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Geochimica et Cosmochimica Acta 159 (2015) 220–230

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

The reduction and oxidation of ceria: A natural abundance triple oxygen isotope perspective

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Received 16 March 2014; accepted in revised form 30 March 2015; Available online 6 April 2015

Abstract

Ceria (CeO_2) is a heavily studied material in catalytic chemistry for use as an oxygen storage medium, oxygen partial pressure regulator, fuel additive, and for the production of syngas, among other applications. Ceria powders are readily reduced and lose structural oxygen when subjected to low pO_2 and/or high temperature conditions. Such dis-stoichiometric ceria can then re-oxidize under higher pO_2 and/or lower temperature by incorporating new oxygen into the previously formed oxygen site vacancies. Despite extensive studies on ceria, the mechanisms for oxygen adsorption–desorption, dissociation–association, and diffusion of oxygen species on ceria surface and within the crystal structure are not well known. We predict that a large kinetic oxygen isotope effect should accompany the release and incorporation of ceria oxygen. As the first attempt to determine the existence and the degree of the isotope effect, this study focuses on a set of simple room-temperature re-oxidation experiments that are also relevant to a laboratory procedure using ceria to measure the triple oxygen isotope composition of CO_2.

Triple-oxygen-isotope labeled ceria powders are heated at 700 °C and cooled under vacuum prior to exposure to air. By combining results from independent experimental sets with different initial oxygen isotope labels and using a combined mass-balance and triangulation approach, we have determined the isotope fractionation factors for both high temperature reduction in vacuum ($\leqslant 10^{-4}$ mbar) and room temperature re-oxidation in air. Results indicate that there is a 1.5‰ ± 0.8‰ increase in the $\delta^{18}O$ value of ceria after being heated in vacuum at 700 °C for 1 h. When the vacuum is broken at room temperature, the previously heated ceria incorporates 3–19% of its final structural oxygen from air, with a $\delta^{18}O$ value of $2.1^{+7.7}_{-4.1}$‰ for the incorporated oxygen. The substantial incorporation of oxygen from air supports that oxygen mobility is high in vacancy-rich ceria during re-oxidation at room temperature. The quantified oxygen isotope fractionation factors are consistent with the direct involvement of O_2 in the rate limiting step for ceria reoxidation in air at room temperature. While additional parameters may reduce some of the uncertainties in our approach, this study demonstrates that isotope effects can be an encouraging tool for studying oxygen transport kinetics in ceria and other oxides. In addition, our finding warns of the special cares and limits in using ceria as an exchange medium for laboratory triple oxygen isotope analysis of CO_2 or other oxygen-bearing gases.

1. INTRODUCTION

Ceria (CeO_2) is a fluorite-type oxide that has been studied and used extensively as an oxygen storage medium in three-way catalysts (Trovarelli et al., 1999), as an oxygen partial pressure regulator (Laachir et al., 1991; Perrichon et al., 1994; Trovarelli et al., 2001), as a fuel additive for the reduction of soot (Lahaye et al., 1996), for the removal of organics from wastewater (Matatov-Meytal and Sheintuch, 1998), and as a fluid cracking catalyst (Trovarelli et al., 1999). In addition, ceria is used in solid oxide fuel cells (SOFCs) (Chueh, 2011) and has shown potential for the production of syn-gas from water and

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http://dx.doi.org/10.1016/j.gca.2015.03.030

CO_2 (Chueh et al., 2010; Chueh and Haile, 2010). It has been known for over half a century that exposing ceria to low pO_2 and/or high temperature conditions will partially reduce ceria (Bevan, 1955; Bevan and Kordis, 1964). At temperatures above 626 °C, ceria can undergo thermal decomposition to a more reduced state (Paparazzo et al., 1991). In addition, storage under ultra-high vacuum conditions is known to induce the formation of oxygen site vacancies (Zhang et al., 2004). Oxygen vacancies in ceria are thought to be dominantly in the form of anion site Frenkel defects created through the generalized reaction:

$$O_o \rightarrow V_o^{\cdot\cdot} + O_i'' \tag{1}$$

where O_o is an oxygen atom in an oxygen site, $V_o^{\cdot\cdot}$ is a positively charged vacancy in the oxygen sub-lattice, and O_i'' is a negatively charged interstitial oxygen atom (Walsh et al., 2011). The key to ceria's behavior is a ready conversion between the Ce^{4+} and Ce^{3+} oxidation states (Perrichon et al., 1994; Demoulin et al., 2007; Graciani et al., 2011). To maintain overall electroneutrality, each newly formed oxygen vacancy and loss of an oxygen atom is balanced by the reduction of two Ce^{4+} atoms to Ce^{3+} (Chueh, 2011).

$$2Ce_{Ce} + O_o \leftrightarrow 2Ce'_{Ce} + V_o^{\cdot\cdot} + \frac{1}{2}O_{2(g)} \tag{2}$$

When exposed to a lower temperature and/or higher pO_2 environments, partially reduced ceria will re-oxidize and fill its oxygen vacancies (Perrichon et al., 1994). When the oxidants are H_2O or CO_2, H_2 or CO will be generated, respectively (Sharma et al., 2000; Singh and Hegde, 2010). This remarkable redox reversibility has resulted in ceria being one of the most useful and studied oxide materials.

