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

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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 1113-1213 K followed an Avrami-Erofeyev nucleation model with an Avrami constant of 1.968 and apparent activation energy of $247.21 \text{ kJ}\cdot\text{mol}^{-1}$. The O_2 partial pressure dependence between 0-20% 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 450-750 K with an apparent activation energy of $58.07 \text{ kJ}\cdot\text{mol}^{-1}$ and no evident dependence on O_2 concentration between 5-100% O_2 -Ar. Solid characterization was performed using scanning electron microscopy and x-ray powder diffraction.

Keywords: Concentrated Solar Energy; Thermochemical Energy Storage; Two – Step Thermochemical Cycle; Cobalt Oxide; Kinetic Analysis

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. in press). 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 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, Agrafiotis et al. 2015c).

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, Kaczmarzka 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 $960 \text{ kJ} \cdot \text{mol}^{-1}$ 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 $892 \text{ kJ} \cdot \text{mol}^{-1}$ 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 $723 \text{ kJ} \cdot \text{mol}^{-1}$ 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 ± 10 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 Co₃O₄ thermolysis and CoO oxidation are determined with thermogravimetry at 1 bar over a range of temperatures and O₂ concentrations. The novelty of this work is aimed towards developing applicable kinetics for Co₃O₄ thermolysis and CoO oxidation that capture the effects of both temperature and O₂ partial pressure over appropriate ranges for concentrated solar power applications.

Experimental Section

Experimentation was carried out using a TGA (Netzsch STA449 F3 Jupiter, ± 1 µg). Powder samples of ~100 mg of Co₃O₄ (Sigma-Aldrich, particle size <10 µm) and CoO (Sigma-Aldrich, ~325 mesh) were placed on a 17-mm-diameter Al₂O₃ crucible. The crucible was in contact with an S-type thermocouple and was covered with a platinum foil to prevent unwanted reactions. The initial mass of each sample was determined using an analytical balance (Mettler-Toledo ML54, ± 0.1 mg), and product gases were temporally monitored with mass spectrometry (MS, OmniStar ThermoStar GSD320 Gas Analysis System) and gas chromatography (GC, Agilent 490 Micro GC equipped with Molsieve and PoraPLOT Q columns). Different initial powder samples for CoO and Co₃O₄ were used due to uncertainty about full conversion. Using different samples ensured sample purity and uniformity between experiments.

Isothermal experiments were performed to examine the Co₃O₄ thermolysis in the high temperature graphite furnace ($T_{\text{max}} = 2273$ K) of the TGA at different temperatures and O₂ concentrations. The

samples were heated at 20 K/min in the graphite furnace with 100 mL_N/min (L_N denotes liters at normal conditions at 273 K and 1 bar) of 80% O₂-Ar entering from the bottom of the graphite furnace to impede the onset of Co₃O₄ thermolysis. Upon reaching the isotherm, the samples were held in 80% O₂-Ar for ~15 min to allow for thermal stabilization, and the atmosphere was then switched to a reducing atmosphere of O₂-Ar to allow the thermolysis to proceed until conversion from Co₃O₄ to CoO was complete. MS and GC measurements showed that ~1.5 min was required to purge to O₂ below 1% from the graphite furnace. Three runs were performed for each condition, and blanks were run at each condition and subtracted from sample runs to mitigate the effects of buoyancy and momentum due to changing temperatures. The $\% \Delta m_{\text{loss}}(t)/m_{\text{initial}}$ for isothermal experiments between 1113 – 1213 K in 0% O₂-Ar are shown in Figure 1a. Mass loss curves have deceleratory rate that is highly temperature-dependent. All samples reached complete conversion with a $\% \Delta m_{\text{loss}}(t)/m_{\text{initial}}$ equal to 6.6%. There was almost an order of magnitude difference between time to complete conversion at the minimum and maximum temperatures tested, and increasing the temperature above 1193 K led to only marginal increases in reaction rate. The rate slowed as the samples reached full conversion. Figure 1b shows the $\% \Delta m_{\text{loss}}(t)/m_{\text{initial}}$ for isothermal experiments at 1213 K in 0-20% O₂-Ar. Mass loss was slightly less consistent as sample conditions approached the thermodynamic limit, but a clear trend of higher O₂ concentrations inhibiting the rate of thermolysis was seen. Approximately twice the time was required to reduce the Co₃O₄ particles under a 20% O₂-Ar atmosphere versus a 0% O₂-Ar atmosphere. Samples at 1213 K did not completely reduce above 20% O₂-Ar, so temperature changes had a demonstrably greater effect on rate than O₂ concentration changes.

