

Study of a catalytic system with sulphur resistance for self reforming of raw biogas with CO₂ emissions reduction (O-12H)

E. Poggio-Fracarri^{1,2*}, L. Alemany², M. Laborde¹, F. Mariño¹

¹ Instituto de Tecnologías del Hidrógeno y Energías Sostenibles, (UBA-CONICET), Departamento de Ingeniería Química, Facultad de Ingeniería, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón de Industrias, Ciudad de Buenos Aires, Argentina

² Laboratorio de Tecnologías Catalíticas, (PROCAT), Departamento de Ingeniería Química, Facultad de Ciencias, Universidad de Málaga, Campus Unversitario de Teatinos 29017, Málaga, España

(*) Pres. and corresponding author: eapoggio@fi.uba.ar

Keywords: Biogas, Hydrogen, Sulphur resistance

1. Introduction

Conversion of methane into H₂ is a mature catalytic process well known in the industry that employs a large variety of primary sources such as natural gas, naphta, heavy oils, or coal. This process reformates the carbon containing molecule supplying more than the 90 % of the H₂ produced worldwide, with carbon oxides as byproducts [1]. However, the current needs to achieve a sustainable development constrains the use of fossil sources in the industry sector. An interesting alternative is the biomass, particularly infrutilized biomass, food waste, or activated sludges. The gasification of solid biomass or the biogas directly obtained by fermentation is a wet mixture of methane and carbon dioxide, which can be catalytic processed to obtain syngas of different CO/H₂ ratios, including an enriched hydrogen stream. The applicability of this raw material is currently hindered by two main causes, the considerable content of CO₂ concurrently obtained, which reduces the efficiency of the process, and the presence of poisons such as traces of sulphur compounds and ammonia [2]. With the purpose of overcoming the first obstacle, CO₂ and water present in the biogas can be used as oxidizing agents in the mixed reforming of methane, also known of birreforming reaction, Eq. (1) [3]. As an additional consequence, a decrease in carbon dioxide emissions is obtained.



The presence of sulphur compounds normally found in different biogas sources, such as H₂S, dimethyl sulphide (DMS), or methyl mercaptan, conduct to the deactivation of Ni/Al₂O₃ commercial reforming catalysts due to their strong adsorption in active sites. Industrially, it is possible to remove these compounds, but the high cost associated to the purification of the methane of the stream may be unaffordable for this process. A conceivable alternative is the employment of sulphur tolerant catalysts. As a result, a multi-metallic sample was tested in the present work, a modified Ni/Al₂O₃ traditional catalyst. The addition of Sn as promoter was used to improve the sulphur resistance [4], while the redox pair Ce⁴⁺/Ce³⁺ enhanced the activity of the sample activating the oxidizing agents and, finally, very small amount of Rh was included with the aim of gasifying coke deposits

[5]. Additionally, a change in the reaction conditions was also studied in order to improve the stability of the samples.

2. Experimental

A multi-metallic NiCeSnRh/Al₂O₃ sample was obtained by simultaneous incipient wetness impregnation of the alumina support (S_{BET}=246 m²/g, V_p= 0.76 cm³/g) with an aqueous solution of the chemical precursors: Ni(NO₃)₂·6H₂O, Ce(NO₃)₃·6H₂O, Rh(NO₃)₃·xH₂O, and a SnC₂O₄ solution in nitric acid. The components were adjusted in order to obtain the following nominal composition: 9 at/nm² of Ni, 5 at/nm², of Ce, Sn:Ni (1:1000 atomic ratio) and Rh:Ni (1:10000 atomic ratio). After the impregnation stage, the sample was kept in stagnant air at 90 °C overnight and then treated in air for 5 h (10 C^o/min). This latter stage was followed by a reduction procedure at 700°C (10°C/min) during 20 minutes in 5% of H₂ (He as balance) with the aim of activating the sample. The XRD patterns have been recorded with an X'Pert MPD PRO diffractometer (PANalytical) using Cu radiation. The catalytic activity evaluation was conducted in an isothermal fixed bed reactor loaded with 200 mg of sample mass and a total flow of 100 ml/min, 45 %vol CH₄, 30 %vol H₂O, 15 %vol CO₂ (N₂ balanced) for bireforming reaction (BRM), and 30%CH₄, 60% of H₂O (N₂ balanced) for steam methane reforming reaction (SMR). The performance analysis in presence of model sulphur compound (Dimethyl Sulphide, hereafter called DMS) was carried out by including 90 ppm of DMS at the gaseous stream previously dissolved in water.

