Applied Catalysis A: General 483 (2014) 25–30

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Coupling catalysis and electrocatalysis for hydrogen production in a solid electrolyte membrane reactor

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ARTICLE INFO

Article history:
Received 14 March 2014
Received in revised form 27 May 2014
Accepted 24 June 2014
Available online 1 July 2014

Keywords:
H_2 production
Methane decomposition
Steam electrolysis
Solid electrolyte membrane reactor
Electrochemical regeneration.

ABSTRACT

This study reports the production of H_2 via catalytic methane decomposition on Pt supported on yttria-stabilized zirconia together with its electrochemical regeneration in a solid electrolyte membrane reactor. Hence, a Pt-YSZ_{porous}/YSZ/Pt double-chamber solid electrolyte cell was prepared and tested under two reaction regimes. In the first regime, under open-circuit conditions, hydrogen and carbon are produced on the catalytically active Pt-YSZ porous catalyst via methane decomposition reaction (CH_4 (g) → C (s) + $2H_2$ (g)). In the second regime, under polarization conditions, steam is electrolyzed at the Pt cathode of the cell ($H_2O + 2e^- \rightarrow H_2 + O^{2-}$) and the produced O^{2-} ions were simultaneously electrochemically pumped to the Pt/YSZ porous catalyst (anode), thereby allowing removal of the previously deposited carbon ($C(s) + O^{2-} \rightarrow CO_2$ (g)) and finally regenerating the Pt/YSZ porous catalyst film. We demonstrated that the carbon generated in the methane decomposition step serves as a depolarizating agent in the steam electrolysis process, thus decreasing the electrical energy input required for electrochemically producing pure H_2. In addition, during the regeneration step, C_2 hydrocarbons (e.g., ethane and ethylene) were obtained as a result of the electrocatalytic methane oxidative coupling on the Pt/YSZ porous catalyst film. The performance and durability of the system was also verified for long operation times in view of the possible practical application of this novel reactor configuration, which combines gas-phase catalysis and electrocatalysis for hydrogen production.

1. Introduction

Hydrogen is considered a promising candidate to be the energy carrier of the future. It is used as fuel in fuel cells to produce electricity. In addition, hydrogen and syngas can be used in a wide range of industrial applications, such us petrochemicals, ammonia, petroleum refining, and methanol synthesis [1–3]. If attention is focused on the use of hydrogen as clean fuel to produce energy by fuel-cell systems, the development of efficient processes for the production of "CO_x-free" H_2 streams becomes important in order to overcome hurdles associated with the use of a conventional multi-step process for its further separation and purification. In this sense, the thermal catalytic decomposition of methane (TCD) into hydrogen and carbon is attracting much research interest since it appears to be a direct, mildly endothermic, attractive way for producing highly "pure" hydrogen with reduced CO_2 emissions [4]. This process become more interesting taking into account the reserves of natural gas and the recent advances in the technology for the extraction of natural gas from impermeable shale formations (commonly named shale gas) [5]. Hence, methane can be thermo-catalytically decomposed into carbon and hydrogen without producing CO_2 according to the following reaction:

$$CH_4(g) \rightarrow C(s) + 2H_2(g) \quad (1)$$

When compared to conventional methane-reforming technologies, TCD has a number of positive aspects, as recently stressed by some authors. For instance, based on the life-cycle assessments, Dufour et al. [6] claimed TCD as the most environment-friendly process for hydrogen production as it presented the lowest total environmental impact and CO_2 emissions in comparison with methane steam reforming coupled with CO_2 capture and methane thermal cracking technologies. Accordingly, different metal-based catalysts have been widely used to decrease the high temperature required for methane decomposition [7–10]. These metal catalysts are generally deactivated by deposited carbon during the course of the reaction, thereby requiring frequent regeneration treatments

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http://dx.doi.org/10.1016/j.apcata.2014.06.025
0926-860X/

for recovering initial activity. This technical barrier has motivated researchers to develop novel reactor designs and specifically membrane reactors [11–13]. In this sense, Karagiannakis et al. [11] reported the electrochemical double-chamber solid electrolyte membrane reactor (SEMR) using a proton-conducting ceramic membrane, $SrCe_{0.95}Yb_{0.05}O_{3d}$ (SCYb). In this approach, the hydrogen produced by the catalytic hydrocarbon decomposition is electrochemically transported through the proton-conducting membrane. In a similar work, the experimental verification and evaluation of a barium cerate mixed conducting membrane perovskite ($BaCe_{0.9}Y_{0.1}O_{3-\delta}$, BCYO) containing Pd catalyst was provided, leading to high-purity hydrogen and carbon production by TCD [14]. In addition, the SEMRs have already been used in other related hydrogen production process, e.g., via steam reforming or partial oxidation reactions [15] and have been described in detail by means of excellent reviews [16–19]. On the other hand, the electrochemical oxidation of carbon in SEMRs (as solid oxide fuel cells, SOFCs) has been previously studied in literature [20–22].

