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Fe_2O_3/β-SiC: A new high efficient catalyst for the selective oxidation of H_2S into elemental sulfur

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ABSTRACT

Over the last decades, sulfur recovery from the H_2S-containing acid gases (issued from oil refineries or natural gas plants) has become more and more important due to the ever increasing standards of efficiency required by environmental protection pressures. The H_2S-tail gas was directly oxidized by oxygen to yield elemental sulfur. A significant improvement of the H_2S conversion and selectivity has been developed, however, the support which is the core of the process still needs to be improved. Recently, β-SiC has been reported to be an efficient and selective catalyst support for the H_2S-to-S reaction. One expected reason for this superior yield should be due to the high thermal conductivity of the support. The high thermal conductivity of the silicon carbide plays an important role in the maintenance of the high selectivity by avoiding the formation of hot spots on the catalyst surface which could favor secondary reactions. On the other hand, insulator supports such as alumina exhibit a poor selectivity due to catalyst surface temperature runaway.

1. Introduction

Hydrogen sulfide, H_2S, is released from different sources, i.e. natural gas plant and refinery. Due to its high toxicity, H_2S must be removed as much as possible before releasing the off-gas into the atmosphere. The general trend is to selectively transform the H_2S into elemental sulfur using the equilibrated Claus process: $2H_2S + SO_2 \leftrightarrow (3/n)S_n + 2H_2O$ [1]. However, the thermodynamic limitations of the Claus equilibrium reaction fix the maximum conversion level at about 97% at a reaction temperature of 230 °C. In this process the sulfur formed was continuously vaporized and further condensed at the cool part of the reactor allowing the avoidance of periodical regeneration to remove the condensed sulfur on the catalyst body. This has led to the development of new processes to deal with the Claus tail gas, based on the direct catalytic oxidation of remaining traces of H_2S (1 vol.%) by oxygen or H_2S absorption/recycling technologies, into elemental sulfur, in order to meet the ever stricter legislation requirements. Details concerning all these processes were recently summarized in a series of reviews published in the literature, but the catalysts, which are the core of the process, still need to be improved [2–5].

Since a decade, it has been reported by several research groups that high surface area silicon carbide (SiC) could be successfully used in the place of traditional oxidic supports such as alumina and silica for several reactions [6–11]. Silicon carbide (β-SiC) with a high specific surface area was effectively used as support for the selective oxidation of H_2S into elemental sulfur at a temperature below the dewpoint (115 °C) [12–14]. It was nevertheless of interest to find new catalysts which could overcome the slight disadvantage of a discontinuous process involving reaction and regeneration periods, and could also allow a continuous H_2S oxidation over the sulfur dewpoint. In such conditions, the main problem in the catalytic oxidation of H_2S was linked to the presence of sulfur and water: most of the oxidic supports used and especially alumina reacted with the reactants leading to a decrease in the catalytic performances or even to the destruction of the catalyst (i.e. sulfation). Furthermore, the formation of hot spots on the catalyst surface, due to the very exothermic nature of the H_2S oxidation (ca. 60 °C temperature increase per percent of H_2S converted in *an adiabatic mode*), could lead to a decrease in the selectivity into elemental sulfur by the formation of SO_2. In this way, silicon carbide is probably one of the most promising catalyst supports for exothermic reactions and especially under very

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corrosive and aggressive conditions. The chemical inertness and the high thermal conductivity of β-SiC coupled with a tuned porosity and a medium surface area lead this material to be a promising substitute for oxidic support.

In the present work the selective oxidation of trace amount of H_2S into elemental sulfur was carried out on the iron supported SiC-based catalyst, in an extrudate form. The reaction was performed in a continuous mode and the sulfur formed during the course of the reaction was vaporized and further condensed in a cool part of the reactor allowing the avoidance of periodical regeneration. The results obtained clearly evidence the high selectivity of the SiC-based catalyst even at relatively high reaction temperature. Such a high selectivity was attributed to the ability of the SiC support to withstand a heat transfer from the active site to the catalyst body and to prevent hot spot formation which could be detrimental for the process selectivity by favorizing the total oxidation reaction leading to the formation of SO_2. The desulfurization results obtained on the SiC-based catalyst were also compared with those obtained on a traditional catalyst, i.e. Al_2O_3-based catalyst, under similar reaction conditions. According to the results, for a given reaction condition, the sulfur selectivity was far lower on the alumina-based catalyst compared to that obtained on the SiC-based catalyst regardless of the nature of the starting active phase, i.e. iron oxide. The high heat homogenisation owing to the high thermal conductivity of the SiC support was again advanced to explain the observed results.

