



# Vanadium-Ceria Structured Catalysts for the Selective Partial Oxidation of H<sub>2</sub>S from Biogas

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The reaction of H<sub>2</sub>S selective partial oxidation to elemental sulfur in the range of temperature of 150-200 °C was studied on cordierite honeycomb-structured catalysts.

The preparation procedure of catalytic cordierite monoliths has been studied, from the washcoating with CeO<sub>2</sub> to the deposition of V<sub>2</sub>O<sub>5</sub> by wet impregnation.

Two different preparation washcoating procedures deposition were studied: in one case the washcoat had been already added with the salts precursors of the active species (joint impregnation method), in other case the active species were added only after the deposition step of the washcoat on the monolith, by impregnation in a solution of the salt precursor (distinct impregnation method).

The catalysts prepared with the two different methods were characterized and the stability was investigated in catalytic activity tests. The catalysts prepared with the "joint impregnation" method have shown a poor catalytic activity and tendency to the deactivation.

Very different results were found for the catalysts prepared with the "distinct impregnation" method, for which the effect of the vanadium content (2-19 V<sub>2</sub>O<sub>5</sub> wt %) was also studied at 200 °C. Good catalytic performances were obtained for both samples that have shown a high H<sub>2</sub>S conversion (~90 %), low SO<sub>2</sub> selectivity (2 %) and a high stability.

## 1. Introduction

Several processes have been described and developed for the elimination of H<sub>2</sub>S from products or off-gases. For the small scale plant, a very interesting solution could be represented by the direct and selective H<sub>2</sub>S oxidation to sulphur as reported in the following reaction  $H_2S + \frac{1}{2} O_2 = \frac{1}{x} S_x + H_2O$  and performed at low temperature in the presence of a very active and selective catalyst (Yasyerly and Dogu, 2004).

In a previous work, we examined the performances of vanadium-oxide based catalysts supported on the metal oxides in the range of temperature of 50 - 250 °C (Palma et al., 2012). Among the investigated samples, V<sub>2</sub>O<sub>5</sub>/CeO<sub>2</sub> catalyst showed the most promising catalytic performances at temperature lower than 200 °C in terms of high H<sub>2</sub>S and O<sub>2</sub> conversion with a very low SO<sub>2</sub> selectivity at a feed ratio H<sub>2</sub>S/O<sub>2</sub>= 2. In order to verify the possibility to further reduce the SO<sub>2</sub> selectivity, additional experimental tests were performed by investigating the effect of the inlet H<sub>2</sub>S concentration, the gas hourly space velocity and the H<sub>2</sub>S/O<sub>2</sub> molar feed ratio (Palma et al., 2013a).

Additional catalytic activity tests were also carried out to study the effect of the vanadium content in the range 2.55-20 wt % V<sub>2</sub>O<sub>5</sub> at different temperatures the results of which of this preliminary screening showed that, in the temperature range of 150 - 250 °C, the vanadium load mainly affected the value of SO<sub>2</sub> selectivity, with not so relevant effects on the catalytic activity. The most selective catalyst was the 20 wt % V<sub>2</sub>O<sub>5</sub>/CeO<sub>2</sub> showing a sulfur selectivity of about 99 % at 150 °C (Palma et al., 2013b).

The aim of this work is to transfer this formulation on a cordierite (2MgO·2Al<sub>2</sub>O<sub>3</sub>·5SiO<sub>2</sub>) honeycomb structured carrier by using a CeO<sub>2</sub> based-washcoat as support for the vanadium oxide deposition (2-19 V<sub>2</sub>O<sub>5</sub> wt %).

Monolithic catalysts can be an attractive replacement of conventional carriers in heterogeneous catalysts (Heck et al., 2001). The development of the cordierite monolithic structure has been stimulated by the

requirements of a widely variety of gas-phase reactions such as catalysis in catalytic combustion of VOCs, automotive application, selective reduction of NO<sub>x</sub>. The main reasons are due to its high mechanical strength, low thermal expansion coefficient, and low-pressure drop (Nijhuis et al., 2001).

