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Honeycomb Structured Catalysts for H₂ Production via H₂S Oxidative Decomposition

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Abstract: Cordierite honeycomb structured catalysts were studied for the reaction of H₂S decomposition in the presence of oxygen to obtain H₂ and sulphur. An Al₂O₃-based washcoat was deposited on the honeycomb monolith by a dip-coating procedure. In particular, three different washcoat percentages (15, 20 and 30 wt%) were deposited on the structured carrier and the obtained samples were characterized by N₂ adsorption and SEM analysis. The evaluation of the catalytic performance of the three samples was carried out at two different temperatures (1000 °C and 1100 °C). The sample with 30 wt% washcoat content showed the lowest SO₂ selectivity at 1000 °C (<0.4%), whereas the H₂S conversion and H₂ yield values were very similar to those achieved for the samples at 15 and 20 wt% washcoat loading. Based on these results, additional tests were carried out on the catalyst with 30 wt% Al₂O₃-based washcoat loading, varying the contact time and the H₂S inlet concentration to identify the operating conditions that minimize the SO₂ formation, obtaining good H₂S conversion and H₂ yield. The comparison of the structured catalyst with the powder alumina sample has shown the same catalytic performance, exhibiting lower SO₂ selectivity.

Keywords: H₂S oxidative decomposition; H₂ production; sulphur; Al₂O₃-based washcoat; cordierite monolith honeycomb

1. Introduction

The direct recovery of H_2 and sulphur from H_2S has attracted strong interest in the scientific community, and several papers on this topic have been published [1]. Nowadays, H_2S is converted to sulphur and H_2O by the Claus process, which is not cost-effective because the price of sulphur is depressed and the hydrogen is lost as H_2O . In this regard, an interesting alternative is to obtain sulphur and H_2 by thermal decomposition of H_2S . However, a H_2S decomposition reaction is highly endothermic and is not favoured from a thermodynamic point of view because, for extremely high temperatures, it requires follow-up separation stages and has high fixed and operating costs [2].

A promising alternative to the Claus process is to carry out the H_2S decomposition reaction with a small concentration of oxygen in order to use the heat produced by the H_2S oxidation to support the endothermicity of the H_2S cracking reaction. In this way, the system could be run in autothermal conditions, obtaining sulphur, H_2O and H_2 [3].

However, the oxygen can represent a problem due to the possible formation of SO_2 , mainly caused by H_2S total oxidation reaction.

The use of a catalyst is necessary to maximize selectivity towards sulphur and hydrogen, minimizing the SO₂ production. Al₂O₃-based catalysts were generally employed because they favour H₂ formation, reducing SO₂ formation by the Claus reaction $(2H_2S + SO_2 = 3/2S_2 + 2H_2O)$ [4].

In our previous works, we have studied the reaction of H_2S thermal oxidative decomposition in homogeneous phase [5,6] and with alumina-based catalyst in powder form [7] by investigating the effect of different operating conditions (temperature, O_2/H_2S , H_2S inlet concentration) on the catalytic performance. In the presence of the catalyst, the SO_2 selectivity was about 0.5% at 1000 °C, significantly lower than that observed in the homogeneous phase (4%).

Starting from the promising results obtained in the presence of the alumina-based catalyst, the aim of this paper is the transfer of the catalytic formulation of the powder to a structured catalyst coated with an alumina-based washcoat.

Honeycomb monolithic catalysts can be an interesting alternative to carriers usually used for the formulation of structured catalysts [8,9].

Cordierite monolithic structure has been studied in different gas phase reactions as well as catalytic combustion of volatile organic compounds and selective reduction of NO_x [8,10].

Cordierite $(2MgO \cdot 2Al_2O_3 \cdot 5SiO_2)$ is a material characterized by high chemical and mechanical stability; and low thermal expansivity coefficient, porosity and pore size distribution. These properties allow good washcoat adherence [11].

Washcoats are coated on the carrier to yield a large specific surface area on which active phases are deposited [12].

The aim is to identify the washcoat loading able to depress the SO_2 formation, ensuring good H_2S conversion and H_2 yield.

The alumina-based washcoat has been deposited on the honeycomb monolith by a dip-coating procedure and three structured catalysts at 15, 20, and 30 wt% of washcoat loading were prepared, characterized from a physical-chemical point of view, and the influence of different operating conditions (reaction temperature, contact time, H₂S inlet concentration) on catalytic performance has been assessed.

2. Results and Discussion

2.1. Structured Catalyst Characterization

Table 1 reports the SSA values of cordierite, before and after the washcoat deposition with the three different loadings.

