

Solar electricity via an Air Brayton cycle with an integrated two-step thermochemical cycle for heat storage based on $\text{Co}_3\text{O}_4/\text{CoO}$ redox reactions II: Kinetic analyses

Alexander P. Muroyama, Andrew J. Schrader, Peter G. Loutzenhiser*

George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0405, USA

Received 16 April 2015; received in revised form 31 May 2015; accepted 4 August 2015

Available online 30 September 2015

Communicated by: Associate Editor Robert Pitz-Paal

Abstract

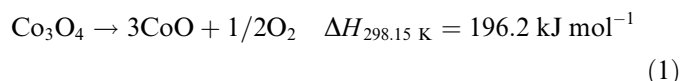
A two-step solar thermochemical cycle based on $\text{Co}_3\text{O}_4/\text{CoO}$ redox reactions integrated into an Air Brayton cycle is considered for thermochemical heat storage. The two-step cycle encompasses (1) the thermolysis of Co_3O_4 to CoO and O_2 driven by concentrated solar irradiation and (2) the re-oxidation of CoO with O_2 to Co_3O_4 , releasing heat and completing the cycle. The cycle steps can be decoupled, allowing for thermochemical heat storage and integration into an Air Brayton cycle for continuous electricity production. Kinetic analyses to identify the rate limiting mechanisms and determine kinetic parameters for both the thermolysis of Co_3O_4 and the re-oxidation of CoO with O_2 were performed using a combination of isothermal and non-isothermal thermogravimetry. The Co_3O_4 thermolysis between 1113 and 1213 K followed an Avrami–Erofev nucleation model with an Avrami constant of 1.968 and apparent activation energy of $247.21 \text{ kJ mol}^{-1}$. The O_2 partial pressure dependence between 0% and 20% O_2 –Ar was determined with a power rate law, resulting in a reaction order of 1.506. Ionic diffusion was the rate limiting step for CoO oxidation between 450 and 750 K with an apparent activation energy of $58.07 \text{ kJ mol}^{-1}$ and no evident dependence on O_2 concentration between 5% and 100% O_2 –Ar. Solid characterization was performed using scanning electron microscopy and X-ray powder diffraction.

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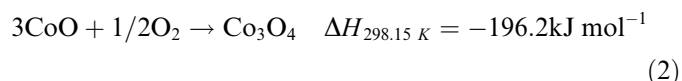
Keywords: Concentrated solar energy; Thermochemical energy storage; Two-step thermochemical cycle; Cobalt oxide; Kinetic analysis

1. Introduction

In a previous work, a thermodynamic analysis of a two-step solar thermochemical cycle for heat storage was performed with integration into an Air Brayton cycle (Schrader et al., 2015). The first step of the cycle is the endothermic thermolysis of Co_3O_4 driven by concentrated solar irradiation, represented as:



Heat is released in the second step of the cycle by re-oxidizing CoO with pressurized air in a non-solar process, represented as:



The resulting Co_3O_4 can be recycled back to the first step to complete the cycle. The cycle steps are decoupled, enabling long-term storage of sunlight to produce

* Corresponding author. Tel.: +1 404 894 3012.

E-mail address: peter.loutzenhiser@me.gatech.edu (P.G. Loutzenhiser).

Nomenclature

E_a	apparent activation energy	t_0	offset time
I	intensity	T	temperature
k	rate constant	<i>Greek letters</i>	
k_0	apparent pre-exponential factor	α	conversion
m	mass	β	fitting parameter
n	Avrami constant	γ	reaction order
p	pressure	ΔH	enthalpy change of reaction
q	measurands	θ	diffraction angle
R	universal gas constant	σ	experimental uncertainty
t	time	χ^2	chi-squared estimation

on-demand electricity. Integration of the heat storage cycle into an Air Brayton cycle with a robust thermodynamic analysis determined theoretical solar-to-electricity efficiencies of up to 44%. Previous studies have assessed the potential of cobalt oxide for a two-step solar thermochemical storage process (Wong, 2011; Neises et al., 2012; Agrafiotis et al., 2014; Karagiannakis et al., 2014; Pagkoura et al., 2014; Agrafiotis et al., 2015b,c).