Figure 1. Measured temporal mass losses normalized with the initial mass from isothermal thermogravimetry for the Co₃O₄ thermolysis for (a) temperatures between 1113 – 1213 K at 0% O₂-Ar and (b) O₂ concentrations between 0-20% O₂-Ar at 1213 K.

Non-isothermal thermolysis experiments were performed by heating Co_3O_4 samples at a rate of 20 K/min in a reducing atmosphere flowing at 100 mL_N/min until complete conversion was achieved. Three runs were performed at each O_2 -Ar condition and blank runs were subtracted from sample runs. Figure 2 shows the $\% \Delta m_{\text{loss}}(t)/m_{\text{initial}}$ for experiments in 0-15% O_2 -Ar. Higher O_2 concentrations prevented the onset of the thermolysis as the reaction was thermodynamically limited. While higher O_2 concentrations would inhibit rate of thermolysis due to the back reaction, this was offset by higher corresponding thermolysis temperatures in non-isothermal experiments, leading to minimal changes in rate between 5-15% O_2 -Ar.

Figure 2. Measured temporal mass losses normalized with the initial mass for non-isothermal thermogravimetry for O_2 concentrations between 0-15% O_2 -Ar with the temporal temperature (dashed) increasing at a rate of 20 K/min.

A series of isothermal TGA runs for CoO oxidation with O_2 were initially performed by heating the sample in Ar and then switching to an O_2 -Ar atmosphere after the isotherm; however, very fast kinetics (i.e., full conversion in less than 30 seconds) coupled with required purge time to remove Ar from the system made it problematic to extract kinetics due to high uncertainties. Therefore, a series of non-isothermal oxidation experiments were performed in the water vapor furnace ($T_{\text{max}} = 1523$ K) of the TGA by heating samples at 10 K/min while keeping a constant oxidizing flow of 100 mL_N/min until the samples fully oxidized. The water vapor furnace introduces reacting gases above the sample, which is more applicable for oxidation reactions. Figure 3 shows the $\% \Delta m_{\text{loss}}(t)/m_{\text{initial}}$ for experiments in 5-100% O_2 -Ar with the sample temperature. Conversion was more gradual for non-isothermal oxidation compared with non-isothermal thermolysis. The onset of the reaction began at ~ 430 K, and all samples reached

complete conversion within TGA error by ~ 800 K with complete conversion corresponding to a $\% \Delta m_{\text{loss}}(t)/m_{\text{initial}}$ of $\sim 7.1\%$. Reaction rate appeared to be independent of O_2 concentration.

Figure 3. Measured temporal mass gains from non-isothermal thermogravimetry for the CoO oxidation in 0-20% O_2 -Ar (markers) with temporal temperature (dashed) increasing at a rate of 10 K/min.

Samples of CoO and Co_3O_4 were repeatedly cycled between oxidized and reduced states via isothermal pressure swing in order to evaluate suitability for solar thermochemical storage application. Samples were heated to 1133 K in the TGA at a rate of 20 K/min, then held at that temperature and repeatedly cycled between 100 mL_N/min 0 and 20% O_2 -Ar, for 15-min intervals without interruption. A temperature of 1133 K was chosen as the isotherm due to thermodynamic favorability for either oxidation or thermolysis depending on atmosphere. Figure 4 shows normalized mass change for six cycles starting with samples of (a) CoO and (b) Co_3O_4 . Theoretical maximum conversion, denoted by dotted lines, was nearly reached for both oxidation and thermolysis during each cycle. The ability to fully reduce or fully oxidize did not diminish over 10 redox cycles. The CoO sample had more rapid mass changes than the Co_3O_4 , likely due to smaller particle sizes and greater surface-area-to-volume ratios.