Multiple kinetic steps have been proposed for the dynamic redox processes involving ceria or mixed ceric oxides and gaseous O_2 or CO_2 (Holmgren and Andersson, 1998; Holmgren et al., 1999; Madier et al., 1999; Galdikas et al., 2004; Duprez, 2006; Sadovskaya et al., 2007). Two key sets of kinetic steps involved in the reduction and re-oxidation of ceria are: (1) dissociative adsorption and associative desorption of the oxygen-bearing oxidant molecule (commonly O_2) on the ceria surface, and (2) diffusion of atomic oxygen within the bulk structure of ceria through a vacancy hopping mechanism (Fig. 1). At higher temperatures, surface reactions are believed to be much slower than bulk oxygen diffusion and are therefore thought to be the rate limiting steps (Holmgren et al., 1999; Duprez, 2006; Chueh and Haile, 2010; Chueh, 2011).

Studies on oxygen transport kinetics between ceria or mixed ceric oxides and O_2 or CO_2 have been conducted for decades. The methods employed include (1) stable oxygen isotope labeling with either subsequent depth profiling and imaging of ^{18}O tracer diffusion in oxides by Secondary Ion Mass Spectrometry (SIMS) (Manning et al., 1997; Lane and Kilner, 2000; Fielitz and Borchardt, 2001; Perkins et al., 2001; Yashiro et al., 2002; De Souza et al., 2005; Kilner et al., 2011; Salazar-Villalpando, 2012) or by subsequent isotope analysis of the evolving O-bearing gases (Gorelov and Kurumchin, 1987; Madier et al., 1999; Cunningham et al., 1999a,b; Dong et al., 2004; Bedrane et al., 2005; Duprez, 2006; Bouwmeester et al., 2009; Anan'ev et al., 2012), (2) measuring electrical and ionic conductivity (Park and Choi, 2008; Waldhausl et al., 2012; Wang et al., 2012), and (3) gravimetric methods (Katsuki et al., 2002; Stan et al., 2004). The different methods have their own merits. Even within the oxygen isotope labeling approach, gas-phase analysis has a purported advantage over depth profiling because it offers mechanistic information on oxygen exchange at the oxide surface (Bouwmeester et al., 2009; Anan'ev et al., 2012).

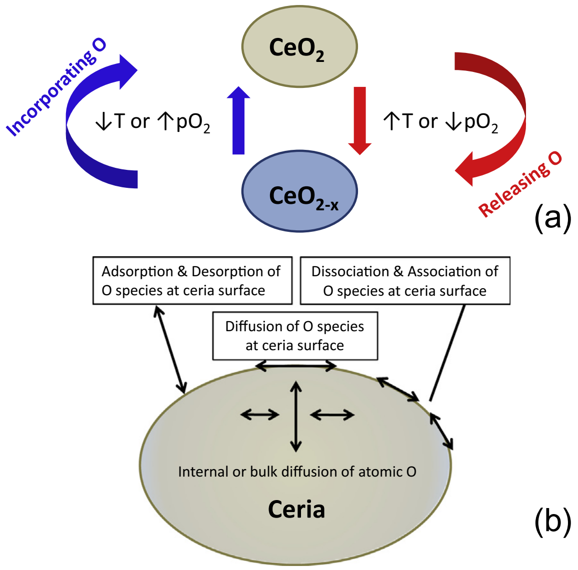

Fig. 1. (a) Ceria redox cycle and (b) potential kinetic steps involved.

Thus far, the stable isotope studies on oxygen transport kinetics involve the use of a highly enriched ^{18}O or ^{17}O tracer (Klier et al., 1963). In these studies isotope fractionation or "the isotope effect" is ignored. The present study, however, examines the degree and sign of these small enrichments during the redox cycling of ceria. The isotope effect has the potential to reveal reaction mechanisms at a quantum chemical level, providing independent mechanistic insights that an enriched ^{18}O tracer often cannot reveal. In this study, we focus on a simple set of room-temperature re-oxidation (RTRO) experiments starting with triple-oxygen-isotope labeled ceria powders. Combining the results from independent sets of experiments with different initial oxygen isotope labels and applying a combined mass-balance and triangulation approach, we have determined the fraction of new oxygen being incorporated as well as the apparent non-equilibrium isotope fractionation factors for both the reduction and re-oxidation of ceria. Our study is the first to quantify oxygen isotope effects for the redox processes of ceria. The isotope effect, as is determined here, can act as a guidepost for future exploration of isotope effects for oxygen transport in ceria and diverse mixed oxides.

Here we specifically focus on ceria's reduction at 700 °C and re-oxidation at room temperature (i.e. 22 °C), a temperature much lower than that used in most previous experimental studies on ceria–gas interactions.