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Kinetic and thermodynamic considerations for oxygen absorption/desorption using cobalt oxide

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Abstract

Cobalt oxide absorbs oxygen as the high-temperature rock-salt CoO structure is transformed into the lower-temperature cubic Co_3O_4 spinel. The absorption and desorption processes are reversible, which makes the material a potential candidate for use in temperature and/or pressure swing absorption modes for the production of oxygen. TGA/DTA experiments were conducted to quantify the kinetics and thermodynamics of the reaction. Over the temperature range investigated, both absorption and desorption were highly dependent on the thermodynamic driving force with faster kinetics occurring as ΔG became more negative. The reaction kinetics were primarily controlled by heat transfer and the thermodynamic driving force. Kinetic data suggest that cobalt oxide of 1 – 5 μm particle size can be oxidized or reduced at temperatures 40° above or below 890 °C in air, in less than 10 min at a bed thickness of 10 mm. A large change in enthalpy ($\Delta H \approx 195$ kJ/mol) as Co_3O_4 is converted to CoO affects heat transfer and the economy of producing oxygen by this method.

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Keywords: Oxygen transport; Reaction kinetics; Thermodynamic driving force; Cobalt oxide

1. Introduction

Oxygen is produced in large quantities by cryogenic distillation using Joule–Thompson refrigeration [1,2]. Nitrogen has a boiling point of 77.4 K and oxygen has a boiling point of 90.18 K and so the air can be easily separated into O_2 and N_2 in a distillation column. The purity of oxygen produced by this method is around 99.5%. The main impurity is argon, which is hard to separate since Ar has a boiling point (87.3 K) close to O_2. Argon is separated by further distillation, producing oxygen of 99.99% purity [2]. Lower purity oxygen (90–95%) is useful for many applications and pressure swing adsorption (PSA) or vacuum swing adsorption (VSA) methods are generally used to supply oxygen and nitrogen when lower-volumes are required [3,4]. A zeolite bed that preferentially adsorbs nitrogen over oxygen is most commonly used. Argon is always an impurity in oxygen produced by this method since both Ar and O_2 do not adsorb on zeolite. Although some nitrogen absorption occurs, PSA and VSA are generally adsorption processes and require high surface area zeolite beds to provide ample sites for nitrogen adsorption.

Absorption methods are generally not cost effective since they require higher temperatures for operation and longer times for oxygen diffusion. Desorption is endothermic and absorption is exothermic, which further complicates efforts to use pressure swings for such reactions. Nonetheless, a number of reversible reactions are under consideration for applications in oxygen storage [5], oxygen delivery [6], or use in chemical reactions [7]. Strategies for dealing with equilibrium-limited reactions, such as reversible reactions where there is a change in valence state of the metal cation, are also known [8].

The reaction between CoO and Co_3O_4, which can be expressed as

$$Co_3O_4 \leftrightarrow 3CoO + \tfrac{1}{2}O_2 \qquad (1)$$

is of interest because equilibrium occurs at 891°C in one atmosphere air [9], a temperature where chemical diffusion is rapid enough to give relatively fast kinetics so that the reaction can go to completion in a reasonably short time using 1 – 5 μm particles [5]. While it is possible to dope cobalt oxide with

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aliovalent cations to change the rates of absorption and desorption [5], the purpose of the present study was to investigate the role of kinetic and thermodynamic factors on oxygen absorption and desorption of undoped cobalt oxide. Furthermore, it was desired to assess whether this reaction could compete with PSA/VSA in supplying oxygen for industrial use.

2. Experimental

Co_3O_4 powder (OMG grade LS, lot C12H8207/1) with surface area of 1.0 m^2/g and a mean particle size of 3.7 μm was deagglomerated by mixing 200 g of cobalt oxide with 250 g of 2-propanol and paint shaking for 2 h inside a high-density polyethylene jar with 250 g of spherical Y-TZP media. The slurry was dried and then heated to 950 °C for 10 h to coarsen the cobalt oxide. The powder was pulverized by paint shaking for 15 min.

Surface area was measured by a multipoint BET method (Mircomeretics Tristar model) and particle size by laser light scattering (Coulter model LS 230). A scanning electron microscope (JOEL model JSM-5900/LV) was used to compare particle size before and after thermal cycling to $\approx$950°C. TGA/DTA measurements (Netzsch model STA409) were made on sample sizes of $\approx$1.6 g in flowing (50 cc/min) air or oxygen. Samples were heated either in 6 mm or 11 mm inner diameter crucibles with 1–14 mm powder depths. Porosity in the powder beds ranged from 77% to 85%. Heating and cooling rates of 20 °C/min were used unless otherwise stated. Time and temperature were varied in a single experiment to obtain kinetic data. A fully desorbed sample was cycled between the desorption temperature (960 °C) and the absorption temperature, which increased from 845 °C to 875 °C. At each absorption temperature the isothermal hold time varied between 5 and 25 min.

