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RESEARCHING THERMAL DISSOCIATION OF SPIRIT OXIDE TO OBTAIN HYDROGEN UNDER THE INFLUENCE OF CONCENTRATED SOLAR RADIATION

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ABSTRACT

Nowadays, more than 45% of this rapidly growing global energy demand is met by renewable fuels. Despite their ease of use, fossil fuels are the main source of anthropogenic emissions of greenhouse gases and other pollutants, which ultimately have a serious impact on the environment and public health. In addition, fossil fuel resources are limited and unevenly distributed around the world, creating additional concerns about the reliability and security of energy supply. Solar energy, a clean, freely available and almost inexhaustible source of energy, appears as an attractive candidate in this context. However, the large-scale use of this renewable resource is associated with a diluted, intermittent and uneven distribution of solar radiation around the world. Thus, to overcome these obstacles, research on solar thermochemical processing aims to identify and develop convenient thermochemical conversion methods to efficiently store continuous solar energy in the form of high-energy-density chemical bonds.

KEYWORDS

Renewable fuels, energy supply, thermochemical conversion, thermochemical cycles, solar-fuel energy conversion, moderate temperatures, thermal contraction.

Introduction

From a strategic point of view, the thermochemical production of solar fuels can proceed along two parallel paths. One of them is a short/medium-term approach involving the use of carbon-based raw materials, the energy content of which is renewed from the original raw materials by introducing solar energy. Examples of such processes are steam reforming of natural gas, thermal cracking of methane and steam gasification of carbonaceous waste, biomass, coal and petroleum coke. Another, long-term route is aimed at producing syngas via H_2O/CO_2 -splitting solar thermochemical cycles.

Materials and Methods

Studies of solar thermochemical cycles have shown that the direct thermal decomposition of H2O/CO2, although conceptually simple, requires very high temperatures for the reactions to proceed. temperatures (> 2500 K) have shown to be severely challenged. to a reasonable extent and the need for high-temperature separation techniques to prevent its formation. An explosive mixture of H2/O2 or CO/O2. To overcome these problems, solar thermochemical cycles perform H2O/CO2 splitting via multistep processes, where H2 and/or CO and O2 are produced in separate steps, thereby bypassing the need for high-temperature separation. these elements. In addition, since the high cycle temperature is typically much lower than that required to effect direct thermolysis of H2O/CO2, material limitations are greatly reduced and reradiation is not possible, hardness - increases by the fourth power. Due to the potential of achieving high efficiency of solar-fuel energy conversion, a group of 2-stage H2O/CO 2 splitting thermochemical cycles based on metal oxide oxidation-reduction reactions is of particular interest. where M represents the metal and M_xO_y. the corresponding metal oxide. The first stage of the cycle is the high-temperature endothermic reduction of metal oxide to metal using concentrated solar radiation:

$$M_xO_y \rightarrow xM + y/2O_2 \ (1.1)$$

Solar redox cycles can be classified as volatile if the oxide sublimates during the high-temperature reduction step, and non-volatile if the oxide remains in the condensed phase throughout the process. Generally, volatile oxides (for example, ZnO and SnO_2) exhibit fast dissociation kinetics, but require rapid quenching of the products with an inert gas to prevent their recombination, while non-volatile oxides (for example, Fe3O4 and CeO_2) have a mechanical effect suffers from secrets. instability and slower reaction kinetics. Criteria for identifying potential redox cycles include large reductions at moderate temperatures, favorable oxidation thermodynamics, fast redox kinetics, and material stability, cost, availability, and toxicity. Among the most favorable candidate metal oxide redox couples for 2-step thermochemical cycles, Fe3O4 /FeO and ZnO/Zn are theoretically achievable due to their relative simplicity and high solar-to-fuel efficiency. However, the need for shutdown imposes an energy penalty and economic burden, which may be a limiting factor for the large-scale use of these processes. Schematic representation of a 2-step solar thermochemical cycle for syngas production using metal redox couples (M: metal; MxOy: corresponding metal oxide). The solar reduction step of the cycle based on the Fe3O4/FeO redox couple was experimentally demonstrated at temperatures ranging from 1673 to 1973 K and pressures from 0.1 to 1 bar in an inert atmosphere. Further oxidation of reduced FeO was studied separately using CO2 and H2O, thermogravimetric studies using mixtures of H2O and CO2 allowed to determine competitive gas adsorption kinetics. Reactants on the surface of FeO particles. An important problem of the Fe3O4/FeO cycle is the rapid quenching of the redox couple caused by sintering and coagulation of the material during the reduction stage. Ultimately, this problem with reduction temperatures above the melting points of Fe3O4 (1808 K) and FeO (1643 K) can be overcome by lowering the partial pressure of O2 in the reacting atmosphere and consequently overcoming it is the temperature required to effect thermal contraction.