2. Experimental

2.1. The support

The beta silicon carbide (β-SiC) was synthesized according to the *Shape Memory Synthesis* (*SMS*) developed by Ledoux et al. [15–17] and prepared by the SICAT Company. The synthesis is carried out at high temperature (1200–1300 °C) under argon atmosphere according to the gas–solid reaction between a carbon solid and SiO vapors ($SiO + 2C \rightarrow SiC + CO$). The starting carbonaceous material made of a pre-shaped polymer (extrudates, monoliths, foam, etc.) containing the right amount of C and O, to which silicon micropowder was added and mixed before drying and shaping, is converted into beta silicon carbide. The β-SiC obtained was finally decarbonized at 700 °C for 2 h under air flow in order to oxidize the excess of carbon untransformed. The SiC support used in this study was in an extrudate form (2 mm diameter and 5 mm length).

2.2. The catalyst preparation

The iron oxide based catalyst was prepared by incipient wetness impregnation of the dry support (2 mm diameter pellets) with an aqueous solution containing 20 vol.% of glycerol ($C_3H_8O_3$, Fluka) and $Fe(NO_3)_3{\cdot}9H_2O$ (Merck). The resulting material was dried at room temperature for 12 h, then in an oven at 150 °C for 12 h and finally calcined in air at 350 °C for 2 h in order to decompose the iron nitrate precursor into its corresponding oxide Fe_2O_3.

A common alumina (γ-Al_2O_3, 2 mm diameter pellets)-based catalyst was synthesized in the same conditions as described previously in order to compare it to our beta silicon carbide based catalyst. The same amount of active phase was impregnated, and only the support was changed (γ-Al_2O_3, AKZO NOBEL S_{BET} = 200 m^2/g).

2.3. H_2S oxidation test

Selective oxidation of H_2S was carried out in an apparatus working isothermally at atmospheric pressure and is presented in Fig. 1. An amount of 1.5 g (2.25 mL) of catalyst was placed on silica wool in Pyrex, heated on a fixed bed reactor (18 mm inner diameter and 600 mm height). The gas mixture was passed downwards through the catalyst bed. The reactor was vertically mounted in an electric furnace, and the temperature was controlled by a K-type thermocouple and a Minicor regulator. The flow rate of gases (H_2S, O_2 and He) was monitored by Brooks 5850TR flowmeters linked to a control unit. The composition of the reactants feed was H_2S (1 vol.%), O_2 (2.5 vol.%), H_2O (30 vol.%) and He (balance), corresponding to a O_2/H_2S ratio of 5 according to Eq. (1), and a gas hourly space velocity (GHSV) varying from 3000 to 4000 h^{-1} (typical GHSV in industrial units is in the range of 1200–1500 h^{-1}).

$$H_2S + \frac{1}{2}O_2 \rightarrow H_2O + \frac{1}{n}S_n \quad \Delta H = -222\,\text{kJ mol}^{-1} \tag{1}$$

Steam was also present in the feed in a relatively large amount (30 vol.%) in order to accurately reproduce the real industrial reaction conditions (the water formed during the Claus process is

