

Selective Oxidation of H₂S to Sulphur from Biogas on V₂O₅/CeO₂ Catalysts

Vincenzo Palma, Daniela Barba*, Paolo Ciambelli

University of Salerno, via Ponte Don Melillo 1, 84084, Fisciano (SA), Italy
 daniela.barba@ymail.com

Ceria supported Vanadium-based catalysts were studied for the selective partial oxidation of H₂S to sulphur at low temperature. The effect of vanadium content was investigated in the range 2.55 – 20 wt% V₂O₅ by catalytic activity tests carried out at different temperature. The samples were characterized by XRD and Raman Spectroscopy techniques. The Raman spectroscopy has confirmed highly dispersed vanadium for low V₂O₅ loading and monovanadate and crystalline forms at V₂O₅ loads higher > 10 wt%. Results of catalytic activity tests showed that the effect of the vanadium content has affected mainly the selectivity to sulfur, while the catalytic activity is very high for all the tested samples that showed high conversions of H₂S (> 90 %) and very close to the thermodynamic values. The most promising catalyst was the sample with the highest Vanadium oxide load (20 wt% V₂O₅/CeO₂) that showed 99 % of sulfur selectivity and equilibrium conversion even at 150 °C.

1. Introduction

Biogas is a renewable energy source that can be produced from biomass, agricultural and industrial waste and sewage sludge. Its main constituents are CH₄, CO₂ but unfortunately are present sulphur based compounds as H₂S, COS (Ciambelli et al., 2010).

Various commercial processes based on physical-chemical treatment (adsorption, absorption in aqueous solutions, physical solvent, membrane separation, biological desulfurization) have been used to treat tail gases containing low concentrations (< 5 % vol); the main problem of these purification processes is linked to the high costs and to the limited overall efficiency (Pettersson and Wellinger, 2009).

Some employ transition-metal oxides and mixed oxides for the catalytic oxidation of H₂S (Li et al., 1997).

For the small scale plant, a very interesting solution can be represented by the direct and selective H₂S oxidation to sulfur at low temperature, that can be realized only if an active and selective catalyst is available (Yasyerly et al., 2004).

In a previous work we examined the performance of vanadium-oxide based catalysts supported on the metal oxide (V₂O₅-TiO₂, V₂O₅-CeO₂, V₂O₅-CuFe₂O₄) that were investigated in the range of temperature of 50 - 250 °C (Palma et al., 2012). Among all the catalysts investigated, the V₂O₅/CeO₂ catalyst has showed the better catalytic performance at low temperature (150 - 250 °C) in terms of H₂S and O₂ conversion with a low selectivity to SO₂ (13 %). To minimize the SO₂ selectivity were performed experimental tests by investigating the effect of the inlet H₂S concentration (250 - 1,000 ppm), the gas hourly space velocity (GHSV = 15,000 - 45,000 h⁻¹), the feed molar ratio (O₂/H₂S = 0.4 - 0.5). Promising results were obtained with a O₂/H₂S = 0.4 for which it was observed a lower selectivity to SO₂ (~4 %) any significant variations of the H₂S, O₂ conversion.

This study presents the catalytic behaviour of V₂O₅/CeO₂ samples at various vanadium loadings amounts (2.55 - 10 wt %) to determine the optimal catalyst formulation and operative conditions to obtain a very high H₂S conversion and the SO₂ selectivity minimization.

2. Experimental

Catalysts based vanadium with different metal loading variable between 2.55 wt% and 20 wt% supported on cerium oxide were prepared by wet impregnation. We started by aqueous solution of ammonium metavanadate (NH_4VO_3), and powder ceria (CeO_2). This solution was placed on a heated plate until to water complete evaporation. After drying of the impregnated sample at 120°C overnight, it was calcined at 400°C for 3 h.

The catalyst prepared was also characterized by different techniques: X-Ray Diffraction and Raman Spectroscopy.

X-ray Diffraction measures were performed with a Bruker D8 diffractometer with a monochromatic $\text{CuK}\alpha 1$ on the fresh catalysts before the catalytic tests and on the CeO_2 used as support.

Raman spectra were recorded in ambient conditions with a Spectroscopy Raman using as the excitation source an ion laser of 785 nm.

The catalytic tests were carried out in a fixed bed flow reactor, made of a steel tube 21 cm long and a 14 mm of internal diameter. The reactor is inserted in an electrical furnace equipped with a PID electronic temperature controller. The reactor has an "isothermal" profile ($\pm 1^\circ\text{C}$) of 3 cm from 8 cm from the inlet where the catalytic bed profile. A thermocouple is inserted in a steel sheath of the inner diameter of 6 mm concentric to the reactor.

