

H₂S REMOVAL FROM A BIOGAS STREAM FED TO MOLTEN CARBONATE FUEL CELLS

Vincenzo Palma*, Emma Palo and Paolo Ciambelli
Department of Chemical and Food Engineering, University of Salerno, Via Ponte Don
Melillo 84084 Fisciano (SA), Italy

Summary

H₂S removal in biogas stream is a key issue, in particular when biogas is fed to a molten carbonate fuel cell. The selective partial oxidation of H₂S at low temperature is one of the most used process for its abatement, with activated carbon and mixed oxides catalysts as the main kind of materials employed for this reaction. Results showed higher performances of mixed oxides, particularly for V₂O₅-TiO₂ based catalyst with respect to activated carbon. The behavior of O₂ and H₂O concentration profile at reactor outlet indicate that very different reaction mechanism may act for the different catalyst samples.

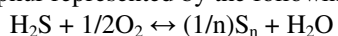
Keywords

Biogas, hydrogen sulphide removal, molten carbonate fuel cell

Introduction

Biogas is a valuable renewable energy carrier and can be employed directly as a fuel or as a raw material for the production of synthesis gas. It is produced by a large number of anaerobic microbial species that ferment the organic matter under controlled temperature, moisture and acidity conditions¹. Its main constituents are methane and carbon dioxide, however it also contains considerable amounts of sulphur compounds, such as hydrogen sulfide and mercaptans. Depending on the composition of the organic material fermented, the H₂S content of biogas can vary from 10 to about 10,000 ppm. Its removal is a crucial step for any eventual utilization of biogas, since in energy-recovery processes it could be converted to highly corrosive compounds such as SO₂ and H₂SO₄². In particular, when the end use technology is represented by a molten carbonate fuel cell, the maximum tolerated H₂S concentration is less than 5 ppm³.

Several methods are employed for biogas purification² and among them there is the selective oxidation of H₂S to elemental sulphur represented by the following reaction:



At very low temperatures (<100°C), and H₂S concentration, this reaction does not have the thermodynamic limitations characterizing the conventional Claus process. The most investigated materials for this kind of reaction belong to two classes: activated carbons and metal oxides. Activated carbons are excellent adsorbents with their specific application related to the properties of molecules to be removed or adsorbed. Several works, carried out by Bandosz et al.⁴ on adsorption/oxidation of H₂S on unmodified carbon at

ambient temperature, showed that a proper combination of surface chemistry and porosity of carbon leads to a good performance of carbons and evidencing that some of the main parameters, determining the process selectivity, are the pH and the carbon prehumidification. On the other hand, among mixed oxides the most investigated ones contain vanadium, sometimes modified with other metals (molybdenum, copper, cerium) to reduce the typical deactivation of vanadium oxide catalyst⁵. Furthermore, novel catalysts and supports such as three dimensional mesoporous carbon aerogels⁶, nanofibrous materials⁷ silicon carbide are employed for this kind of reaction.

The aim of this work is to study the H₂S selective oxidation, in order to reduce hydrogen sulphide concentration below the tolerated limit for a MC fuel cell. Different kind of catalyst, carbon or mixed oxides were investigated, as well as the influence of operating parameters such as temperature, H₂S concentration, O₂/H₂S molar feed ratio. Preliminary results are here reported.

Experimental

Three kind of catalysts were preliminary investigated: impregnated steam activated carbon provided by Norit, CuO-MnO₂ mixed oxide provided by Sud-Chemie, and a V₂O₅-TiO₂ prepared in our lab. The catalytic activity were carried out with a laboratory plant consisting of mass flow controllers to feed the H₂S and the O₂ to the reactor. When added, water was fed by saturating a nitrogen stream at temperature controlled conditions. The reaction was

* e-mail: vpalma@unisa.it

carried out in a quartz reactor inserted in an electrical furnace equipped with a PID temperature controller. The exhaust stream was analyzed by a quadrupole filter mass spectrometer equipped with a sulphur trap in order to follow all the reactants and the gaseous product at the reactor outlet. The preliminary tests were carried out at a $15,000 \text{ h}^{-1}$ GHSV, at fixed temperature of 50°C , by feeding 1000 ppm of H_2S , 500 of O_2 and balance nitrogen.