After the selection of the cordierite as structured carrier, the attention will be focused on the washcoat impregnation with the active phase (V<sub>2</sub>O<sub>5</sub>). To this scope, two different techniques will be used in order to verify the possibility to obtain a one-step catalytic washcoat deposition procedure. The different structured samples will be characterized in terms of mechanical stability test by ultrasonic vibration to investigate the adhesion of ceria washcoat on cordierite and compared in terms of catalytic activity tests.

## 2. Experimental

### 2.1 Materials

Cordierite honeycomb monoliths (9 channels) with 30 mm in length, 6 mm in width, 6 mm in height and 226 cells/in<sup>2</sup> (cpsi) were used as the substrate on which a commercial Ceria-Zirconia washcoat (Ecocat) was deposited. For the active phase deposition (V<sub>2</sub>O<sub>5</sub>) we started by aqueous solution of ammonium metavanadate (Aldrich).

### 2.2 Catalysts preparation

Before the washcoat deposition on the cordierite monolith, the carrier was predried and evacuated at 550 °C for 2 h.

The monoliths were impregnated with the washcoat by dip coating technique and the excess suspension inside the channels of the cordierite substrate was blown off. More precisely the excess suspension was evacuated from the channels by a vacuum pump and after the monoliths were dried at 120 °C for 30 min. Since the monolith cannot be coated sufficiently by a single impregnation, multi-impregnation were required. In order to get more homogeneous washcoatings, it was preferable to use diluted suspensions and perform more than one immersion.

The target of the washcoating procedure was to deposit about 20 wt % of washcoat on the monoliths, in order to completely cover the monoliths channels with a thin layer of washcoat; for the following impregnations the procedure was the same as the first one, until a 20 wt % increase was obtained. Finally the washcoated monoliths were calcined in air at 550 °C for 2 h.

Two different washcoating procedures deposition were studied.

In a case, the solution of the salt precursor of the active phase is added to the washcoat slurry and the monolith is dipped into a suitable slurry (joint impregnation method). After the removing of the excess suspension, the catalysed monolith was dried and also calcined at 400 °C for 3 h.

In the other case the monolith, after washcoat deposition and stabilization by calcination at 550 °C for 2 h, is dipped into the solution of the salt precursor of the phase active (distinct impregnation method).

The impregnation/drying steps into the solution of the salt precursor of the phase active were performed for many times until it was reached the desired content of the active phase. Finally the monoliths were calcined at 400 °C for 3 h.

Catalysts with a vanadium content variable between 2 wt % and 19 wt % were prepared with this last preparation method.

The catalysts prepared was also characterized by different techniques: X-ray diffraction measures, Raman spectroscopy; furthermore the adhesion of the washcoat was evaluated using an ultrasonic technique.

One of goals of this study was to find out a good preparation route to obtain a mechanically stable washcoated cordierite monolith with catalytic activity at least as good as the powder catalyst.

The catalytic tests were carried out in a fixed bed flow reactor, made of a pyrex glass tube 0.21 m long and a 0.014 m of internal diameter, inserted in an electrical furnace equipped with a PID electronic temperature controller.

Preliminary tests were carried out at atmospheric pressure and GHSV of 21,000 h<sup>-1</sup> (~170 ms), in the temperature range 150 - 250 °C, with 500 ppm of H<sub>2</sub>S, 250 ppm of O<sub>2</sub> and N<sub>2</sub> to balance.

The exhaust stream (H<sub>2</sub>S, O<sub>2</sub>, H<sub>2</sub>O) was analyzed by a quadrupole filter mass spectrometer while the concentration of SO<sub>2</sub>, which may be present in the stream leaving the reactor, is monitored instead by an analyzer FT-IR Multigas in continuous.