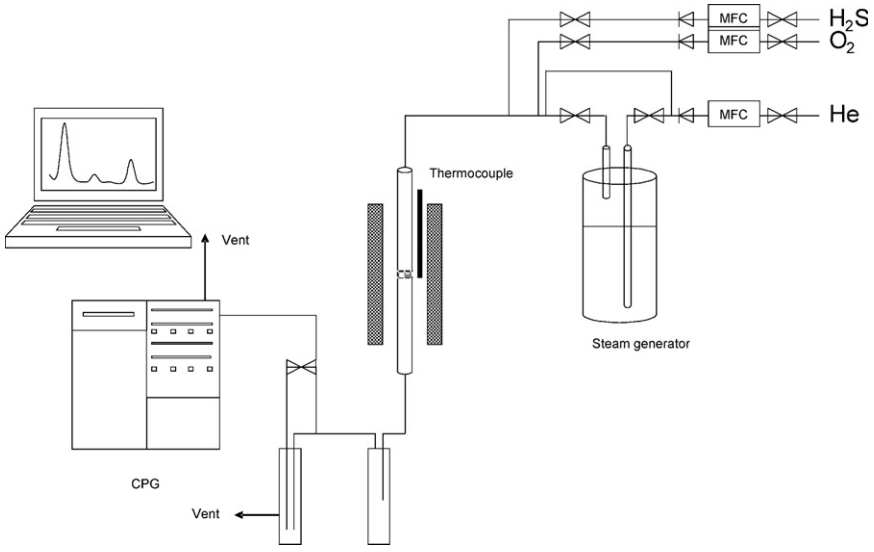

Fig. 1. Schematic diagram of the apparatus used for the H_2S oxidation test.

not removed and remains in the tail gas). The steam was provided by a saturator kept at the required temperature. The sulfur produced condensed in the lower part of the reactor and melted down with the help of a thermal stripper or a heating tape in order to be stocked in a sulfur trap allowing continuous operation. All the lines were maintained at 120 °C with a heating tape to avoid condensation before the chromatographic analysis.

Analysis of the inlet and outlet gases was performed on-line using a Varian CP-3800 gas chromatograph equipped with a Chrompack CP-SilicaPLOT capillary column allowing the detection of O_2, H_2S, H_2O and SO_2, a catharometer detector (TCD) and a calibrated six-port loop (250 μl). Before the reaction, the reactor was purged with helium at room temperature until no trace of oxygen could be detected by gas chromatography at the exit of the reactor, then the dry helium flow was replaced by the one containing steam. The catalyst was heated from room temperature to the reaction temperature and the wet helium flow was replaced by the reactant flow.

2.4. Characterization techniques

2.4.1. X-ray diffraction

Structural characterization of the samples was done by powder XRD carried out with a Bruker Diffractometer Model D8 Advance equipped with a Vantec detector, using a Cu Kα radiation. The mean crystallite size was determined from the Scherrer equation with the normal assumption of spherical crystallites. The nature of the crystalline phase in the sample was checked using the database of the Joint Committee on Powder Diffraction Standards (JCPDS).

2.4.2. Nitrogen adsorption

The pore size and the surface area measurements were performed with a Micromeretics Tristar 3000 porosimeter using N_2 as adsorbent. S_{BET} is the surface area of the sample calculated from the nitrogen isotherm using the BET method.

Mercury intrusion porosimetry was used to determine the porous distribution of the macroporosity which could not be measured by N_2 adsorption.

2.4.3. TEM microanalysis

TEM and EDS microanalysis techniques are used to provide information on the dispersion of the active phase, the particle size, its morphology, and its composition. TEM and EDS were carried out in a Topcon model EM200B operating at 200 kV equipped with beryllium window, with a point-to-point resolution of 0.17 nm.

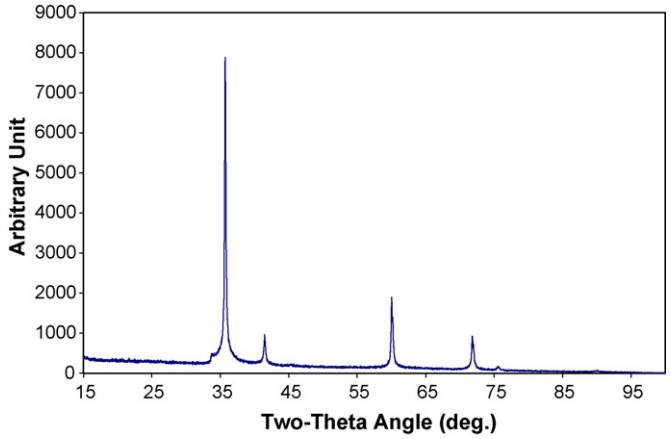

Fig. 2. X-ray patterns of the silicon carbide support iron oxide based catalyst prepared by incipient wetness impregnation.

