ELSEVIER

Catalysis Today 53 (1999) 535–542

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Direct oxidation of H_2S into S. New catalysts and processes based on SiC support

Nicolas Keller [a], Cuong Pham-Huu [a], Claude Crouzet [a], Marc J. Ledoux [a,*], Sabine Savin-Poncet [b], Jean-B. Nougayrede [b], Jacques Bousquet [b]

[a] *Lab. de Chimie des Matériaux Catalytiques, ECPM-Univ L. Pasteur and CNRS, 25, rue Becquerel, 67087 Strasbourg, France*

[b] *Elf Aquitaine, Lacq and Solaize, France*

Abstract

Nickel sulphide, supported on SiC, exhibits a very high activity and selectivity for the direct oxidation of H_2S into S at medium temperatures (100–120°C) or at room temperature (20–40°C). Iron oxide, also supported on SiC, is highly reactive, and selective, for the same reaction at higher temperatures (210–240°C). This support is very stable, insensitive to steam and to any sulphur compounds in this range of temperature. ©1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Refiners and gas processors should comply with environmental protection pressures and, in particular, should diminish the SO_2 release at the incinerator level, which results in particular from gas purification hydrotreatment operations involving H_2S. This gas is conventionally treated by the well-known Claus process to produce elemental sulphur and steam according to the reactions:

$$H_2S + \tfrac{3}{2}O_2 \rightarrow SO_2 + H_2O$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

According to thermodynamics, the catalyst and the number of successive reactors, the maximum efficiency cannot be >98%. This means that, for a conventional sulphur plant, the SO_2 emissions may amount to many thousand tons per year released into the atmosphere. A typical tail gas may contain SO_2 (~6000 ppm), H_2S (~12000 ppm), COS and CS_2 (~700 ppm).

Several processes have been applied to extract the last remaining sulphur based on different concepts [1,2]. The entire tail gas can be burned and all the molecules containing sulphur are transformed into SO_2, or can be catalytically hydrotreated in order to obtain only H_2S. Then absorption processes can extract either SO_2 or H_2S and after desorption these gases can be recycled into the Claus plant. These processes based on the absorption concept can be >99.9% efficient; however, they generally require expensive investments and running costs.

Another concept is based on the catalytic oxidation of the remaining H_2S by air into S and water. This requires that the upstream Claus processes work in an excess of H_2S in order to have no SO_2 remaining in the tail gas (COS and CS_2 can be hydrolysed into H_2S). There are other processes based on different concepts, such as Clauspol by IFP [3]. The catalytic oxidation of H_2S can be performed above the sulphur dew point (180°C) and the elemental sulphur

---

[*] Corresponding author.

0920-5861/99/$ – see front matter ©1999 Elsevier Science B.V. All rights reserved.
PII: S0920-5861(99)00141-8

condensed at the outlet of the reactor. The Superclaus process by Comprimo B.V. [4–8] was first developed in 1985, then regularly upgraded to reach an efficiency of 99.5% at temperatures around 240°C and is based on Fe and Cr catalysts supported on alumina or silica. The BSR high activity process by Parsons [3] reaches the same performance and is based on Fe supported on modified alumina. The catalytic oxidation of H_2S can also be performed below the sulphur dew point. In this case, the elemental sulphur remains on the catalyst and should be regularly regenerated by heating the reactor to allow sulphur to melt and flow outside the catalytic bed. Among these, the Doxosulfreen process of Elf and Lurgi [9,10] is based on Cu catalysts supported on modified alumina, and working in an adiabatic system between 90°C and 140°C and can reach an efficiency of 99.9%; the low temperature preventing a too large total oxidation of H_2S into SO_2.

The main problems in the catalytic oxidation of H_2S are the very high activity of the catalyst leading to the formation of SO_2 and, thus, decreasing the selectivity of the reaction

$$H_2S + \tfrac{1}{2}O_2 \rightarrow S + H_2O$$

and the stability of the catalyst. In the presence of sulphur and steam, most of the used oxide supports are sulphated with time leading to a decrease in activity or even to the destruction of the catalyst.

