CHEMICAL ENGINEERING TRANSACTIONS

VOL. 29, 2012

Guest Editors: Petar Sabev Varbanov, Hon Loong Lam, Jiří Jaromír Klemeš
Copyright © 2012, AIDIC Servizi S.r.l.,
ISBN 978-88-95608-20-4; **ISSN** 1974-9791

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at: www.aidic.it/cet

DOI: 10.3303/CET1229106

H_2S Removal in Biogas by Direct Catalytic Oxidation to Sulphur on V_2O_5/CeO_2 Catalysts

Vincenzo Palma[a], Daniela Barba*[a], Paolo Ciambelli[a]

[a]University of Salerno, Department of Industrial Engineering, via Ponte Don Melillo - Fisciano (SA) - Italy
daniela.barba@ymail.com

The direct and selective partial H_2S oxidation to elemental sulphur at low temperature may be an interesting alternative to the traditional methods of H_2S abatement if an active and selective catalyst is available.

In our previous works, a screening of vanadium-based catalysts supported on the metal oxide (V_2O_5-TiO_2, V_2O_5-CeO_2, V_2O_5-$CuFe_2O_4$) was performed in the range of temperature 50-250 °C; among all the catalysts investigated, the V_2O_5/CeO_2 catalyst has showed the better catalytic performance in terms of H_2S conversion (>95 %) and a low SO_2 selectivity (~13 %) at T= 250 °C.

Based on these promising results, further investigations on V_2O_5/CeO_2 catalyst were performed to investigate the influence of the inlet concentration of H_2S (250-1000 ppm), the gas hourly space velocity (GHSV=15,000-45,000 h^{-1}) and the molar feed ratio (O_2/H_2S=0.4-0.5) in order to minimize the selectivity of the system to SO_2.

Preliminary results relevant to the effect of the gas hourly space velocity and the inlet concentrations of H_2S, showed that they did not contribute to reduce significantly the SO_2 selectivity, while interesting result in terms of SO_2 selectivity was obtained with a sub-stoichiometric feed ratio (O_2/H_2S = 0.4), for which it is resulted drastically reduced from 13 % to 4 % without any significant reduction of the H_2S and O_2 conversions.

From these good results, future works will performed to investigate the effect of vanadium load by studying samples in the range 2.55-10 %wt in order to determine the optimal catalyst formulation and operative conditions to obtain a very high H_2S conversion and the SO_2 selectivity minimization.

1. Introduction

Biogas generated from anaerobic digestion processes is a clean and environmentally friendly renewable fuel. Due to the particular composition, biogas can be used in a large number of applications where it's expected the utilization of the natural gas: direct generation of heat (industrial boilers), production of energy and heat (internal combustion engines, gas turbines).

In addition, in these last years, the attention is also focused on the possibility to use the biogas for energy production in unconventional systems as the molten carbonate fuel cells.

The main real limitation to the utilization of the biogas as fuel for MCFC is represented by the poisoning of the anode, of the electrolyte, and the deactivation of catalyst oxidation sites by sulphur based compounds (H_2S, COS) that are always presents in biogas (Ciccoli et al., 2010). Even if present at low concentration level, they must be depressed at ppm values, because the sulphur content allowed in the MCFC is lower than 5 ppm. For these reasons, a H_2S clean-up stage must be considered (McPhail et al., 2009).

Please cite this article as: Palma V., Barba D. and Ciambelli P., (2012), H_2S removal in biogas by direct catalytic oxidation to sulphur on V_2O_5/CeO_2 catalysts, Chemical Engineering Transactions, 29, 631-636

The most applied technique for the H_2S abatement in large scale plants is represented by the classical absorption process, characterized by high costs and a limited overall efficiency (Petersson et al., 2009, Zicari 2003).

For the small scale plant, a very interesting solution can be represented by the direct and selective H_2S catalytic oxidation to sulphur at low temperature.

Among all the catalysts investigated, the V_2O_5/CeO_2 catalyst has showed the better catalytic performance in terms of H_2S and O_2 conversion with a high sulphur yield and therefore it could be a good candidate for this reaction.

2. Experimental

The V_2O_5/CeO_2 catalyst with a nominal V_2O_5 load of 2.55 %wt was prepared by wet impregnation method. We started by aqueous solution of ammonium metavanadate (Aldrich), and powder ceria (Aldrich). 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. For reaction test, catalyst has been reduced to the size 180-355 µm.

The catalyst prepared was also characterized by different techniques.

