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Hydrogen production in solar reactors

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Abstract

The present work summarizes the recent activities of our laboratory in the field of solar-aided hydrogen production with structured monolithic solar reactors. This reactor concept, ‘‘transferred’’ from the well-known automobile exhaust catalytic after-treatment systems, employs ceramic supports optimized to absorb effectively solar radiation and develop sufficiently high temperatures, that are coated with active materials capable to perform/catalyze a variety of ‘‘solar-aided’’ reactions for the production of hydrogen such as water splitting or natural gas reforming. Our work evolves in an integrated approach starting from the synthesis of active powders tailored to particular hydrogen production reactions, their deposition upon porous absorbers, testing of relevant properties of merit such as thermomechanical stability and hydrogen yield and finally to the design, operation simulation and performance optimization of structured monolithic solar hydrogen production reactors. This approach, among other things, has culminated to the world’s first closed, solar-thermochemical cycle in operation that is capable of continuous hydrogen production employing entirely renewable and abundant energy sources and raw materials – solar energy and water, respectively – without any CO_2 emissions and holds, thus, a significant potential for large-scale, emissions-free hydrogen production, particularly for regions of the world that lack indigenous resources but are endowed with ample solar energy.

Keywords: Solar hydrogen; Monolithic reactors; Water splitting; Steam reforming; Redox materials; Catalytic materials

1. Introduction

The harnessing of the huge energy potential of solar radiation and its effective conversion to chemical energy carriers such as hydrogen is a subject of primary technological interest. There are basically three pathways for producing hydrogen with the aid of solar energy [1]: electrochemical, photochemical and thermochemical. The latter is based on the use of concentrated solar radiation as the energy source for performing high-temperature reactions that produce hydrogen from transformation of various fossil and non-fossil fuels via different routes such as water splitting (to produce hydrogen and oxygen) [1–4], natural gas steam reforming (to produce syngas) [5–8] and natural gas cracking (to produce hydrogen and carbon black nanoparticles) [9–12]. All of these routes involve in some step endothermic reactions that make use of concentrated solar radiation as their energy source of high-temperature process heat.

Obviously, the ideal raw material for hydrogen production is water, due to its abundance, low value and the absence of CO_2 emissions during its dissociation (water splitting) to hydrogen and oxygen. However, although conceptually simple, the single-step thermal dissociation of water (known as water thermolysis):

$$H_2O \rightarrow H_2 + 0.5O_2 \qquad (1)$$

is a reaction not favoured thermodynamically; extremely high temperatures (>2200 °C) are required for obtaining some significant dissociation degree [1]; moreover, requires the energy intensive process of high-temperature oxygen–hydrogen separation coupled with expensive membrane technology [13] and therefore is considered of little chance for technical and economical viability in the near future [4]. The current state-of-the-art of solar chemistry for water splitting and hydrogen production is focused on the so-called redox pair cycles. These are two-step processes, based on redox materials that can

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Nomenclature

c_i	gas phase concentration of species i
c_{1w}	vapor concentration close to the wall
c_{pi}	molar specific heat capacity of species i
c_{pw}	specific heat capacity of the material of the monolith
E_{lo}	activation energy of water splitting reaction
E_{reg}	activation energy of regeneration reaction
f_i	molar flow rate of species i
ΔH_{lo}	heat of water splitting reaction
ΔH_{reg}	heat of regeneration reaction
k_{lo}	rate constant of water splitting reaction
$k_{lo,o}$	frequency factor of water splitting reaction
k_{reg}	rate constant of regeneration reaction
$k_{reg,o}$	frequency factor of regeneration reaction
k_D	mass transfer coefficient in the channel
k_H	heat transfer coefficient in the channel
L	length of the monolith channel
N	number of discretization intervals
P	pressure
Q	solar heating rate per channel
R	universal gas constant
t	time
T	gas temperature
T_w	wall temperature
w	wall thickness
y	fractional surface coverage
Y	average fractional coverage of the monolith
z	coordinate along the monolith