A system of three-way valves allows to send the stream feed to the reactor, or in by-pass position, to send the stream feed to analysis.

Catalytic activity tests were carried out at atmospheric pressure and GHSV of $9.5 \cdot 10^4 \text{ h}^{-1}$ (40 ms), in the temperature range $150 - 250^\circ\text{C}$, with 200 ppm of H_2S , 100 ppm of O_2 and N_2 to balance. For reaction test, catalyst has been reduced to the size 38 - 180 micrometer.

The exhaust stream was analysed by a quadrupole mass spectrometer equipped with a sulphur trap in order to follow all the reactants and the gaseous product at the reactor outlet.

The H_2S conversion, and the SO_2 selectivity were calculated by using the following equations, by considering negligible the gas phase volume change:

$$x_{\text{H}_2\text{S}}, \% = (\text{ppm of H}_2\text{S reacted} / \text{ppm of H}_2\text{S fed}) \cdot 100$$

$$y_{\text{SO}_2}, \% = (\text{ppm of sulphur dioxide} / \text{ppm of hydrogen sulphide reacted}) \cdot 100$$

3. Results and Discussion

Figure 1 gives XRD patterns of the CeO_2 support and $\text{V}_2\text{O}_5/\text{CeO}_2$ catalysts at different loading before of the catalytic test. All the samples showed the characteristic peaks of CeO_2 while the typical V_2O_5 reflections cannot be detected likely due to the low metal loading and the good dispersion on the support (Soriano et al., 2009).

The X-Ray reflections of ceria were observed at $2\theta \sim 28.3^\circ, 32.8^\circ, 47.3^\circ$ and 56.1° by showing a typical cubic crystal structure of fluorite type cerium oxide (Radhika and Sugunan, 2006).

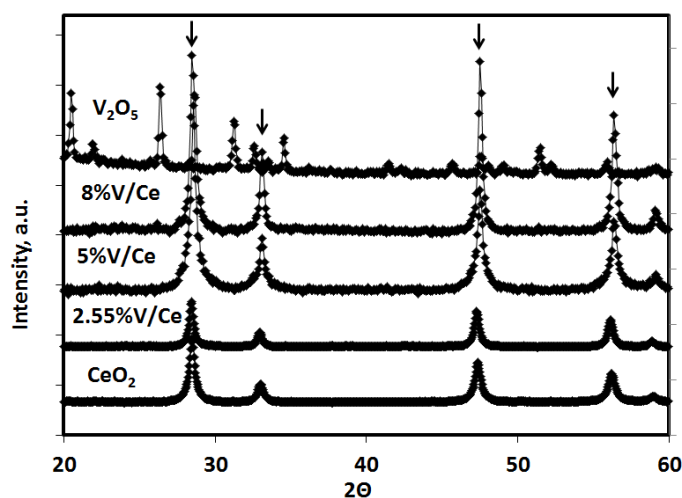


Figure 1: X-Ray diffraction patterns of CeO_2 , V_2O_5 and the $\text{V}_2\text{O}_5/\text{CeO}_2$ catalysts before of the catalytic test

In Figure 2 are shown the Raman spectra of CeO_2 and $\text{V}_2\text{O}_5/\text{CeO}_2$ catalysts. The characteristic Raman peak of CeO_2 has been identified around 458 cm^{-1} (Xiaodong Gu et al., 2006), while bulk V_2O_5 have shown typical Raman peaks around 289, 305, 410, 530, 706, 998 cm^{-1} . These bands can refer to the vibrational modes of crystalline V_2O_5 (Holgrado et al., 2010). The peak at around at $1,023\text{ cm}^{-1}$, observed on the sample 5 % $\text{V}_2\text{O}_5/\text{CeO}_2$, was assigned to the V=O stretching vibration of an isolated monovanadate species (VO_4^{3-}) (Soriano et al., 2009). It is also important to note that the presence of significant amount of crystalline V_2O_5 cannot be detected up to 20 % V_2O_5 load.

