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

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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 environmentally 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.
The selection of the material, employed as anode in the H\textsuperscript{+}-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\textsubscript{2}S/H\textsubscript{2}O decomposition, ii) high electronic conductivity, iii) good adherence on solid electrolyte, and iv) tolerance against H\textsubscript{2}S and S compounds [5].

In this context, and prior to electrochemical tests, a series of transition metal catalysts, supported on CeO\textsubscript{2}, were synthesized and evaluated, in terms of their catalytic activity and stability for H\textsubscript{2}S decomposition, in the absence/presence of H\textsubscript{2}O.

2 Materials and methods

Y-doped barium zirconate (BaZr\textsubscript{0.85}Y\textsubscript{0.15}O\textsubscript{3-δ}, 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\textsubscript{3}, Y\textsubscript{2}O\textsubscript{3} and ZrO\textsubscript{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\textsubscript{2} were synthesized employing the wet-impregnation method. La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3-δ} (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\textsubscript{2}) in the absence/presence of H\textsubscript{2}O

The evaluation of anode materials was carried out by determining the H\textsubscript{2}S decomposition performance both in the absence and presence of H\textsubscript{2}O. In Figure 2 the catalytic performance of the direct H\textsubscript{2}S decomposition, M/CeO\textsubscript{2} (where M: Co, Ni, Fe, Cu), at 20 wt.% metal loading towards the direct H\textsubscript{2}S decomposition, is depicted. For comparison purposes, the performance of bare ceria and the H\textsubscript{2}S 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\textsubscript{2}-catalyst exhibited the superior performance.

In order to evaluate the catalysts at simulated Black Sea conditions, the H\textsubscript{2}S decomposition reaction was examined also in the presence of H\textsubscript{2}O. Initially, preliminary experiments were performed at two different feed compositions (i.e., 1% H\textsubscript{2}S / 90% H\textsubscript{2}O / 9% Ar and 90% H\textsubscript{2}O / 10% Ar), where the rate of H\textsubscript{2} production was monitored. The experimental results clearly revealed that the H\textsubscript{2}O conversion is essentially negligible, both in the absence/presence of catalyst (90% H\textsubscript{2}O/ 10% Ar). However, it was generally observed that the presence of H\textsubscript{2}O enhances the H\textsubscript{2}S conversion, as predicted by thermodynamics. In Figure 3, the H\textsubscript{2} production rate of bare CeO\textsubscript{2} in comparison with the 20 and 30 wt.% Co/CeO\textsubscript{2} catalysts, both in the absence and presence of H\textsubscript{2}O, is examined. The results clearly indicate the superiority of Co/CeO\textsubscript{2} catalysts under both dry and wet conditions. Specifically, the 20 wt.% Co/CeO\textsubscript{2} catalyst exhibited the optimum performance in the absence of H\textsubscript{2}O, while the 30 wt.% Co/CeO\textsubscript{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.
The optimum catalyst 30 wt.% Co/CeO$_2$ 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 CeO$_2$, although the steady state of H$_2$ 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 H$_2$ 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. H$_2$ production vs. time on stream (10 h) in the presence of H$_2$O for 30 wt.% Co/CeO$_2$ (Fresh, Used, H$_2$ addition) and CeO$_2$ catalysts.

4 Conclusions

In the present work, a series of transition metal catalysts (Co, Ni, Fe, Cu) supported on CeO$_2$ were prepared and evaluated concerning their performance, with respect to their activity and stability in the H$_2$S decomposition reaction. The experimental results in the absence of H$_2$O showed that the 20 wt.% Co/CeO$_2$ catalyst exhibited the optimum performance, achieving H$_2$S conversions close to those predicted by thermodynamics. In the presence of H$_2$O, the 30 wt.% Co/CeO$_2$ 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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