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Oxygen exchange reaction kinetics for cerium(IV) oxide at 1000 °C

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ABSTRACT

Bulk oxygen exchange rate kinetics on CeO_2 at 1000 °C were observed to have a first order dependence on the fraction of reaction remaining and to be independent of oxygen partial pressure, total pressure, particle size, and specific surface area. This suggests that the exchange reaction is dominated by an internal chemical reaction that is occurring throughout the bulk of the material, and not at the material surface. Oxygen exchange rates were limited by this internal chemical reaction for all CeO_2 powders studied (15 nm to −325 mesh), and had a rate constant of $1.19 \times 10^{-2}\ s^{-1}$ with a time to completion of 617 s. These results are similar to the exchange rates observed previously on PuO_2, suggesting that oxygen exchange on PuO_2 may also be dominated by an internal chemical reaction under similar conditions. This work will help guide future experiments on $^{238}PuO_2$ oxygen exchange reactions.

1. Introduction

Radioisotope power systems (RPS) employed in space exploration utilize the heat generated by the radioactive decay of ^{238}Pu to generate electricity using various forms of energy conversion technology. Unfortunately, the heat generating α radiation produced by ^{238}Pu undergoes an (α,n) reaction with the naturally occurring ^{17}O and ^{18}O isotopes present in the currently used PuO_2 fuel form. This (α,n) reaction is the primary cause of the increase in neutron emission rate (NER) from ~2600 n s^{-1} g^{-1} for ^{238}Pu metal [1] to 15,000–20,000 for $^{238}PuO_2$ [2,3]. Elevated NER is a significant concern for worker dose rates as well as its impact on spacecraft components and scientific instrumentation. Performing an isotopic exchange reaction between $^{17}O/^{18}O$ and ^{16}O helps minimize the NER and provide a safer working environment for both the people and the spacecraft involved in any RPS project [2–6].

^{16}O exchange reactions have been successfully performed on PuO_2 using both oxygen gas [2–4] and H_2O[5] depleted in ^{17}O and ^{18}O at temperatures ranging between 700 and 1550 °C, but only a limited understanding of the kinetics and reaction mechanisms were obtained from these early works. Critical kinetic, thermodynamic, and mechanistic information was not obtained in these previous studies, such as: dependence on gas composition and partial pressures, the effect of particle characteristics, and whether the rate is limited by a chemical reaction or diffusion. A more complete understanding of the isotopic exchange reaction is necessary to help users of PuO_2 adapt to processing changes and understand currently unexplained phenomena without the need for extensive developmental work. Water has been observed to undergo a reaction with PuO_2 to produce a superstoichiometric form of plutonium dioxide [7,8], and this superstoichiometric form may be responsible for the production of strong gaseous oxidizing agents which may chemically react with nearby materials in RPS systems. [8,9] Considering the potential detrimental effects of the superstoichiometric form of PuO_2 generated via exposure to water, this report will focus on the exchange reaction using oxygen gas.

Given the hazards and costs associated with Pu experimentation, it makes sense to perform initial studies on CeO_2, which is a common cold surrogate for PuO_2, because of its highly similar structural and chemical properties [10]. The bulk oxygen isotopic exchange process, as opposed to just the surface exchange reaction, has been studied at lower temperatures (350–520 °C) on pure CeO_2, [11–14] and at higher temperatures (up to 1000 °C) for 10–31% Gd doped CeO_2 [15–17]. Unfortunately, there do not appear to be any studies on the bulk oxygen exchange for pure CeO_2 at temperatures above 520 °C, and oxygen exchange reactions on Gd doped CeO_2 show that the doping causes a significant change in the rate constant [14,15]. This suggests that high temperature studies on Gd doped CeO_2 may not be representative of the exchange mechanism for pure CeO_2 or, subsequently, PuO_2. Additionally, studies on Gd doped CeO_2 concluded that the rate limiting step in the exchange mechanism changes above 700 °C [15], suggesting that lower temperature studies on

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CeO_2 may not be representative of the exchange mechanism above ~700 °C. Since rapid and complete PuO_2 isotopic oxygen exchange is desired for practical purposes, previous oxygen exchange studies on PuO_2 have always been performed at temperatures ≥700 °C [3–6]. Thus, studying the oxygen exchange on pure CeO_2 at temperatures above 700 °C is necessary for these surrogate experiments to properly correlate to the conditions utilized for $^{238}PuO_2$ processing.

Understanding the high temperature mobility of oxygen in pure CeO_2 will also likely be of interest to several other fields of study including catalytic surfaces and solid oxide fuel cells [18,19]. Isotopic oxygen exchange is one technique that is used to help better understand the kinetics and thermodynamics of oxygen mobility in CeO_2. Since we are unaware of any previous studies that obtained isotopic oxygen exchange kinetics at temperatures >700 °C on pure CeO_2, this work will help expand the knowledge base of these fields regarding the behavior of pure CeO_2 at high temperatures.