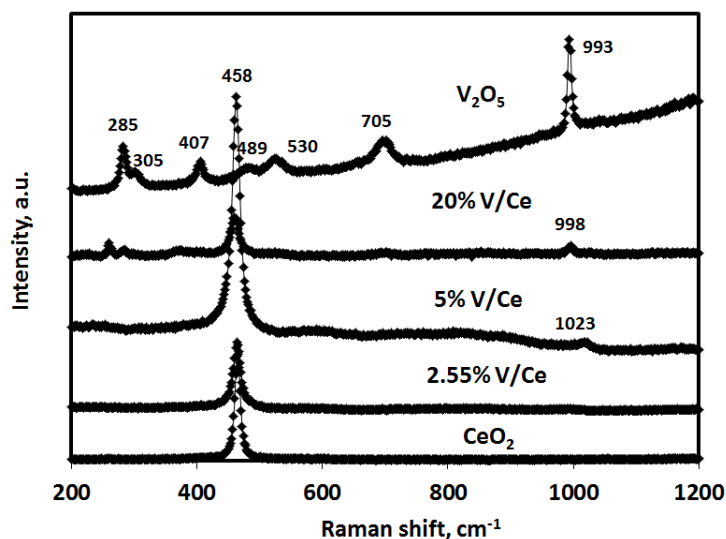


Figure 2: Raman spectra of CeO_2 and the fresh catalysts $\text{V}_2\text{O}_5/\text{CeO}_2$ before of the catalytic test.

Prior to carry out the activity tests on $\text{V}_2\text{O}_5/\text{CeO}_2$ catalysts, they have been verified the performances of the separate bulk V_2O_5 and the CeO_2 in terms of H_2S conversion and SO_2 selectivity as function of temperature as reported respectively in the Figure 3 and Figure 4.

From the data reported in Figure 3, an almost complete H_2S conversion was observed on the bulk V_2O_5 in the overall temperature range, while for the support the values of the H_2S conversion were only ~95 % at higher temperature, and lower at lower temperatures, reaching about 50 % at 150 °C.

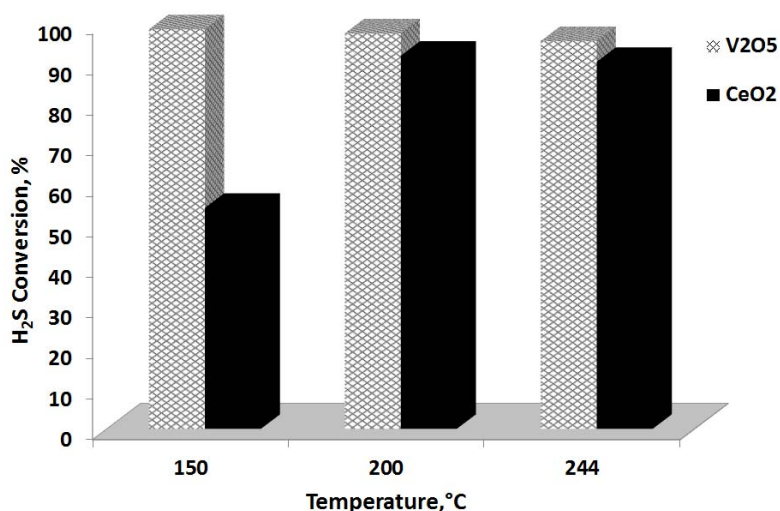


Figure 3: Comparison in terms of H_2S conversion of active phase (V_2O_5) and support (CeO_2) in the range of temperature 150 - 245 °C

The results relative to the SO_2 selectivity to increase of the temperature are showed in the Figure 4.

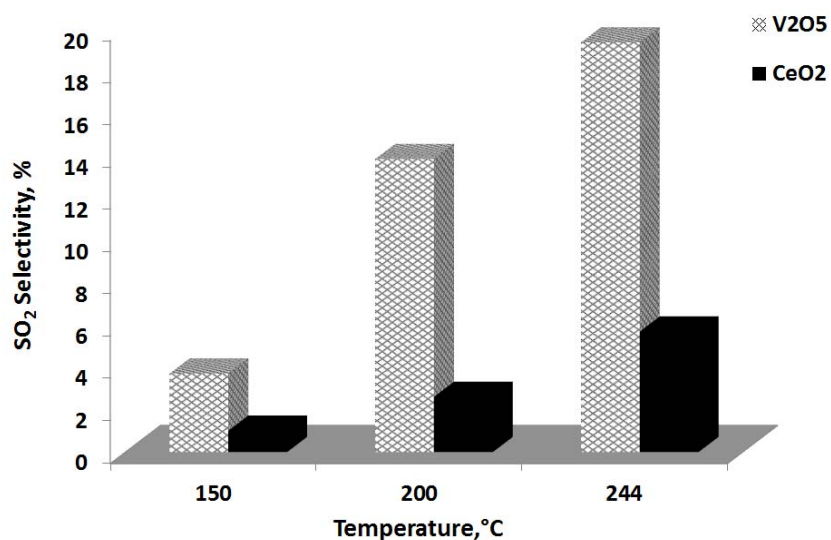


Figure 4: Comparison in terms of SO₂ selectivity of active phase (V₂O₅) and support (CeO₂) in the range of temperature 150 - 245 °C

