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Investigation of thermal and carbothermal reduction of volatile oxides (ZnO, SnO_2, GeO_2, and MgO) via solar-driven vacuum thermogravimetry for thermochemical production of solar fuels

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ABSTRACT

This study addresses the solar thermogravimetry analysis of high-temperature reduction reactions involving volatile metal oxides for application in solar thermochemical fuel production via two-step H_2O and CO_2 splitting. The redox cycles encompass the thermal or carbo-thermal reduction of a metal oxide using concentrated solar energy followed by its oxidation with CO_2 and/or H_2O to produce solar-derived fuels (CO and/or H_2). A new solar-driven vacuum thermogravimeter has been developed for the investigation of the high-temperature thermochemical reactions. The system is designed for reduced pressure operation down to a few mbar with flowing purge gas for studying low-pressure conditions, while the weight change of the solid reactants is continuously monitored during high-temperature solar heating under non-linear heating profile. The method was applied to investigate the kinetic rates of the thermochemical solid/gas reactions involving ZnO, SnO_2, GeO_2, and MgO volatile oxides in a controlled atmosphere. The reaction rates were determined as a function of the temperature for different pressures in the system. Metal oxides reduction under low pressure was shown to be of special interest because the reaction rate is greatly enhanced and the required temperature to achieve a given reduction rate is significantly lowered. In contrast to inert gas dilution, a total pressure decrease also reduces the need for a diluent gas, thus simplifying the process and avoiding energy penalties associated with inert gas recycling.

1. Introduction

The production of fuels from the ultimate products of combustion, namely H_2O, CO_2, and heat (ideally provided by solar energy, mimicking the natural photosynthesis process [1]), is of major concern. This innovative approach to solve both fossil fuel scarcity and rising CO_2 emissions may be a great step forward in the mastery of the combustion process, by enabling its reversal. Combustion being an oxidation reaction, its inversion proceeds via the reduction of the products, yielding CO and H_2.

$$CO_2 = CO + 0.5O_2 \;\; \Delta G^{\circ} < 0 \;\; \text{for } T > 3065\,^{\circ}C \tag{1}$$

$$H_2O = H_2 + 0.5O_2 \;\; \Delta G^{\circ} < 0 \text{ for } T > 4080\,^{\circ}C \tag{2}$$

These species, whose mixture is syngas, have a high energy potential that can be released through combustion, or further densified through processing to liquid hydrocarbon fuels (and high value chemical by-products [2]) by using industrial-scale Fischer–Tropsch process. The highly endothermic nature of these thermolysis reactions and the associated high temperatures make their large-scale implementation unlikely. Several approaches have been proposed and studied to circumvent this limit [3,4]. The two-step redox thermochemical cycles present the advantage of directly using high-temperature solar heat, offering a more direct conversion path (as compared to electrolysis, which requires the intermediate production of electricity). This approach uses a metal oxide redox pair as an oxygen carrier, and splits the overall chemical reaction into two steps [5]. In a first solar-driven step, the metal oxide is reduced at high temperature in an endothermic reaction. In the second exothermal step, the oxygen-deficient specie reduces H_2O or CO_2 to generate H_2 or CO, regenerating the metal oxide for the next cycle:

$$MO_x = MO_{x-1} + \frac{1}{2}O_2 \qquad T > 1200\,^{\circ}C, \Delta H \gg 0 \tag{3}$$

$$MO_{x-1} + CO_2 = MO_x + CO \;\; T < 1000\,^{\circ}C, \; \Delta H < 0 \tag{4}$$

Alternatively, a carbonaceous reducer (e.g., solid carbon) can be used to decrease the temperature of the solar step [6]. A large

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variety of redox cycles have been evaluated during the past years [7]. The non-volatile oxides, chiefly represented by ferrite- [8,9] and ceria-based oxides [10–12], present the advantage of remaining in solid phase throughout the cycle, but offer a limited thermal stability (sintering) and a low fuel productivity (the reduction reaction is generally partial and proceeds via the formation of oxygen vacancies in crystal lattice). Volatile oxide cycles, mainly represented by ZnO/Zn [13] and SnO_2/SnO couples [14], proceed through the vaporization of the reduced species during the first step (the boiling temperature of products is lower than the reduction temperature), which are then condensed downstream into nano-sized particles. Despite a relatively higher reduction temperature, this ensures that the specific surface area is regenerated at each cycle, and the fuel productivity is potentially higher due to stoichiometric reactions. On the other hand, the separation of the inert carrier gas for recycling and of the products (i.e. oxygen and reduced specie) can be problematic, requiring a quenching that impedes heat recovery.

The first high-temperature step of the cycles presents most of challenges. The theoretical temperature is elevated and thus, any mean for its reduction and for heat integration over the whole cycle is crucial. Reducing the partial pressures of the products is generally considered to favor the reactions at lower temperatures, either through dilution with an inert gas or reduced pressure operation. Both solutions imply an energy cost, either required for the heating and separation of the inert gas or for the pumping work.

The quenching required for volatile oxide cycles makes the dilution a heat sink. Studies have been devoted to the analysis of these parasitic energy losses for non-volatile oxides ([12,15,16]), by taking into account only the cost of the separation of the inert gas from the oxygen released, and tend to show that this cost is almost negligible (estimated to be 20 $\mathrm{kJ\,mol^{-1}}$ [12]). Therefore, the other option consisting of the reduction of the total pressure may appear pointless (reduced pressure implies higher capital and operating costs for the reactor).