Accurate determination of the chemical kinetics of both reactions is of key importance for developing chemical reactor technologies to realize both cycle steps. Metal oxides generally follow the principles of solid-state kinetics, based on a variety of models and mechanisms that include nucleation and nuclei growth, geometrical contraction, diffusion, and simple reaction order (Khawam and Flanagan, 2006). The limiting mechanisms proposed in previous works for Co_3O_4 thermolysis include nucleation (Hutchings et al., 2006; Wong, 2011), heat transfer (Hutchings et al., 2006), and diffusion (Reti et al., 1966). Previous studies have proposed diffusion (Gulbransen and Andrew, 1951; Hsu and Yurek, 1982; Tomlinson and Easterlow, 1985; Morin and Dieckmann, 1990; Kaczmarek et al., 2012) or nucleation (Reti et al., 1966; Ott and Rankin, 1979; Wong, 2011) as the limiting mechanism for CoO oxidation.

Prior work using non-isothermal thermolysis and isothermal re-oxidation in air with a thermogravimetric analyzer (TGA) determined an apparent activation energy of 960 kJ mol^{-1} for Co_3O_4 thermolysis using a nucleation model (Wong, 2011). Another study used a TGA to perform multi-cyclic temperature reduction and re-oxidation in air or O_2 , finding apparent activation energies of 439 and 892 kJ mol^{-1} for thermolysis in air and O_2 , respectively, using a model based on thermodynamic driving force (Hutchings et al., 2006). A recent work used downstream O_2 measurements in an air-blown furnace system with a simplified kinetic model, resulting in apparent activation energies of 723 kJ mol^{-1} for Co_3O_4 thermolysis and -249 kJ mol^{-1} for CoO oxidation (Pagkoura et al., 2014). An earlier study investigated the initial oxidation rate of CoO at high

temperatures by monitoring temporal pressure changes in a closed container filled with the oxide and oxygen and reported an apparent activation energy of 60 kJ mol^{-1} (Reti et al., 1966). A later marker study found the total layer growth kinetics of CoO oxidation to have an apparent activation energy of $70 \pm 10 \text{ kJ mol}^{-1}$ in the 973–1048 K temperature range (Tomlinson and Easterlow, 1985).

Other works have analyzed the kinetics of other metal oxide redox pairs for solar applications, including Zn/ZnO (Berman and Epstein, 2000; Möller and Palumbo, 2001; Perkins et al., 2007; Chambon et al., 2009; Ernst et al., 2009; Loutzenhiser et al., 2009; Schunk and Steinfeld, 2009; Levêque and Abanades, 2013; Venstrom and Davidson, 2013), SnO/SnO₂ (Chambon et al., 2009; Abanades, 2012; Levêque and Abanades, 2013), FeO/Fe₃O₄ (Go et al., 2008; Loutzenhiser et al., 2009), Mg/MgO (Gálvez et al., 2008), MnO/Mn₂O₃ (Francis et al., 2010; Botas et al., 2012), perovskites (McDaniel et al., 2014), and ferrites (Go et al., 2008; Neises et al., 2010; Scheffe et al., 2013; Kostoglou et al., 2014). These and other redox pairs have been examined predominantly for solar thermal syngas production and are detailed in an extensive review (Agrafiotis et al., 2015a).

In the present work, apparent chemical kinetic parameters for Co_3O_4 thermolysis and CoO oxidation are determined with thermogravimetry at 1 bar over a range of temperatures and O_2 concentrations. The novelty of this work is aimed towards developing applicable kinetics for Co_3O_4 thermolysis and CoO oxidation that capture the effects of both temperature and O_2 partial pressure over appropriate ranges for concentrated solar power applications.

2. Experimental section

Experimentation was carried out using a TGA (Netzsch STA449 F3 Jupiter, $\pm 1 \mu\text{g}$). Powder samples of $\sim 100 \text{ mg}$ of Co_3O_4 (Sigma–Aldrich, particle size $< 10 \mu\text{m}$) and CoO (Sigma–Aldrich, ~ 325 mesh) were placed on a

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