The catalysts were characterized by thermal analysis, N_2 adsorption, Boehm titration and surface pH evaluation.

Results and discussion

Preliminary results of H_2S removal activity are reported in Figure 1a-c.

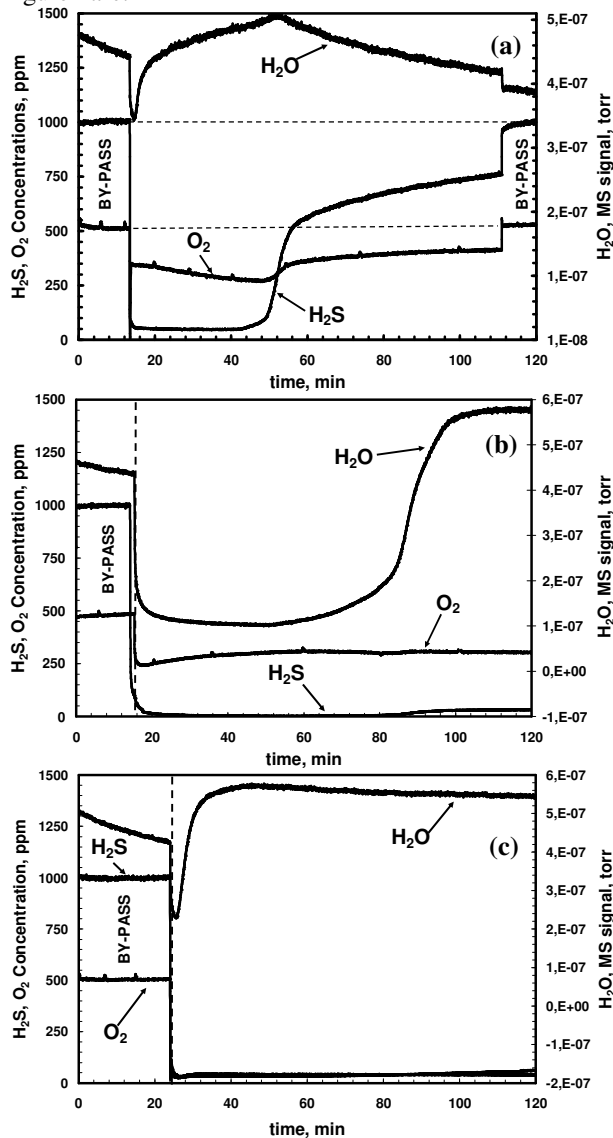


Figure 1. Catalytic activity tests on steam activated carbon (a), CuO-MnO_2 (b) and $\text{V}_2\text{O}_5\text{-TiO}_2$ (c) mixed oxides

Experimental results showed very different catalytic behavior of the selected catalysts. In the case of activated carbon, after the by-pass phase, the H_2O concentration increases with a simultaneous decrease of O_2 and H_2S

concentrations that reaches about 50 ppm. After about 30 min, H_2S concentration suddenly increase, reaching about 500 ppm, simultaneously to the H_2O signal decrease. In the case of CuO-MnO_2 based catalyst, after the by-pass phase, H_2S is completely converted with simultaneous decrease in H_2O concentration. After about 60 min a slight decrease in the catalytic activity can be observed, since about 30 ppm of H_2S are detected at the reactor outlet. Better performances were shown by the $\text{V}_2\text{O}_5\text{-TiO}_2$ based catalyst. After the by pass phase, very high H_2S and O_2 conversions were observed, but more important, higher stability with respect to carbon based material are proved, since any remarkable difference in catalytic activity can be observed after 120 min of test.

Conclusions

A preliminary investigation was carried out on different catalysts for H_2S selective partial oxidation at low temperature. Results showed higher performances of mixed oxides, particularly for $\text{V}_2\text{O}_5\text{-TiO}_2$ based catalyst with respect to activated carbon. The behavior of O_2 and H_2O concentration profile at reactor outlet indicate that very different reaction mechanism may act for the different catalyst samples.

Acknowledgments

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