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An investigation into the stability and use of non-stoichiometric $YBaCo_4O_{7+\delta}$ for oxygen enrichment processes

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A B S T R A C T

$YBaCo_4O_{7+\delta}$ has been reported to have a large oxygen capacity which can be accessed on practical timescales by both temperature and pressure swings below 400 °C. One potential use of this oxygen capacity is for oxygen enrichment of process gas streams for e.g. application in oxy-fuel combustion and auto-thermal reforming. In this work, $YBaCo_4O_{7+\delta}$ powders were produced by a solid state synthesis and their material properties studied with a view to use as a process stream oxygen enricher. The stability of the material as a function of temperature in both CO_2 and reducing gases (CO and H_2) was investigated. The kinetics of oxygen uptake and release was studied by following the response to swings in oxygen partial pressure (pO_2) and temperature. To demonstrate the potential for employing this reversible oxygen capacity, the material was successfully used to supply oxygen into a gas stream with a pO_2 of 0.31 bar after oxidation in an air stream (pO_2 = 0.21 bar).

1. Introduction

Oxygen enrichment of process gas streams can be useful in many chemical processes such as the oxygen enhanced water-gas shift reaction (OWGS) [1,2], auto-thermal reforming of methane (ATR) [3], the removal of H_2S from a gas stream (Claus reaction) [4,5], ammonia synthesis [7] and oxy-fuel combustion [6]. The characteristics and potential benefits of such processes are summarised in Table 1.

One process of particular interest to the current work is oxy-fuel combustion. In this process, the fuels are combusted in a stream of CO_2 and O_2 instead of air [8,9]. The major advantage of this process is that it prevents nitrogen from entering the combustion system, yielding an exhaust rich in CO_2 (as opposed to N_2 in a traditional air-fed furnace) which can be readily captured. Additionally, the absence of N_2 reduces the amount of NO_X formed during combustion, potentially removing the need for additional treatments (unless an N-rich fuel is used) [10]. Part of the CO_2 exhaust is recycled and oxygenated to a high enough pO_2 (typically 0.3 bar) for combustion. Studies have shown that a pO_2 lower than 0.3 bar cannot sustain the flame due to the higher specific heat capacity of CO_2 [11,12].

There are several different processes currently used for oxygen enrichment. The simplest of these methods involves the use of cryogenic distillation or pressure swing absorption (PSA) to produce oxygen which is subsequently injected into a process stream. However, cryogenic distillation is energy intensive and the purity of oxygen produced by PSA is lower, typically ~95% [13,14]. Additionally, both methods generally operate on a large scale, and it is uncommon for smaller stationary units to be present for use at an individual process site. Oxygen separation using membranes which allow the selective transport of oxygen into a process stream can be a local, small-scale alternative for oxygen production. Although these units suffer from high operating costs, relatively low mechanical stability and the requirement of large areas of operation [15].

Oxygen separation through redox cycling of an oxygen storage material has the potential to improve on several of these issues. These materials can be used to selectively uptake oxygen (e.g. from air) during an oxidation step before releasing this incorporated oxygen into a process stream during an oxygen release step, caused by a change in temperature or pO_2. Two classes of materials have been studied for this thermo-chemical oxygen production. Simple transition metal oxides such as Mn_2O_3, Co_3O_4 and CuO have relatively high oxygen storage capacities, up to ~10 wt% of the material, but suffer from sintering [16]. On the other hand, non-stoichiometric oxides, primarily perovskites, are much more resistant to sintering, albeit offering lower oxygen storage capacities [17]. Both types of materials typically operate at temperatures above 800 °C due to either kinetic or thermodynamic limitations.

$YBaCo_4O_{7+\delta}$ is an oxygen hyper-stoichiometric material which has been shown to reversibly incorporate a large excess of oxygen ions into its crystal structure in ambient air, at temperatures between 300 and 400 °C, which is lost upon further heating [18–21]. *In-situ* x-ray diffraction (XRD) investigations of the material have shown that in a pO_2

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Table 1
List of processes which can potentially benefit from the addition of controlled amounts of oxygen.

Process	Process characteristic of oxygen addition
OWGS	In the presence of a suitable catalyst, a small amount of O_2 co-fed with the WGS feed can selectively improve the conversion of CO whilst maintaining a high yield of H_2 in the product stream [1,2]
ATR	Partially combusts methane to provide the heat required for the otherwise endothermic methane reforming [3].
Claus process	Oxygen used to convert H_2S to SO_2 and water which can be further processed to allow recovery of sulfur and removal of acid gas from exhaust streams [4,5]
Ammonia synthesis	Oxygen enrichment can be used to control the nitrogen to hydrogen ratio during ammonia synthesis, improving the efficiency of the reactor [7]
Oxy-fuel combustion	Combustion of fuel in a stream of CO_2 and O_2 instead of air can produce a CO_2-rich exhaust that can be easily captured with minimal gas separation and treatment [6]

of 1 bar the material undergoes complex crystallographic changes, namely a transition from a hexagonal to an orthorhombic space group upon oxygen incorporation at 300 °C. Further heating of the sample to temperatures above 400 °C returns the original hexagonal structure [22]. The oxygen storage capacity of this material is one of the highest among non-stoichiometric materials investigated so far, approximately 3.5% by weight (equal to a change in δ of 1.5) [23]. Furthermore, as the operating temperature of the material is only ~400 °C, much lower than its synthesis temperatures of 1200 °C, it is likely that $YBaCo_4O_{7+\delta}$ would be less prone to further thermal sintering during operation. Whilst the potential of $YBaCo_4O_{7+\delta}$ for oxygen separation has been demonstrated qualitatively, no detailed study of how the release of oxygen from the material changes in different pO_2's has been conducted.