SAMPLE	SSA (m ² /g)
Cordierite	0.8
Washcoat 15 wt%	8
Washcoat 20 wt%	13
Washcoat 30 wt%	29.0

Table 1. SSA of the structured catalysts.

It is possible to observe that the SSA of the cordierite is very low (<1 m²/g), probably due to the low porosity of the sample. By increasing the washcoat load, the SSA is increased from 8.6 up to $29 \text{ m}^2/\text{g}$ [13,14].

The objective of the washcoating procedure was to obtain an average washcoat cover on the monoliths channels walls of ~100 μ m.

The uniformity of the washcoat layer and the probable presence of the large pores of the support were studied with SEM analysis.

The SEM images of the cordierite and the cordierite after the washcoat deposition are shown in Figure 1.



Figure 1. SEM images of cordierite before (a) and after the washcoat deposition (b).

On the cordierite (Figure 1a), the clear presence of macropores can constitute anchoring points for the washcoat; the presence of these macropores is also justified by the low value of SSA (<1 m^2/g).

From Figure 1b, it clearly appears that after the washcoating procedure, the macropores in the cordierite walls were entirely covered and filled by the washcoat. Moreover, Figure 1b also shows small cracks on the washcoat layer. As confirmed by the literature, this kind of small crack may act as additional anchoring points for the active phases, producing other surfaces available for the chemical reaction [15].

The mechanical stability of the washcoat layer deposited on the cordierite was investigated by ultrasonic tests. Figure 2 reports the weight loss of the samples as a function of ultrasonic exposure time.



Figure 2. Adhesion test stability for three different washcoat loads.

A better adhesion of the washcoat to the cordierite is obtained for the sample at 30 wt%, for which we observed a weight loss lower than 0.5 wt%. A higher weight loss was instead obtained for the sample with the lower washcoat content.

However, the results obtained for all three samples denote the good adhesion and stability of the washcoat on the carrier, confirming the effectiveness of the preparation method.

2.2. Catalytic Activity Test

2.2.1. Effect of the Washcoat Loading

Preliminary tests were performed to investigate the influence of the washcoat loading on the catalytic performance at 1000 and 1100 °C (Figure 3). These tests were performed at fixed contact (20 ms) and at 10 vol% H_2S inlet concentration. The results obtained were compared with the equilibrium data.



Figure 3. Cont.



Figure 3. Effect of the washcoat loading at T = 1000 °C (left), T = 1100 °C (right), in terms of H₂S conversion (**a**,**b**), H₂ Yield (**c**,**d**), SO₂ selectivity (**e**,**f**).

At 1000 °C reaction temperature, an increase of the H_2S conversion and a small decrease of the H_2 yield were observed by increasing the washcoat loading.

The lowest SO₂ selectivity value was obtained with the sample 30 wt% of washcoat content at 1000 °C, while, with the same sample, the SO₂ selectivity seems to be higher at 1100 °C with respect to the other two washcoat loadings. However, we have chosen the sample at 30 wt% washcoat loading because this content allows us to maintain the SO₂ selectivity at values lower than 0.4% for both investigated temperatures.

In fact, the main objective of the our work is to improve the selectivity of the reaction system towards sulphur and H_2 , minimizing the SO₂ selectivity and giving the process at "quasi" zero SO₂ emissions, also when the reaction temperature is different.

The H₂S conversion and H₂ yield exhibit at 1100 °C the same trends as those obtained at 1000 °C; the only difference was observed for the SO₂ selectivity, which was negligible at the lower washcoat loadings (15–20 wt%) and about 0.2% for the sample at 30 wt% washcoat content.

At the highest washcoat percentage, there is a better approach to the equilibrium for the H_2S conversion, but a slight decrease of the H_2 yield, likely because the oxidation reactions are a little more favoured, as confirmed by the SO_2 selectivity values.

Based on the results obtained, further investigations were performed using the catalyst having the highest washcoat content (30 wt%).

2.2.2. Influence of the Contact Time and H₂S Inlet Concentration

The influence of the contact time (20–30 ms) is reported in Figure 4.



Figure 4. Catalytic performance of cordierite, washcoat + cordierite in terms of H_2S conversion (**a**), H_2 yield (**b**), SO_2 selectivity (**c**) (T = 1100 °C).

For the catalysed samples, we obtained a H_2S conversion (50%) very close to the thermodynamic equilibrium one, while for the case of the bare cordierite (Figure 4a) the values of H_2S conversion and H_2 yield are much lower than the equilibrium ones (Figure 4a,b), but do not seem be affected by the variation in the contact time. Relative to the SO_2 selectivity, for the cordierite the value is 0.4% while for the sample catalysed it is 0.2% (Figure 4c).