X-ray diffraction measures were performed with a Brucker D8 diffractometer with a monochromatic CuKα1 on the calcined catalyst before and after 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 pyrex glass tube 0.21 m long and a 0.02 m of internal diameter. The reactor is inserted in an electrical furnace equipped with a PID electronic temperature controller. The catalytic bed is located in the furnace in a selected region with an “isothermal” profile (±1°C).

A system of four-way valves allows to send the stream feed to the reactor, or in by-pass position, to send the stream feed to analysis. In the by-pass configuration, an independent MFC allows to send nitrogen to the reactor.

Preliminary tests were carried out at atmospheric pressure and GHSV of 15,000 h^{-1}, in the temperature range 50-250 °C, with 1000 ppm of H_2S, 500 ppm of O_2 and N_2 to balance.

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

The H_2S, O_2 conversions, and the SO_2 selectivity were calculated by using the following equations, by considering negligible the gas phase volume change:

xH_2S, % = (ppm of H_2S reacted / ppm of H_2S fed) ·100

xO_2, % = (ppm of O_2 reacted / ppm of O_2 fed) ·100

ySO_2, % = (ppm of sulfur dioxide / ppm of hydrogen sulfide reacted) ·100

3. Results and Discussion

In the Figure 1 are compared XRD patterns of the CeO_2 support with catalyst V_2O_5/CeO_2 before and after the catalytic test.

All the samples exhibited the characteristic peaks of CeO_2; reflections cannot be detected for V_2O_5, likely due to the low metal loading (2.55% wt) and the good dispersion on the support (M.D. Soriano et al., 2009).

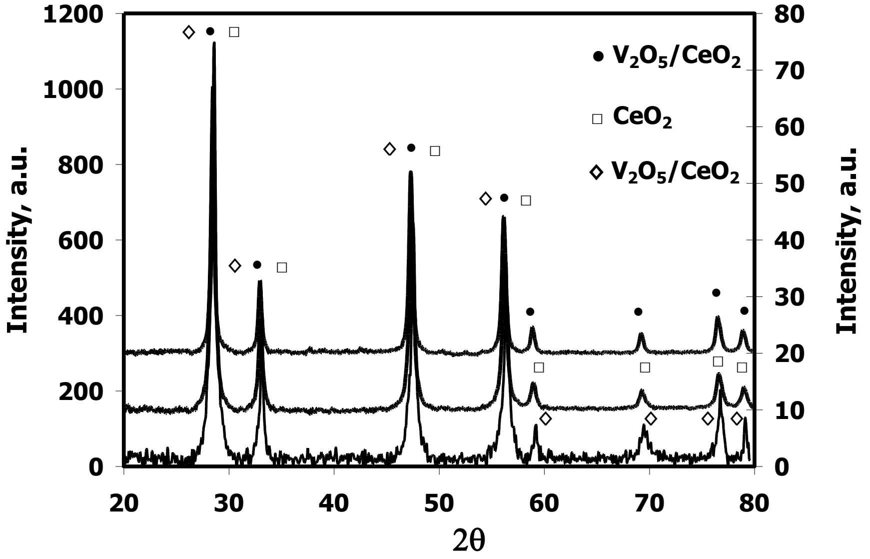

Figure 1: *X-Ray diffraction patterns of CeO_2 and of the catalyst V_2O_5/CeO_2 before (•) and after the catalytic test (◊).*

The Raman spectra of CeO_2 and V_2O_5/CeO_2 catalysts are shown in the Figure 2; the only peaks are relative to the CeO_2, revealing the highly dispersed state of vanadium.
A characteristic Raman peak of CeO_2 has been identified around 465 cm^{-1} (Xiaodong Gu et al., 2006).

