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Low-temperature selective oxidation of hydrogen sulfide into elemental sulfur on a NiS_2/SiC catalyst

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Nickel sulfide supported on SiC exhibits a very high activity and selectivity for the direct oxidation of H_2S into elemental sulfur at low reaction temperature (60 °C). The presence of water on the catalyst surface could explain the absence of deactivation even at high sulfur loading of the surface. The chemical inertness of the SiC support allowed any detrimental reactions between the active phase and the support itself to be avoided.

Keywords: selective H_2S oxidation, low reaction temperature, nickel sulfide supported catalyst, silicon carbide

1. Introduction

Hydrogen sulfide, H_2S, contained in the acid gases generated by oil refineries or natural gas plants, must be transformed before release into the atmosphere, due to its high toxicity. Many processes have been developed by the industry to treat these effluents and to meet the requirements of the new legislations. The general trend is to selectively transform the H_2S into elemental sulfur, which is a valuable product, by the modified Claus process [1,2]. However, due to the 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. For this reason, new processes to deal with the Claus tail gas were developed based on the direct oxidation of H_2S by oxygen or H_2S absorption/recycling technologies. Details concerning these processes were recently summarized in a series of reviews published in the literature [3–6].

In our previous articles [7,8] it has been reported that the nickel-sulfide-based catalyst supported on high surface area SiC was an active and very selective catalyst for the oxidation of H_2S into elemental sulfur at temperatures around 100 °C, in the presence of an oxygen excess and a high relative humidity ($\geqslant$20 vol% of steam). The aim of this work is to report the catalytic results for the total selective oxidation of H_2S into elemental sulfur in a discontinuous mode (reaction/regeneration cycles) on the NiS_2/SiC catalyst at low reaction temperature (60 °C) [8,9].

2. Experimental

2.1. Catalysts and materials

Silicon carbide grains used as supports were synthesized at the CRV-Pechiney according to the method previously described [10–14]. The SiC had a surface area of 30 m^2/g with a pore size distribution centered around 20 nm. The SiC was used after a calcination at 700 °C without further chemical treatment.

The nickel-based catalyst was prepared by incipient wetness impregnation of the dried support with an aqueous solution of $Ni(NO_3)_2\cdot H_2O$ (Merck). The catalyst after impregnation was dried at 120 °C for 14 h and calcined at 350 °C for 2 h in order to form NiO. This material was then *in situ* sulfided with a large excess of gas or liquid elemental sulfur at 300 °C, leaching the solid, in the same way that the catalyst will subsequently be regenerated. This had no effect on the active phase dispersion.

2.2. Characterization techniques

The metal loading was obtained by atomic absorption spectroscopy (AAS) performed at the Service Central d'Analyse of the CNRS, Vernaison, France. Structural characterization of the samples was performed by powder XRD measurements, carried out with a Siemens diffractometer model D-5000, using Cu Kα radiation and operating at 40 kV and 20 mA. BET surface areas were measured by means of a commercial BET unit (Coulter SA 3100, Coultronic SA) using N_2 adsorption at -196 °C and pore size distributions were obtained from the desorption branch of the isotherms according to the method developed by Barrett et al. [15]. The gross morphology of the catalysts was ob-

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served by scanning electron microscopy (SEM) (Jeol model JSM-840) working at 20 kV and 10 mA.

2.3. Selective oxidation test

The experiments were carried out in the apparatus already described in a previous publication [8]. The catalyst was placed on a silica wool in a Pyrex tube (30 mm internal diameter and 600 mm height). The catalyst weight was varied between 2.5 and 3.5 g giving a catalyst volume of 5.0 ± 0.1 cm^3. The composition of the reactant mixture was constant and contained H_2S (2000 ppm vol%), O_2 (3200 ppm vol%), 20% of steam and balance helium. Steam was provided by a saturator kept at constant temperature. In order to avoid condensation, all the lines were maintained at 120 °C with a heating tape. The volume hour space velocity (VHSV) was 1000 h^{-1}, a typical value used in industrial processes.

The products from the reactor unit were analyzed on-line by gas chromatography using a Varian CX-3400 chromatograph equipped with a TCD.