3. Results and discussion

3.1. Catalyst characterizations

3.1.1. XRD patterns

The X-ray pattern of the iron based catalyst (3 wt.% Fe loading) is presented in Fig. 2 and only showed diffraction lines corresponding to β-SiC suggesting that Fe_2O_3 is present in an amorphous phase or in a very dispersed crystallised phase. No traces of other compounds such as SiO_2 or Si were detected, meaning that such species if present were either in a very small crystalline amount or in a superficial amorphous form which could not be accurately detected by the XRD technique [18,19]. Previous works clearly indicate the high dispersion of iron oxide, nickel oxide and MoO_3 on a β-SiC surface by using a viscous (glycerol) agent in the impregnation solution [20,21]. The small size of the iron particles was confirmed by TEM experiment and is discussed in the next section.

3.1.2. TEM analysis

Previous characterization using high-resolution TEM and XPS has shown that the SiC support was partially covered by thin 1–3 nm thick amorphous layers SiO_xC_y and SiO_2 on the surface of the SiC [22], which is not detected by XRD, as presented in Fig. 3A. TEM image of the starting Fe_2O_3 particle dispersed on the β-SiC surface is presented in Fig. 3B. Statistical TEM analysis

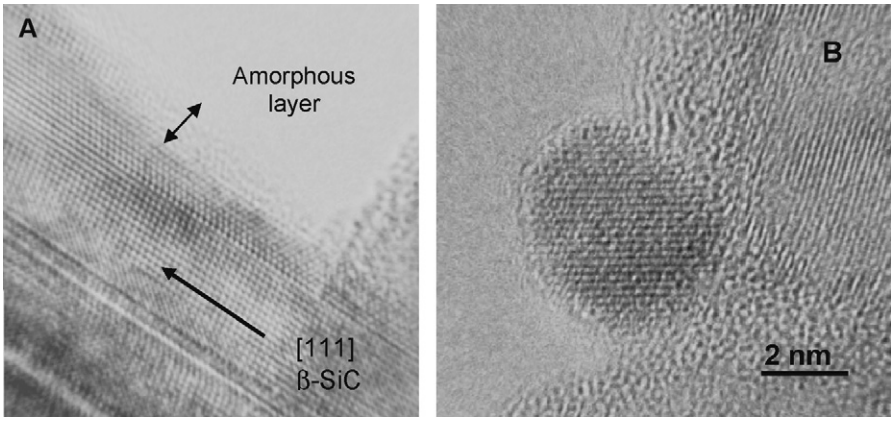

Fig. 3. TEM micrograph (high resolution) of the β-SiC (A) and of the iron based catalyst (B). The amorphous layer coupled to the peculiar surface of the silicon carbide permits to have a high dispersion of the active phase.

over 400 particles confirms the high dispersion of the Fe_2O_3 phase on the SiC surface with an average particle size centred at around 4 nm. The use of the viscous solution by the addition of glycerol played an important role in the dispersion of the iron precursor and the final particles size. In fact, several catalysts were prepared by the incipient wetness impregnation, with water as solvent and with water/glycerol. The XRD pattern (not reported) of the samples prepared without any addition of glycerol presented diffraction lines corresponding to the iron oxide. The high dispersion was attributed to the existence of a strong interaction between the deposited salt and the SiO_x topmost layer present on the SiC surface.

3.1.3. Surface area and pore size distribution

The silicon carbide used during this study was optimized as much as the porous distribution (especially the macroporous network) as the specific surface area. Fig. 4 reports the macroporous distribution of the support obtained by mercury intrusion and the mesoporous distribution obtained by nitrogen adsorption. The Fe_2O_3/SiC catalyst exhibited on the whole the same surface area (ca. S_{BET} = 25 m^2/g) as the support. After a screening of different support (pore size distribution and specific surface area), we found that the optimal macroporous size should be higher than 0.1 μm [23]. This could be explained by the need of large pores to make the diffusion of the reactants easier (gain in conversion). Moreover, the selectivity in sulfur is enhanced by the ease of evacuation of the sulfur avoiding the formation of SO_2. The specific surface area must be greater as much as 10 m^2/g to avoid or to diminish the sintering of the active phase on stream.

