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CARDOTHERMIC DISSOCIATION OF ZINC OXIDE TO PRODUCE HYDROGEN UNDER CONCENTRATED SOLAR RADIATION

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ABSTRACT

Solar 2-step Zn/ZnO redox reactions to decompose H_2O and CO_2 have the potential to achieve high solar energy-to-fuel efficiency and ultimately economic competitiveness. It consists of: (1) endothermic dissociation of ZnO into Zn and O_2 by concentrated solar energy and (2) subsequent exothermic reaction of Zn with H_2O/CO_2 to H_2/CO (called mixed syngas) and initial ZnO; the second is processed into the first stage. In this paper, several aspects of solar reactor technology to realize the first stage of the redox cycle are investigated experimentally and numerically.

A two-dimensional dynamic numerical model of a 10 kW solar reactor prototype for the thermal dissociation of ZnO is constructed based on a detailed analysis of radiation heat transfer associated with conduction, convection, and chemical reaction effects.

Quartz glass is considered as a semi-transparent glass layer with spectral and direction-dependent optical properties. Model validation is performed by comparing the cavity temperature, reaction rate, and quartz glass temperature distribution measured by IR thermography with experimental results obtained with a 10 kW solar reactor prototype. Experimentally obtained solar energy conversion efficiencies are reported and various energy flows are quantified.

An engineering design and experimental demonstration of a 10 kW extended solar thermochemical pilot plant for thermal dissociation of ZnO is presented. The solar reactor consists of a rotating cavity-receiver made of a rigid self-supporting structure of Al2O3 pieces. The innermost coating of the cavity consists of a layer of ZnO particles that are directly exposed to the concentrated solar radiation entering through the window opening. Experiments were conducted in a solar oven by introducing a special solar reactor to concentrated radiation streams and a solar radiation power of 140 kW/h. The solar reactor was operated at temperatures up to 1936 K, which gave the Zn molar fraction of the condensed products in the range of 12-49%, which largely depended on the Ar flow rate to quench the gaseous products formed.

The performance of a 10 kW solar reactor is also numerically investigated using the developed reactor model. Ray tracing adapted to incorporate the geometry of the solar reactor is used to calibrate a 10 kW reactor to the high flux solar radiation delivered by the solar oven. After the optical characterization of the heliostats, the ray tracing code was able to predict the solar radiative power of the reactor with 98% accuracy. Experimental validation of the reactor model is performed in a solar reactor by comparing the predicted temperature and degree of ZnO dissociation with measured data from a 10 kW solar reactor. Experimentally obtained solar energy conversion efficiencies are reported and various energy flows are quantified.

1. Introduction. The world's primary energy demand is estimated at $508 \cdot 10^{18}$ analyzed to increase by 51% by 2035 under current policy scenarios, which is primarily due to the rapid growth of the world's population and the continued economic development of emerging markets. Today, 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.

It is known to be totally dependent on fossil fuels. In 2009, more than 46% of transportation energy demand was met by renewable energy carriers. With around 19% of global energy use and 23% of energy-related CO_2 emissions, the transport sector is the biggest polluter and one of the few industries where emissions are still growing. Based on current trends, energy demand for motorized mobility is projected to increase by nearly 40 percent by 2030 and by more than 75 percent by 2050. Meeting this rapidly growing demand, while stabilizing atmospheric GHG concentrations at current targets, poses a serious challenge for sustainable development and requires the large-scale introduction of carbon-neutral transport fuels (including electricity) in the near future. . While electricity is expected to play an important role in transforming the global energy economy, the huge need for liquid fuels for the transportation sector cannot be avoided. In particular, the aviation and heavy machinery subsectors, where electricity is not a suitable energy source, may continue to be heavily dependent on liquid fuels. Thus, the environmental impact of fossil fuel consumption combined with the sustainable global dependence on liquid fuels requires a transition to sustainable fuel production technologies derived from renewable energy sources. 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 has focused on identifying and developing convenient thermochemical conversion methods to efficiently store continuous solar energy in the form of high-energy-density chemical bonds. efficient renewable fuel production.