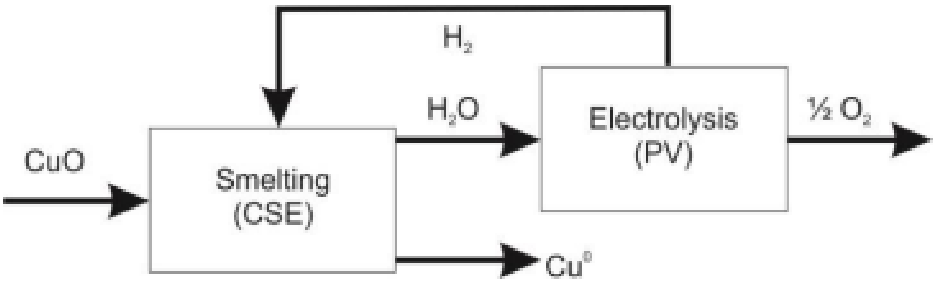

Figure 1. Thermal dissociation of spirit oxide to obtain hydrogen under the influence of concentrated solar radiation

However, in terms of energy conversion efficiency, there were no estimates reported in the last study. Another promising cycle in the class of volatile systems is based on the SnO/SnO2 redox couple, which has similar properties to the analogous Zn/ZnO cycle. Neglecting the energy penalty associated with the high heating value of H2 produced and the consumption of inert gas, the exergy and energy efficiency of the cycle were estimated to be 30% and 36%, respectively. However, it was observed that the decomposition of H2O by SnO proceeds at a slower rate than the hydrolysis of Zn. Among the many other redox materials previously discussed and explored for use in 2-step solar thermochemical cycles, the Zn/ZnO redox couple has been identified as a promising route due to its potential to achieve high solar energy - the efficiency of converting energy into fuel. This oxidation-reduction cycle is expressed as follows:

Step 1: $ZnO \rightarrow Zn + 0{,}5O_2$ ΔH 298K = 350,5 kJ·mol^{-1}

Step 2:

$$Zn + H_2O \rightarrow ZnO + H_2 \; \Delta H \; 298K = -62{,}0 \; kJ \cdot mol^{-1}$$

$$Zn + CO_2 \rightarrow ZnO + CO \; \Delta H \; 298K = -67{,}5 \; kJ \cdot mol^{-1}$$