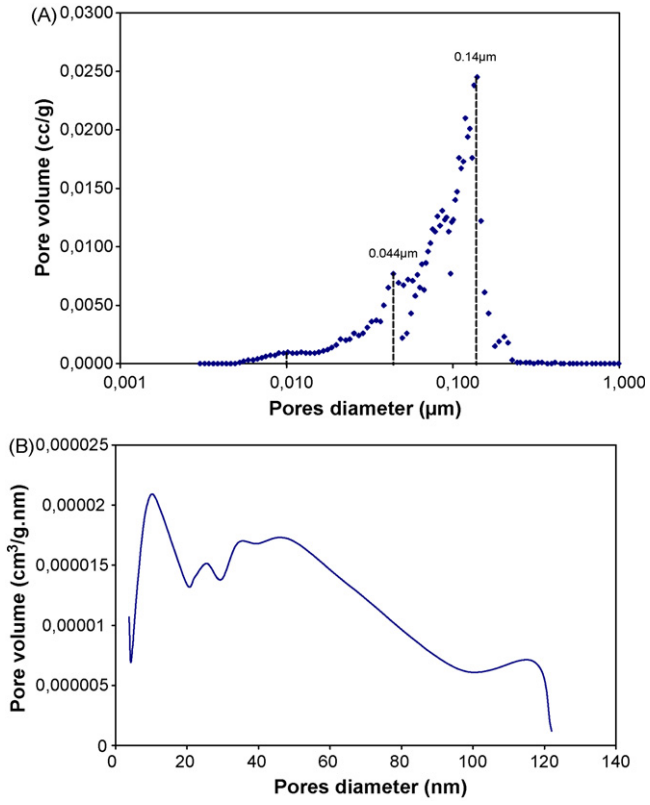

Fig. 4. (A) Pore size distribution by Hg intrusion; most of the pores are centred around 0.14 μm in their diameter. (B) Pore size distribution obtained by N_2 adsorption; the porosity range goes from 5 to 100 nm.

3.2. Catalyst performances

3.2.1. Influence of the reaction temperature

In a previous work the author presented the high potential of beta silicon carbide used as support for the selective oxidation of H_2S into S in Claus tail gas conditions (230 °C, 1% [H_2S] = 1 vol.%) [29]. The superior yield of the silicon carbide could be explained by the chemistry surface of the β-SiC or the tuned porosity of the material or its thermal conductivity. Van den Brink and Geus [27] reported the sensitivity of a silica based catalyst (4% Fe supported on SiO_2, S_{BET} 40 m^2/g) toward the reaction temperature. By increasing the reaction temperature, the selectivity dropped strongly (i.e. <70% at 300 °C). We assumed that the surface of the porous silicon carbide is a mix of an oxicarbide and amorphous silica, so we can exclude the role of the surface chemistry of the support for the unmatched yields for the SiC-based catalyst. One other suspected reason for superior yields was the tuned porosity of the support, but it could not explain the stability of the catalyst in unconventional reaction conditions (elevated temperatures and high H_2S concentration). The thermal conductivity of the support might be a good candidate to explain superior yields. Investigating catalyst performance at elevated temperatures can give an overview of the thermal conductivity effect of the tested supports.