3. Results and discussion

The XRD pattern of the fresh sample showed different crystalline phases, cerianite, CeO₂ (PDF#43-1002), NiO, bunsenite (PDF#47-1049), NiAl₂O₄ (PDF#10-0339), and no marked alumina signals, except for that located close to 66°, which may indicate the presence of almost an amorphous support (patterns not showed). Additionally, no Sn or Rh species were observed, probably by the low content existing in the solid. the crystallite size of fluorite and bunsenite species were estimated by Scherrer equation presenting a higher value for NiO in comparison with CeO₂, in agreement with the higher atomic content of Ni present in the sample, Table 1. After the activation procedure (catalysts reduction), an increase of the crystallite size of the fluorite particles was observed in conformity with the lower BET surface area

measured. Since NiO signals were not identified, and perceptible lines of NiO appeared, a possible incorporation of Ni to fluorite lattice might be disregarded.

Table 1. Results of BET and XRD techniques

Parameter	Fresh	Reduced
BET (m ² /g)	150	124
d _{fluorite} (nm)	5.4	5.9
d _{Ni/NiO} (nm)	8.5 (NiO)	5.9 (Ni ⁰)

Two different samples were submitted to a long term run analysis at 700 °C during several hours: a clean catalyst, and a sulphurized one in order to determine the effect of the DMS in the activity. This latter sample was obtained by impregnating a concentrated solution of DMS over a previously reduced sample, achieving a value close to 0.1 wt.% (sulphur/catalyst mass ratio). The results of methane conversion, Figure 1, showed three stages: an initial decrease present in both samples (t < 2 hours) probably by the stabilization of the catalyst, followed by a further decrease in the case of the poisoned solid (2 < t < 14 hours), while the activity of the clean remained almost unchanged. Finally, a more marked decrease was found for the poisoned solid (t > 14 hours). These results suggest a clear influence of the DMS in the activity and stability of the catalyst in comparison with the clean solid. On the other hand, the CO₂ conversion of the clean sample decreased at the end of the test simultaneously with the increase in the H₂/CO ratio, probably indicating an obstruction by coke of the active sites for CO₂ activation. The values presented by the sulphurized catalyst were almost constant with a clear decrease in the final stage in agreement with the CH₄ conversion plot suggesting catalyst deactivation. The H₂/CO ratio was higher than theoretical of Dry Reforming of Methane (DRM), and remarkably close to the corresponding of BRM, suggesting the occurrence of this reaction irrespective of the presence of DMS.

With the purpose of determining the effect of DMS in a continuous flow, an additionally BRM reaction test was performed. This test was also conducted with reactivation stages in order to analyse the feasibility of reversible deactivation. Therefore, a BRM reaction stage was followed by SMR; the results are reported in Figure 2. Methane conversion values achieved by the sample at the initial step were close to 65%, decreasing to 55% after 24 hours.

These results suggest an improved performance of the sample in the current operation conditions. Otherwise, the sample evaluated at SMR reaction conditions achieved a CH₄ conversion in the range 80-85% with a slight decrease with the time on stream (TOS). The different trends found for BRM and SMR with TOS probably indicates a gasification of carbon deposits (reversible deactivation) and might also suggest a partial removal of the sulphur compound from the catalyst surface.