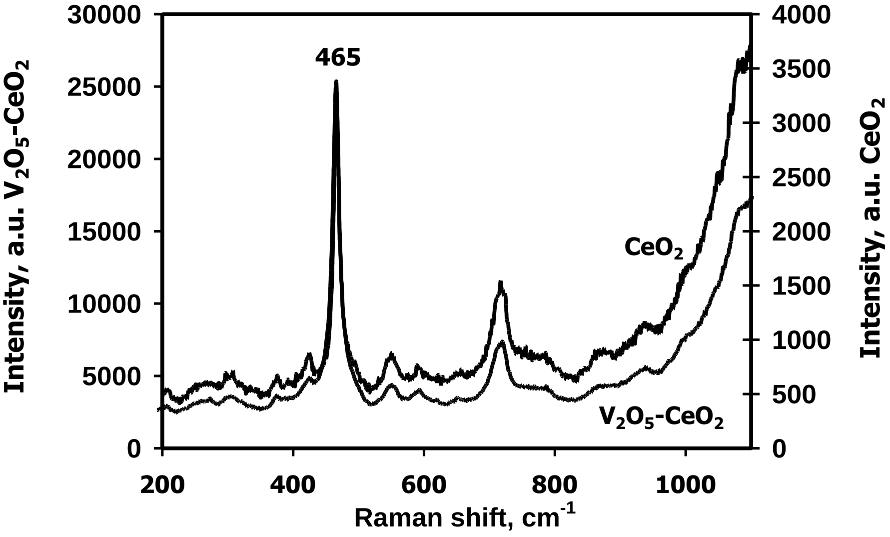

Figure 2: Raman spectra of CeO_2 and of the catalyst V_2O_5/CeO_2 before of the catalytic test.

In Figure 3 are reported results of catalytic activity test obtained at GHSV value of 15000h^{-1}. The figure shows the behavior of the H_2S, O_2 conversions and SO_2 selectivity as function of temperature with an inlet H_2S concentration of 1000 ppm and an O_2/H_2S molar feed ratio of 0.5.

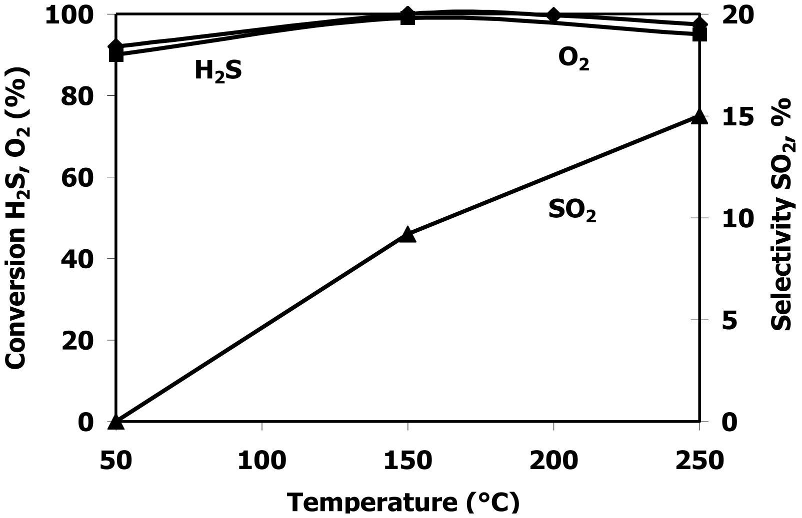

Figure 3: Conversion of H_2S, O_2 and SO_2 selectivity in the range T=50-250 °C

The experimental results show a very high H_2S and O_2 conversion, that is always higher than 90 %, and simultaneously a very low SO_2 production that increase with temperature, reaching the maximum selectivity value of 14 % at the highest temperature tested.

The results of catalytic activity of V_2O_5-CeO_2 catalyst at T=250 °C as function of time are reported in Figure 4.

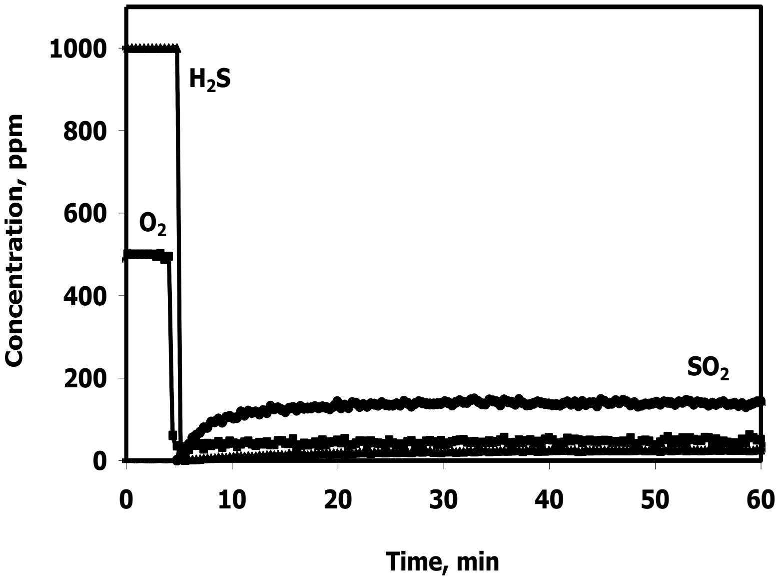

Figure 4: Stability test of V_2O_5/CeO_2 at T=250 °C (1000 ppm H_2S, O_2/H_2S=0.5).