The H_2S desulfurization performances obtained on the Fe_2O_3–3 wt.%/Al_2O_3 catalyst as a function of reaction temperature (230–300 °C) are presented in Fig. 5. The optimal catalytic results are observed for a reaction temperature of 250 °C (86% for the sulfur yield). Even at very high temperature (more than 350 °C) the H_2S conversion is not complete, but a significant gain could be observed when the reaction temperature increased from 230 to 280 °C with a conversion of about 92% to ca. 99% respectively. It can be observed that the catalytic performances, in terms of sulfur yield, continuously decreased to reach 41% when the reaction temperature increased from 250 to 350 °C. This loss in sulfur yield is due to the decrease of the selectivity with the elevation of temperature. The formation of SO_2 is sensitive to the reaction temperature and an elevation of 20 °C (230–250 °C) decreases the selectivity for more than 5%. This tendency is more pronounced at higher temperatures. These results are in accordance with the literature and especially the results obtained for the first and the second generation of the Superclaus catalysts [24–27]. For a silica based catalyst (commercial one), the trend is the same with a huge loss in selectivity by increasing the reaction temperature, for more details see Ref. [27].

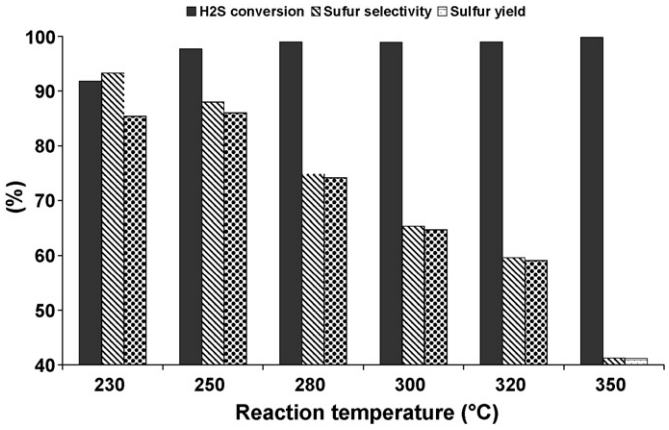

Fig. 5. Influence of the reaction temperature on the desulfurization performances obtained over iron oxide supported on alumina (reaction conditions: H_2S (1 vol.%), O_2 (2.5 vol.%), H_2O (30 vol.%) and He (balance), GHSV = 3000 h^{-1}).

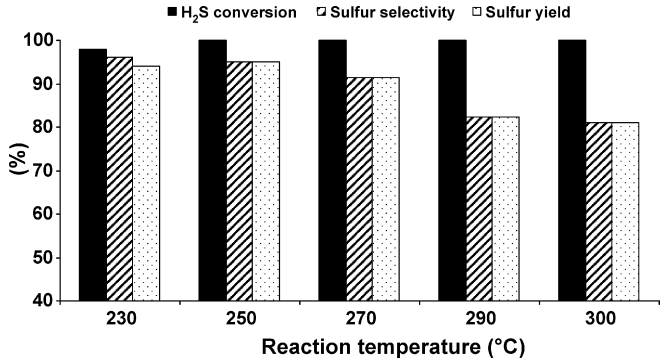

Fig. 6. Influence of the reaction temperature on the desulfurization performances obtained over iron oxide supported on silicon carbide (reaction conditions: H_2S (1 vol.%), O_2 (2.5 vol.%), H_2O (30 vol.%) and He (balance), GHSV = 3000 h^{-1}).

Fig. 6 reports the desulfurization performances obtained on the Fe_2O_3/SiC catalyst as a function of the reaction temperature. Contrary to the alumina-based catalyst, the silicon carbide one is much more active even at low temperatures. The conversion is complete at 250 °C with a sulfur yield of 95% (selectivity of 95%) which is the highest performance reported in the literature in these conditions up to now, and especially at high space velocity this exceptional activity is still observable at GHSV = 4000 h^{-1}. One of the most surprising catalyst behaviours is the relative stable sulfur selectivity versus the temperature reaction. In fact, an increase of 50 °C produces a loss of 14% in the selectivity which reaches 81% at 300 °C.

Comparison of the desulfurization performances of the two catalysts as a function of the reaction temperature is presented in Fig. 7. This graph clearly shows the higher selectivity of the silicon based catalyst which permits to process at higher conversions (by increasing the reaction temperature). The alumina-based catalyst can be subject to the retro Claus reaction, especially at high reaction temperatures (>300 °C), and this could explain the low selectivity of the catalyst at such temperatures. The surface reactivity of the beta silicon carbide could not explain the gain in selectivity; it could be expected that the intrinsic thermal conductivity of the beta silicon carbide material also acted an important role. The porous beta silicon carbide presents an intrinsic thermal conductivity 6 times higher as a porous alumina. In fact, the effective thermal conductivity of the reactor depends on the intrinsic conductivity of the catalytic solid λ_s.