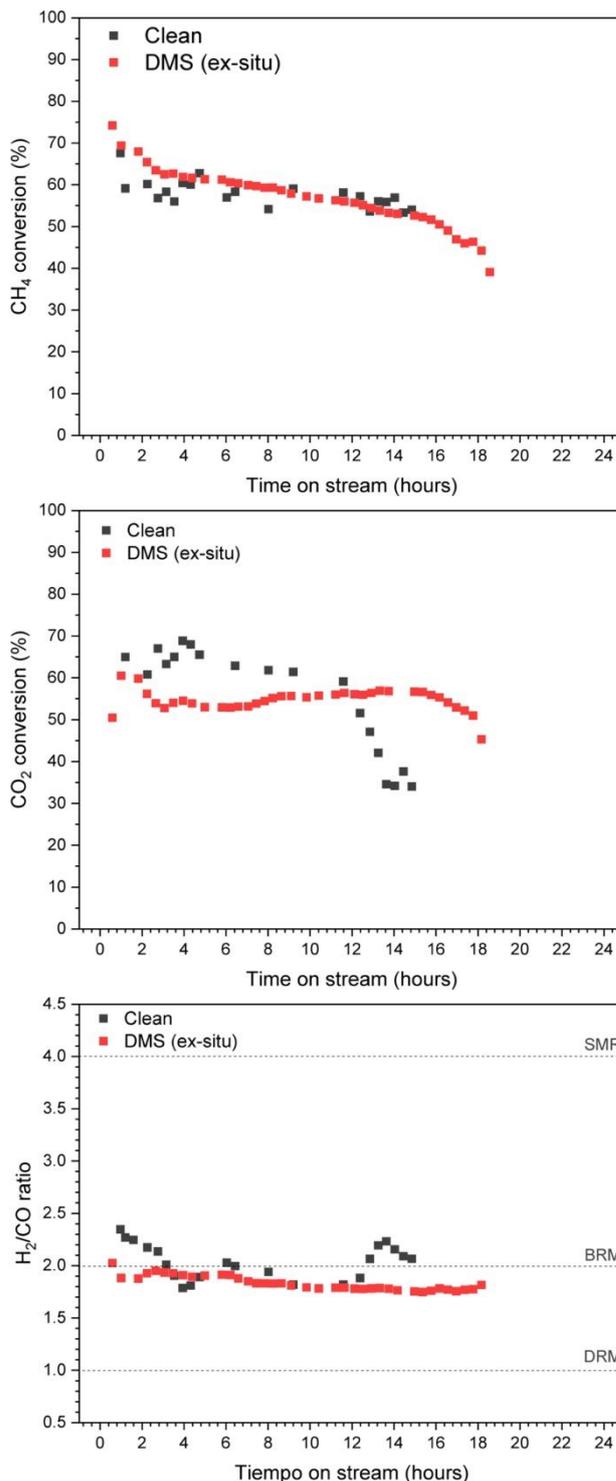


Fig. 1. Long term run of the two tested samples, clean and sulphurized at 700 °C in BRM reaction, a) CH₄ conversion, b) CO₂ conversion, c) H₂/CO ratio.

The CO₂ conversion presented scattered values in the 65-75% range indicating the successful activation of this stable molecule at 700 °C during the entire test.