where ZnO is thermally dissociated in the first endothermic reduction step to Zn and O2 at around 2000 K using concentrated solar energy. After separation from O2, the produced Zn/H2O and CO2 undergo an exothermic reaction in a low-temperature oxidation reactor to form syngas and primary metal oxides, which are recycled to the solar reactor. Since the two stages are separated, syngas production can be carried out in convenient geographical locations, regardless of solar energy. The relevant thermodynamic quantities of the ZnO dissociation reaction depend on the reaction temperature. The quantities, namely standard reaction enthalpy ΔH r o, standard Gibbs free energy change ΔG r o, and equilibrium constant Kp, were calculated at 1 bar using the HSC Outokumpu code. Above 234 0 K, ΔG r o < 0 and the reaction proceeds spontaneously to the right, giving ΔH r 0. Energy requirements (ΔHr o, ΔGr o) and equilibrium constant (Kp) for the ZnO dissociation reaction. The minimum flow rate of A_r necessary to control the dissociation is determined based on the thermodynamics of chemical equilibrium until the reaction can be completed at temperatures below 2340 K. The kinetics of ZnO dissociation were studied using an equation solar-driven thermogravimeter, where a packed bed of ZnO particles was exposed to direct high-flux solar radiation at peak concentration ratios of up to 2400 solar did. In this study, isothermal runs performed between 1800 - 2100 K were fitted by linear regression to a zero-order Arrhenius rate law of the form r"=k'0 with 95% confidence. exp (Ea / RT), Ea =361±53 kJ mol^{-1} gives the apparent activation energy and the pre-exponential factor k'0= 14.03·106 ± 2.73·106 kg·m-2·s^{-1} . Similar values of Ea obtained in other experimental devices by non-solar thermogravimetric and non-solar gravimetric analyzes confirm the basic physics of Lvov's mechanical model, in which Ea. specified as a configuration-independent parameter. Alternatively, an inverse method using dynamic O_2 concentration measurements at the reactor outlet in conjunction with transient heat/mass transfer models is used to determine Ea. with an uncertainty of 10%. On the other hand, the pre-exponential factor k'0 showed a strong dependence on the mass transport properties of the specific configuration. For example, it has been shown that doubling the flow rate of the inert carrier gas (Ar) used to clean the evolving gaseous products causes k'0 to be twice the original measured value. Also, measurements in an aerosol flow reactor resulted in k'0 three orders of magnitude larger than values measured in stationary reactors. Studies on the kinetics of the extrasolar second step have mainly focused on the oxidation of Zn by H2O equation and CO2 equation. individual reactions. Simultaneous splitting of H2O and CO2 for syngas production was experimentally demonstrated using a packed layer of Zn/ZnO particles, where the particle mixture was shown to be an effective inert aid to prevent sintering and subsequent passivation of Zn. An experiment using samples produced in a solar reactor (25 wt % Zn) gave up to 96% conversion of molar Zn to ZnO. Early experiments on solar thermal dissociation of ZnO were conducted using small-scale and directly irradiated solar reactors. These studies served to investigate the formation of Zn decomposition and subsequent condensation of Zn(g), as well as to determine the various chemical and physical factors controlling the overall efficiency of the process. Subsequently, various solar reactor concepts, including attracted currents, packed beds, and rotating cavity receivers, have been experimentally investigated to realize ZnO dissociation. Thermal dissociation of ZnO particles in an aerosol stream was demonstrated in the range 1873–2023 K using an electrically heated transport tube apparatus. A packed bed reactor was the concept. It is investigated in a chamber filled with pressed ZnO forming a partial slope in a directly irradiated chamber. Regarding the rotating cavity-receiver concept, the 10-kW solar reactor configuration presented in is discussed in detail in the next chapter. Numerical modeling has become an important tool to understand the basic heat and mass transport mechanisms occurring in such high-temperature solar reactors and to identify the main sources of heat loss. This, in turn, provided the understanding needed to optimize and scale up solar reactor technology. The effect of dynamic thermal conductivity and sintering from the experimentally determined irradiance properties for a shrinking wrapped layer of ZnO particles with a solar concentration ratio in the range of 1225–2133 K and a surface temperature in the range of 1834–2109 K checked using spectroscopic goniometry system. A Monte Carlo method was used to solve the unsteady radiative heat transfer in a chemically reacting medium for a suspension of thermally dissociated ZnO particles. As an alternative to quenching, electrolytic methods of in situ separation of Zn(g) and O 2 at high temperatures have been experimentally demonstrated in small-scale reactors. Study of the condensation of Zn in the presence of O 2 by fractional crystallization in a tube furnace with a temperature gradient. The oxidation of Zn is a heterogeneous process in which Zn (g) can be in a metastable state in the absence of O 2. nucleation sites.

Conclusion

Using an optimized quencher attached to a solar-powered thermogravimeter, it was experimentally shown that Zn yields greater than 90% can be achieved at partial pressures of ~100 Pa Zn >100,000 K·s -1 and cooling rates. Although experimental observations qualitatively agree with numerical model calculations, a quantitative comparison is not yet possible because the rate constants of the elementary reactions describing the nucleation, growth, and deoxidation of Zn are still unknown. A quencher was installed at the outlet of the 10-kW solar reactor to rapidly reduce the effluent temperature by injecting Ar into a water-cooled annular outlet, resulting in an average solids deoxidation rate of 39%.

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