The H<sub>2</sub>S conversion and the SO<sub>2</sub> selectivity were calculated by using the following equations, by considering negligible the gas phase volume change:

$$x_{\text{H}_2\text{S}}, \% = ((\text{H}_2\text{S}^{\text{IN}} - \text{H}_2\text{S}^{\text{OUT}}) / \text{H}_2\text{S}^{\text{IN}}) \cdot 100 \quad (1)$$

$$y_{\text{SO}_2}, \% = \text{SO}_2 / (\text{H}_2\text{S}^{\text{IN}} - \text{H}_2\text{S}^{\text{OUT}}) \cdot 100 \quad (2)$$

### 3. Results and Discussion

The Raman spectra of the samples with a  $V_2O_5$  content of 20 wt % prepared with the different impregnation techniques have shown in the following figures (Figure 1a-b).

For the sample prepared with the "joint impregnation" method, it is possible to identify the characteristic peak of  $CeO_2$  at  $458\text{ cm}^{-1}$  and other peaks ( $260, 377, 785, 792, 857\text{ cm}^{-1}$ ) ascribable to the presence of the cerium vanadate -  $CeVO_4$  (Gu et al., 2006) Figure 1a.

The Raman spectra of the catalyst prepared by the "distinct impregnation" method have shown in the Figure 1b.

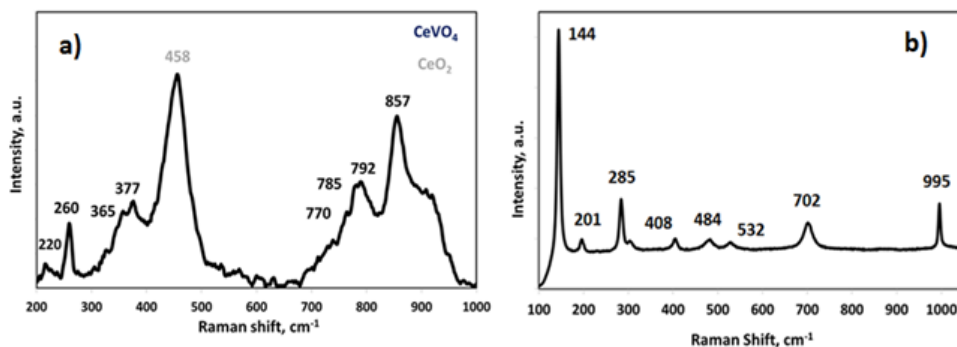


Figure.1: Raman spectra of the fresh catalysts prepared with the joint impregnation (a), and with the distinct impregnation (b)

From the Raman spectra shown in Figure 1b, it is possible to attribute all the peaks to  $V_2O_5$  crystalline species, that exhibited Raman characteristic peaks at  $144, 203, 283, 302, 404, 489, 523, 697, 994\text{ cm}^{-1}$  (Daniell et al., 2002).

The washcoat adhesion test, performed by exposure to ultrasounds showed only some very low, or almost negligible washcoat weight loss during the first cycles of adhesion test, indicating a good adherence to the cordierite support.

The optimal washcoat thickness was determined starting from three different thickness ( $50, 150, 226\text{ }\mu\text{m}$ ) at temperature of  $200\text{ }^\circ\text{C}$  and under conditions far from the thermodynamic equilibrium to better evaluate a difference of the  $H_2S$  conversion values (Figure 2).

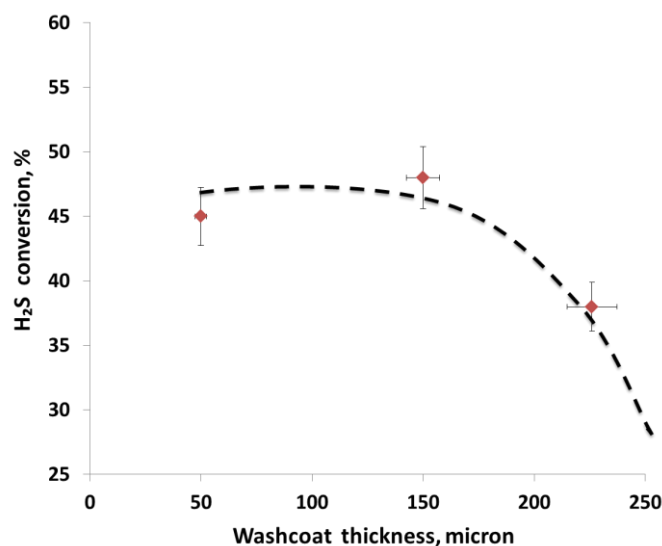


Figure.2: Influence of the washcoat thickness on the catalytic activity ( $Q=800\text{ Ncm}^3/\text{min}$ ,  $T=200\text{ }^\circ\text{C}$ )

A decrease of the  $H_2S$  conversion value was observed for a washcoat thickness greater than  $150\text{ }\mu\text{m}$ , likely due to the internal diffusion phenomena inside the washcoat.