Greek letters

α	size of the side of the monolith channel
ρ_s	density of the material of the monolith
Ψ	storage capacity of the wall

act as effective water splitters at lower temperatures [1–4]. According to this idea, in the first step (water splitting) the activated redox reagent (usually the reduced state of a metal oxide) is oxidized by taking oxygen from water and producing hydrogen via reaction (2) below. During the second step the oxidized state of the reagent is reduced, to be used again (regeneration), delivering some of the oxygen of its lattice according to reaction (3):

$$MO_{red} + H_2O(g) \rightarrow MO_{ox} + H_2(g) \tag{2}$$

$$MO_{ox} \rightarrow MO_{red} + \tfrac{1}{2}O_2 \tag{3}$$

The disadvantage is that a two-step process is required, consisting of a water splitting and a regeneration (oxygen release) step. The advantage is the production of pure hydrogen and the removal of oxygen in separate steps, avoiding the need for high-temperature separation and the chance of explosive mixtures formation.

The redox materials that have been evaluated consist of oxide pairs of multivalent metals such as Fe_3O_4/FeO, Mn_3O_4/MnO – the most representative of which can be considered the Fe_3O_4/FeO system [14] – systems of metal oxide/metal (e.g. ZnO/Zn) [15] and their combinations, e.g. doped ferrites such as $(A,B)Fe_2O_4$ with elements A and B being bivalent metal cations such as Mn, Ni or Zn [16]. Reaction (2) is slightly exothermic whereas reaction (3) is highly endothermic. For example for the system $Mn_{0.5}Zn_{0.5}Fe_2O_4$ a thermodynamic evaluation provided enthalpies of +300 kJ/mol for the O_2 releasing step and between −35 and −68 kJ/mol for the water splitting step [16]. Therefore, water splitting is taking place at temperatures below 900 K while the reduction of the metal oxide, takes place at much higher temperatures. The concept has been proven experimentally, however the regeneration temperatures are still high imposing a barrier towards integration of a two-step water splitting process with a concentrating solar system. For full exploitation of the potential of such cycles, there is a need for materials with high water-splitting activity and regenerability at moderate temperatures, with long-term stability and no properties' degradation over extended cyclic operation under concentrated solar irradiation.

Therefore, at least for a transition period, hydrogen supply at a competitive cost can only be achieved from hydrocarbons—essentially natural gas (whose principal component is methane) using well-known commercial processes like steam reforming where methane and steam are converted to syngas according to reaction (4):

$$CH_4 + H_2O(g) \Leftrightarrow 3H_2 + CO, \qquad \Delta H_{298K} = 206\,\text{kJ/mol} \tag{4}$$

In the conventional process, natural gas is fed together with steam to the reformer, where reacts over a catalyst at temperatures between 800 and 1000 °C. In the solar process, it is possible to provide all necessary heat by solar energy [8]. Current state-of-the-art catalytic systems for natural gas steam-reforming are based either on highly expensive precious metals or on systems of significantly lower cost based on Ni-metal supported on mixed oxides of Ca–Al [17] or Mg–Al [18] of the spinels and hexa-aluminates structures (e.g. $MgAl_2O_4$ or $CaAl_6O_7$, respectively). The mixed oxide supports are traditionally synthesized by co-firing of the corresponding oxides at high temperatures (>1600 °C) for extended periods [19] or from wet chemistry routes that also involve sintering of precipitated powders (even though at lower temperatures). This firing is followed by a second calcination step at 500–700 °C under H_2 flow to reduce NiO to "active" Ni. Nevertheless, the use of natural gas as a chemical feedstock and as a fuel in the current hydrogen production processes induces emissions of large quantities of carbon dioxide.

Alternatively, thermal cracking of methane to gaseous hydrogen and carbon black particles according to reaction scheme (5) below, is another promising pathway, towards a more sustainable production of hydrogen, due to carbon sequestration before fuel usage:

$$CH_4 \rightarrow C(s) + 2H_2, \qquad \Delta H_{298K} = 75\,\text{kJ/mol} \tag{5}$$