The influence of the H_2S inlet concentration at 1100 °C and at a fixed contact time of 30 ms is displayed in Figure 5.





Figure 5. Effect of H₂S inlet concentration on H₂S conversion (**a**), H₂ yield (**b**), SO₂ selectivity (**c**) (T = 1100 $^{\circ}$ C, τ = 30 ms).

With the increase in H_2S concentration, it is possible to note a progressive decrease of H_2S conversion, H_2 yield, and SO_2 selectivity. In particular, it was negligible when the H_2S inlet concentration was higher than 10 vol%, likely because the kinetic of the Claus reaction is more favoured at higher H_2S concentrations. However, it must be stressed that the H_2S conversion is rather high (>40%) and the H_2 yield is close to the equilibrium value, also for the catalytic test carried out at the higher tested H_2S inlet concentration (40 vol%).

2.2.3. Comparison between Powder and Structured Catalyst

Finally, the comparison between the catalysed monolith and the powder catalyst was performed at 1100 °C reaction temperature and 30 ms contact time. The results of the alumina powder catalyst refers to our previous work [7]. The amount of powder catalyst used in the test is equal to 0.2 g; the mass of washcoat deposited on the cordierite monolith (at 30 wt%) is 0.2, considering that the weight of structured catalyst used in the test was 0.67 g.

The catalytic performances of the two samples are listed in Table 2.

	Powder Catalyst	Structured Catalyst
H ₂ S Conversion, %	57 ± 5	56 ± 5
H ₂ Yield, %	21 ± 3	21 ± 3
SO ₂ Selectivity, %	0.5 ± 0.05	0.2 ± 0.05

 Table 2. Catalytic performances of the powder and structured catalyst.

For both the catalysts we obtained the same values of H_2S conversion and H_2 yield, while the SO_2 selectivity observed for the structured catalyst is about half that of the other, evidencing no limitation to the internal diffusive transport in the washcoat layer [16].

3. Experimental and Methods

3.1. Materials

Cordierite honeycomb monoliths provided by Corning (New York, NY, USA) (226 cpsi, average wall thickness 0.23 mm) were employed as the carrier (nine channels).

The monoliths have the following size: 30 mm in length, 6 mm wide, and 6 mm high.

For the washcoat procedure, boehmite (AlOOH), provided by Sigma Aldrich (St. Louis, MO, USA), nitric acid (60–65 wt%) and distilled water were used. For the slurry preparation, a known amount of boehmite (36 g) was added to 300 cm³ of distilled water, in order to obtain the solid percentage desired (10 wt%).

3.2. Structured Catalyst Preparation and Characterization Tests

Before the dip-coating procedure, the monoliths were pre-treated at 500 $^{\circ}$ C in a muffle furnace for 2 h in static air. The slurry formation was obtained by adding the nitric acid (HNO₃) to the suspension in agitation in order to obtain a pH value of 1–2, to ensure good rheological properties that are necessary for the achievement of a uniform and homogeneous washcoat deposition [17,18].

The dip-coating procedure was realized by dipping the ceramic support in the slurry for 1 h (Figure 6).



Figure 6. Monolith dipped in the washcoat.

After the impregnation of the monolith, the excess suspension inside the channels of the cordierite was removed by a vacuum pump. Afterward, the monoliths were dehydrated at 120 °C for 12 h and afterwards calcined at 500 °C for 2 h. The same procedure was adopted until the desired washcoat load was reached (15, 20 or 30 wt%).

The amount of the deposited washcoat was evaluated by considering the initial weight of the monolith and the weight after each step of impregnation/calcination. After the achievement of the desired washcoat load, the monoliths were calcined at 900 $^{\circ}$ C for 1 h at a 20 $^{\circ}$ C/min heating rate (Figure 7).



Figure 7. Structured catalyst after calcination at 900 °C for 1 h.

The estimation of the average thickness of the washcoat layer deposited on the cordierite was made through the evaluation of the apparent density of the powder alumina obtained after the calcination at 500 $^{\circ}$ C for 2 h and the calculation of the overall exposed surface of the monolith.

The average thickness of the washcoat is then evaluated according to the following relationship (Equation (1)):

$$Average \ thickness = \ \frac{\rho_{APP} \cdot washcoat \ weight}{S}, \tag{1}$$

where ρ_{APP} : apparent density of alumina, (g/cm³); washcoat weight: mass of the washcoat deposited, (g); S: total surface of the monolith, cm².

The obtained values are listed in Table 3.

Samples	Average Thickness (µm)
Washcoat 15 wt%	46
Washcoat 20 wt%	64
Washcoat 30 wt%	90

Table 3. Average thickness of washcoat layer.