Concerning the volatile oxide cycles, although some of the first studies have considered solar reactor operation under reduced pressure [17], the other developed prototypes have involved massive inert gas dilution [18]. For the 100 kW prototype, a partial pressure of products of 5 Pa is required to obtain about 50% of ZnO reduction yield, equivalent to a dilution ratio of about 10^4. Even though most of the inert gas is introduced through the quenching system located downstream of the solar reactor itself, a minimum flow is required inside to screen the window but also to favor the reaction and to direct the gaseous products toward the outlet. Since the heating of one mole of nitrogen from 25 °C to 1800 °C requires about 60 kJ (33 kJ if argon is used instead [19]), even a dilution as low as 7 for ZnO and 9 for SnO_2 (respectively 13 and 21 with argon) more than doubles the heat required in the solar reactor for the heating (of inert gas and reactant) and the reaction enthalpy, which is lost during the quenching. On the basis of these considerations, reduced pressure operation may represent an alternative option to avoid energy penalties associated with inert gas recycling.

Concerning thermal reductions, reaction kinetics have been scarcely studied. ZnO solid–gas decomposition to Zn and O_2 is generally considered as a zero order reaction, with an activation energy of about $313 \pm 31\ \mathrm{kJ\,mol^{-1}}$ [20,21]. For SnO_2 reduction, a higher activation energy of about $353 \pm 18\ \mathrm{kJ\,mol^{-1}}$ [22,21] is reported and reducing the pressure in the reactor allows decreasing the temperature required for a given reaction rate [22]. Concerning GeO_2 reduction, there is no available published kinetic data.

Concerning carbothermal reductions, the case of ZnO is the most documented [23] and the observed reaction mechanism is a 3D volume contraction-type, yielding an activation energy of 201.5 $\mathrm{kJ\,mol^{-1}}$ [24]. For MgO, various studies have been conducted with a large variety of carbon sources (graphite, charcoal, coke), each resulting in different values of activation energy (from 201 to 468 $\mathrm{kJ\,mol^{-1}}$), underlining the high dependence on the carbon type [25–27]. More generally, reduction in presence of carbon is considered to follow a two-step reaction path:

$$MO_x + CO = MO_{x-1} + CO_2 \tag{5}$$

$$CO_2 + C = 2CO \tag{6}$$

Few studies have focused on the particular impact of pressure and dilution on the reaction kinetics.

Thus, this study focuses on the thermal and carbothermal reduction of various volatile oxides under reduced pressure and/or dilution with an inert gas in a solar thermogravimeter. The kinetic investigation of the reduction reactions is conducted for the potentially applicable redox compounds including ZnO, SnO_2, GeO_2, and MgO. To our knowledge, this is the first time that the reduction rates of these volatile oxides are experimentally reported in a wide range of pressures and temperatures.

2. Thermodynamic background

The thermal and/or carbothermal reduction of ZnO, SnO_2, GeO_2, and MgO is considered. A summary of the main thermodynamic data and corresponding sources is proposed in Table 1 for the thermal reductions and in Table 2 for the carbothermal reductions. The written reactions are the thermodynamically most favorable.

The equilibrium constant $K(T)$, applied to reaction Eq. (3), can be expressed as a function of the oxygen partial pressure. Considering the reactant conversion α at thermodynamic equilibrium and the inert gas dilution d, the following relations arise:

$$p_{O_2} = \frac{p_{MO_{x-1}}}{2} = \frac{n_{O_2}}{n_{O_2} + n_{MO_{x-1}} + n_{\mathrm{inert}}} P_t = \frac{0.5\alpha}{1.5\alpha + d} P_t \tag{7}$$

$$\text{with, } \alpha = 1 - \frac{n_{MO_x,\ \mathrm{final}}}{n_{MO_x,\ \mathrm{initial}}} \tag{8}$$

$$\text{and, } d = \frac{n_{\mathrm{inert\ gas}}}{n_{MO_x,\ \mathrm{initial}}} \tag{9}$$

Table 1
Thermodynamic data and corresponding references for purely thermal reduction ($C = 5000$, $I = 1\ \mathrm{kW\,m^{-2}}$). The temperature corresponds to the theoretical inversion temperature and $\eta_{\mathrm{Solar\text{-}to\text{-}fuel}}$ to the solar to fuel efficiency as defined in [30].

	Temperature	Reaction	ΔH° ($\mathrm{kJ\,mol^{-1}}$)	$\eta_{\mathrm{Solar\text{-}to\text{-}fuel}}$	Refs.
MgO	3440 °C	$MgO \rightarrow Mg(g) + 0.5\ O_2$	603	–	–
ZnO	2070 °C	$ZnO \rightarrow Zn(g) + 0.5\ O_2$	378	29% (@ 2000 °C)	[28]
SnO_2	2060 °C	$SnO_2 \rightarrow SnO(g) + 0.5\ O_2$	519	29.8% (@ 1600 °C)	[14]
GeO_2	1830 °C	$GeO_2 \rightarrow GeO(g) + 0.5\ O_2$	469	34.6% (@ 1500 °C)	[29]