



Kinetic analysis of high-temperature solid–gas reactions by an inverse method applied to ZnO and SnO₂ solar thermal dissociation

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HIGHLIGHTS

- An inverse method to identify the kinetics of high-temperature solid–gas reactions.
- The method was applied to the case of ZnO and SnO₂ solar thermal dissociations.
- The reactions were carried out in a high-temperature solar chemical reactor.
- The inverse method involves the online diagnosis of outlet gas and a reactor model.
- The activation energy of dissociations was 313 ± 31 kJ/mol for ZnO and 353 ± 18 kJ/mol for SnO₂.

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ABSTRACT

This study addresses the kinetic investigation of solid–gas reactions in a high-temperature solar chemical reactor. An inverse method was developed to identify the kinetics of metal oxide thermal dissociation as part of a two-step thermochemical redox cycle for solar splitting of H₂O and CO₂. This method was applied and further validated by studying ZnO and SnO₂ solar thermal dissociation. A solar chemical reactor enabling continuous solid reactant processing was developed in which both the oxide reactant temperature at the front surface and the O₂ concentration in the off gas were measured dynamically. The aim of the inverse method was to identify the intrinsic kinetics of the dissociation reaction using only the available experimental data.

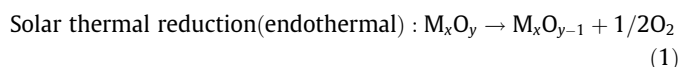
Different approaches were proposed and compared to investigate the kinetics of solid–gas reactions. The activation energy of the reaction was first estimated roughly using an iso-conversional model-free approach, which can be used as an initialization value for further refinement with the inverse method. The inverse method consists in identifying the reaction kinetics from only the online diagnosis of outlet O₂ concentration and using a model enabling parameters fitting via an iterative process. Depending on the considered approach and assumptions for predicting the temperature profile within the reacting oxide rod (succession of stationary states assumption or unsteady state operation), the activation energy of the dissociation reaction was found to be 313 ± 31 kJ/mol for ZnO and 353 ± 18 kJ/mol for SnO₂. Such a method may be implemented for the kinetic analysis of any kind of solid–gas reactions in high-temperature solar reactors.

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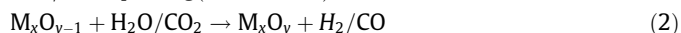
1. Introduction

Thermochemical cycles involving metal oxide redox pairs have been rising much interest during the last decades for their capability to reduce water and carbon dioxide, leading to potential CO₂-free production of solar hydrogen (from water) and syngas (mix of carbon monoxide and dihydrogen from the co-splitting of water and carbon dioxide) [1–9]. When using syngas as a chemical precursor for the production of solar liquid fuels (using the well-

known Fischer–Tropsch process for instance) or hydrogen as a clean energy vector, the development of metal redox pairs may become a major step toward the reduction of the environmental impact of widespread energies. The two-step thermochemical cycle involving metal oxide redox pairs encompasses the following reactions:



H₂O/CO₂ splitting(exothermal) :



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