Desorption temperatures varied between 905 and 950 °C in air, with times ranging between 3 and 25 min. Fig. 1 shows how the variation in temperature was used to study desorption kinetics in air by keeping the absorption temperature constant at 780 °C and varying the desorption temperature from 900 to 950 °C. Fig. 1 shows substantial desorption of oxygen at 950 °C in a 5-min hold time, with less desorption occurring as the temperatures was lowered to 910 °C. No desorption was observed below 910 °C during these short 5-min hold times.

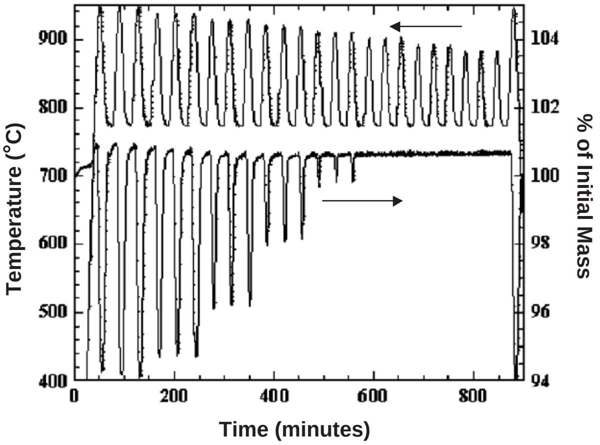

Fig. 1. Desorption of oxygen in air at 950, 940, 930, 920, and 910 °C with 5-min isothermal holds. Each cycle was repeated three times. Note that no desorption was observed below 910 °C.

Desorption data were obtained in flowing oxygen as well as air. The shift in partial pressure in oxygen necessitated a shift in the temperatures used to collect the desorption data, since the equilibrium temperature for the coexistence of CoO and Co_3O_4 is a function of the oxygen partial pressure. Desorption times in oxygen varied between 2 and 25 min with temperatures ranging between 955 and 980 °C.

A phenomenological equation [10] was used to fit the rate of transformation between the two phases as:

$$X(t) = 1 - \exp(-kt^n) \tag{2}$$

where $X(t)$ is the fraction transformed at time t, with k and n being time-independent constants. Rearrangement of this equation yields:

$$\ln \ln(1/(1 - X(t))) = \ln(k) + n\ln(t) \tag{3}$$

so that a linear relationship is expected when $\ln \ln (1/(1-X(t))$ is plotted as a function of $\ln t$, giving a slope n and y-intercept of $\ln k$. Once the time-independent constants were determined, time–temperature–transformation (T–T–T) diagrams, or isothermal transformation diagrams, for both absorption and desorption were generated.

A three-dimensional finite element code (Topaz3D—Lawrence Livermore National Labs) was used to analyze the heat transfer to the powder bed within the TGA test furnace. The model included the ceramic cup filled with the Co_3O_4 powder and convective/radiation boundary conditions from the semi-infinite surroundings representing the furnace cavity. The semi-infinite boundary temperatures were those temperatures and ramps measured in the TGA experiments. A lumped temperature dependent heat flux term (h_{equiv}) was used as the boundary condition to the exposed surfaces (cup and top of bed). This flux term consisted of a natural convection term and a linearized radiation term. At temperatures above the transition temperature (T>891 °C) and heating rates of 20 °C/min, the surface temperature of the cup is within 4 °C of the furnace temperature. At these conditions, the highly non-linear temperature dependent radiation terms ($T_{\mathrm{hot}}^4 - T_{\mathrm{cold}}^4$) can be factored into a temperature dependent constant ($h_{\mathrm{radiation}}$) and a linear temperature dependent term ($T_{\mathrm{bc}} - T_{\mathrm{cup}}$), assuming the temperature differential between the boundary condition (T_{bc}) and the cup (T_{cup}) is small.

The thermal conductivity of the cobalt oxide was based on data from Salamon et al. [11] correcting for effects of temperature and porosity [12]. Heat capacity data were taken from Barin [13]. An additional simplification was made in the model wherein the heat of formation during the phase change was rolled into the specific heat of the powder bed and occurred over a 1°C window. This simplification also aided in the numerical convergence of the finite element calculations. From this model, the heat transfer effects of cup geometry (diameter and depth) and thermal boundary conditions were