The objective of this article is to present the use of a stable catalyst working in all the ranges of temperature, above 180°C and below, based on a new silicon carbide support, and allowing an extremely high performance in terms of activity and selectivity because of the peculiar dispersive properties of such a material and its remarkable chemical stability [11–13].

2. Experimental

2.1. Reaction conditions and micropilot

All the catalysts were tested in a heated fixed-bed reactor containing 5–100 g of catalyst, according to the needs of the reaction. A system of mass flow controllers were used to fix the flows and partial pressures of H_2S, O_2 and He (used as dilutent). The partial pressure of H_2S could be as high as 2% (20 000 ppm). Steam was provided by a saturator working at the required temperature allowing variation of the partial pressure from 0% to 40%. Elemental sulphur was recovered below the reactor in a cool flask, either directly when working above the dew point or after heating when working below. The analysis of the inlet and outlet gas was done using a Varian CX-3400 gas chromatograph equipped with a column allowing the separation of H_2S, H_2O and SO_2, a TCD detector and a computer. Before entering the column, the gas was dried through a bed of $CaCl_2$. Careful analyses were made to check that no absorption phenomena were disturbing the analytical process. Because of the poor sensitivity for SO_2 detection, an additional system using Draeger analytical tubes and a calibrated pump was directly connected to the outlet of the reactor. The limit of detection and the absolute error was at 5 ppm for SO_2 and 10 ppm for H_2S. This means that when no sulphur was detected either by chromatography or by the analytical tubes no more than 15 ppm of total sulphur was released in the vent. Sulphur mass balance was calculated both, from the continuous chromatographic analysis and by weighing the sulphur deposit. The agreement was always better than $100 \pm 1\%$. The reaction partial pressures, temperatures, flows and mass of catalyst will be provided in Section 3.

2.2. Catalyst preparation and characterization

The SiC support was prepared according to the two synthesis methods already published [14–16]. In the first method, pre-shaped activated charcoal (powder or extrudates) was reacted with SiO vapor generated by the reaction of Si and SiO_2, according to the following two equations :

$$Si + SiO_2 \rightarrow 2SiO$$

$$SiO + 2C \rightarrow SiC + CO$$

in a batch reactor heated to ca. 1300°C and maintained under low pressure. This synthesis generated SiC with a surface area ranging from 20 to 80 m^2/g [17]. In the second method performed by Pechiney, charcoal powder was pre-mixed with a fine powder of silicon into a polyfuran resin. This past was shaped into grains, extrudates or spheres, then dried and heated in a rotating reactor at about 1300°C in a counter flow of Ar. This process was continuous. This synthesis generated

SiC with a surface area ranging from 20 to 40 m^2/g. Many test reactions have shown that these two types of SiC have strictly identical properties for the reactions studied in this article. In both cases, the β-form was obtained. Generally, calcination at 600°C was performed after synthesis in order to burn the remaining unreacted charcoal.

The precursor of the active phase, either Ni nitrate or Fe nitrate, was impregnated following the wet impregnation process with a water solution of these salts. The dried solid was then calcined at 350°C for Ni and 400°C for Fe in order to decompose the nitrate and form either NiO or Fe_2O_3. The activation of the catalyst will be presented in detail in Section 3. Different characterization methods were used mainly to identify the nature of the different phases (XRD, SEM, TEM) and to localize sulphur on catalysts working below the dew point.

3. Results and discussion

3.1. Sub-dew point reactions

β-SiC was impregnated with nickel nitrate in order to obtain different concentrations of Ni on the support. Catalysts containing 3.9, 5.6 and 10 wt.% of Ni were tested and did not show significant differences. In activity below 3%, a decrease was observed. Fig. 1 shows a TEM micrograph of NiO–3.9%/SiC and the particle distribution in terms of diameter measured for 1000 particles on a statistical sample of micrographs. It is clear that the majority of the particles had a diameter between 30 and 50 Å.