3. Results and discussion

3.1. Characteristics of the NiS_2/SiC catalyst

The nickel concentration measured by the AAS technique was 4.9 wt%. The XRD patterns of the catalyst in the oxidic and the sulfided forms are presented in figure 1. The SiC-supported NiO exhibited broad diffraction lines of the metal oxide meaning a high dispersion on the SiC support. This result was confirmed by HRTEM measurements, which showed that NiO particles were well dispersed throughout the catalyst surface with a distribution centered at around 5–10 nm of diameter [8]. The surface area of the catalyst was 30 m^2/g. The XRD pattern of the sulfided catalyst showed SiC and the sharp diffraction lines corresponding to the NiS_2 phase according to the JCPDS card and the surface area was decreased from 30 to 26 m^2/g. The loss in surface area when going from NiO to NiS_2 was attributed to a sintering of the supported phase during sulfidation, leading to nickel sulfide particles having a larger diameter than the original NiO. Similar results have already been reported by different authors in the literature. Groot [16] has suggested that during sulfidation, even at low temperature, considerable sintering took place due to a structure alteration. This phenomenon was explained by the fact that during the replacement of oxygen atoms by sulfur atoms, cleavage and formation of atomic bonds might temporarily lead to a phase which is more mobile and hence prone to sinter.

3.2. Desulfurization activity on NiS_2/SiC

The results obtained during the selective oxidation of H_2S into elemental sulfur over the NiS_2/SiC catalyst at 60 °C in the presence of 20 vol% of steam in the reactant feed are presented in figure 2(a) as a function of time on stream. The desulfurization activity was maximum at the beginning of the test and no deactivation was observed up to 90 h on stream. The oxidation was totally selective and no traces of SO_2 were detected at the exit of the reactor. The amount of sulfur deposited on the catalyst was identical to that expected. Such a result was in close agreement with those reported in the literature on similar systems, where SO_2 or other sulfur oxidized compounds were only pro-