Main part:

1. Production of solar thermochemical fuel

Solar thermochemical processes use concentrated solar radiation as an energy source of high-temperature process heat to drive highly endothermic reactions. By exploiting the entire solar spectrum while operating at high temperatures, solar thermochemical processes offer a sustainable and efficient way to produce storable and transportable chemical fuels. The target solar fuel proposed here is syngas: a mixture of H_2 and CO. Unlike solar hydrogen (another potential renewable energy carrier for the future energy economy), the ease of production of syngas is that the latter can be converted to gasoline, diesel, kerosene, methanol, and other alternative liquid fuels through conventional Fischer-Tropsch or other catalytic reforming processes. organic commodity that can be processed to synthetic hydrocarbon fuels such as I . transport sector infrastructure without existing global changes. From a strategic point of view, the thermochemical production of solar fuels can proceed along two parallel paths. one is the short/medium term route involving the use of carbon feedstocks, whose energy content is upgraded from the original feedstock by incorporating solar energy.Examples of such processes include steam reforming of natural gas, thermal cracking of methane, and steam gasification of carbonaceous waste, biomass, coal and petroleum coke Another, long-term route focuses on the production of syngas via H_2O/CO_2-splitting solar thermochemical cycles.

2. Termochemical cycles

Studies of solar thermochemical cycles have shown that the direct thermal decomposition of H_2O/CO_2, although conceptually simple, requires very high temperatures for the reactions to proceed. temperatures (> 2500 K) have shown to be severely challenged. Explosive mixture of H_2/O_2 or CO/O_2. To overcome these problems, solar thermochemical cycles perform H_2O/CO_2 splitting via multistep processes, where H_2 and/or CO and O_2 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 H_2O/CO_2, material limitations are greatly reduced and reradiation is not possible. hardness - increases by the fourth power.

A group of 2-stage H_2O/CO_2 splitting thermochemical cycles based on metal oxide redox reactions is of particular interest due to the potential to achieve high solar-fuel energy conversion efficiency. A schematic view of the 2-step solar redox cycle is shown in the figure, 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)

The second, low-temperature step is the non-solar exothermic oxidation of the metal with H_2O and CO_2, forming syngas (a mixture of H_2 and CO) and the corresponding metal oxide: If CO_2 is taken directly from atmospheric air, the solar thermochemical cycle becomes a closed material carbon source of liquid hydrocarbon fuels.

Different metal oxide redox couples suitable for $2O/CO_2$ fission thermochemical cycles were studied. 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. Usually, 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, Fe_3O_4 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, Fe_3O_4 /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 Fe_3O_4/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 the reduced FeO was studied using CO_2 and H_2O separately, and thermogravimetric studies using mixtures of H_2O and CO_2 revealed competitive gas adsorption kinetics. Reactants on the surface of FeO particles. An important problem of the Fe_3O_4/FeO cycle is the rapid quenching of the redox couple resulting from the sintering and coagulation of the material during the reduction step. Ultimately, this problem with reduction temperatures above the melting points of Fe_3O_4 (1808 K) and FeO (1643 K) can be overcome by lowering the partial pressure of O_2 in the reacting atmosphere and consequently overcoming it. the temperature required to effect thermal contraction. However, this benefit comes at the expense of a large energy penalty due to the increased amount of inert gas consumed to achieve the low O_2 partial pressure. Alternatively, partial replacement of Fe in Fe_3O_4 with other metals such as cobalt (Co), nickel (Ni), manganese (Mn) and zinc (Zn) can produce mixed type $(M_xF_{y-x})_3O_4$ ferrites. Fe_3O_4 can be reduced at lower temperatures. The use of zirconium supports was not only shown to be very important to facilitate the high temperature sintering of mixed ferrites, but it was observed that molten iron plays an important role in the reaction mechanism. Perhaps one of the main disadvantages of mixed ferrites is the low percentage of O_2 release and consequently the limited H_2O/CO_2 production rate per unit mass of reactants. Recently, the non-stoichiometric cycle based on the redox couple of CeO_2/CeO_2 -cerium oxides has attracted much scientific attention due to its high selectivity and fast redox kinetics compared to other non-volatile metal oxides. However, similar to ferrite-based oxides, the series cycle suffers from low specific O_2 release and consequently limited fuel yield due to only partial reduction of the oxide. Theoretically, solar-to-fuel energy conversion efficiencies of 20% have been shown to be achievable, while heat recovery to the system can increase this efficiency to values close to 30%. An experimental demonstration of simultaneous CO_2/H_2O splitting was first performed using a series of porous felts, then replacing the felt with a meshed porous ceramic structure resulted in significantly higher reactor performance, resulting in a solar-to-fuel = 3.53%. As an alternative to series-based cycles, the use of nonstoichiometric perovskite-type materials in the form has also been recently explored. Thermodynamic predictions and experimental observations have shown that, although larger oxidation yields are expected for the base materials, in the absence of heat recovery, the series is expected to achieve greater solar fuel efficiency primarily for the base materials. materials do not oxidize stoichiometrically and have almost twice the heat capacity compared to ceria. The improvement in redox