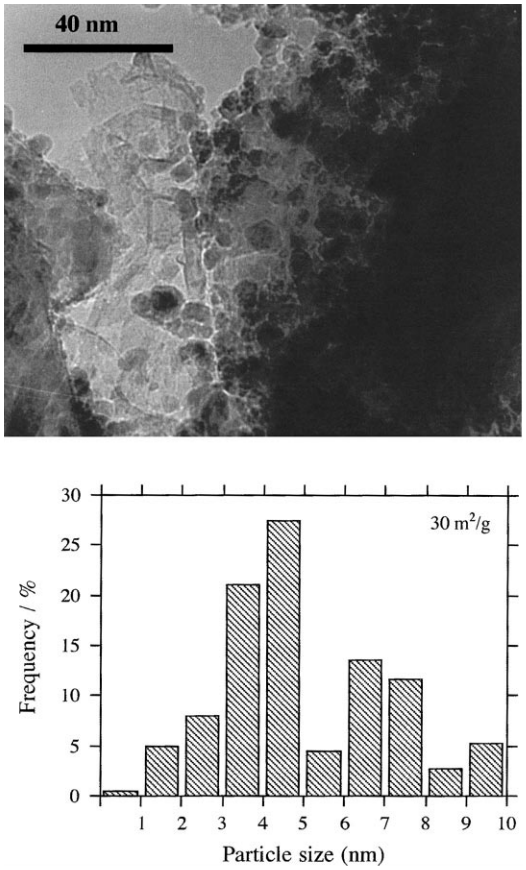

Fig. 1. TEM and particles distribution of NiO/SiC-3.9%.

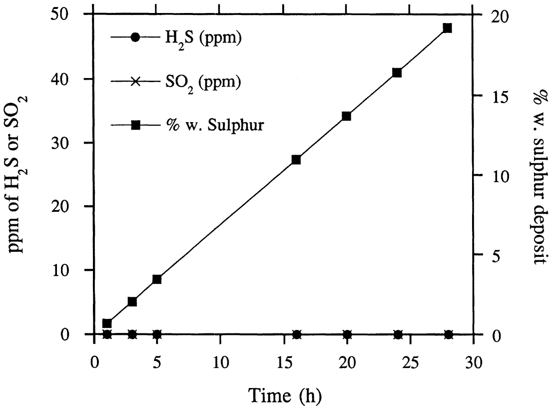

Fig. 2. Activity and selectivity of NiS_2/SiC-3.9% at 100°C.

A large excess of elemental sulphur was dropped into the top of the catalyst bed (NiO/SiC) and the system was heated under H_2S/He-2% flow at 300°C. When all the sulphur had gone through the catalyst, the reactor was cooled down to room temperature and an XRD diagram of the material was produced (identical to the diagram in Fig. 4(a)). The catalyst only contained NiS_2 and β-SiC as crystalline phases. This activated catalyst was heated to 100°C under a flow of pure He and then switched to a flow containing 2000 ppm of H_2S, 3200 ppm of O_2, 20% steam (complement to the He atmosphere), at a volume hour space velocity (VHSV) of 1050 h^{-1} for a contact time of 3.4 s. Fig. 2 shows that no H_2S or SO_2 were detected at the outlet of the reactor up to 30 h, meaning thereby that 100% conversion with 100% selectivity

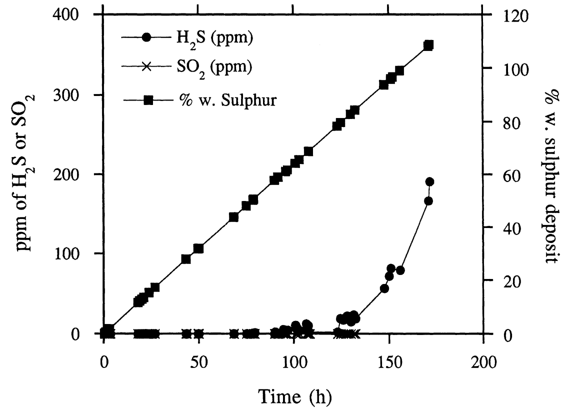

Fig. 3. Activity and selectivity of NiS$_2$/SiC-10% at 100°C during 180 h.

took place. The sulphur balance calculated (from chromatography of the inlet gas) and measured by weighing the catalyst before, and after, melting the sulphur deposit was 100%. After 30 h, the catalyst bed had stored almost 20% in weight of sulphur. The same test was run on NiO-10%/SiC and exhibited the same results (Fig. 3). But, instead of stopping the test after 30 h, it was carried on for 180 h. No SO$_2$ was ever detected. After 100 h, some ppm of H$_2$S could be found in the outlet gas, but it was only after 150 h that the catalyst started to lose some activity with 200 ppm of H$_2$S at 180 h. During this period, the catalyst had stored >100% of its weight as elemental sulphur in its pores.

