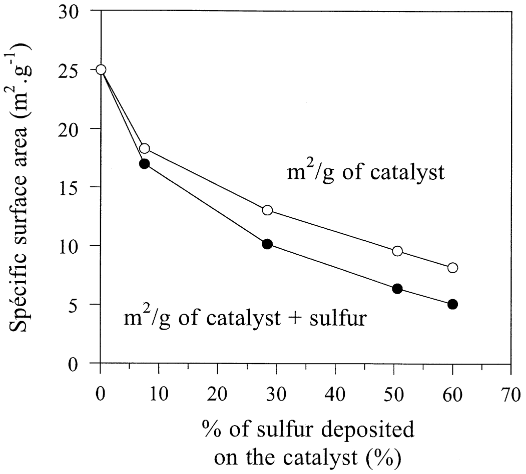

Fig. 2. Surface area modification as a function of sulfur deposition. The test was carried out in the presence of 20 vol.% of steam in the feed. Separate experiments have shown that sulfur had no surface area, <1 m^2/g.

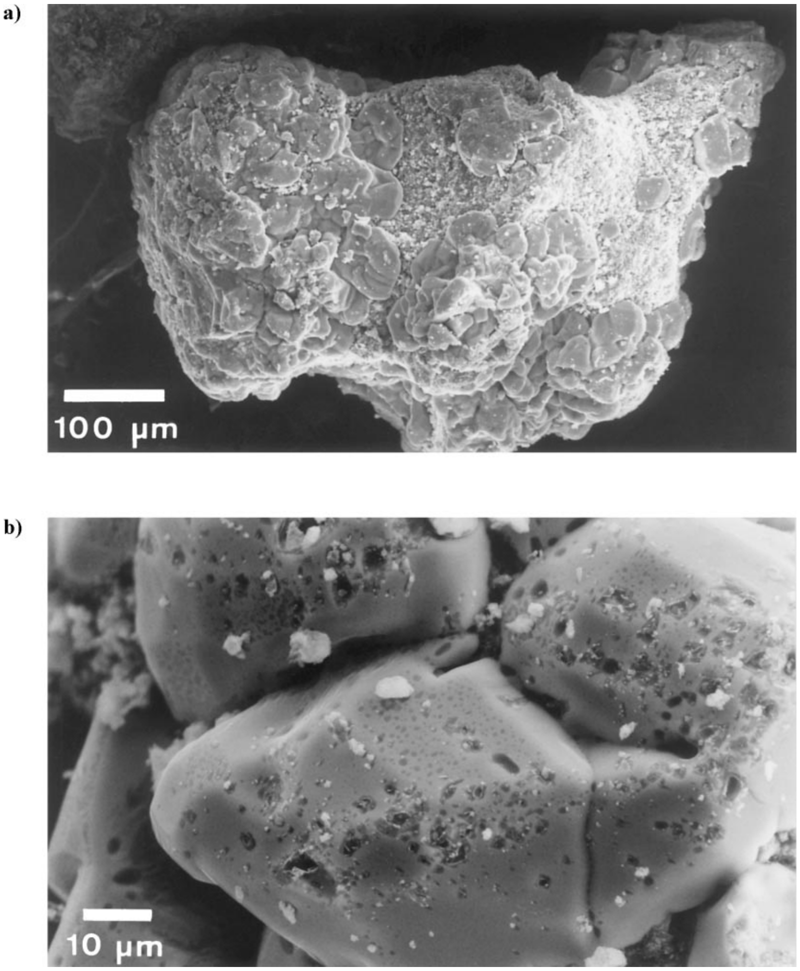

Fig. 3. SEM micrographs of the catalyst and the sulfur morphology after the desulfurization test: (a) general morphology showing the presence of large aggregates of solid sulfur; (b) high magnification of the sulfur particle evidencing the pore size network.

the hydrophilic part, in the pores. The water film, constantly wetting the catalyst, can act as a conveyor belt, transporting away the sulfur freshly generated by the particles of the active phase, cleaning these particles and storing the elemental sulfur where the water film stops, i.e. the hydrophobic part, out of the pores.

The selectivity into sulfur remained stable and total from the beginning of the test. This high selectivity was attributed to the low reaction temperature and to the absence of any harmful microposity, generally detrimental to the selectivity, because of artificially increasing the local contact time allowing the total oxidation into SO_2.

3.2. Post-reaction characterization

On the fresh catalyst the diffraction lines due to the support, SiC, and the active phase, NiS_2, were detected and no other nickel oxide or sulfur species were observed. After reaction at 60°C in the presence of 20 vol.% water, a large amount of sulfur was deposited on the catalyst surface evidenced by the sharp diffraction lines of sulfur in the XRD diagram (not shown). The sulfur deposition induced a significant drop in the surface area of the catalyst (Fig. 2). However, it is important to note that even after more than 60 wt.% of sulfur deposition part of the catalyst

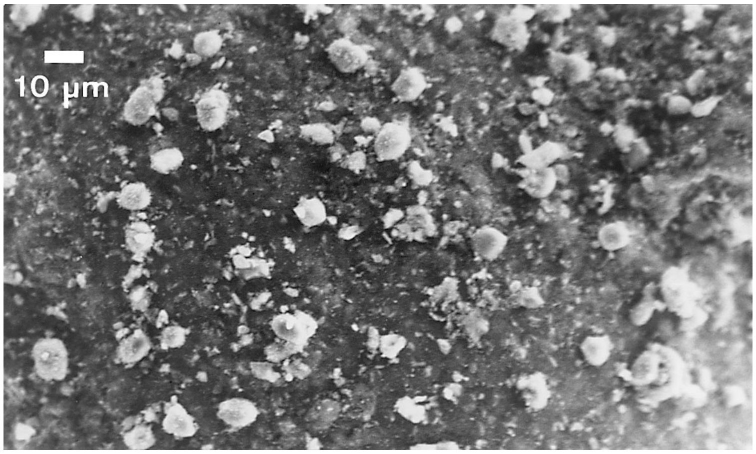

Fig. 4. SEM micrograph of the catalyst and the sulfur morphology after the desulfurization test in the absence of steam in the feed. The sulfur particles formed were smaller in size and their distribution was more homogeneous compared to that observed on the catalyst tested in the presence of steam presented above.

