



Honeycomb-structured catalysts for the selective partial oxidation of H₂S



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ABSTRACT

The reaction of H₂S selective partial oxidation to elemental sulfur was studied on cordierite honeycomb-structured catalysts in the range of temperature of 150–200 °C.

The preparation procedure of catalytic cordierite monoliths has been studied, from the washcoating with CeO₂ to the deposition of V₂O₅ 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 V₂O₅ wt %) was also studied at 200 °C. Good catalytic performances were obtained for both samples that have shown a high H₂S conversion (~90%), low SO₂ selectivity (3%) and a high stability.

The catalytic tests performed to varying the contact time with the temperature have allowed to identify the possible reaction pathway and the optimal operating conditions for which were obtained good catalytic performance.

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1. Introduction

The dependence on conventional fossil fuels involves the requirement of renewable energy sources such as hydro, solar, wind and biomass.

Energy recovery from biomass i.e. bio-fuels and organic fraction of industrial and domestic waste streams is a desirable development because it provides a means of reducing emissions (politically most important, those of CO₂) linked to energy production (Mirata et al., 2005).

Furthermore, the biomass can be also used as raw material for the hydrogen production for energy and mobile applications in a renewable way (Miltner et al., 2010).

In particular, possible uses of the biogas are the its combustion to produce combined heat and power unit or the biomethane

production and subsequent injection to the gas grid or use in transports (Ravina and Genon, 2015).

The biogas production by anaerobic fermentation is a promising method in order to obtain an energy carrier from biomass resources while achieving multiple environmental benefits, such as the fossil energy substitution, carbon emission reduction, and pollution abatement (Zhang et al., 2013).

The anaerobic digestion process can be divided in four steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis. Proteins, lipids, and carbohydrates are hydrolyzed to amino acids, long-chain fatty acids, and sugars, respectively. These small molecules are then converted by fermentative bacteria (acidogens) to a mixture of volatile fatty acids and other minor products such as alcohol. Acetogenic bacteria further convert the volatile fatty acids to acetate, carbon dioxide, and/or hydrogen, which provide direct substrates for methanogenesis (Zheng et al., 2014).

During this process some problems can occur, as inhibitory phenomena that can result of the accumulation of fatty acids,

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ammonia (NH₄ and NH₃) and production of H₂S (Montingelli et al., 2015).

The interest in anaerobic digestion (AD) and biogas production technology has grown rapidly over the years, mainly due to the increasing importance of renewable energy deployment with respect to structured mitigation of greenhouse gas (GHG) emissions (Poeschl et al., 2012).

The main compounds of the biogas are CH₄, CO₂ but they are also sulfur compounds such as H₂S, COS.

Several processes have been described and developed for the elimination of H₂S from products or off-gases. The most common commercial methods are based on chemical and physical treatment such as dry processes (adsorbents, iron and zinc oxide) physical solvent, chemical absorption in aqueous solution (amine), biological desulfurization, membrane separation that are characterized by high operating costs and low yields (Zicari, 2003).

For the small scale plant, a very interesting solution could be represented by the direct and selective H₂S oxidation to sulfur as reported in the following reaction $H_2S + \frac{1}{2}O_2 = \frac{1}{x}S_x + H_2O$ (Eq. 1) 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, V₂O₅/CeO₂ catalyst showed the most promising catalytic performances at temperature lower than 200 °C in terms of high H₂S and O₂ conversion with a very low SO₂ selectivity at a feed ratio H₂S/O₂ = 2. In order to verify the possibility to further reduce the SO₂ selectivity, additional experimental tests were performed by investigating the effect of the inlet H₂S concentration, the gas hourly space velocity and the H₂S/O₂ molar feed ratio (Palma et al., 2013a).

Further catalytic activity tests were also carried out to study the effect of the vanadium content in the range 2.55–20 wt % V₂O₅ at different temperatures the which results of this preliminary screening showed that, in the temperature range of 150–250 °C, the vanadium load mainly affected the value of SO₂ selectivity, with not so relevant effects on the catalytic activity. The most selective catalyst was the 20 wt % V₂O₅/CeO₂ 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·2Al₂O₃·5SiO₂) honeycomb structured carrier by using a CeO₂/ZrO₂ based-washcoat as support for the vanadium oxide deposition (2–19 V₂O₅ wt%). The ceramic honeycombs are generally produced from cordierite or anisotropic crystalline magnesium aluminosilicate and inherently have a low surface area (<2 m²/g). The pore structure of the cordierite honeycombs facilitates the deposition of the catalytic support.

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_x. 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 (V₂O₅). 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 performance of the different structured samples will be compared in catalytic activity tests. The effect of the contact time at 150–200 °C was also investigated in order to identify the possible reaction pathway.

2. Experimental

2.1. Materials

Cordierite honeycomb monoliths (9 channels) with length variable between 10 and 50 mm, 6 mm in width, 6 mm in height and 226 cells per square inch (cps) were used as the substrate for washcoating.

A commercial Ceria-Zirconia washcoat (EcoCat) having an initial solids content of 40 wt% was deposited on the cordierite. For the active phase deposition (V₂O₅) we started by aqueous solution of ammonium metavanadate (NH₄VO₃).

2.2. Catalysts preparation and characterization

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 corresponding to the washcoat addition. 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 (0.02 M) 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 catalyzed 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 active phase 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.

2.3. Experimental setup

Catalytic tests were carried out using the experimental setup shown in our previous works (Palma and Barba, 2014). Preliminary tests were carried out at atmospheric pressure and GHSV of 21,000 h⁻¹ (~170 ms), in the temperature range 150–250 °C, with 500 ppm of H₂S, 250 ppm of O₂ and N₂ to balance.

The H₂S conversion (xH₂S) and the SO₂ selectivity (ySO₂) were calculated by using the following equations (Eqs. (2) and (3)), by considering negligible the gas phase volume change:

$$xH_2S, \% = ((H_2S_{IN} - H_2S_{OUT})/H_2S_{IN}) \cdot 100 \quad (2)$$

$$ySO_2, \% = SO_{2OUT}/(H_2S_{IN} - H_2S_{OUT}) \cdot 100 \quad (3)$$

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