Many cycles of reactions at 100°C and sulphur removal at 250–300°C under inert gas (or gas containing H$_2$S) were performed without showing any deactivation or degradation of the catalyst. In Fig. 4 are reported the XRD diagrams of the catalyst containing 20% elemental sulphur (clearly evidenced in Fig. 4(b)) and the 10× cycles catalyst (Fig. 4(a)).

The porosity of the material (Fig. 5) was measured before activation, NiO/SiC; low mesoporosity between 30 and 80 Å and large macroporosity between 200 and 500 Å, initially found, had disappeared on the activated catalyst NiS$_2$/SiC. This phenomenon was attributed to a slight sintering of the particles when going from NiO to NiS$_2$, blocking the access to the smallest pores. This was clearly indicated, both by the loss in surface area, from 30 to 24 m^2/g and by the TEM micrograph shown in Fig. 6. The high resolution TEM exhibited a well-crystallized NiS$_2$ particle (the two

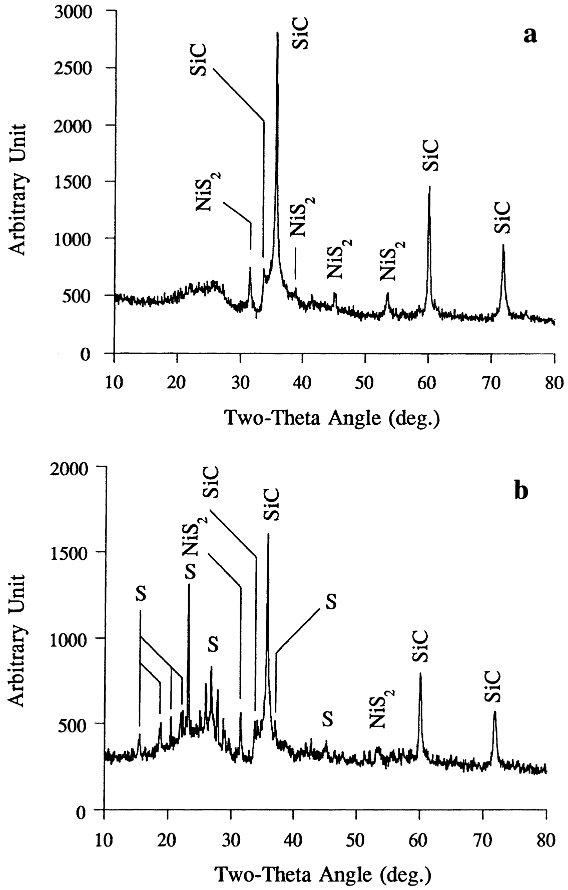

Fig. 4. XRD diagrams of NiS$_2$/SiC (a) before, and (b) after reaction.

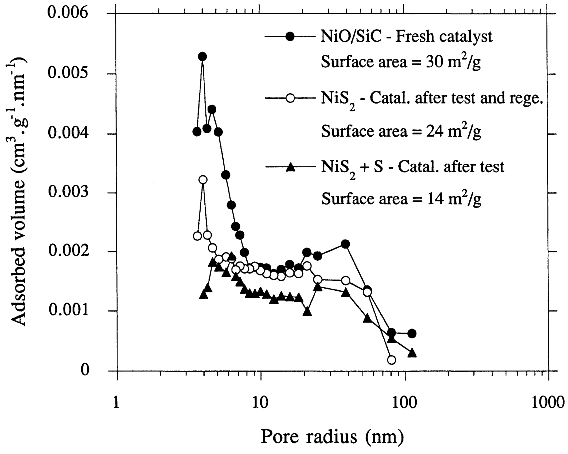

Fig. 5. Pore distribution and specific surface area of NiO/SiC, NiS$_2$/SiC and NiS$_2$/SiC after test.