The figure shows that the catalyst in the first hour of time on stream any deactivation is evident, and the catalyst exhibits a very high H_2S and O_2 conversion, but also a significant SO_2 concentration (140 ppm).

Further results concerning the effect of the gas hourly space velocity at constant inlet H_2S concentrations and O_2/H_2S molar feed ratio on the SO_2 selectivity are showed in Table 1, where despite the sensible change in the GHSV values, any significant variations of the H_2S, O_2 conversions and SO_2 selectivity are obtained.

Table 1: Effect of the gas hourly space velocity on the catalytic activity of V_2O_5/CeO_2 (T=250 °C, $O_2/H_2S=0.5$).

GHSV, h^{-1}	X_{H2S}, %	X_{O2}, %	Y_{SO2}, %
15,000	97	91	14
45,000	97	100	13

In Table 2 the effect of the inlet H_2S concentration (from 250 ppm to 1000 ppm) in the feed gas at constant temperature and O_2/H_2S molar feed ratio are reported in terms of H_2S conversion and SO_2 selectivity.

Table 2: Effect of the H_2S concentrations on the catalytic activity of V_2O_5/CeO_2 (T=250 °C, $O_2/H_2S=0.5$).

H_2S, ppm	O_2, ppm	X_{H2S}, %	Y_{SO2}, %
1000	500	98	14
500	250	98	17
250	125	100	26

In this case, the results reported in Table 2 show that there is a measurable effect of the initial concentration of H_2S in the gas supply only on the selectivity to SO_2.

Moreover, it is also evident that even significantly reducing the initial concentration of H_2S, is not found a similar reduction in the selectivity to SO_2.

In contrast with the very good results in terms of H_2S conversion, the SO_2 selectivity is not so bad when the O_2/H_2S feed ratio is 0.5. As a consequence, additional catalytic tests were performed at lower O_2/H_2S molar feed ratio values, and the relevant results are reported in Table 3, where a very good result in terms of SO_2 selectivity was obtained for the O_2/H_2S value of 0.4, for which the SO_2 selectivity results drastically reduced from 13 % to 4 % without any significant reduction of the H_2S and O_2 conversions.

Table 3: Effect *of the feed ratio on the catalytic activity of V_2O_5/CeO_2 (T=250 °C, $O_2/H_2S=0.5$, GHSV=45,000 h^{-1})*

O_2/H_2S	X_{H2S}, %	X_{O2}, %	Y_{SO2}, %
0.5	97	100	13
0.4	94	100	4

4. Conclusions

A vanadium-based catalyst supported on ceria with a nominal load of 2.55 %wt was prepared via impregnation method, and studied for the selective reaction of H_2S oxidation to sulfur.
XRD and Raman characterization results showed that no signals relevant to the presence of isolated V_2O_5, suggesting that vanadium oxide is well dispersed on the CeO_2 surface.
The V_2O_5/CeO_2 catalyst showed very good performances in terms of catalytic activity, stability and SO_2 selectivity. The effect of the gas hourly space velocity and the inlet concentrations of H_2S did not contribute to reduce significantly the SO_2 selectivity.
An interesting result to reduce SO_2 selectivity from 14 % to 4 %, was obtained by decreasing the O_2/H_2S feed ratio from the stoichiometric one ($O_2/H_2S = 0.5$) to a slightly lower value ($O_2/H_2S = 0.4$).

5. Acknowledgments

This work was performed and financed in the framework of the Italian MSE-ENEA research agreement “Studi sulla produzione elettrica locale da biomasse e scarti”.

References

Ciccoli R., Cigolotti V., 2010, Molten carbonate fuel cells fed with biogas: combating H_2S, Waste Management 30, 1018-1024.

McPhail S., Moreno A., Bove R., 2009, International Status of Molten Carbonate Fuel Cell (MCFC) Technology, Report RSE,.181.

Petersson A., Wellinger A., 2009, Biogas Upgrading Technologies-developments and innovations, IEA Bioenergy.

McKinsey S.Z., 2003, Removal H_2S biogas using cow-manure compost”, Thesis, Faculty of Science of Cornell University, 2-54.

Soriano M:D., Jimenez J., 209, “Selective oxidation of H2S to sulphur over vanadia supported on mesoporous zirconium phosphate heterostructure, App. Catal. B, 92, .271-279.

Xiaodong Gu, Jiazen Ge, 2006, Structural, redox and acid - base properties of V_2O_5/CeO_2 catalyst,“ Thermochimica Acta, 451, 84-93.