Honeycomb V_2O_5-CeO_2 Catalysts for H_2S Abatement from Biogas by Direct Selective Oxidation to Sulfur at Low Temperature

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Honeycomb V_2O_5/CeO_2 structured catalysts were prepared for the H_2S abatement from biogas by direct selective catalytic oxidation to sulphur and water at low temperature.

Two commercial CeO_2-based washcoats (Ecocat, Mel Chemicals) and a CeO_2-based washcoat prepared in laboratory, used as a support for the active phase deposition, were deposited on a honeycomb monolith made of cordierite by dip coating procedure; after washcoat deposition and stabilization, the active phase (V_2O_5) was deposited by wet impregnation.

The washcoats were characterized by X-Ray Diffraction, X-Ray Fluorescence (ED-XRF). The adhesion of the different washcoats on cordierite was investigated by ultrasonic vibration, by studying also the effect of the addition of the alumina binder on the catalyst properties.

Different washcoats uncatalysed and catalysed with 2 wt% of V_2O_5 were tested in catalytic activity test at 200°C in order to compare the catalytic performance in terms of H_2S abatement efficiency and resistance to the deactivation.

1.Introduction

Biogas is produced by the anaerobic digestion or fermentation of biodegradable materials such as biomass, manure, sewage, municipal waste, green waste, plant material, and crops. Biogas comprises primarily methane (CH_4), carbon dioxide (CO_2) and small amounts of hydrogen sulfide (H_2S).

The direct utilization of biogas as fuel without removal of H_2S leads to the formation of sulphur dioxide (SO_2), which is another toxic pollutant and a major contributor to acid rain in the atmosphere.

H_2S can be removed by a variety of processes, based on physical–chemical treatment characterized by high costs and a limited overall efficiency (Abatzoglou and Boivin, 2009).

The catalytic oxidation-based processes as the Claus Process were widely employed for the abatement of H_2S (Sassi and Gupta, 2008). In this way, an alternative process for the removal of H_2S at low concentrations from a simulated biogas stream could be based on the partial selective catalytic oxidation to Sulphur and water ($H_2S + ½ O_2 -> S + H_2O$).

For this process, vanadium-ceria catalysts were identified as catalytic systems very active and selective to sulphur, minimizing the SO_2 formation (Palma et al., 2013). In our previous works, many investigations were carried out on these catalysts, such as the effect of the different vanadium loading, temperature and contact time (Palma and Barba, 2014c).

The goal of this work was to transfer the formulation used for the powder catalysts to a honeycomb structured catalyst carrier prepared by using a CeO_2/ZrO_2 based-washcoat as a support for the vanadium oxide deposition.

Monolithic catalysts have found many applications in industrial chemistry (Cybulski and Moulijn,1994).

Cordierite, with the formula $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$, is a material with high chemical and mechanical durability, low thermal expansivity and low dielectric constant, porosity and pore size distributions suitable for ease of washcoat application and good washcoat adherence (Williams, 2001).

Washcoat materials are coated on the honeycomb surface to provide a stable and large surface area on which catalytic materials are deposited. For low-temperature use, the washcoat material is required to have a high surface area and to give a high dispersion of the catalytic materials deposited on it (Kikuchi et al., 2003).

The preparation procedure of the structured catalysts by the carrier washcoating to vanadium oxide deposition by wet impregnation was studied; the catalytic activity of the three different washcoats on which a vanadium loading was deposited (2 wt%) was investigated.

2.Experimental and Methods

2.1 Catalysts Preparation and characterization

Cordierite honeycomb monoliths (226 cpsi, average wall thickness 0.23 mm, apparent density of 0.47 g/cm^3) rectangular in shape, with 30 mm in length, 6 mm in width, 6 mm in height were used as the substrate.

Two commercial Ceria-Zirconia-based washcoats (Ecocat, Mel Chemicals) and a Ceria-based washcoat prepared in laboratory were impregnated on a cordierite honeycomb having 9 channels.

The CeO_2-based washcoat was prepared starting by a suspension of 1.1 g of methylcellulose dissolved in 100cm^3 of distilled water under stirring for 8 h. Subsequently 40 g of CeO_2 were added and the final suspension was left under stirring for 6 h. Before use, the cordierite monoliths, were pretreated at 550 °C for 2 h.

The monoliths were impregnated with the washcoat by dip coating technique and the excess slurry inside the channels of the cordierite substrate was removed by blowing air with a vacuum pump; afterward the monoliths were dried at 120 °C for 30 min. In order to get more homogeneous washcoatings, it was preferable to use diluted suspensions, having a solid concentration in the slurry equal to 20 wt% (Palma et al., 2014 a-b). The aim 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.