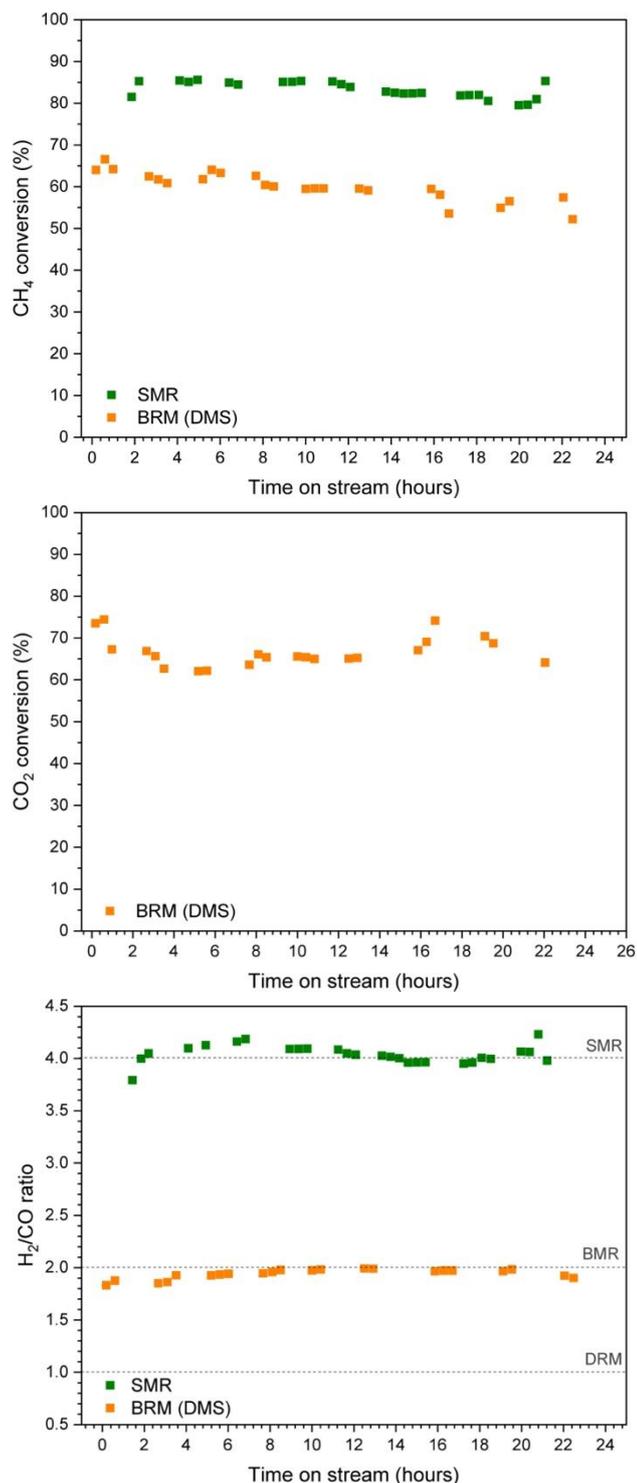


Fig. 2. Long term run of the tested sample at BRM and SMR cycles carried out at 700 °C, a) CH₄ conversion, b) CO₂ conversion, c) H₂/CO ratio.

Regarding the H₂/CO ratio, it can be observed that the sample practically achieved the theoretical values during BRM and SMR reaction conditions. In fact, the ratio was close to 4 for SMR, indicating the incidence of Water Gas Shift reaction decreasing the amount of CO and simultaneously increasing the H₂ produced; however, gasification of the coke previously deposited should not be disregarded. Under BRM reaction conditions, an acceptable and stable H₂/CO ratio was observed, suggesting the occurrence of this reaction in the entire TOS range. In addition, the deactivation observed by the decrease in the methane conversion may be mainly induced by the blocking effect of the DMS in the active sites, with a lower contribution of the coke deposition as it was observed for the clean sample in Figure 1.

4. Conclusions

The catalyst presented a relevant performance in sulphur-free conditions, not only in activity but also in stability. The test carried out in the presence of DMS showed that this multimetallic catalyst has an acceptable sulphur-resistance. The alternating operation between BRM/SMR allowed to operate in optimal conditions improving the stability of the sample, probably due to the gasification of coke deposits, which partially regenerates the active sites blocked by the sulphur compound. The approach presented in this work, multimetallic sample together with alternated reaction conditions, is a promising technology capable of carrying out biogas self-reforming process without any pretreatment or composition adjustment

Acknowledgements

The authors thank to University of Buenos Aires, CONICET and the ANPCyT for their financial support.

References

- [1] P. Ferreira-Aparicio, M. Benito, *Catal. Rev. Sci. Eng.* 47 (2005) 491-588.
- [2] S. Rasi, A. Veijanen, J. Rintala, Trace compounds of biogas from different biogas production plants, *Energy*, 32 (2007) 1375-1380.
- [3] A. Farooqi, M. Yussuf, N. Zabidi, R. Saidur, K. Sanaullah, A. Farooqi, A. Khan, B. Abdullah. *Int. J. Hydro. Energ.* In Press (2022).
- [4] M. Rangan, M. Yung, J. Medlin, *J. Catal.* 282 (2011) 249.
- [5] García-Dieguez M, Finocchio E, Larrubia M, Alemany L, Busca G, *J. Catal.* 274 (2010) 11.