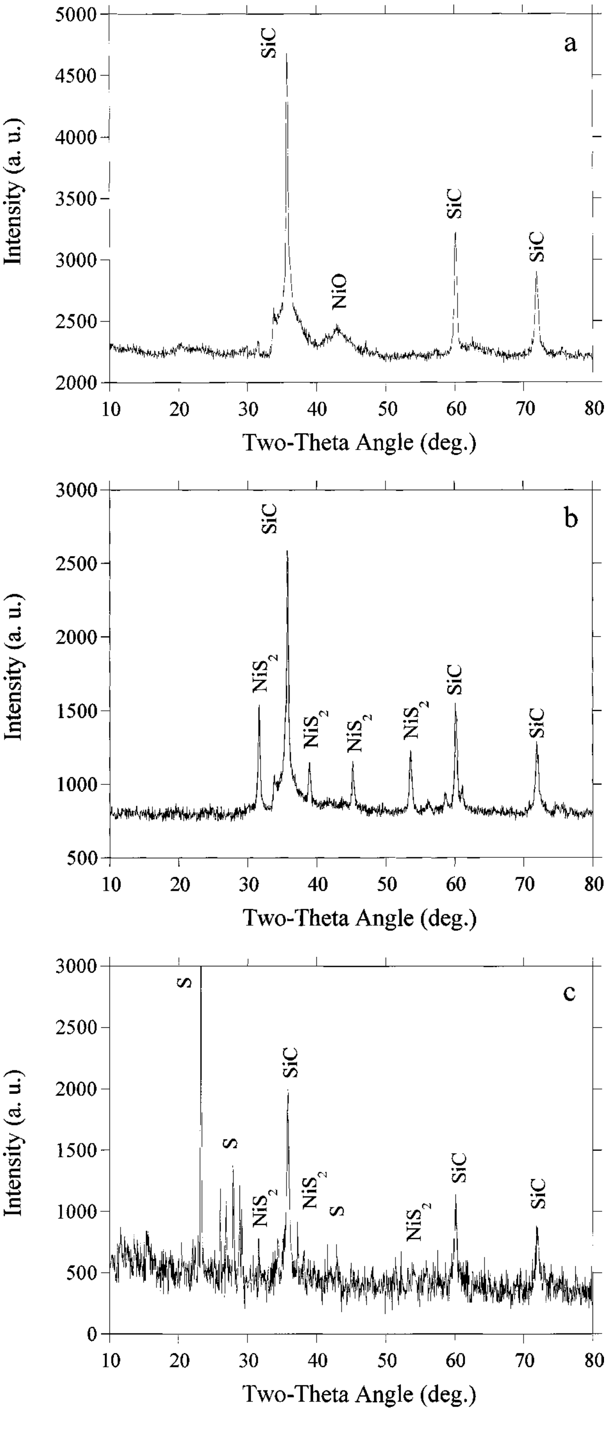


Figure 1. XRD pattern of the silicon-carbide-supported nickel catalyst after calcination in air at 350 °C (a), followed by sulfidation in the presence of sulfur at 300 °C for 2 h (b), and after desulfurization test (c).

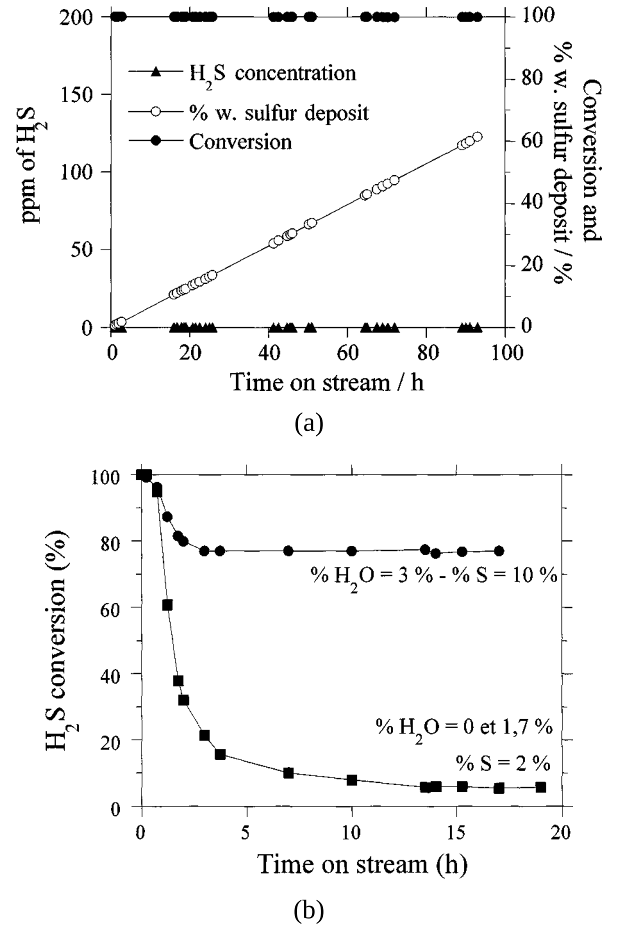
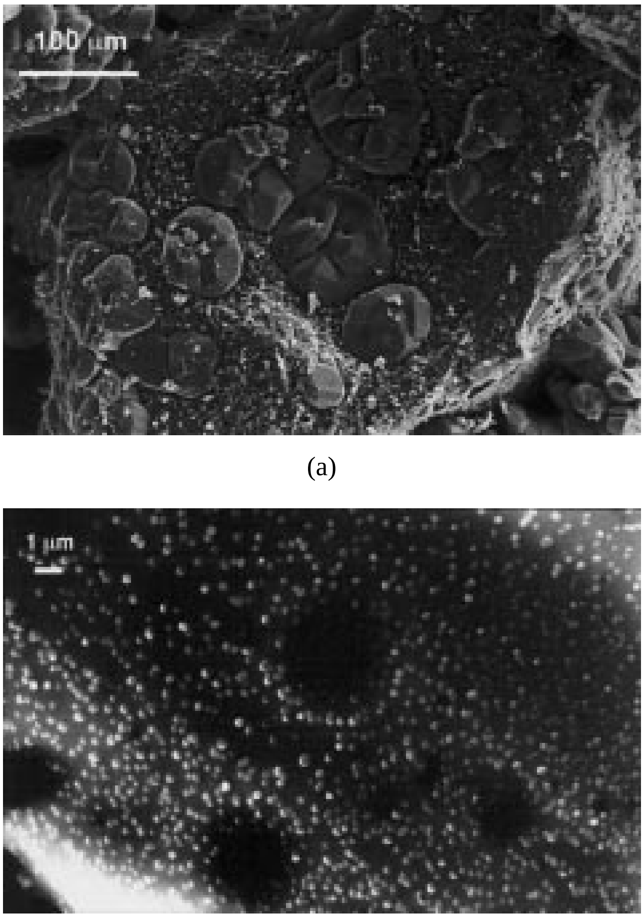


