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Design and operation of a solar-driven thermogravimeter for high temperature kinetic analysis of solid–gas thermochemical reactions in controlled atmosphere

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Abstract

A novel solar-driven thermogravimeter has been developed for on-sun kinetic analysis of solid–gas thermochemical reactions at high temperature in controlled atmosphere. The proposed concept includes a cavity-type solar receiver and a separate tubular reaction chamber that aims at ensuring a reliable reaction temperature measurement during thermochemical processing while enabling on-line gas analysis. Other features include high temperature and heating rate capabilities (1600 °C, up to 150 K min^{-1}), controlled atmosphere including reduced pressure or vacuum conditions or different flowing gas atmospheres, and precise measurement of mass variations (resolution of 10^{-5} g over the whole range, capacity 220 g). Since the available incident solar power absorbed by the reactor was determined by the size of the parabolic dish concentrator (about 1 kW), a thermal analysis was performed to design properly the cavity size for reaching the desired temperature level. Limestone calcination and ZnO thermal reduction were successfully performed to validate the set-up reliability. The temperature- and pressure-dependent drift was determined and corrected using the mass variation observed during the heating period of the reactant. The device was finally operated to investigate the kinetics of ZnO and SnO_2 solar thermal dissociation.

Keywords: Thermogravimeter; Solar reactor; Thermochemical cycles; Kinetics; Metal oxides; Thermal dissociation

1. Introduction

Recent solar concentration technologies provide carbon-free heat at high temperature levels. Derived solar thermochemistry is a growing research field, and the technico-economic feasibility of various chemical processes is being re-assessed (Steinfeld and Palumbo, 2001; Lemus and Martínez Duart, 2010; Weimer, 2012; Acar and Dincer, 2014). Among those, efficient solar fuels production through thermochemical redox cycles is a prime example. Thermochemical cycles were first developed for the coupling with a nuclear heat source available below 1000 °C. At this temperature, a minimum of three chemical steps is necessary for splitting water into its elements (Funk and Reinstrom, 1966; Abraham and Schreiner, 1973, 1974) with inherent limitations. With solar concentrating technologies, the process temperature may be increased, allowing new chemical routes and materials. Metal oxide redox cycles are presently among the most advanced paths for solar thermochemical fuel production (Xiao et al., 2012, and references therein). Such a cycle is composed of two steps (Fig. 1): (1) a highly endothermic reduction during which the metal oxide is reduced into a lower valence oxide or dissociated to the pure metal at high temperature using concentrated solar power to drive the reaction; (2) an

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Nomenclature

α	chemical conversion
β	extinction coefficient
κ	absorption coefficient
λ	thermal conductivity, $W\ m^{-1}\ K^{-1}$
ρ	density, $kg\ m^{-3}$
σ_s	scattering coefficient
$\overline{\overline{\sigma}}$	viscous stress tensor, $kg\ m^{-1}\ s^{-2}$
ϕ	scattering phase function
Ω	solid angle
DNI	direct normal irradiation, $W\ m^{-2}$
E_a	activation energy, $kJ\ mol^{-1}$
h	enthalpy, $kJ\ mol^{-1}$
I	directional intensity of radiation $W\ m^{-2}\ st^{-1}$
I_b	black body intensity
k_0	pre-exponential factor, s^{-1}
$\dot{m}_i$	mass flow inlet of the gas i, $kg\ s^{-1}$
P	pressure, Pa
$\mathbf{r}$	position vector
R	gas constant, $J\ mol^{-1}\ K^{-1}$
$\mathbf{s}$	unit direction vector
T	temperature, K
$\mathbf{u}$	gas velocity vector, $m\ s^{-1}$
v_i	inlet velocity of the gas i, $m\ s^{-1}$

exothermic re-oxidation of the reduced species in presence of H_2O and/or CO_2 to produce H_2 and/or CO and to regenerate the metal oxide.