Figure 4. Mass change normalized with initial mass (solid lines) for redox cycling (a) CoO and (b) Co₃O₄ with theoretical maximum conversion (dotted) and O₂ concentration (dot-dashed) shown.

Kinetic Analysis

The temporal conversion of Co₃O₄ to CoO or CoO to Co₃O₄ was determined using TGA measurements as:

$$\alpha(t) = \frac{m(t) - m_{\text{initial}}}{m_{\infty} - m_{\text{initial}}} \quad (3)$$

where t is time; $m(t)$ is temporal sample mass measured by TGA; m_{initial} is the initial sample mass; and m_{∞} is the mass calculated for full conversion. Weighted non-linear regression (Alper and Gelb 1990) was used to fit data to the appropriate rate laws using the least squares criterion for best fit by minimizing chi-squared using a multidimensional unconstrained non-linear minimization algorithm (Nelder-Mead), represented generically as:

$$\chi_{\min}^2 = \sum_j \left(\frac{F_j}{\sigma_j} \right)^2 \quad (4)$$

where F is a function of measured properties and values that are initially unknown, represented as:

$$F_j = f(q_{1j}, \dots, q_{nj}; \beta_1, \dots, \beta_r) = 0 \quad (5)$$

where q denotes n measurands assumed as known, and β represents r fitting parameters assumed initially as unknown. The standard error was estimated as:

$$\sigma_j^2 = \sum_{i=1}^n \left(\frac{\partial F_j}{\partial q_{ij}} \right)^2 \sigma_{ij}^2 \quad (6)$$

where σ_{ij} represents the experimental uncertainty of the parameter. Ninety-five percent confidence limits for the β 's were estimated using Monte Carlo analyses (Alper and Gelb 1990) with greater than 200 iterations by stochastically varying σ_{ij} 's according to a Gaussian probability distribution function (pdf) and a uniform pdf for frequentist and Bayesian errors, respectively (Gleser 1998).

The rate limiting mechanism for Co_3O_4 thermolysis was related to random nucleation where imperfections in surface of the solid reactant material minimize the activation energy (Khawam and Flanagan 2006). Nucleation has been proposed as the mechanism for several decomposition reactions (Malinin and Tolmachev 1975, Hutchings et al. 2006, Khawam and Flanagan 2006, Wong 2011). A pressure dependence power rate law was included to account for the $3\text{CoO} + \frac{1}{2}\text{O}_2 \rightarrow \text{Co}_3\text{O}_4$ back reaction (2), which impedes the forward reaction (1). The Avrami-Erofeyev model with a power rate term to resolve O_2 partial pressure functionality from literature (Vyazovkin et al. 2011, Pagkoura et al. 2014) for solid-gas reactions captured the reaction mechanism, given as:

$$k \left(1 - \frac{p_{\text{O}_2}}{p_{\text{O}_2,\text{eq}}(T)} \right)^\gamma (t - t_0) = [-\ln(1 - \alpha)]^{1/n} \quad (7)$$

where n is the Avrami constant; p_{O_2} is the O_2 partial pressure, $p_{\text{O}_2,\text{eq}}$ is the O_2 partial pressure at equilibrium determined using thermophysical property data (Roine 2011); γ is the reaction order; t_0 is the offset time required to resolve the latency from switching from 80% O_2 -Ar to 0-20% O_2 -Ar and small grain growth during the onset of nucleation. For isothermal experiments performed with 0% O_2 -Ar, the back reaction is small (i.e., $p_{\text{O}_2}=0$) as the O_2 evolving during the reaction is continuously removed. The reaction mechanism is represented as:

$$k(t - t_0) = [-\ln(1 - \alpha)]^{1/n} \quad (8)$$

The limiting mechanism for CoO oxidation was found to be ionic diffusion through a Co_3O_4 oxide layer forming at the surface and becoming thicker as the reaction proceeds, according to Wagner's theory of metal oxidation (Wagner 1933, Wagner 1975). The reaction rate is limited by the outward mobility of Co^{2+} and Co^{3+} cations from the CoO core and the inward diffusion of O^{2-} anions. The 3D diffusion model is represented as:

$$kt = \left(1 - (1 - \alpha)^{1/3}\right)^2 \quad (9)$$

The rate constants were assumed to follow an Arrhenius-type temperature dependency, represented as:

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \quad (10)$$

where k_0 is the pre-exponential factor; E_a is the apparent activation energy; R is the universal gas constant; and T is the temperature.

Results and Discussion

Kinetic analyses were performed for Co_3O_4 thermolysis and CoO oxidation with O_2 , and the results are described in this section.

Co₃O₄ Thermolysis

Figure 5a shows a comparison of the modeled and experimental conversion for Co_3O_4 thermolysis between 1113-1213 K at 0% O_2 -Ar. $n = 1.968 \pm 0.058$ was determined for Co_3O_4 thermolysis with good agreement between the model and experiment as t_0 was used to account for the switching from 80% O_2 -Ar to 0% O_2 -Ar. This deviation was less pronounced at higher temperatures due to favorable thermodynamics at higher O_2 concentrations. Figure 5b shows the modeled and experimental conversion for Co_3O_4 thermolysis at 1213 K between 0-20% O_2 -Ar. $\gamma = 1.506 \pm 0.022$ was determined by fitting all data simultaneously and using k 's and n 's determined at 0% O_2 -Ar between 1113-1213 K. The γ term captures the complex dependence of reaction rate on p_{O_2} . Agreement between the modeled and experimental conversions is particularly strong at lower O_2 concentrations where thermolysis takes place relatively quickly, but deviates more as O_2 concentrations approach the thermodynamic limit of thermolysis.

Figure 5. Experimental (markers) and fitted (solid) conversion for Co_3O_4 thermolysis (a) for temperatures between 1113 – 1213 K at 0% O_2 -Ar and (b) O_2 concentrations between 0-20% O_2 -Ar at 1213 K.

The rate constants were determined from isothermal experiments at 0% O_2 -Ar and fitted to an Arrhenius-type temperature dependency, with k_0 and E_a , given with 95% confidence limits as:

$$k = 1.104 \pm 0.043 \times 10^9 \text{ s}^{-1} \exp\left(-\frac{247.21 \pm 0.38 \text{ kJ} \cdot \text{mol}^{-1}}{RT}\right) \quad (11)$$

The Arrhenius-type temperature dependency is shown in Figure 6 for Co_3O_4 . The k 's are strongly dependent on temperature and exponentially increase with increasing temperature. The apparent activation energy is similar in magnitude to the enthalpy change of reaction, consistent with observations about metal oxide thermolysis (Malinin and Tolmachev 1975). The value is also consistent with the observation that self-diffusion activation energies in spinels are typically $250\text{-}350 \text{ kJ} \cdot \text{mol}^{-1}$ (Oshcherin 1975). The apparent activation energy is lower than some previously reported values (Hutchings et al. 2006, Wong 2011, Pagkoura et al. 2014); however, the apparent activation energy can be highly dependent on experimental conditions, sample preparation, and chosen reaction mechanism.

Figure 6. Arrhenius plot for isothermal Co_3O_4 thermolysis showing experimental (markers) and fitted (solid) kinetic parameters

CoO Oxidation

Figure 7 shows experimental and modeled conversion for dynamic CoO oxidation. All runs have the same temperature profile and thus have the same modeled conversion given the O_2 partial pressure independence. The 3D diffusion model has very good agreement within the 450-750 K range. The differential form of Equation 6 was used to produce the fitted curve given the same initial α , using a 6-term finite-difference approximation for $\frac{d\alpha}{dt}$ (Tannehill et al. 1997). The fitted conversion curve started after some initial conversion because the differential form of Equation 6 becomes undefined as α approaches zero. There was no dependence on p_{O_2} as Co and O ion migration is the limiting mechanism, rather than O_2 adsorption at the surface. Previous literature has shown that Co oxidation rate is independent of p_{O_2} in the 593-793 K range (Chattopadhyay and Measor 1969) and relatively independent of p_{O_2} in the 873-1073 K range (Hsu and Yurek 1982). Other literature has suggested that CoO oxidation to form Co_3O_4 is diffusion-controlled with a virtually constant k in the intermediate O_2 pressure range (Kaczmariska et al. 2012). The present work supports this observation, particularly in the T and p_{O_2} ranges tested.