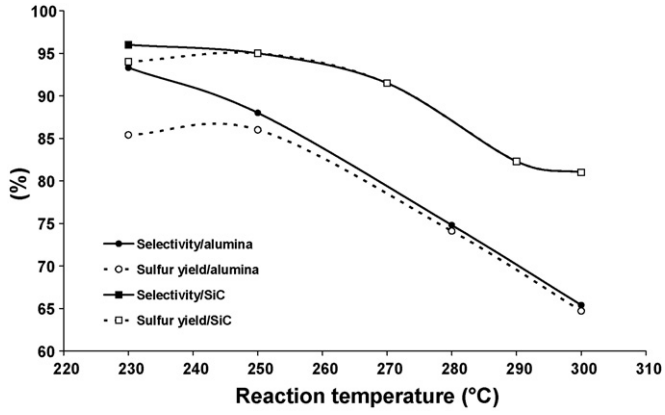

Fig. 7. Comparison of the catalytic performances of the two iron based catalysts supported on alumina and silicon carbide as a function of the reaction temperature.

This bed parameter (λ_{ax}^{eff}) is given by the relationship recommended by Vortmeyer and Schfer [28]:

$$\lambda_{ax}^{eff} = \lambda_f \left(\frac{\lambda_s}{\lambda_f}\right)^n \quad (2)$$

with

$$n = 0.280 - 0.757 \log(\varepsilon) - 0.057 \log\left(\frac{\lambda_s}{\lambda_f}\right)$$

where λ_f and λ_s are the intrinsic conductivity of the gas phase and the solid phase respectively, and finally ε is the porosity of the catalyst bed. In a previous work, the author took values of λ_s for silicon carbide and alumina found in the literature (150 and 30 W/m K^{-1} respectively) [29]. These values were attributed for dense material without porosity but we assumed that the ratio between dense and porous materials would be the same. In the mean time, the λ_s for the porous beta silicon carbide and alumina was measured (by flash laser method) and the values were around 4, and 0.6 W/m K^{-1} respectively.

For the beta silicon carbide based catalyst, the heat (coming from the oven and produced by the reaction) is homogenised from the surface to the heart of each extrudate and from the top at the end of the catalytic bed. It is commonly accepted that the heat transfer in a catalytic reactor (gas–solid reaction) is operated by the gas phase. But at low GHSV the solid phase could also bring a contribution in the heat transfer by a grain to grain conduction. Some calculation clearly shows the effect of the intrinsic thermal conductivity of different supports (β-SiC, alumina, cordierite) to the thermal profile of the catalytic bed [29]. For the isolating supports (alumina, cordierite), the calculation predicted a sharp hot spot, while the beta silicon carbide with a higher λ_s and λ_{ax}^{eff} exhibits a smoother thermal profile of the bed [29]. The selectivity of the reaction is directly linked to the temperature inside the catalytic bed and surely explains the differences of the catalysts especially for the selectivity at high temperatures (according to the very high sensitivity of the selectivity toward the reaction temperatures).

3.2.2. Influence of the H_2S concentration

Following the hypothesis advanced above, one should expect that the intrinsic thermal conductivity of the silicon carbide should be beneficial when the H_2S concentration in the feed is increased. Indeed, the selective oxidation of H_2S is a very exothermic reaction (ΔH = −222 kJ mol^{-1}) and the adiabatic temperature for 1% of H_2S converted is close to 60 °C ($\Delta T_{ad} = (\omega_0/MC\,p_g)(-\Delta H)$), where ω_0 is the weight fraction of H_2S in the feed. In the case of 2% H_2S being totally converted, we might expect that the intrinsic thermal conductivity of the silicon carbide would be much more beneficial to the sulfur yield by lowering the hot spot on the catalyst body and also to evacuate as rapid as the heat formed from the reaction. Fig. 8 reports the catalytic performances of the silicon carbide based catalyst as a function of the H_2S concentration in the feed.