Figure 2. Catalytic activity and theoretical sulfur weight deposited on the catalyst during selective oxidation of H_2S on NiS_2/SiC catalyst at 60 °C: (a) 20 vol% of steam, (b) as a function of steam partial pressure: 3 and 0%.



(b)

Figure 3. SEM micrographs of the NiS_2/SiC catalyst after a desulfurization test at 60 °C.

duced at higher temperatures [17–20]. The extremely high selectivity into elemental sulfur observed in this test could thus be attributed to the low reaction temperature used. The XRD pattern of the catalyst after the desulfurization test is presented in figure 1(c) and only exhibited diffraction lines corresponding to SiC, NiS_2 and elemental sulfur. No traces of other compounds such as NiO or $NiSO_4$ were detected in the pattern.

After many reaction cycles, the catalyst was washed several times with deionized water at room temperature in order to dissolve any potential nickel sulfate present on its surface. Elemental analysis of the resulting water showed no evidence of any nickel confirming the absence of Ni sulfate.

At 60 °C, a large fraction of the steam in the feed condensed on the catalyst surface during the desulfurization test due to the difference between the steam generation temperature (85 °C) and the reaction temperature. However, this seemed not to affect the desulfurization activity. In contrast, it has been reported that a liquid film, formed by condensation of water on the catalyst surface, was required to perform desulfurization at low temperature over high surface area activated charcoal [20,21]. According to these different authors, the catalytic reaction could take place in the water phase faster than in a gas–solid system [17,20–22]. Some authors suggested that dissolved O_2 was cracked into reactive radicals and could react with partially dissociated H_2S [17,23]. In addition, Primavera et al. [20] reported also that the presence of water could slow down the deactivation process, by promoting sulfur deposition on different carbon sites and/or by mechanically removing sulfur from active sites.

It is significant to note that after 90 h on stream the amount of elemental sulfur deposited on the catalyst was around 62% of the total weight of the starting catalyst while no deactivation was observed. Such a phenomenon meant that the active sites remained accessible for the reactants even with a high sulfur loading. Water present in the feed could then promote the deposition of sulfur on the edge of the active sites partly on the support, or mechanically remove the sulfur from the sites to the support, as suggested by Primavera [20]. Such an explanation was confirmed by SEM of the sulfur-loaded catalyst (figure 3(a)). Sulfur formed during the reaction was agglomerated into large crystallites leaving free a large fraction of the catalyst surface. In addition, the crystallites formed in the presence of steam were highly porous according to the SEM micro-