For this reason, the catalysts will be prepared by using a washcoat thickness between 50 - 150  $\mu\text{m}$ .

Table.1 Effect of the different washcoating procedure on the catalytic activity

	Joint impregnation	Distinct impregnation
$X_{\text{H}_2\text{S}}$ , %	77	90
$Y_{\text{SO}_2}$ , %	1	2

The effect of the different washcoating procedure (joint and distinct impregnation) on the catalytic performances was studied on catalysts having a vanadium loading of 2 wt % at 200 °C.

The results, in terms of H<sub>2</sub>S conversion and SO<sub>2</sub> selectivity are reported in Table 1.

From the results obtained it is possible to observe quite similar values of SO<sub>2</sub> selectivity and an higher H<sub>2</sub>S conversion only for the catalyst prepared with the distinct impregnation of the active phase respect to washcoat.

Based on these results, other catalysts will be prepared with the distinct impregnation method of the washcoat with the active phase. The effect of the V<sub>2</sub>O<sub>5</sub> loading variable between 2 wt % and 19 wt % was investigated on the catalytic performances and in particular relatively to the SO<sub>2</sub> minimization at temperature of 150-200 °C.

The catalytic test performed on the catalyst with the lowest vanadium content (2 wt %), reported in the Figure 3 at 200 °C, shows the concentration of the reactants (H<sub>2</sub>S, O<sub>2</sub>) and the products (SO<sub>2</sub>, H<sub>2</sub>O) as function of time.

The feed stream is sent in by-pass to the reactor for 30 min to obtain stable concentration values of H<sub>2</sub>S and O<sub>2</sub>; the strong decrease of the reactants concentration and the increase of the products concentration, denotes the sending of the feed mixture to the reactor.

During the test (70 min), it was obtained a good catalytic activity and a high stability.

By the concentration profiles of H<sub>2</sub>S and oxygen from the mass fragment, it is possible to note the achievement of stationary values just after 30 min of the test with a final conversion of H<sub>2</sub>S equal to 90 %. It was found a low SO<sub>2</sub> formation, the concentration of which from the outset has reached a steady state value of 10 ppm. The formation of H<sub>2</sub>O, stable during the test, is indicated by the presence of mass fragment 18.

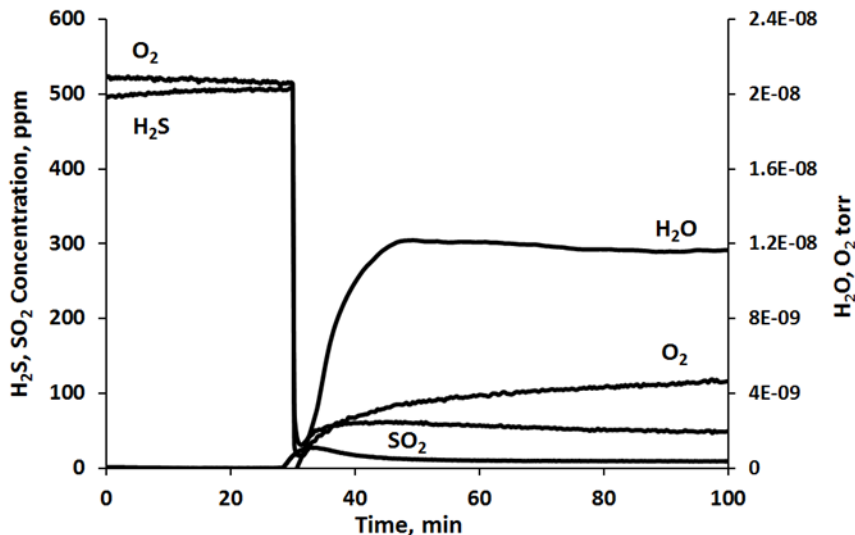


Figure.3: Catalytic activity test on monolith with 2 wt % V<sub>2</sub>O<sub>5</sub> (T=200°C)

