PEER REVIEWED

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Metal oxides and the thermochemical storage of solar energy

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ABSTRACT

Metal oxides are used in concentrated solar energy plants (CSP) to store heat, which can be used in the absence of the sun to generate electricity or produce solar fuels. Energy can be stored in this form for long periods, being released when necessary. Two step redox thermochemical cycles using metal oxides are a valuable solar energy storage option to produce H_2 and CO.
This brief review paper summarizes the role of metal oxide on the sustainable production of alternative fuels. It contemplates the formation of oxygen vacancies, combination of metals and the progress made to date on the utilization of metal oxides as promising materials with potential application in water splitting for production of clean hydrogen and solar fuels.

THE THERMOCHEMICAL STORAGE OF SOLAR ENERGY

The sun is an unlimited source of energy. This energy can be converted and stored in the form of chemical fuels, such as hydrogen or syngas (synthesis gas), being an ecological alternative to fossil fuels (1). Solar energy stored in the form of solar fuels can be transportable and stored for long periods. Hydrogen is a promising fuel option as it allows high storage capacity and energy density. Hydrogen can be generated from solar energy by electrochemical, photochemical or thermochemical processes (Figure 1) (2).

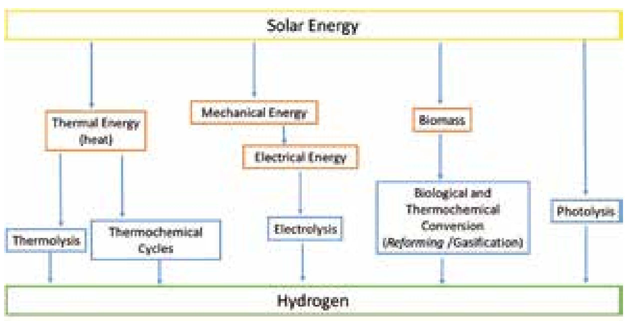

Figure 1. Methods of producing hydrogen from solar energy (adapted from (2)).

Recently, Steinfeld and coworkers reviewed important aspects concerning thermochemical energy storage using concentrated solar radiation (3). Through thermochemical cycles, there is no need to separate oxygen from hydrogen, produced in different stages, at temperatures below the thermolysis process and there is no need to consume electrical energy as through electrolysis, where it is necessary to consume large amounts of electricity.
Metal oxides are used in concentrated solar energy plants (CSP) to store heat and in the absence of sun, to generate electricity or produce solar fuels (3).

THE REDOX CYCLE OF METAL OXIDES

Thermochemical cycles allow storing energy in the form of reduced metal oxides, $MO_{1-□}$ (Figure 2) (2).
In the first step, the metal oxide (MO) is reduced in an endothermic process at a low oxygen partial pressure and high temperature. Concentrated sunlight heat energy is used in this step as source of energy.

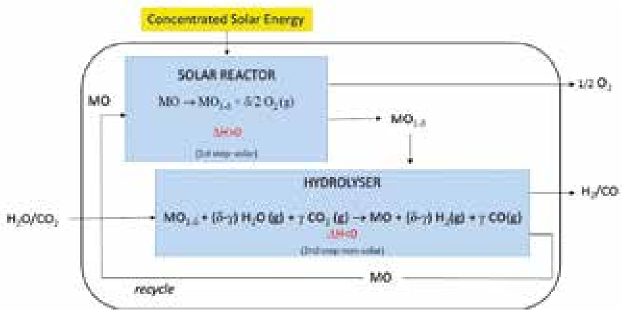

Figure 2. Production of H_2 /CO using thermochemical metal oxide technology (adapted from (2)).

In the second step, a non-solar step, the metal oxide is reoxidized, reacting with CO_2 and H_2O to produce H_2 and CO. The energy is stored in the reduction step and used in the oxidation step, with the reduced metal oxides used as intermediate material. The amount of energy that is stored in the reduction step determines the efficiency of the process. The maximum amount of fuel possible to be produced is directly related to the oxygen storage capacity of the oxides, □, known as non-stoichiometric oxygen (3).
Metal oxides used in this process are continuously recycled. According to the transformations occurred, the two-step redox cycles can be divided into volatile cycles, non-volatile stoichiometric cycles and non-stoichiometric cycles (Table 1) (4). In volatile cycles, the metal oxides suffer a solid-gas phase transition. The capacity for oxygen exchange is higher in these cycles. The volatile products should be destroyed quickly to avoid recombination and the process is not energy efficient. Non-volatile stoichiometric cycles led to partial reduction of the metal. In the non-volatile non-stoichiometric cycles, the oxides remain in stable crystalline structure. Their anion or cation accommodates changes in the number of voids.