Also in terms of SO₂ selectivity very different results were observed for the bulk V₂O₅ and CeO₂. The bulk V₂O₅ showed higher values of SO₂ selectivity at 200 °C and 244 °C, respectively equal to 14 % and 20 %. The support, instead, has showed an intrinsic lower selectivity even at the highest temperature (~6 %) and a value almost negligible at temperature of 150 °C. Based on the preliminary results relative to the unsupported V₂O₅ and Ceria support, the attention was focused on the V₂O₅/CeO₂ catalysts and in particular to the influence of the V₂O₅ loading on the catalytic performance.

In the Figure 5 it is showed the catalytic activity in terms of H₂S conversion in the range of temperature 150 - 244 °C.

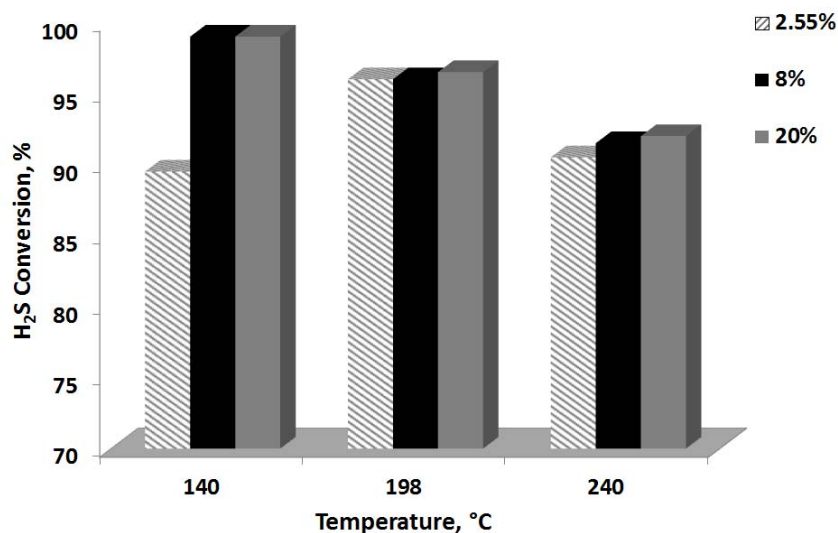


Figure 5: H₂S conversion to varying the temperature for V₂O₅/CeO₂ catalysts with different metal loading

The figure shows that, for all the samples, the higher H₂S conversion values were obtained at the lower temperature (150 °C), except to the sample 2.55 wt% V₂O₅/CeO₂, for which the H₂S conversion was ~90 %; the H₂S conversion was about 100 % for the other samples.

At temperature of 200 °C, they are not appreciable significant difference, because all the catalysts have shown a H₂S conversion about 96 %, while the catalyst with higher metal loading (20 wt% V₂O₅) has showed a higher value (98 %).

At high temperature (240 °C), the catalyst with higher V₂O₅ loading (8 wt% - 20 wt%) have exhibited values of H₂S conversion higher than 90 %; in particular for the 20 wt% V₂O₅/CeO₂ the value was ~93 %.