In this work, a feasibility study was conducted to demonstrate how $YBaCo_4O_{7+\delta}$ could be used for oxygen enrichment processes. This work aims to find suitable operating conditions for both oxygen incorporation and release, in order to demonstrate the ability of this material to incorporate oxygen from air (pO_2 of 0.21 bar) and to release this oxygen at a higher pO_2 of 0.31 bar over reasonable timescales, using a small temperature swing to create a driving force. Additionally, the material stability in various reactive gases is investigated to elucidate for which oxygen enrichment processes this material may be suitable.

2. Experimental

2.1. Sample synthesis

Powders of $YBaCo_4O_{7+\delta}$ were produced by a solid state synthesis described in ref. [24]. Stoichiometric amounts of Y_2O_3, Co_3O_4 and $BaCO_3$ (Sigma Aldrich, 99.99, 99.7 and 99% + purity respectively) were ground together by mortar and pestle and underwent a two stage calcination in air with intermittent grinding. The first calcination step occurred at 1000 °C and lasted 12 h and the second calcination was performed at 1200 °C for 12 h with the sample cooled to room temperature in-between. A heating and cooling rate of 1 °C/min between room temperature and the target temperature was used for both steps.

2.2. Sample characterisation

X-ray powder diffraction (XRD) of the as-synthesised and used material was performed at ambient conditions with a Panalytical X'Pert Pro diffractometer using CuKα radiation (40 kV, 40 mA) for 2θ between 10 and 90° with a step size of 0.033°. EDX analysis of samples was conducted using a Rontec Quantax unit.

Thermogravimetric analysis (TGA) of the material was conducted using a Rubotherm dynTHERM unit. The gas molar flow rates of all TGA experiments were regulated at 8.8×10^{-3} mol/min with Brooks mass flow controllers and a sample of particles with mass between 200 and 400 mg and size between 80 and 160 μm was used for each experiment. For each experiment, the sample was pre-treated by heating in helium (BOC, 99.995% purity) to 500 °C and dwelling for 4 h to achieve a stable final mass (δ change < 0.001 over 1 h), corresponding to $\delta = 0$ according to other studies [25], and subsequently cooled to the required starting temperature.

Two types of TGA experiments were conducted in this work: temperature programmed reactions (TPR) in a constant atmosphere, and oxygen cycling experiments.

To investigate the stability of the material in CO, H_2 and CO_2, TPR experiments were performed in 5 mol% CO in He, 5 mol% H_2 in He and 50 mol% CO_2 in He respectively (provided by BOC), from 100 to 500 °C (800 °C in the case of CO_2) with a heating rate of 1 °C/min.

To determine the effect of pO_2 on the temperature at which oxygen release begins, a set of experiments were conducted where the pre-treated samples were first exposed to different pO_2's ranging from 0.05 to 0.42 bar at 300 °C for 10 h, followed by step changes in temperature in 5 °C increments up to 430 °C, allowing for 1 h between each change.

Oxygen cycling experiments were conducted in order to measure the rate of incorporation and release of oxygen as a function of temperature. During these experiments, after the sample underwent the helium pre-treatment, the sample was cooled in helium to the required starting temperature. Once the required starting temperature, between 280 and 370 °C, was reached, the gas environment was switched from helium to the required pO_2 where the material was allowed to dwell for 1 h for oxidation. After oxidation the gas environment was switched to helium and held for another hour to release oxygen from the sample.

To fully demonstrate the potential of the material for oxygen enrichment, a sample of $YBaCo_4O_{7+\delta}$ was allowed to dwell for 2 h in an air stream ($pO_2 = 0.21$ bar) at 310 °C to incorporate oxygen before a temperature swing in a pO_2 of 0.31 bar was used to release this incorporated oxygen. During this oxygen release step, the sample was heated at a rate of 20 °C/min to 430 °C, starting at the same time as the gas switch and allowed to dwell isothermally for 54 min, before rapidly cooling to the starting temperature of 310 °C.

The stability of the material in water vapour was also examined by exposing 1 g of the material in a packed bed (internal diameter 5 mm) to a pH_2O of 0.05 bar, balanced in Ar (99.995% purity) at 450 °C for 3 h, with a flow rate of 2×10^{-3} mol/min controlled by Brooks mass flow controllers.

3. Results and discussion

3.1. Material stability

The results of several TPRs of $YBaCo_4O_{7+\delta}$ in common reactive gases found in an exhaust stream from a potential oxy-fuel combustion process are shown in Fig. 1.

It can be seen from Fig. 1(a) that during TPR with $pCO = 0.05$ bar, the sample maintained a constant mass until approximately 250 °C, after which a small weight gain of approximately 0.1% was observed. This gain was attributed to carbon deposition on the material via the Boudouard reaction and was confirmed by EDX measurements which showed an increased carbon loading on the material compared to fresh powder. Between 350 °C and 500 °C, the sample mass decreased slightly to 99.6% of the initial mass, most likely due to the reduction of the material by CO. The insert in Fig. 1(a) compares XRD patterns of a