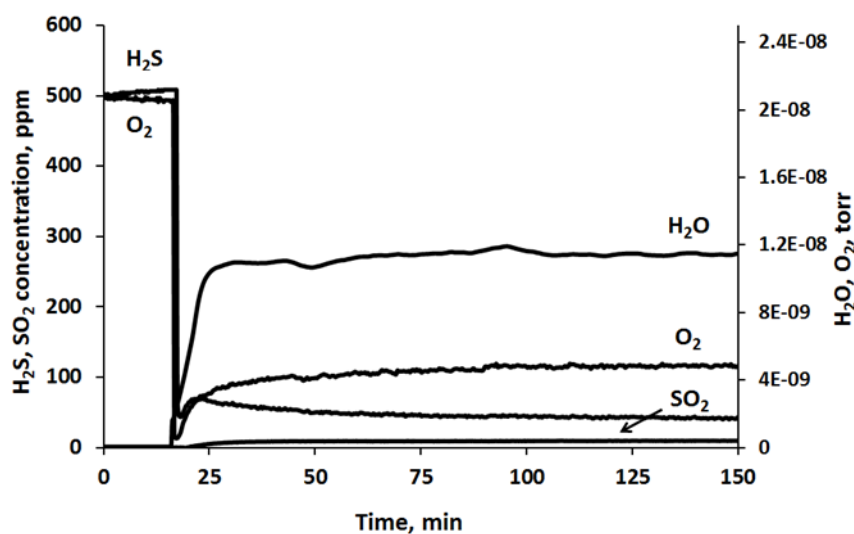


Figure.4: Catalytic activity test on monolith with 19 wt %  $V_2O_5$  ( $T=200^\circ C$ )

Similar results were also obtained in the case of the catalytic test performed with the catalyst having a vanadium loading of 20 wt %, where the  $H_2S$  final conversion was about 92 % with a low value of  $SO_2$  selectivity (2 %), corresponding to about 9 ppm of  $SO_2$  (Figure 4).

Even in this case, during the test (~ 2 h), the sample did not show evident deactivation phenomena.

#### 4. Conclusions

The reaction of  $H_2S$  selective partial oxidation to elemental sulfur in the temperature range of 150-200 °C was studied on specifically prepared honeycomb-structured catalysts obtained starting by honeycomb cordierite monoliths and a commercial Ceria based washcoat, at which the V active species was added.

The ultrasound tests showed that the washcoat anchors and interlocks well on the substrate and the high calcination temperature promotes the stability of the washcoat (Boix et al., 2003).

Raman spectra obtained on the catalysts prepared with the two different methods, showed the formation of different species, likely responsible of the sensibly altered catalytic activity.

In the catalytic tests, the so prepared catalyst showed a moderate  $H_2S$  conversion, corresponding to about 77 % at 200 °C, and at the same time, a low durability, with a strong tendency to the deactivation.

Very different results were found for the catalysts prepared with the "distinct impregnation" method for which the effect of the vanadium content (2 wt % - 19 wt %) was also investigated in the range 150-200 °C. The results obtained at 200 °C for the two Vanadium load were very similar, in terms of  $H_2S$  conversion (~90 %) and  $SO_2$  selectivity (2 %). The absence of a sensible effect of the different  $V_2O_5$  on the catalytic performances, can be likely due to the very good catalytic activity of the two samples, that in the selected operating conditions (150 – 200 °C) reached a  $H_2S$  conversion close to the thermodynamic equilibrium.

The worst catalytic performances obtained for the samples prepared with the "joint impregnation" method, may be attributed to the presence of  $CeVO_4$  instead of the  $VO_x$ , that are reported in the literature as the most active species for the desired reaction.

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