thermodynamics was demonstrated in a subsequent experimental study, where the use of alternative perovskite compositions in the shape was reported to produce significantly more fuel than cerium when reduced at 1350 °C and reoxidized at 1000 °C. 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 the H2 produced and the inert gas consumption, the exergy and energy efficiency of the cycle were estimated to be 30% and 36%, respectively. The ability of SnO powders to be effective However, it was observed that the decomposition of H2O by SnO proceeds at a slower rate compared to the hydrolysis of Zn.

3. Zn/ ZnO cycle

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. - efficiency of converting energy into fuel. This oxidation-reduction cycle is expressed as follows:

Step 1:

$ZnO + C \rightarrow Zn + CO\ \Delta H\ 298K = 350{,}5\ kJ \cdot mol^{-1}$

Step 2:

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

where ZnO is thermally dissociated in the first endothermic reduction step to Zn and CO at around 2000 K using concentrated solar energy. After separation from CO, the produced Zn/H2O undergoes an exothermic reaction in a low-temperature oxidation reactor to form H2 and the initial metal oxide, which is 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.

4. Thermodynamics of ZnO dissociation

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, $\Delta G_r^{o} < 0$ and the reaction proceeds spontaneously to the right, giving an amount of ΔH_r^{o}. in the form of, for example, solar process heat. Based on Le Chatelier's principle, the temperature required by the thermodynamics of the process can be reduced by lowering the partial pressure of the gaseous products, for example, by lowering the total pressure of the system. Alternatively, an inert carrier gas (e.g., Ar) can be used to dilute the gaseous products and consequently change the thermodynamic equilibrium. Although the use of an inert gas introduces an energy penalty associated with spent gas recycling, it allows the system to be operated at atmospheric pressure, thus avoiding the high engineering costs typically associated with vacuum processes.

Energy requirements (ΔH_r^{o} , ΔG_r^{o}) and equilibrium constant (Kp) for the ZnO dissociation reaction. The minimum flow rate of Ar necessary to control the dissociation is determined based on the thermodynamics of chemical equilibrium until the reaction can be completed at temperatures below 234^{0} K. For this purpose, let's look at common reversible chemicals, the reaction is described as follows: In which represents the stoichiometric

coefficients of the gases involved in the reaction. Using these coefficients, it can be shown that the chemical equilibrium constant Kp is given by: where p is the partial pressure of the corresponding gases and p0 is the reference pressure. By applying Eq. to the ZnO dissociation reaction, the required molar flow rate of Ar, assuming that the condensed ZnO phase does not play a role in the equilibrium composition. It can be calculated as follows: Normalized with respect to the molar flow rate of ZnO dissociation. If the reactor is operated at 2000 K. It produces Ar. Alternatively, a reduced amount of inert gas can be used in such a way that higher reduction rates can be achieved without driving the dissociation to completion, altering the thermodynamic equilibrium. In this regard, the calculated molar fractions of Zn(g) in the equilibrium composition depending on the reaction temperature and ratios are shown.