In this work, we propose a novel approach based on the ability of SEMRs to both, produce carbon and H_2 and to electrochemically oxidize the carbon deposited over an electrode. It consists of a solid electrolyte membrane reactor that allows to electrochemically regenerate a Pt catalyst from the carbon deposition in the TCD reaction. Hence, a Pt-YSZ_{porous}/YSZ/Pt (YSZ = yttria-stabilized zirconia) double-chamber cell operating under two reaction regimes have been developed. In the first regime, hydrogen and carbon are produced on the catalytically active Pt/YSZ porous film via TCD under open-circuit conditions. In the second regime, under closed-circuit conditions, steam is electrolyzed at the Pt cathode of the cell (reaction 2), thereby simultaneously generating O^{2-} ions that are electrochemically pumped to the Pt/YSZ porous catalyst film (anode) assisting in the removal of the previously deposited carbon (reaction 3):

$$H_2O + 2e^- \rightarrow H_2 + O^{2-} \quad (2)$$

$$C(s) + O^{2-} \rightarrow CO_2(g) \quad (3)$$

This way, the second reaction regime allows to electrochemically regenerate the active Pt/YSZ porous film by a carbon-assisted steam electrolysis process leading to the further production of hydrogen. The use of carbon-containing molecules such as CH_4 [23], CO [24], or carbon [25] as depolarizating agents is of great interest for the electrolytic production of H_2, since it allows to strongly decrease the required electrical power input for the process. Consequently, the herein proposed double-chamber configuration allows the in situ valorization of the produced carbon as a depolarizating agent during the steam electrolysis process.

2. Experimental

2.1. Solid electrolyte cell preparation and characterization

The solid electrolyte cell consisted of an yttria-stabilized zirconia (YSZ) tube closed at one end, with 15 cm length, 1.8 cm internal diameter, and 1.5 mm thickness (supplied by CERECO). On both faces of the closed side tube (Fig. 1), two kind of Pt catalysts were prepared. Firstly, in the inner side of the tube, a continuous Pt catalyst film was prepared on the dense YSZ by application of a thin coating of Pt paste (METALOR), followed by two calcination steps, at 300 °C (2 h) and 850 °C (2 h). The final Pt loading was around 5 mg Pt/cm^2. A Pt/YSZ porous catalyst film based on Pt nanoparticles supported on YSZ was furnished on the outer side of the YSZ tube. For that purpose, a porous YSZ interlayer was firstly deposited as follows. YSZ powder was mixed with an organic binder (Decoflux, Zschwimmer, and Schwartz) in a 1:1 (w/w) ratio and then it was spin-coated on the outer face of the tube. The assembly was dried at

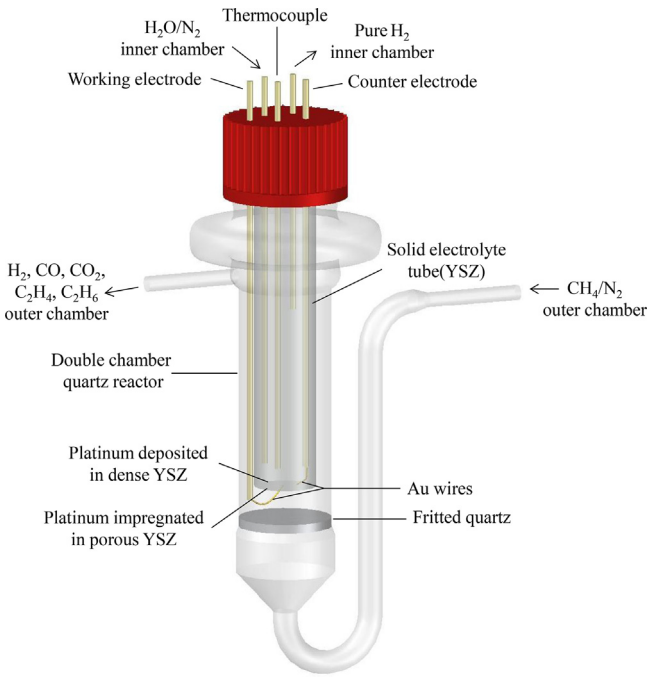

Fig. 1. Scheme of the double-chamber solid electrolyte cell reactor.

100 °C for 1 h in an oven and then calcined at 850 °C for 6 h in order to ensure good adherence. Then, the Pt active catalytic particles were deposited on the porous YSZ interlayer. The Pt particles were prepared by an impregnation technique consisting of successive steps of deposition and thermal decomposition of the 2-propanol solution of 0.1 M H_2PtCl_6. Initially, 10 μl of precursor solution was deposited on the YSZ substrate using a plastic circular mask in order to obtain a 2.01 cm^2 geometric area of the catalytic film. Then, evaporation of the solvent took place at 70 °C for 10 min, followed by drying of the sample at 120 °C overnight and then calcination at 850 °C for 2 h. Several successive steps of this deposition procedure followed by drying and heating were repeated until a final metal loading of 0.6 mg Pt was obtained. It led to a highly dispersed Pt/YSZ electrode, with a poor electrical conductivity. Then, a catalytically inert Au current collector was added to the Pt/YSZ porous catalyst film for polarization purposes. Hence, the electrical contact of the Pt electrode and the Au current collector was carried out by gold wires, which were in turn connected to a potentiostat–galvanostat Voltalab 21 (Radiometer Analytical). The prepared solid electrolyte cell was placed on a quartz tube with appropriate feed-through for both reaction sides as shown in Fig. 1. Before the catalytic activity measurements, the Pt porous catalyst film was reduced under H_2 stream at 450 °C for 1 h.

The Pt porous catalyst film was characterized by X-ray diffraction (XRD) with a Philips PW 1710 instrument using Ni-filtered Cu Kα radiation. The diffractograms were compared with the JCPDS-ICDD references. The Pt porous catalyst film was also characterized via scanning electron microscopy (SEM) with BSE signal using a JEOL 6490 LV microscope. Linear voltammetry measurements were also performed with the potentiostat–galvanostat Voltalab 21 under different reaction atmospheres and different Pt catalytic states (regenerated and deactivated) and were recorded at a sweep rate of 100 mV s^{-1}.

2.2. Catalytic activity measurements

The reaction gases (Praxair, Inc.) were certified standards of 10% CH_4/N_2, and N_2 (99.999% purity) was used as the carrier gas. The gas flow was controlled by a set of calibrated mass flow-meters