The reduction step concentrates most of the technological challenges, regarding both the solar reactor and the reactive material. On the one hand, commercial high-temperature constructing refractory materials can be used for solar applications such as chemical reactors by selecting the most thermally and chemically stable reactor wall materials for the solar receiver and the reaction chamber, and the challenge resides mainly in the appropriate reactor design and the scale-up. On the other hand, specific reactants are widely under investigation on the viewpoints of thermodynamics and kinetics, long-term structural and thermal stability, reactivity and cyclability of materials, and several oxides have been proposed including SnO_2, ZnO, Fe_3O_4, CeO_2, and mixed oxides for the most studied (Abanades et al., 2006; D'Souza, 2013 and references therein). The corresponding redox pairs are either stoichiometric (i.e. the reduction produces a lower valence species, as for ZnO/Zn) or non-stoichiometric (the reduction produces oxygen defects in the oxide lattice, e.g. $CeO_2/CeO_{2-\delta}$), and products can be either volatile (if the reduced specie is obtained in gas phase, as for $ZnO/Zn_{(g)}$ or $SnO_2/SnO_{(g)}$) or not. Of major concern for any thermochemical process is the kinetic rate of the solar step, which depends on the temperature, pressure (total and oxygen partial pressure) and composition (effect of doping, impurities, etc.).

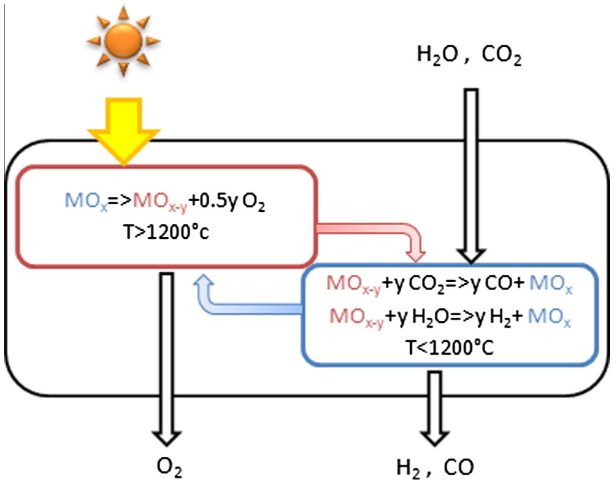

Fig. 1. The two-step thermochemical cycle using metal oxide for H_2/CO production from solar power and H_2O/CO_2.

Most of studies have mainly used commercial conventional systems such as thermogravimetric analysis (TGA) to derive the kinetics of the reduction reactions. Despite of the practical use of TGA with controlled atmosphere (vacuum or neutral atmosphere conditions), no system shows appropriateness to approach solar reactor conditions encompassing severe high-temperature heating, high heating rate, controlled atmosphere, and solar irradiation.

A solar thermogravimetry device was used for studying ZnO thermal reduction to $Zn_{(g)}$ (Schunk and Steinfeld, 2009). The system consists of a horizontally irradiated insulated cavity receiver with a pellet of dense ZnO in its center that is held in a cylindrical 20 mm-i.d., 40 mm-length Al_2O_3 sample holder. This holder is mounted on an alumina rod connected to a balance for continuous monitoring of the sample weight. The temperature is estimated by pyrometry. Main issues concern the accuracy of both the weight (measured mass losses from 30 ± 10 mg to 300 ± 10 mg) and the temperature measurements (a large thermal gradient exists in the sample in addition to the uncertainty due to pyrometer accuracy). More recently, this set-up was improved by adding a pyrometer to measure the temperature at the rear of the sample (after effective emissivity measurement) and gas analyzers (Alonso et al., 2013; Bellan et al., 2013; Gonzalez-Aguilar et al., 2012). The revised device was used to study Mn_2O_3 and Mn_3O_4 reduction, but problematic temperature gradient and issues with temperature determination were still pointed out.