The effect of Ar on the resulting balance is noticeable. 1 and 2000 K bring the Zn(g) molar fraction to about 0.1 and increase when the reactor is operated at Ar. The Ar consumption coefficient allows driving 10 times until the dissociation reaction ends at the same temperature. Likewise, the same Zn(g) mole fraction that can be achieved by Ar operates at 1 and 2100 K could theoretically be reached 200 K lower with increasing Ar. Finally, Ar offers 100 while the theoretical potential to reach thermodynamic equilibrium drives the following reactor. Effect of inert carrier gas on Ar Zn mole fraction reached at thermodynamic equilibrium.

5. Analysis of the second law

shows a model flow diagram used to determine the theoretical maximum cycle efficiency by second law (exergy) analysis. The process is assumed to be carried out under 1 bar and steady state conditions. The reactor is modeled as a perfectly insulated black-body cavity-receiver, and its solar energy absorption efficiency is defined as Molar flow rate, Stefan-Boltzmann constant, I - normal radiation insolation, C - average solar concentration ratio, Tr is the temperature of the solar reactor and Tamb is the ambient temperature. As defined, absorption represents the ability of the reactor to absorb incoming solar radiation, but does not include losses due to radiation spillage, as they are separately taken into account in the optical efficiency of the solar concentration system. Solar energy conversion efficiency is defined as the fraction of solar energy converted to chemical energy:

Model flow diagram of a 2-step solar thermochemical cycle for syngas production via H_2O/CO_2 splitting via Zn/ZnO redox reactions.

6. Kinetic analyses

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. (Ea/RT), gives the apparent activation energy *Ea* =361±53 kJ $mol^{-1}$and the pre-exponential factor k'_0=14,03·10^6 ± 2,73·10^6 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 higher than values measured in stationary reactors. Studies on the kinetics of the extrasolar second step have mainly focused on the oxidation of Zn by the H_2O equation and the CO_2 equation. individual reactions. The simultaneous splitting of H_2O and CO_2 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.

7. Technology of solar reactors

Early experiments on solar thermal dissociation of ZnO were conducted using small-scale and direct-irradiated solar reactors. These studies served to investigate the formation of Zn decomposition and subsequent condensation of Zn(g), as well as to identify various chemical and physical factors that control the overall efficiency of the process. Subsequently, various solar reactor concepts, including drawn-flow, packed-bed, and rotating cavity receivers, were 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 effects of dynamic thermal conductivity and sintering were investigated using experimentally determined irradiance properties for a shrinking wrapped layer of ZnO particles exposed to solar concentration ratios in the range of 1225–2133 K and surface temperatures in the range of 1834–2109 K. 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. Recently, a two-dimensional reactor model was developed in which the simultaneous effects of radiation, convection, and heat conduction were coupled to the reaction kinetics of ZnO dissociation occurring in the shrinking domain. Separation of the gaseous products, Zn(g) and O_2, was first considered using an inert gas to dilute and rapidly quench the gases evolved below the Zn saturation and freezing points. As an alternative to quenching, electrolytic methods for in situ separation of Zn(g) and O_2 at high temperatures have been experimentally demonstrated in small-scale reactors. Although refrigeration is the main source of irreversibility, it is still the preferred method due to its simplicity. Study of the condensation of Zn in the presence of O_2 by fractional crystallization in a temperature gradient tube furnace 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. 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 reoxidation rate of 39%. 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 the experimental observations qualitatively agree with numerical model calculations, a quantitative comparison is not yet possible because the rate constants of the elementary reactions that describe the nucleation, growth, and reoxidation of Zn are still unknown.

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