

H₂S in Black Sea: Turning an environmental threat to an opportunity for clean H₂ production via an Electrochemical Membrane Reactor. Research progress in H₂S-PROTON Project

Tzoulia Kraia^{1,2}, Michalis Konsolakis³ and George E. Marnellos^{1,2,a}

¹ Chemical Process & Energy Resources Institute (C.P.E.R.I.), Centre for Research and Technology Hellas (C.E.R.T.H.), P.O. Box 60361, 57001, Thessaloniki, Greece

² Department of Mechanical Engineering, University of Western Macedonia, Bakola & Sialvera, 50100, Kozani, Greece

³ Technical University of Crete, School of Production Engineering and Management, Chania, 73100, Crete, Greece

Abstract. The present study aims to examine and evaluate the concept of H₂S decomposition to H₂ production in (H⁺)-conducting electrochemical reactors. In such a complex process, one of the major issues raised is the optimal selection of materials for the electrochemical cell. Specifically, the anode electrode should exhibit high catalytic activity and electronic conductivity, in order to make the process efficient. In this context, and before the electrochemical tests, a number of transition metal catalysts supported on CeO₂ were prepared using the wet impregnation method and tested for their performance regarding the activity/stability of the H₂S decomposition reaction, in the absence and presence of H₂O. The experimental results are accompanied by the corresponding thermodynamic calculations, at various reaction conditions. The physico-chemical characteristics of the employed catalysts were determined using the BET, XRD, SEM and elemental analysis methods. The experimental results showed that the catalysts 20% wt. Co/CeO₂ and 30% wt. Co/CeO₂ exhibit high H₂S conversions, in the absence and presence of H₂O respectively, comparable to conversions indicated by thermodynamics and with remarkable stability, which is attributed to the in-situ sulfation of catalysts' active components during their exposure at the feedstock mixture.

1 Introduction

Fossil fuels still remain the primary feedstock supply for energy production, leading as a consequence to important environmental and socioeconomic implications [1]. In view of these adverse effects, an innovative and environmental friendly approach has to be adopted. H₂ is in general considered as a promising energy carrier towards a more sustainable future [2].

Apart from the harmful effects to human health and the surrounding ecosystem, the H₂S contained in Black Sea (BS) may serve as a H₂ source [1,4]. From theoretical calculations, it has been found that it is possible to produce 270 Mtons of H₂, corresponding to 808 Mtons of gasoline or 766 Mtons of natural gas [1,4]. The Hydrogen production process from Black Sea consists of the following steps: a) pumping of sea water at ~1000 m depth, b) extraction of concentrated H₂S/H₂O mixtures, c) co-electrolysis of H₂S and H₂O to H₂ in H⁺-conducting electrochemical reactors. The decomposition of H₂S to H₂ can be achieved using various technologies categorized as thermal, thermochemical, electrochemical, photochemical and plasmochemical methods [4]. The electrochemical processes, which operate at intermediate

temperatures (700-1000 K), are seen as the most promising approach. The conventional homogeneous/catalytic decomposition of H₂S, takes place at significantly higher temperatures, in order to achieve conversions exceeding 80%. To overcome this issue, a novel approach based on ceramic H⁺-conducting electrochemical reactors/fuel cells is proposed (Figure 1).

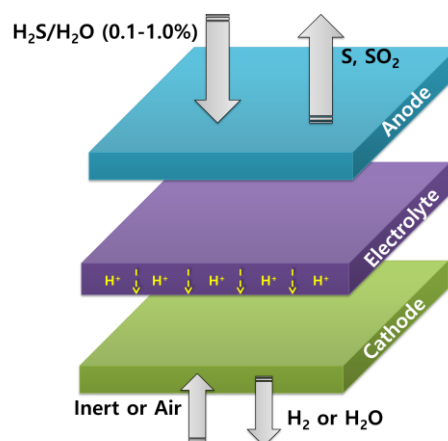


Figure 1. Schematic representation of H₂S decomposition in an electrochemical membrane reactor.

^a Corresponding author: gmarnellos@uowm.gr

The selection of the material, employed as anode in the H^+ -conducting high temperature solid oxide fuel cell/reactor, is crucial for the successful operation of the proposed process. For this specific application, the anodic electrode has to exhibit: i) high catalytic activity towards the H_2S/H_2O decomposition, ii) high electronic conductivity, iii) good adherence on solid electrolyte, and iv) tolerance against H_2S and S compounds [5].