Figure 7. Experimental (markers) and fitted (solid) conversions for non-isothermal CoO oxidation with temporal temperature (dashed) over a range of O_2 concentrations between 5-100% with a heating rate of 10 K/min.

Figure 8 shows the Arrhenius plot for CoO oxidation fitting in the 477-708 K range with a k determined as:

$$k = 22.16 \pm 1.20 \text{ s}^{-1} \exp\left(-\frac{58.07 \pm 0.26 \text{ kJ} \cdot \text{mol}^{-1}}{RT}\right) \quad (12)$$

The apparent activation energy for oxidation shows relatively strong agreement with previous studies (Reti et al. 1966, Tomlinson and Easterlow 1985) and is significantly lower than that for thermolysis due to a much weaker dependence on temperature. However, the rate constant increases exponentially with increasing T . The fit slightly under-predicts k at higher T and over-predicts k at lower T .

Figure 8. Arrhenius plot for dynamic CoO oxidation showing experimental (markers) and fitted (solid) kinetic parameters

Cycling

Figure 9a shows the first, third, and fifth cycle of oxidation and thermolysis superimposed to highlight slight changes that took place during each cycle, starting with CoO. The CoO sample experienced a minuscule decrease in oxidation rate and increase in thermolysis rate that only took place after the first cycle. The parity plot shown in Figure 9b shows some deviation from the initial conversion. However, parity for the third and fifth cycles is almost identical. Parity fits with 95% confidence limits for conversion during the third and fifth cycles were determined as $\alpha_{3^{\text{rd}} \text{ cycle}} = (0.9878 \pm 0.0062)\alpha_{1^{\text{st}} \text{ cycle}}$ and $\alpha_{5^{\text{th}} \text{ cycle}} = (0.9854 \pm 0.0061)\alpha_{1^{\text{st}} \text{ cycle}}$, respectively. These results are indicative of initial sample conversion rate degradation as the 95% confidence intervals do not include unity.

Figure 9. For initial sample of CoO, (a) superimposed reduction/oxidation cycles comparing normalized mass change and (b) parity plot comparing conversions with first cycle

The Co_3O_4 sample had more pronounced changes in rate, although in the opposite direction as shown in Figure 10a. Thermolysis took place more slowly and oxidation became slightly faster after a few cycles, and these changes diminished with increasing cycles. The more dramatic changes in the Co_3O_4 sample reaction rates are possibly due to the larger particle size leading to more noticeable changes in the surface morphology. The parity plot given in Figure 10b shows some deviation from the initial conversion with the greatest changes occurring during initial cycling. Parity fits with 95% confidence limits for conversion during the third and fifth cycles were determined as $\alpha_{3^{\text{rd}} \text{ cycle}} = (0.9886 \pm 0.0073)\alpha_{1^{\text{st}} \text{ cycle}}$ and $\alpha_{5^{\text{th}} \text{ cycle}} = (0.9803 \pm 0.0090)\alpha_{1^{\text{st}} \text{ cycle}}$, respectively. These results confirm initial sample conversion rate degradation during cycling. However, overall sample redox performance was largely unaffected by cycling, consistent with previous literature demonstrating good redox cyclability and thermomechanical stability (Hutchings et al. 2006, Agrafiotis et al. 2014, Pagkoura et al. 2014, Agrafiotis et al. 2015b, Agrafiotis et al. 2015c).