The samples were characterized by scanning electron microscopy (SEM) and specific surface area (SSA).

In particular, the morphology of the samples was examined using a Scanning Electron Microscope (SEM) (model LEO 420 V2.04, ASSING, Rome, Italy).

The specific surface area (SSA) was evaluated with a Costech Sorptometer 1040 (Milan, Italy) using the BET method multipoint analysis based on N₂ adsorption/desorption isotherms at $-196 \degree$ C after the pre-treatment of the sample at 150 °C for 1 h in an He flow (99.9990%).

The mechanical stability tests were carried by ultrasonic tests to examine the washcoat adhesion on the carrier. The monoliths were placed in a beaker with petroleum ether (Carlo Erba, Milan, Italy) and positioned in an ultrasonic bath CP104 (EIA S.p.A, 36 kHz) filled with distilled water, at 25 °C, working at 60% of rated power for 0.5 h.

The weight variations were recorded during the test at 5-min intervals after monoliths drying at 120 °C and cooling up to ambient temperature.

The samples' weight losses were calculated according to the following equation:

$$Weight \ Loss = \frac{Initial \ Weight - Final \ Weight}{Initial \ Weight} \cdot 100.$$
(2)

The *"initial weight"* and *"final weight"* represent the washcoat weight before and after the ultrasonic tests.

3.3. Experimental Setup

The catalytic activity tests were performed in the laboratory apparatus displayed in Figure 8 and described in detail in our previous work [5].



Figure 8. Scheme of the laboratory plant.

A system of three-way values allows us to send the feed stream (H_2S , O_2 , N_2) to the reactor and the products to the analyser; in bypass position, the reactants go directly to the analyser in order to check the composition of the feeding gas.

Experiments were carried out in a fixed-bed quartz tubular reactor. The measurement of the temperature in the catalytic bed was realized with a thermocouple placed in a quartz sheath, concentric to the reactor. Sulphur produced by the reaction was trapped by using a quartz-wool filter, located after the reactor in the quenching zone [7].

The gaseous streams were analysed by a mass spectrometer (Hiden HPR 20, Warrington, UK).

The catalytic activity tests were performed with the following operating conditions: temperature: 1000–1100 °C; H₂S concentration: 10–40 vol%; feeding O_2/H_2S molar ratio: 0.2; contact time (V_{cat}/total flow rate): 20–30 ms; total flow rate: 700–1180 Ncm³/min.

The evaluation of the H_2S conversion, SO_2 selectivity, and H_2 yield were realized using the following equations:

where:

 zH_2S^{IN} : Inlet H_2S volumetric fraction [-] zH_2S^{OUT} : Outlet H_2S volumetric fraction [-] zSO_2^{OUT} : Outlet SO_2 volumetric fraction [-] zH_2^{OUT} : Outlet H_2 volumetric fraction [-].

4. Conclusions

Structured catalysts starting with a cordierite carrier were prepared with the objective of realizing a structured catalyst for the reaction of H_2S thermal oxidative decomposition at high temperature. The washcoat deposition on the cordierite carrier was realized by a dip-coating technique.

Interesting results were obtained through the characterization techniques, relating to the chemical and structural properties of the washcoat.

In particular, the washcoat exhibited good adhesion capacity with the support, showing quasi-negligible weight losses after ultrasonic testing. Complete coverage of the macroporosity of the cordierite was observed from the SEM analysis, supporting the effectiveness of the deposition method; furthermore, the microcracks observed on the washcoat layer could act as supplementary anchoring points for the possible active phases deposition.

The effect of three different washcoat loadings (15, 20 and 30 wt%) was tested at temperatures of 1000 °C and 1100 °C in terms of catalytic performance expressed as H_2S conversion, H_2 yield and SO_2 selectivity. The better performance, especially in terms of SO_2 selectivity (0.2%), was obtained at 1100 °C for the sample catalysed with a washcoat loading of 30 wt%.

Lower catalytic activity was observed for bare cordierite in comparison with the catalysed sample. The influence of the contact time and the H_2S concentration was investigated on this sample at a temperature of 1100 °C; at a lower contact time and at higher H_2S concentrations, the SO₂ formation was depressed, obtaining good H_2S conversion and H_2 yield.

Finally, the suitability of the preparation and the correct transfer of the catalytic formulation from the powder to the monolith were confirmed from the same behaviour of the structured catalyst with the respective powder sample. Furthermore, the structured catalyst has evidenced the absence of transport diffusive phenomena, thus making this formulation an innovative solution for the reaction of H_2S oxidative decomposition to produce hydrogen and sulphur simultaneously with negligible SO_2 emissions.

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