As it can be observed, the total sulfur yield is still extremely high despite a high H_2S concentration in the feed. At such high H_2S concentration and high conversions, the T_{ad} is very important (over 115 °C) and we might expect a rise in the temperature at the surface of the catalyst and inside the catalytic bed. The high selectivity is attributed to the high intrinsic thermal conductivity of the silicon carbide, which takes place in the factor of the effective conductivity [29]. In this way, the temperature of each extrudate on which the exothermic reaction takes place has a homogenisation of the temperature from the surface to the core of the material. Furthermore, the temperature in the catalytic bed is also homogenised in the three dimensions and this avoids probably an over-shoot of temperature in the first stage of the catalytic bed

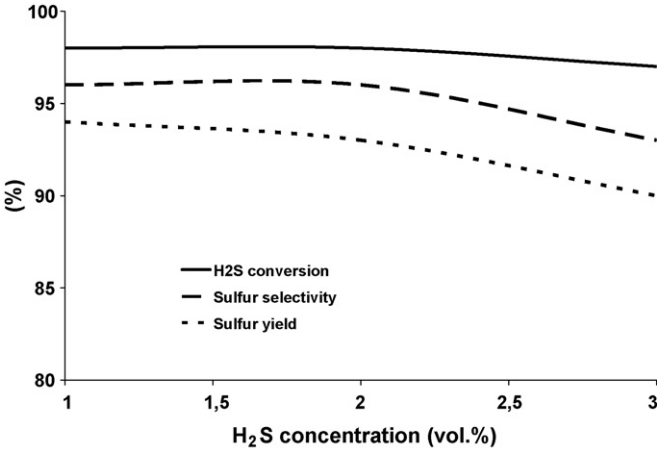

Fig. 8. Desulfurization performances obtained over Fe_2O_3/SiC catalyst as a function of the inlet H_2S concentration.

or local hot spots. The high thermal conductivity of the beta silicon carbide could consider treating high H_2S concentrations and in this case to by-pass the second or the third catalytic stage of the Claus process or to minimize the volume of the catalyst in the reactor.

In summary, the superior yields observed for the silicon carbide catalyst can be mainly attributed to the intrinsic thermal conductivity of the material which prevents hot spot formation and thus total oxidation reaction leading to the formation of SO_2. The surface layer (SiO_2/SiO_xC_y on the surface) allows dispersing the active phase and when combined with the tuned porosity makes the β-SiC a performing support in terms of conversion and selectivity for the studied reaction. The thermal conductivity of the β-SiC can explain higher selectivity at elevated reaction temperatures and at high H_2S concentrations.

4. Conclusions

The tuned porosity combined with the surface properties and the thermal conductivity of SICAT's porous silicon carbide allows to prepare very active and selective catalyst for the selective oxidation of H_2S into S. The beta silicon carbide used for this study was optimized in the porous network (macro and meso) as well as the specific surface area. The high intrinsic thermal conductivity of the silicon carbide is one of the most promising physical properties of this material. This paper aimed to report the huge potential to process with a beta silicon carbide based packed bed. The high thermal conductivity of the material will homogenise temperature inside the bed, avoiding hot spots and overheating. Contrary to other supports which are usually isolating supports, our catalyst permits to work at higher temperature without any loss in selectivity. In other words, using a beta silicon carbide based catalytic bed will allow working at higher sulfur yields.

High concentrations of H_2S (2.7%) could be treated over this catalyst without deactivation, and without any significant loss in sulfur selectivity. The beta silicon carbide is able to evacuate and to rapidly homogenise the heat of the reaction. The direct consequence is to work either with a lower volume of catalyst, or to by-pass the second or the third Claus reactor. β-SiC can be a performing support especially during the startup of an industrial plants and when fluctuation of the feed gas occurs. By limiting temperature runaway, the catalysts lifetime can be extended, and by the way human intervention during the process can be limited.

Acknowledgements

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