As the monolith cannot be coated adequately by a single impregnation, multi-impregnation were required.

The coating procedure was repeated, to reach a value of the loading of active material (CeO_2 washcoat layer) equal to 20 wt%, defined as the washcoat weight divided by the initial weight of the monolithic substrate.

Finally the washcoated monoliths were calcined in air at 550 °C for 2 h.

For deposition of the active phase (V_2O_5) we started by aqueous solution of ammonium metavanadate (0.05 M), where the washcoated monoliths calcined were dipped. The samples were impregnated at 70 °C for 15 min, after they were dried at 120 °C in an oven for 30 min.

The impregnation/drying steps into the solution of the salt precursor of the active phase repeated until it was reached the desired content of the active phase (2 wt% V_2O_5).

Furthermore, at the end of each cycle impregnation / drying, the samples were calcined at 400 °C for 2h, in order to avoid that the salt deposited in the solution could melt again in the following impregnations. Finally the monoliths were calcined at 400 °C for 2 h.

The washcoat was characterized by using different technique: X-Ray Diffraction (XRD), Energy Dispersive X-Ray Fluorescence (ED-XRF) and ultrasonic vibration.

The mechanical stability tests were performed by ultrasonic vibration to investigate the adhesion of the different washcoats on cordierite. The samples have been immersed in a beaker containing petroleum ether, and the whole was placed in an ultrasonic bath filled with distilled water, at temperature of 25 °C for 30 min. The weight changes were recorded during the test at regular intervals of 5 min after monoliths drying at 120 °C and cooling up to room temperature.

The samples weight losses were evaluated according to the following formula (Eq.1):

$$Weight\,loss = \frac{initial\,weight - final\,weight}{initial\,weight} \cdot 100 \qquad \text{Eq.1}$$

The catalytic tests were carried out in a stainless-steel fixed bed-tubular reactor, with an internal diameter of 14 mm and a length of 21 cm, inserted in an electrical furnace equipped with a PID (proportional-integrative-derivative) electronic temperature controller.

Experimental tests were carried out at atmospheric pressure at 150 and 200 °C, at a contact time of ~170 ms (GHSV of $2,2 \cdot 10^4$ h^{-1}) by feeding 500 ppm of H_2S, 250 ppm of O_2 and N_2 to balance.

The exhaust stream (H_2S, O_2, H_2O) was analyzed by a mass spectrometer while the concentration of SO_2 is monitored instead by an analyzer FT-IR Multigas in continuous. The H_2S conversion (Eq.2) and the SO_2 selectivity (Eq.3) were calculated by using the following equations, by considering negligible the gas phase volume change:

$$xH_2S, \% = ((H_2S^{IN} - H_2S^{OUT})/ H_2S^{IN}) \cdot 100 \qquad \text{Eq.2}$$
$$ySO_2, \% = SO_2/(H_2S^{IN} - H_2S^{OUT}) \cdot 100 \qquad \text{Eq.3}$$

3.Results and Discussion

3.1 Washcoat characterization

The XRD patterns of the three washcoats impregnated on the honeycomb cordierite are shown in Figure 1a-b. The ceria-alumina based-washcoat has shown the typical peaks attributable to the cubic crystalline structure of the CeO_2 at $2\Theta = 28.8°, 33.3°, 47.6°$ and $56.5°$ (Radhika and Sugunan, 2006).
In the case of the commercial washcoats (Ecocat, Mel Chemicals) four main peaks attributable to the CeO_2-ZrO_2 solid solution were identified. (Figure 1a).
The spectra of the Mel Chemicals washcoat were slightly shifted of 1.2° compared to those of the Ecocat washcoat due to likely to the higher content of zirconia, as shown also by the greater intensity of the peaks (Figure 1b) (Maya, 2006).
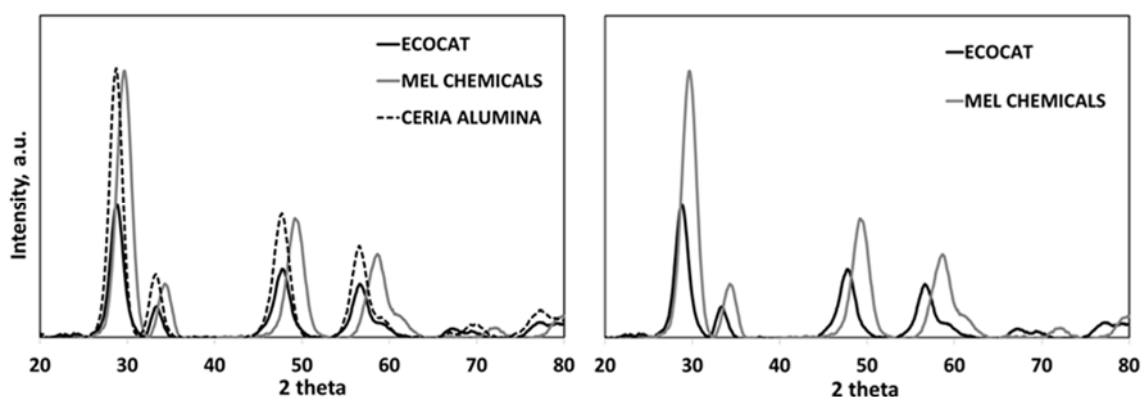