surface remained accessible, i.e. $5\,m^2/g$, meaning that the catalyst surface was not completely covered by sulfur. The sulfur formed had no surface area ($<1\,m^2/g$) and thus, if all the catalyst surface area was covered by sulfur one should expect to obtain a much lower surface area than $5\,m^2/g$.

In the presence of a significant amount of steam, i.e. >5 vol.%, large particles of solid sulfur were observed by SEM analysis (Fig. 3). The sulfur was deposited on the catalyst surface in an aggregate form (Fig. 3a), probably on the hydrophobic part. High magnification of the sulfur aggregates showed that the sulfur was highly porous (Fig. 3b) and this porosity was attributed to the process of aggregation at the edge of the water film. On the big aggregates the presence of small sulfur particles could also be identified in agreement with the unusual mode of sulfur removal.

In dry reaction conditions without the removal action of the water film, only small sulfur aggregates were observed (Fig. 4). In this case, the sulfur deposition occurred on the hydrophilic part and consequently hindered the access to the NiS_2 active sites for the reactants. This direct blockade by the sulfur deposit caused the rapid deactivation of the catalyst.

3.3. *Influence of the reaction temperature*

In this section the desulfurization test was carried out at lower temperature, 40°C instead of 60°C, and the results obtained are presented in Fig. 5. The catalyst required a few hours activation period on stream before reaching 100% conversion. This activation period was attributed to the time required by the NiS_2 phase to be superficially transformed into a new active phase, i.e. formation of an oxysulfide phase by oxygen and sulfur atom exchange [24]. The activation period could be by-passed by a slight activating pretreatment under an oxygen flow at 40°C for 1 h. After

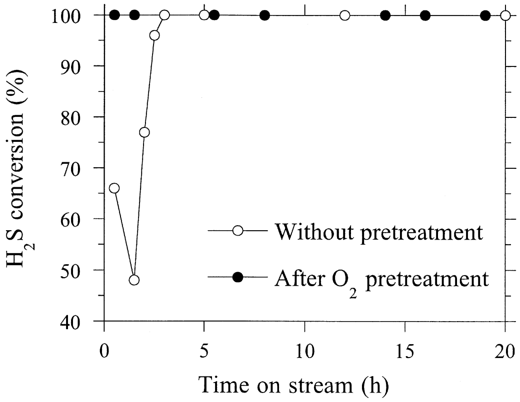

Fig. 5. Influence of reaction temperature on the desulfurization behavior of the NiS_2-5%/SiC catalyst. At 40°C an activation period was observed during the first few hours on stream. Such an activation period could be by-passed by submitting the catalyst to a slight oxidative treatment at 40°C for 1 h.

this oxidative treatment, the catalyst was directly active (see the same figure). In both cases the selectivity into sulfur remained total and stable on stream. The lack of any activation period observed on the test carried out at 60°C was attributed to the higher reactivity at 60°C compared to 40°C, between the sulfur and the oxygen, which considerably shortened the time necessary for the formation of the oxysulfide.

3.4. Stability as a function of test and regeneration cycles

After the desulfurization test (sulfur loading of the used catalyst varying from 2 to 60 wt.%) the catalyst was regenerated by heating under helium flow at 250°C for 2 h in order to vaporize the sulfur. No structural change was observed between the fresh and the regenerated catalyst. Only a slight decrease in surface area was observed after the first regeneration, 18 m^2/g instead of 25 m^2/g. This phenomenon was attributed to the fact that a part of the nickel sulfur particles could sinter during the regeneration. No further change in the surface area was observed for the following cycles.

The desulfurization stability was studied by submitting the catalyst to several cycles of catalytic tests and regenerations. No deactivation was observed on the NiS_2/SiC catalyst after several cycles. This high stability was attributed to the chemical inertness of the support which could avoid (i) the reaction between the active phase and the support itself, and (ii) the chemical modification of the support by reaction with the reactants, steam or sulfur compounds, both drawbacks limiting sulfur recovery efficiency in the case of alumina-based supports.

4. Conclusion

The use of a new type of support, i.e. SiC, and a nickel-based active phase allowed an active, extremely selective and stable catalyst for the oxidation of H_2S into elemental sulfur by oxygen at relatively low temperature (60°C) to be obtained. The catalyst exhibited a high and stable H_2S conversion even at a sulfur loading of more than 60%. Water played a determinant role to maintain the desulfurization activity, while in the absence of water in the feed, a rapid deactivation was observed. The role of water was explained in terms of a mechanical removal and transport of the elemental sulfur formed by the particles of active phase on the hydrophilic part of the support (i.e. oxycarbide or oxide of Si) to the hydrophobic part (i.e. SiC), leaving free access to the active particles even at high sulfur loading. The high selectivity was attributed to the low reaction temperature and the absence of microporosity.

The catalyst also exhibited a high desulfurization activity at lower reaction temperature, i.e. 40°C instead of 60°C. However, at 40°C an activation period was required in order to superficially transform the NiS_2 starting phase into an oxysulfide phase, the probable active phase. Such an activation could be by-passed by a slight oxygen pretreatment of the sulfide catalyst at 40°C.

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