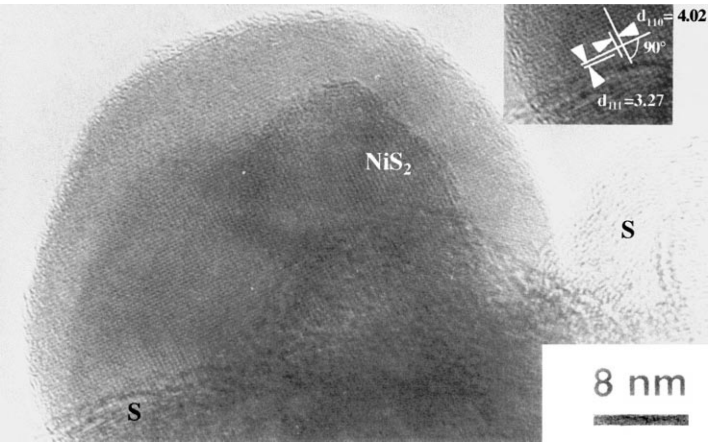

Fig. 6. TEM micrograph of NiS_2/SiC after reaction.

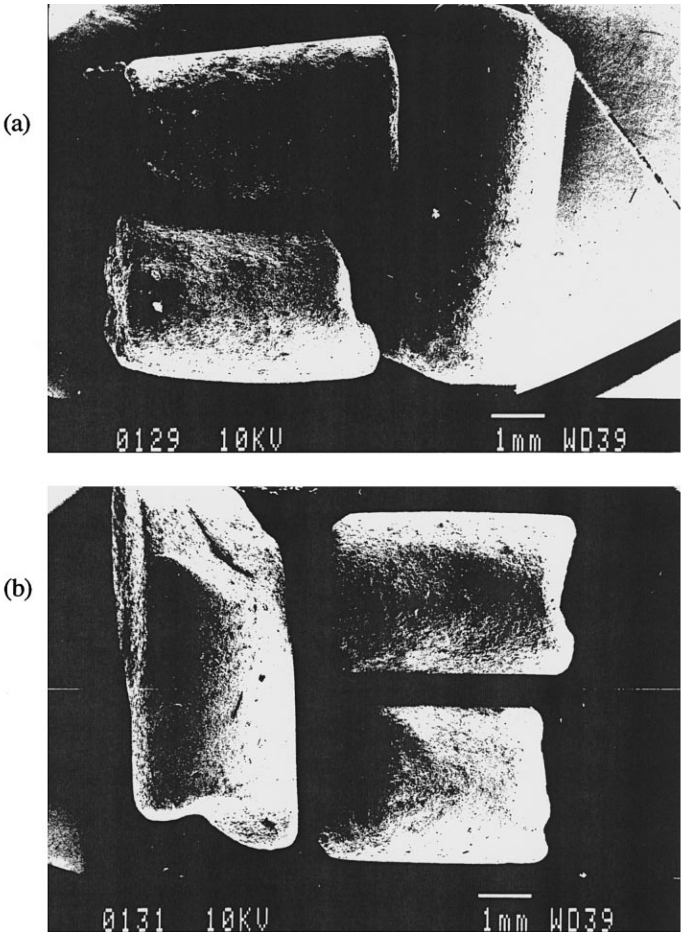

Fig. 7. Low magnification SEM micrographs of extrudates (a) before, and (b) after reaction.