Figure 1: XRD patterns of the three washcoats impregnated on the honeycomb cordierite (a) and comparison of the commercial washcoats (b)

The higher content of zirconia is also confirmed from the ED-XRF analysis which was performed in order to identify qualitatively and quantitatively the elemental composition of the different washcoats relatively to the presence of the ceria (Ce), zirconium (Zr) and aluminum (Al) (Table 1). From the results reported in Table 1, the zirconium content in the Mel Chemicals washcoat was about one magnitude order higher (57 wt%) than obtained in the Ecocat washcoat (5 wt%). The aluminum content, observed in the commercial washcoat, is imputable to the Al_2O_3 of the cordierite.

Table 1: Elemental composition (wt%) of different washcoats by ED-XRF analysis

	Ce, wt%	Zr, wt%	Al, wt%
ECOCAT	58	5	31
MEL CHEMICALS	38	57	5

Ultrasonic testing was performed on the washcoated catalysts to evaluate the adhesion and the stability of the washcoat on the mechanical support. The results are reported in Figure 2 in terms of percent weight loss of the washcoat deposited on the cordierite as function of the exposure time to the ultrasonic vibration cycles. Different values of the weight loss were obtained for the commercial washcoat: Ecocat has exhibited the lowest weight loss of the washcoat (~3 wt%) while Mel Chemicals, after seven cycles, has shown a weight loss of about 20 wt%.
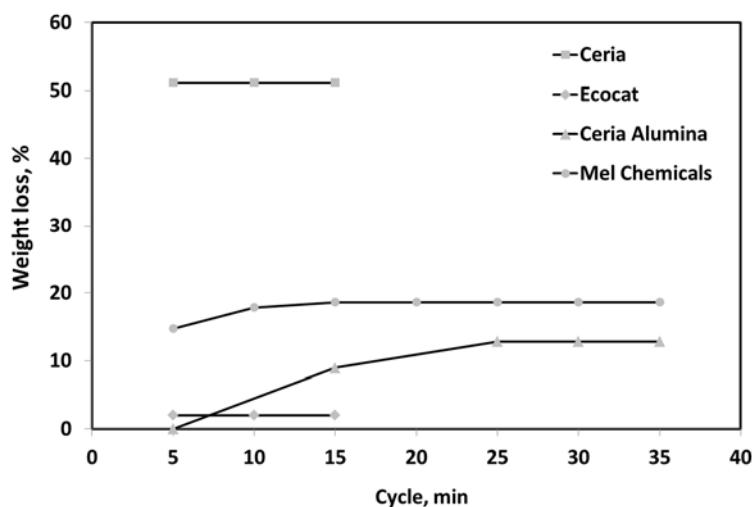
Figure 2: Weight loss as a function of the number of ultrasonic vibration cycles of commercial (Ecocat, Mel Chemicals) and non commercial washcoats (Ceria, Ceria-Alumina)

Non commercial Ceria-alumina based-washcoat has shown a weight loss of about 12 wt %. The effect of the addition of the alumina as binder is very important for the stability of the washcoat; in fact the ceria based-washcoat without binder has shown a high weight loss (~50 wt%) of about four times larger than ceria based-washcoat with alumina as binder.

3.2 Catalytic Activity Tests

The catalytic activity of the different washcoats was investigated at temperature of 200 °C. The results are showed in Table 2 in terms of H_2S conversion and SO_2 selectivity.