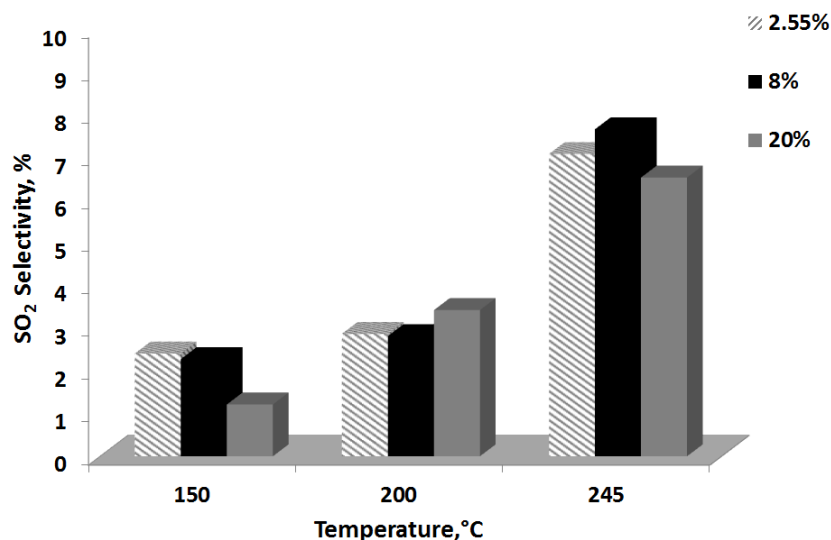


Figure 6: SO₂ selectivity to varying the temperature of V₂O₅/CeO₂ catalysts

From the data of Figure 6 it is clear that for all catalysts the formation of SO₂ increases with increasing temperature, but it is also important to note that the catalyst 20 % V₂O₅/CeO₂ showed a SO₂ formation tendency slightly lower than value obtained for the sample.

In particular, at 150 °C, the catalysts with the higher vanadium load exhibited a very low SO₂ selectivity of only 1 %.

4. Conclusions

In this work, vanadium-based catalysts supported on CeO₂ with different vanadium loading, were used for the H₂S removal by selective partial oxidation at low temperature.

From the characterization techniques, it was obtained that the vanadium oxide was well dispersed on the support when the loading was low (2.55 wt%, 5 wt%, 8 wt% V₂O₅), while in the case of samples having a loading exceeding the 10 wt%, they have been identified peaks attributable (1,023 cm⁻¹) to monovanadate forms of vanadium (VO₄³⁻) and crystalline forms of vanadium (998 cm⁻¹).

From the evaluation of the influence both of the active phase and the support respect to the oxidation reaction, it was obtained, relatively to the formation of SO₂, a more oxidizing effect of the bulk V₂O₅ than the CeO₂ support, and the difference is much more pronounced as the temperature increases.

The screening carried out on catalysts has showed that the effect of the load of vanadium has affected especially on the value of SO₂ selectivity, but not on the catalytic activity because all the samples showed high conversions of H₂S (> 90 %) in the range of temperature 150 - 250°C. The catalyst more selective to sulfur (99 %), for the partial oxidation reaction at low temperature (150 °C), was 20 wt% V₂O₅/CeO₂, suggesting that the polyvanadate species are the most active and selective.

References

- Ciambelli P., Palma V., 2010, Low temperature catalytic steam reforming of ethanol. 2. Preliminary kinetic investigation of Pt/CeO₂ catalysts, Applied Catalysis B: Environmental, 96, 190-197.
- Holgado J.P., Soriano M.D., Jimenez J., 2010, Operando XAS and Raman study on the structure of a supported vanadium oxide catalyst during the oxidation of H₂S to sulfur, App. Catal. B, 92, 271-279.
- Li K.-T., Yen C.-S., Shyu N.-S., 1997, Mixed-metal oxide catalysts containing iron for selective oxidation of hydrogen sulfide to sulphur, Appl. Catal. A: Gen., 156, 117-130.

- Palma V., Barba D., Ciambelli P., 2012, Screening of Catalysts For H₂S Abatement From Biogas To Feed Molten Carbonate Fuel Cells, *Int. Hydrogen Energy*, 38, 328-335. DOI 10.1016/j.ijhydene.2012.10.010.
- Petersson A., Wellinger A., 2009, Biogas Upgrading Technologies-developments and innovations, IEA Bioenergy, <www.iea-biogas.net/_download/publi-task37/upgrading_rz_low_final.pdf>, accessed 2010.
- Radhika T., Sugunan S., 2006, Structural and catalytic investigation of vanadia supported on ceria promoted with high surface area rice husk silica, *Journal of Molecular Catalysis A: Chemical*, 250, 169-176.
- Soriano M.D., Jimenez J., 2009, Selective oxidation of H₂S to sulphur over vanadia supported on mesoporous zirconium phosphate heterostructure, *App. Catal. B* 92, 271-279.
- Gu X, Jiazen Ge J., Zhang H., Aurox A., Shen J., 2006, Structural, redox and acid - base properties of V₂O₅/CeO₂ catalyst, *Thermochimica Acta* 451, 84-93.
- Yasyerly S., Dogu G., Ar I., Dogu T., 2004, Dynamic analysis of removal and selective oxidation of H₂S to elemental sulfur over Cu-V and Cu-V-Mo mixed oxides in a fixed bed reactor, *Chem. Eng. Sci.* 59, 4001-4009.