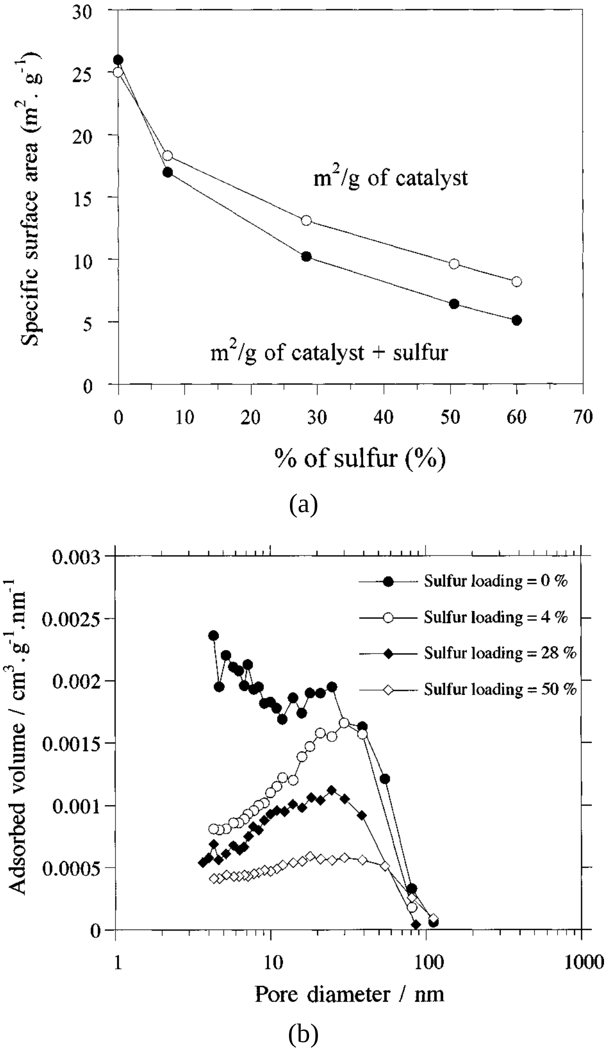


Figure 4. Evolution of the catalyst surface area (a) and pore size distribution (b) as a function of the sulfur deposit.

graph (figure 3(b) at a larger resolution than 3(a)), and this porosity probably allowed the reactants access to the covered active sites. The role of steam is confirmed by tests made at different steam partial pressure (see figure 2(b)).

3.3. Catalyst surface area evolution as a function of elemental sulfur deposition

The catalyst surface area and pore size distribution as a function of sulfur deposition are reported in figure 4 (a) and (b). The catalyst surface area monotonously decreased as the amount of sulfur deposit increased (figure 4(a)), at 8 wt% of elemental sulfur the surface area was decreased from 26 to 18 m^2/g and at 62 wt% the catalyst surface area was down to 5 m^2/g.

The pore size distribution (figure 4(b)) showed a strong modification as the sulfur deposit amount increased. At the beginning, i.e., 4 wt%, the small mesopores were the first filled. Increasing the amount of sulfur affected the whole pore distribution, meaning that probably at this stage a mechanical movement of sulfur was occurring on the surface (steam) and that the absorption was not only due to capillary forces.

3.4. Catalyst stability as a function of catalytic tests and regeneration cycles

Regeneration carried out in the presence of helium at 250 °C for 2 h allowed the removal of all the sulfur deposit by gasification–liquefaction without modification of the active phase nature, i.e., NiS_2 as proved by XRD (not reported). The desulfurization activity was unchanged even after several cycles of catalytic tests and regenerations. Such stability was attributed to the chemical inertness of the support which hindered any reaction between NiS_2 and SiC during the helium regeneration at 250 °C. In addition, no modification was observed in the catalyst surface area after several cycles, i.e., the surface area after regeneration remained unchanged at around 18 m^2/g. It has been reported by Primavera et al. [20] that selective oxidation of H_2S could also be carried out at ambient temperature over high surface area activated charcoal. However, the carbon-based catalyst was less stable as a function of the regeneration cycles, i.e., after the first run followed by a heated helium flow regeneration, the total conversion was significantly decreased along with the decrease in the sulfur storage capacity from 54 to 36 wt%.

4. Conclusion

The SiC-supported NiS_2 catalyst was found to be a very active and selective catalyst for H_2S oxidation into elemental sulfur at temperatures as low as 60 °C. Desulfurization activity in the presence of 20 vol% steam concentration was still maximal even after more than 60 wt% of sulfur deposit. Such a phenomenon was explained by the fact that active sites remained accessible during the course of the reaction: the condensed water film probably promoted deposition of the sulfur in big crystallites leaving a large part of the surface of the catalyst free, or the sulfur could be mechanically removed from active sites by the water. In addition, the porosity of the crystallites of sulfur allowed access to the covered sites by the reactants. The catalyst also exhibited an extremely high stability as a function of catalytic tests and regeneration cycles due to the absence of chemical reactions between the active phase NiS_2 and the support itself.

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