In this context, and prior to electrochemical tests, a series of transition metal catalysts, supported on CeO_2 , were synthesized and evaluated, in terms of their catalytic activity and stability for H_2S decomposition, in the absence/presence of H_2O .

2 Materials and methods

Y-doped barium zirconate ($BaZr_{0.85}Y_{0.15}O_{3-\delta}$, BZY) is selected as the proton-conducting solid electrolyte material for the electrochemical reactor, prepared using the solid state reaction method by calcining a mixture of $BaCO_3$, Y_2O_3 and ZrO_2 powders for 10 h at 1573 K in an alumina crucible [6,7]. For the anode material, transition metal (Co, Ni, Fe, Cu) catalysts, supported on CeO_2 were synthesized employing the wet-impregnation method. $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) was employed as cathode material and prepared by the sol-gel citrate method.

The catalytic activity and stability experiments were performed in an automated apparatus consisting of the feeding unit, the fixed bed quartz U-tube reactor (9.6 mm, i.d.) loaded with 250 mg catalyst admixed with an equal amount of quartz, the heating system of the reactor and the gas analysis system (SHIMADZU 14B). The above description of the apparatus and the corresponding experimental conditions are presented in our previous work [8].

3 Results and discussion

3.1. Effect of the nature and loading of the transition metal catalysts (M/ CeO_2) in the absence/presence of H_2O

The evaluation of anode materials was carried out by determining the H_2S decomposition performance both in the absence and presence of H_2O . In Figure 2 the catalytic performance of the transition metal catalysts, M/ CeO_2 (where M: Co, Ni, Fe, Cu), at 20 wt.% metal loading towards the direct H_2S decomposition, is depicted. For comparison purposes, the performance of bare ceria and the H_2S conversion under homogeneous (absence of a catalyst) conditions, is also presented. It is clear that the presence of a catalyst obviously enhances the obtained conversion. The 20 wt.% Co/CeO_2 catalyst exhibited the superior performance.

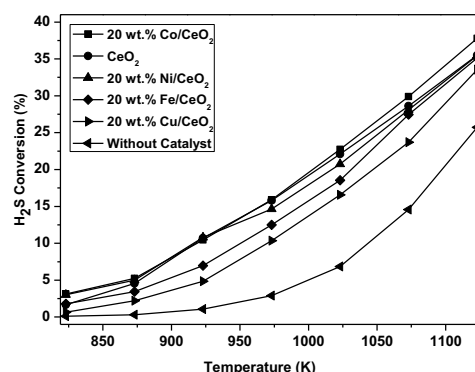


Figure 2. H_2S conversion as a function of reaction temperature over different 20 wt.% M/ CeO_2 catalysts

In order to evaluate the catalysts at simulated Black Sea conditions, the H_2S decomposition reaction was examined also in the presence of H_2O . Initially, preliminary experiments were performed at two different feed compositions (i.e., 1% H_2S / 90% H_2O / 9% Ar and 90% H_2O / 10% Ar), where the rate of H_2 production was monitored. The experimental results clearly revealed that the H_2O conversion is essentially negligible, both in the absence/presence of catalyst (90% H_2O / 10% Ar). However, it was generally observed that the presence of H_2O enhances the H_2S conversion, as predicted by thermodynamics. In Figure 3, the H_2 production rate of bare CeO_2 in comparison with the 20 and 30 wt.% Co/CeO_2 catalysts, both in the absence and presence of H_2O , is examined. The results clearly indicate the superiority of Co/CeO_2 catalysts under both dry and wet conditions. Specifically, the 20 wt.% Co/CeO_2 catalyst exhibited the optimum performance in the absence of H_2O , while the 30 wt.% Co/CeO_2 demonstrated the best performance in the presence of water. This confirms that a specific Co loading is required to achieve the optimum performance, which is depending strongly on the specific reactions conditions.

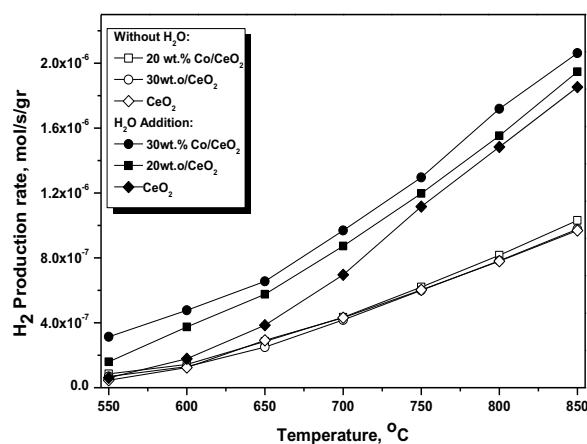


Figure 3. H_2 production rate as a function of temperature for 20 and 30 wt.% Co/CeO_2 and CeO_2 catalysts.