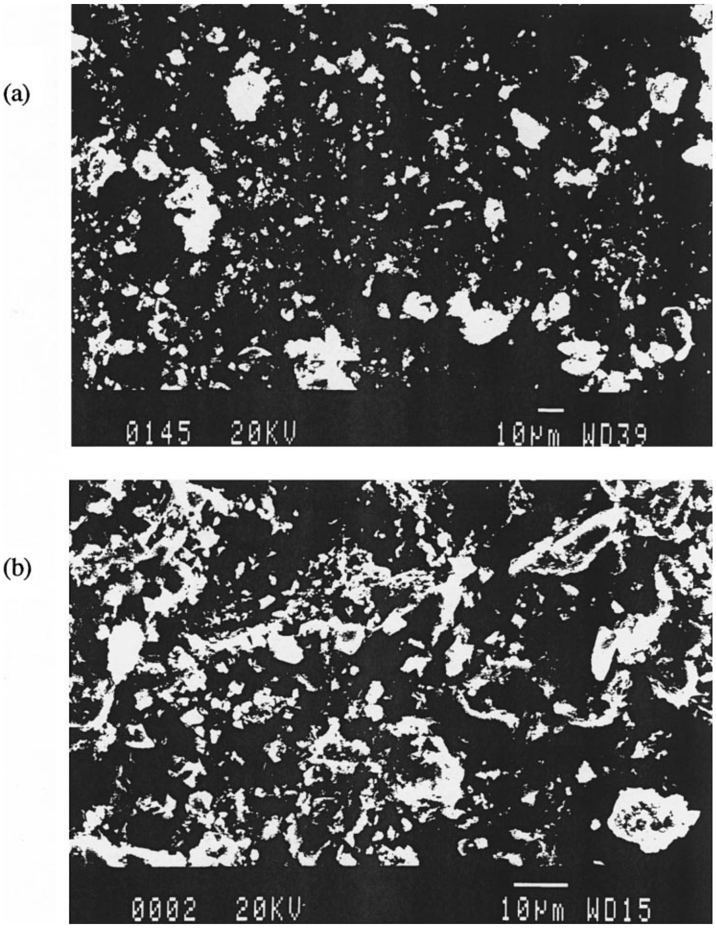

Fig. 8. High magnification SEM micrographs of extrudates (a) before, and (b) after reaction.

orthogonal plans [110] and [111] were clearly identified with distances of 4.02 Å and 3.27 Å respectively) at about 400 Å. Statistical analysis showed that the average size was smaller and around 100 Å. From Fig. 5, it was clear that most of the sulphur deposit was filling the mesoporosity between 40 and 200 Å.

SEM micrographs of the extrudates before reaction (without elemental sulphur), and after (containing 20% sulphur), are shown in Figs. 7 and 8. At low magnification (Fig. 7), the extrudates are identical, meaning that sulphur was contained inside them. At higher magnification (Fig. 8), it is clear that some sulphur was not inside the mesopores, but filling the gap between the SiC grains inside the extrudate (macroporosity and channel).

The NiS_2/SiC catalyst was tested under the same flow conditions at 120°C, which is the average temperature of sub-dew point processes. The catalyst was too reactive at the beginning of the reaction; typical concentrations of SO_2 were found at levels around 1000 ppm with a total conversion of H_2S. In order to obtain a more efficient catalyst, it was necessary to neutralize NiS_2 by a flow of air just after the regeneration, leading probably in this case to an oxysulphide of Ni. After such a treatment, only 300 ppm of SO_2 were released at the beginning of the reaction and the total amount of sulphur ($SO_2 + H_2S$) never exceeded the limit of 300 ppm and averaged 150 ppm for most of the period of test. This is clearly shown in Fig. 9 on NiS_2–5.6%/SiC.

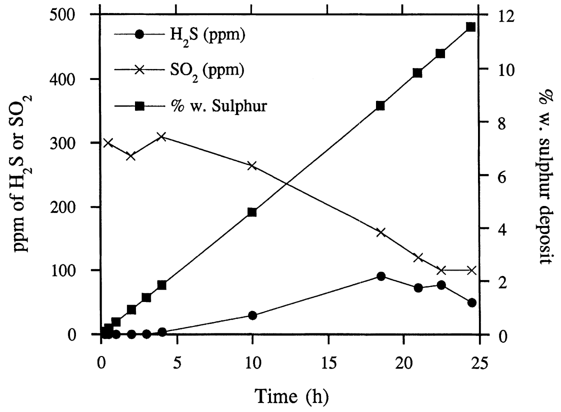

Fig. 9. Activity and selectivity of NiS_2/SiC-5.6% at 120°C.