Figure 10. For initial sample of Co_3O_4 , (a) superimposed reduction/oxidation cycles comparing normalized mass change and (b) parity plot comparing conversions with first cycle

Solid Characterization

Particle microstructures were examined using scanning electron microscopy (SEM, Zeiss Leo 1550). Figure 11 shows SEM pictures of the Co_3O_4 particles before and after conversion. Co_3O_4 has a spinel structure. Figure 11a shows the Co_3O_4 particles having smoother, more angular surfaces than the CoO . After the Co_3O_4 is thermolyzed (Figure 10b), the structure becomes more porous and less defined.

Figure 11. Images from scanning electron microscopy for (a) Co_3O_4 and (b) Co_3O_4 after thermolysis

Figure 12 shows SEM pictures of the CoO particles before and after conversion. Figure 12a shows the smaller particle size and large surface area for reaction. After CoO is oxidized (Figure 12b), the particles expand slightly and still appear to have a large surface area with no distinctive spinel structures being formed.

Figure 12. Images from scanning electron microscopy for (a) CoO and (b) CoO after oxidation

X-ray diffraction (XRD, PANalytical X'Pert PRO Alpha-1 diffractometer) was performed on samples before and after TGA. PDF4+ data were used to verify crystal structures corresponding with CoO and Co_3O_4 in the $20\text{--}80^\circ$ diffraction angle range. Plots of intensity as a function of angle are shown in Figure 13. Converted sample peaks showed good agreement with the equivalent unconverted sample peaks, confirming the presence of each oxide without intermediaries. The converted samples do show some peaks slightly shifted to higher diffraction angles, also noted in previous work (Agrafiotis et al. 2014, Pagkoura et al. 2014).

Figure 13. Intensity versus angle from x-ray diffraction measurements for (a) an unreacted CoO sample and CoO from thermolyzed Co_3O_4 and (b) an unreacted Co_3O_4 sample and Co_3O_4 from oxidized CoO.

Conclusions

$\text{Co}_3\text{O}_4/\text{CoO}$ redox reactions were analyzed using thermogravimetry for application in two-step solar thermochemical cycle integrated into an Air Brayton cycle to store heat. Apparent kinetic parameters were determined for Co_3O_4 thermolysis and CoO oxidation with Arrhenius-type temperature dependencies. The thermolysis followed a nucleation model with an Avrami constant equal to 1.968. O_2 partial pressure dependence of thermolysis was given by a reaction order of 1.506. The apparent activation energy for thermolysis was $247.21 \text{ kJ}\cdot\text{mol}^{-1}$. Non-isothermal thermolysis demonstrated the thermodynamic limit of spontaneous reaction due to the presence of O_2 . Non-isothermal oxidation in the 450-750 K range was described by ionic diffusion through an oxide. No O_2 partial pressure dependence for oxidation was observed. The apparent activation energy for oxidation was $58.07 \text{ kJ}\cdot\text{mol}^{-1}$.

Cycling between reduced and oxidized states via pressure swing was performed using thermogravimetry to demonstrate repeatability and material robustness. Virtually no deviation in the total mass change for either sample was observed over 10 cycles, although very slight changes in reaction rates were observed.

These variations in rate diminished with cycling, presumably due to the morphological changes that occurred during the first cycle. Scanning electron microscopy was used to identify minor structural changes in the samples and small particle size leading to faster reaction times, and x-ray diffraction confirmed the presence of the expected metal oxide without intermediaries after complete conversions. The kinetics developed in this work serve to guide both solar thermochemical reactor designs to efficiently realize Co_3O_4 thermolysis and chemical reactor designs for CoO oxidation operating within the temperatures ranges and O_2 partials pressures presented.

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Nomenclature

E_a	apparent activation energy
I	intensity
k	rate constant
k_0	apparent pre-exponential factor
m	mass
n	Avrami constant
p	pressure
q	measurands
R	universal gas constant
t	time
t_0	offset time
T	temperature

Greek Letters

α	conversion
β	fitting parameter
γ	reaction order
ΔH	enthalpy change of reaction
θ	diffraction angle
σ	experimental uncertainty
χ^2	Chi-squared estimation

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