Table 2: Results of the catalytic activity tests of different washcoats at 200 °C

Washcoat Type	H_2S Conversion (%)	SO_2 selectivity (%)
Ecocat	56	0.5
MEL Chemicals	53	0
Ce/Al	64	0

Three washcoats showed a modest H_2S conversion and a negligible selectivity to SO_2. The Ecocat washcoat, that has shown a good stability during the test reaching a final value of H_2S conversion equal to 56 %. The test of catalytic activity performed on the sample impregnated with Ce/Al washcoat, exhibited similar results to the Mel Chemicals washcoat, showing poor stability and tendency to the deactivation, related to the formulation of the washcoat, also confirming the results obtained from the ultrasonic testing. For comparison, in Table 3 are reported the results of three washcoats catalyzed with 2 wt % of V_2O_5 at the same temperature.

Table 3: Results of the catalytic activity tests of the different washcoats catalyzed with 2 wt% of V_2O_5 at 200 °C

Washcoat Type	H_2S Conversion (%)	SO_2 selectivity (%)
Ecocat	90	2
MEL Chemicals	87	1.3
Ce/Al	90	1

The results of the final structured catalysts have underlined an improvement of the catalytic activity and a low formation of SO_2 with selectivity values lower than 2 %. The better catalytic performance and a good stability was obtained for the Ecocat washcoated catalyst.

For comparison, in Figure 3a-b, are showed the catalytic activity test of the Ecocat washcoat with the same washcoat catalysed with 2 wt% of V_2O_5. It is worth noting that when the feed stream was sent to the reactor, an immediate decrease of the H_2S concentration and the SO_2 production was verified.

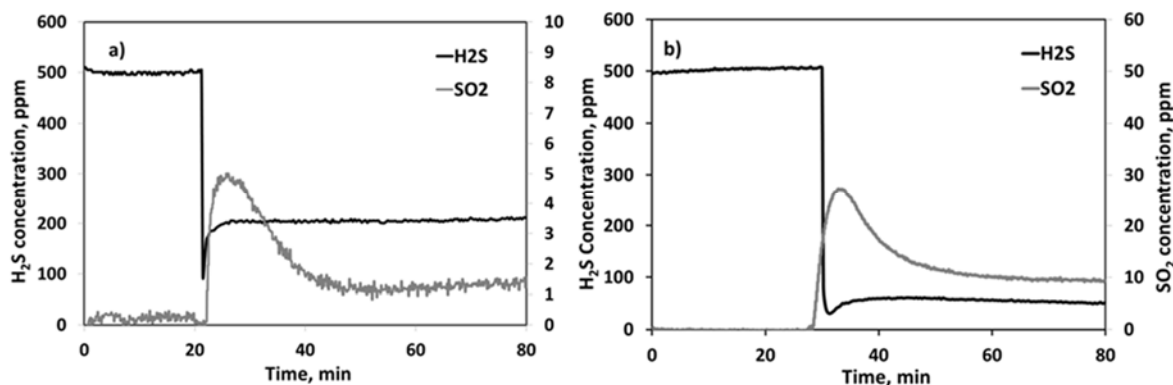Figure 3: Catalytic activity test at 200 °C of the washcoat ECOCAT (a) and the washcoat ECOCAT catalysed with 2 wt% of V_2O_5 (b)

The trend of the H_2S and SO_2 concentration, is similar and steady for the both samples; in fact no deactivation phenomena were observed during the test. However very different results, as already reported in Table 3, were obtained in terms of H_2S conversion and SO_2 concentration. The final SO_2 concentration observed on the catalysed sample was about twice (10 ppm) than that observed on the un-catalysed sample (~4 ppm).

4.Conclusions

Structured vanadium-based catalysts were prepared starting from a support "*Honeycomb*" of Cordierite on which were deposited three different washcoats by impregnation method to which the vanadium active species (2 wt%V_2O_5) was added. Two commercial washcoats and one synthesized in laboratory were characterized by different techniques concerning the chemical and structural properties of the commercial washcoat.

The ultrasonic tests have shown the better adhesion of the Ecocat washcoat on the cordierite support, giving almost negligible weight losses after ultrasonic bath treatment (~3 %) respect to the MEL Chemicals and Ceria-based alumina washcoat for which the weight loss were 20 % and 12 %, respectively. (Boix et al, 2003). The catalytic activity tests performed at 200 °C on the un-catalysed washcoat have shown that the Ecocat washcoat was the only stable support that has not presented phenomena deactivation.

For the washcoats catalysed with the vanadium active phase, it was found a decisive improvement of the catalytic performance obtaining a H_2S conversion about 90 % and a very low value of SO_2 selectivity (≤ 2 %).

Based on these results, the Ecocat washcoat has represented the best compromise between good adhesion to the support and good catalytic performance, both in terms of conversion of H_2S and selectivity to SO_2.

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