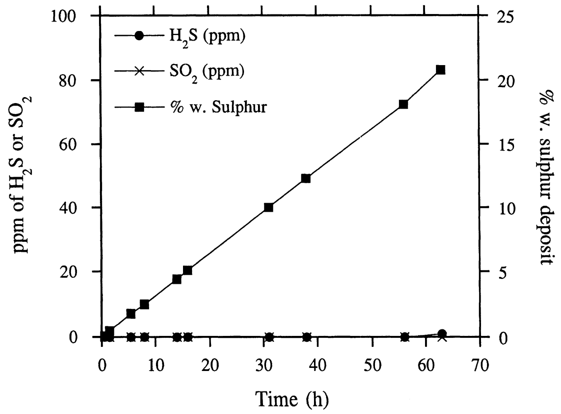

Fig. 10. Activity and selectivity of NiS_2/SiC-5.6% at 40°C.

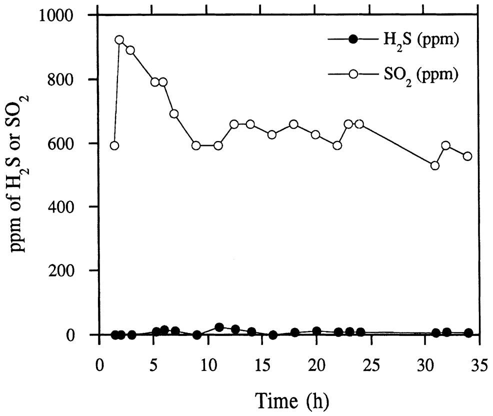

Fig. 11. Activity and selectivity of Fe_2O_3/SiC-5% at 240°C.

In view of the extremely high activity of this catalyst, it was decided to test it at room temperature (in fact, at 40°C in an adiabatic system). With a slightly lower VHSV (720 h^{-1}) and a longer contact time (5 s), the catalyst was 100% selective for a conversion of 100% during 63 h (Fig. 10). No report has ever been published with such results. Trovarelli et al. [18,19] reported that active charcoal exhibited high activity in similar reaction conditions, but the catalyst rapidly deactivated with time-on-stream and sulphur loading. At this temperature, a large fraction of the steam condensed at the head of the reactor and trickled down through the catalyst. The condensed water was analysed and did not contain any detectable sulphur, and its pH was equal to 6.4, a somewhat neutral value. The mass balance of sulphur measured and calculated was 100%. This meant that the catalyst was able to oxidize H_2S contained in small amounts in water, a possible new process to treat acidic aqueous effluent containing H_2S.

3.2. Above-dew point reactions

Many active phases supported on SiC have been tested in this study. Only Fe_2O_3/SiC–5%Fe is reported here (Fig. 11). Without any activation, the catalyst was placed in a fixed bed reactor under a flow containing 0.9%H_2S, 2.29%O_2, 20%steam at 240°C, with a VHSV of 1500 h^{-1}, and a contact time of 2.4 s. The conversion was almost total (a few ppm of H_2S were detected) and the amount of SO_2, measured at 600 ppm at the beginning increased to 900 ppm in the first 5 h to level at 600 ppm for as long as many tens of hours. The measured and calculated mass balance of sulphur was 100%. These results mean that, with such a catalyst, an overall efficiency of 99.8% can be reached which is better than the existing over dew-point processes which do not exceed 99.5% under similar conditions.

There are two hypothesis which can explain these results at low, medium and high temperatures. The SiC support allows the formation of a very specific active phase (Ni or Fe oxysulphide) which cannot be properly stabilized on oxide supports, such as alumina or silica, because of the interference between the oxygen atoms of the support and the active phase. Many authors have already suggested the intervention of the sulphate as the active material [7,20,21]. Different tests which will be published later [22] have proved that sulphate is not the active phase in the supported SiC system, but a compound close to a sulphide containing some oxygen atoms, at least on the surface. The second hypothesis is based on the fact that SiC allows an optimal dispersion of the active particles, small enough to present the required number of active sites and large enough to not be too reactive and less selective. Better dispersed catalysts prepared on SiC by another impregnation procedure give extremely active but not very selective catalysts. These results will be published later [22]. These two hypothesis are not exclusive.