The optimum catalyst 30 wt.% Co/CeO₂ was further examined at long-term stability experiments. As it is shown in Figure 4, after the initial activation period, the performance of the optimum catalyst was stabilized at a value, similar to that indicated by the activity experiments and remained stable until the end of the 10 h duration. On the other hand, in the case of pure CeO₂, although the steady state of H₂ formation rate was achieved earlier, the activity slightly degraded with time on stream. In the case of the aged catalyst, it was observed that approximately half of the time was required for the H₂ production rate to reach steady state. This observation indicates that the remarkable stability of the catalyst can be attributed to the in-situ sulfation of catalyst under reaction atmosphere.

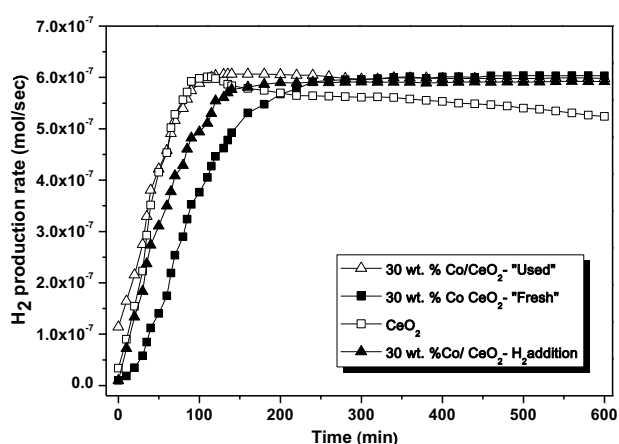


Figure 4. H₂ production vs. time on stream (10 h) in the presence of H₂O for 30 wt.% Co/CeO₂ (Fresh, Used, H₂ addition) and CeO₂ catalysts.

4 Conclusions

In the present work, a series of transition metal catalysts (Co, Ni, Fe, Cu) supported on CeO₂ were prepared and evaluated concerning their performance, with respect to their activity and stability in the H₂S decomposition reaction. The experimental results in the absence of H₂O showed that the 20 wt.% Co/CeO₂ catalyst exhibited the optimum performance, achieving H₂S conversions close to those predicted by thermodynamics. In the presence of H₂O, the 30 wt.% Co/CeO₂ catalyst exhibited the superior behaviour, as well as remarkable stability, while the "aged" catalyst reached faster the steady state. Moreover, the observed remarkable stability was attributed to the in-situ sulfation of catalysts' active components during their exposure to feedstock mixture.

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References

1. A. Midilli, M. Ay, A. Kale, T.N. Veziroglu, *Int. J. Hydrogen Energy*, **32**, 117 (2007).
2. G.E. Marnellos, C. Athanasiou, S.S. Makridis, E.S. Kikkinides, **Ch.3**, p. 23 in: N. Lymberopoulos, E.I. Zoulias (Eds.), *Hydrogen based autonomous power systems*, (2008).
3. J. Zaman, A. Chakma, *Fuel Proc. Technol.*, **41**, 159 (1995).
4. S.Z. Baykara, E.H. Figen, A. Kale, T.N. Veziroglu, *Int. J. Hydrogen Energy*, **32**, 1246 (2007).
5. M. Gong, X. Liu, J. Trembly, C. Johnson, *J. Power Sources* **168**, 289 (2007).
6. K.D. Kreuer, *Ann. Rev. Mater. Res.*, **59**, 33 (2003).
7. Li J, Luo JL, Chuang KT, Sanger AR., *Electrochim. Acta.*, **53**, 3701 (2008)
8. D. Ipsakis, Tz. Kraia, G.E. Marnellos, M. Ouzounidou, S. Voutetakis, R. Dittmeyer, A. Dubbe, K. Haas-Santo, M. Konsolakis, H.E. Figen, N.O. Guldal, S.Z. Baykara, *Int. J. Hydrogen Energy*, **40**, 7530 (2015).