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A novel lab-scale solar reactor for kinetic analysis of non-volatile metal oxides thermal reductions

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Abstract

Thermal reduction of metal oxides is of primary interest within the R&D field of solar driven thermochemistry, because it is frequently involved in processes such as thermochemical cycles for hydrogen production or in thermochemical energy storage systems for solar thermal power plants. A lab-scale solar reactor has been designed to test and analyze solar-driven reduction of non-volatile metal oxides arranged in a packed bed. The test bed allows monitoring of oxygen evolution to determine the reaction rate. Experimental tests with Mn_2O_3, Mn_3O_4 and CeO_2 have been carried out and the performance of each reaction has been analyzed. Total conversion is obtained for Mn_2O_3 reduction. However, only some zones of the Mn_3O_4 and CeO_2 samples achieve reaction temperature. Different types of sample-holders have been used to hold the particles packed-bed, in order to enhance the conversion. The high influence of the irradiance distribution on the sample surface is demonstrated by a testMn_3O_4 reduction.

Keywords: Non-volatile metal oxides; solar reactor; solar thermochemistry; kinetic analysis.

1. Introduction

Solar thermochemistry is a promising long term prospect for commercially developing clean, efficient and sustainable energy systems [1].Thermochemical processes carried out using concentrated solar energy have been widely demonstrated [2, 3] being the production of synthetic fuels, thermochemical storage and hydrogen generation the most investigated processes. Metal oxides reductions are involved in thermochemical processes and represent one of the most critical stages because they take place at the highest temperature of the process. Most of them usually occur at the temperature range of 1100-2300 K that is typically obtained at solar tower systems. Because of that, thermal reductions of metal oxides are very interesting as processes to be carried out by concentrated solar power. To develop them, different configurations of solar reactors have been conceived [4]. A solar reactor should ensure the optimal

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operating conditions to enhance the chemical reaction and also provide a tool to get a deep understanding of reaction features. Particularly, reaction rates including chemical kinetics are often a major concern. Most of the studies for kinetic determinations have been done employing non-solar techniques such as thermogravimetry [5-7]. Some solar devices have been also used to determine kinetics at high radiation fluxes. The thermal decomposition of ZnO in a 45-kW concentrating solar furnace was studied at PSI (Paul Scherrer Institute, Villigen, Switzerland) [8,9] in a cavity-type solar reactor and a solar-driven thermogravimeter. The kinetic parameters were calculated from the sample mass loss. A revised version of the same solar thermogravimenter setup has been successfully applied for analyzing the kinetics of non-volatile metal oxides at PSI's 50-kWth high flux solar simulator [10]. The chemical kinetics was also determined from carrier gas composition analysis at reactor downstream for the TREMPER reactor [11] at PSI's solar furnace and spherical transparent reactors [12] in a vertical solar furnace at CNRS-PROMES, Odeillo, France. In both cases, the sample was enclosed in a transparent sealed cover to keep controlled atmosphere during operation.

In this work, the experimental reduction of some non-volatile oxides under high flux of radiation is presented. Non-volatile metal oxides facilitate the recovery the solid product obtained after the thermal treatment and also simplify the separation of oxygen released, avoiding the use of quenching or other complex separation processes. Particularly, manganese oxides, Mn_2O_3, Mn_3O_4 and cerium oxide, CeO_2 are studied. Manganese oxides reductions are involved in the thermochemical cycle proposed by Sturzenegger [13] and they occur according to this mechanism or chemical route:

$$6\ Mn_2O_3 \rightarrow 4\ Mn_3O_4 + O_2 \tag{1}$$

$$2\ Mn_3O_4 \rightarrow 6\ MnO + O_2 \tag{2}$$

A background on the work previously done on these oxides reduction is found in [14]. In relation to cerium oxide, Abanades *et al*. [15] proposed a two-step thermochemical cycle based on CeO_2/Ce_2O_3.Thermodynamical studies indicated the reduction gave rise to non-stoichiometric species:

$$CeO_2 \rightarrow CeO_{2-x} + x/2O_2 \tag{3}$$

where $0<x<0.5$. A complete thermochemical cycle to water and CO_2 splitting was then developed by Chueh *et al*. [16]. Regarding reduction step, they concluded the oxygen evolution kinetics was limited predominantly by the heating rate.

In the present work, reductions are carried out in a novel solar reactor where reactants are arranged in a packed-bed.

Nomenclature

X_a	Conversion of reactant "a"
m_a	Initial mass of reactant "a"
PM_a	Molecular weight of reactant "a"
$[O_2]$	Oxygen concentration