4. Conclusion

SiC supported Ni or Fe catalysts were found to be extremely reactive and selective for the oxidation of H_2S into elemental sulphur. Three temperature ranges were investigated. Below water dew point, it appeared that, under such conditions, the catalyst is 100% efficient with no carryover of active phase and no acidification of the removed water. Between water and sulphur dew points, at 120°C an overall efficiency of 99.95% was observed. At temperatures typical of over-dew point processes an overall efficiency of 99.8% was found.

Acknowledgements

Elf Aquitaine and Pechiney, both from France, have financially supported this research. C. Estournes and J. Guille for the SEM and G. Ehret for the TEM, all from the IPCMS in Strasbourg, are thanked for their participation.

References

[1] Sulphur 231 (1994) 35.
[2] L. Connock, Sulphur 257 (1998) 34.
[3] Sulphur, 250 (1997) 60.
[4] P.F.M.T. van Nisselrooy, J.A. Lagas, Catal. Today 16 (1993) 263.
[5] P.H. Berben, J.W. Geus, in: Calgary, M.J. Phillips, M. Ternan (Eds.), Proc. 9th Int. Congress on Catalysis, vol. 1, 1988, 284 pp.
[6] P.J. van den Brink, R.J.A.M. Terörde, J.H. Moors, A.J. van Dillen, J.W. Geus, in:P. Ruiz, B. Delmon (Eds.), New Developments Selective Oxidation by Heterogeneous Catalysis, Studies in: Surface Science and Catalysis, vol. 72, Elsevier, Amsterdam, 1992, 123 pp.
[7] P.J. van den Brink, PhD Dissertation, University of Utrecht, The Netherlands, 1992.
[8] P. H. Berben, PhD Dissertation, University of Utrecht, The Netherlands, 1992.
[9] S. Savin, O. Legendre, J.B. Nougayrède, C. Nedez, Sulphur 96, 523 pp. (preprints).
[10] S. Savin, J. Nougayrède, W. Willing, G. Bandel, Int. J. Hydrocarbon Eng., 1998, 54 pp.
[11] A. Philippe, J. Nougayrède, S. Savin-Poncet, M.J. Ledoux, C. Pham-Huu, C. Crouzet, French Patent Application No. 94-13752, 1994
[12] M.J. Ledoux, J. Nougayrède, S. Savin-Poncet, C. Pham-Huu, N. Keller, C. Crouzet, French Patent Application No. 97-16617, 1997.
[13] M.J. Ledoux, J. Nougayrède, C. Pham-Huu, N. Keller, S. Savin-Poncet, C. Crouzet, French Patent Application No. 98-11941, 1998.
[14] M.J. Ledoux, S. Hantzer, C. Pham-Huu, J. Guille, M.P. Desaneaux, J. Catal. 114 (1988) 176.
[15] M.J. Ledoux, S. Hantzer, J. Guille, D. Dubots, US Patent No. 4 914 070.
[16] M.J. Ledoux, J. Guille, C. Pham-Huu, H.M. Dunlop, M. Prin, US Patent No. 5 468 370, 1991.
[17] N. Keller, C. Pham-Huu, S. Roy, M.J. Ledoux, C. Estournes, J. Guille, J. of Materials Science, in press.
[18] A. Primavera, A. Trovarelli, P. Andreussi, G. Dolcetti, Appl. Catal. A: General 173 (1998) 185.
[19] A. Trovarelli, F. Felluga, C. de Leitenburg, P. Andreussi, G. Dolcetti, in: G. Centi et al. (Ed.), Proc. 1st Environmental Catalysis, Pisa, 1–5 May 1995, 667 pp.
[20] A. Piéplu, PhD Dissertation, University of Caen, France, 1994.
[21] A. Piéplu, A. Janin, O. Saur, J.C. Lavalley, in: G. Centi et al. (Ed.), Proc. 1st Environmental Catalysis, Pisa, 1–5 May 1995, 303 pp.
[22] N. Keller, C. Pham-Huu and M.J. Ledoux, in preparation.