This report will study how sample size, oxygen partial pressure, total pressure, oxygen isotope, specific surface area, and the addition of an inert gas affects the rate of the isotopic oxygen exchange reaction between CeO_2 and oxygen gas at 1000 °C by continuously monitoring the composition of the gas phase in a sealed reaction tube using a quadrupole residual gas analyzer (RGA). 1000 °C was chosen because this should produce a rapid isotopic exchange rate while remaining significantly below the temperature where initial phase sintering is expected to occur (i.e. ~half the melting point, or 1200 °C). ^{18}O was chosen as the primary exchange material because enriched ^{18}O gas is readily available commercially and better analytical results can be obtained from ^{18}O because of the very high natural abundance of ^{16}O (~99.7%) found in commercial CeO_2. From these experiments it will be possible to obtain a better understanding of the rate laws governing the oxygen isotopic exchange reaction with CeO_2. This data will then be compared to oxygen isotopic exchange data for PuO_2 in the literature. Results from this work will help better inform future oxygen exchange experimentation on PuO_2.

2. Materials and methods

2.1. Instrumentation

Fig. 1A presents a schematic of the apparatus used to perform the oxygen exchange reactions. Stainless steel tubing and compression fittings were used to assemble the various components of the apparatus. A 0.25% accuracy pressure gauge (Ashcroft, Stratford, CT) was used to measure the system pressure. 51 mm o.d. fused silica reaction tubes (United Silica, Franklin, NJ) were sealed using a silicone o-ring based stainless steel compression flange with two ports that acted as the inlet and outlet for the reagent gases. The flange had two 2.4 mm holes drilled through it to allow an Inconel 718 sheathed Type-K thermocouple and a 1.6 mm by 0.18 mm i.d. stainless steel sampling line to be brought into the reaction tube. These holes were sealed using a low outgassing ($<1\times10^{-9}$ Torr) vacuum epoxy. A bench-top sized fan was used to cool the reaction tube flange to below 60 °C to prevent thermal damage to the silicone o-rings and the epoxy seals. The thermocouple was attached to an in-house constructed temperature controller which powered the furnace. A metering valve rated for shut-off service was attached to the sampling line to limit the flow into the vacuum chamber that housed the Extorr XT200M RGA (New Kensington, PA). The metering valve was adjusted until the analytical sampling delay between the RGA and the reaction tube was between 30 and 40 s. This flow rate resulted in <3% drop in total pressure during each hour of operation.

During the operation of the apparatus presented in Fig. 1A, significant quantities of oxygen were brought into the vacuum chamber and RGA, resulting in significant oxidation of the RGA filament, ionizer, and quadrupole. Fortunately, since this work performs all of its calculations using relative quantities, the reduction in sensitivity caused by this oxidation did not affect the analytical results. However, in order to minimize this damage during future experimentation, the instrument was redesigned as shown Fig. 1B. Replacement filaments and ionizers were obtained for experiments using Fig. 1B design and the quadrupole was cleaned using factory recommended procedures. Considering the similarities between the designs, only the major differences in Fig. 1B will be discussed. First, the fused silica tube (also United Silica) used was 25 mm o.d. and open on both ends, requiring two silicone o-ring based compression flanges and allowing the gas inlet to be moved to the opposite end of the tube from the outlet and sampling lines. Second, a flow splitter was added with a 200 μm pinhole/restriction to reduce the amount of gas entering the RGA/high vacuum chamber. Heating tape, operated at ~400 °C, was used on the inlet side of the tube primarily to keep more of the tube at elevated temperatures and minimize the number of moles of ^{18}O used to obtain the necessary pressures. The outlet side of the tube was not heated in order to maintain minimal flow through the metering valve. A flow controller with a bypass was added for potential future experiments, but was not utilized here. This improved design significantly increased the sampling delay (~90 s) and required an increase in the pressure drop over an experiment (~6% per hour), but did not alter the analytical results. Experiments performed on Fig. 1A design produced results that were similar to Fig. 1B design, therefore we will not differentiate between designs when discussing the experimental results (see Supplemental information).

2.2. Reagents

Powdered CeO_2 samples with nominal particle sizes of 15–30 nm and 70–100 nm were obtained from Alfa Aesar (Ward Hill, MA), while a <5 μm powder was obtained from Sigma-Aldrich (St. Louis, MO) and a −325 mesh powder was obtained from Materion (Milwaukee, WI). Sintered CeO_2 pellets (9 mm diameter by 5 mm thick) were also obtained from Alfa Aesar. All CeO_2 was a minimum 99.5% purity. The density of the sintered pellets was measured to be 96% of the theoretical density using the Archimedes method (assuming a theoretical density of 7.21 g cm^{-3}). Grain sizes in the sintered pellets were measured using ASTM E112-10. Grain sizes in the powder samples were determined visually using transmission electron microscopy (TEM). Specific surface area (a_s) and particle size distribution data was obtained from a commercial laboratory, Particle Technology Labs (Downers Grove, IL) who used a 3-point BET (a_s) and laser diffraction analysis (particle size distribution). Both 99.8% and 50% isotopically purified ^{18}O gases were obtained from Isotech, Inc. (Miamisburg, OH). The 50% ^{18}O purified gas was packaged as a 1:4 mixture with N_2 to minimize pure oxygen safety concerns while the 99.8% purity gas was unmixed. Helium, Argon, Neon, and Ultra Zero Air were obtained from AirGas (Radnor, PA) with the noble gases being ultra-high purity grade. Ultra Zero is a high purity grade of synthetic air that contains only N_2 and O_2 in natural isotopic abundances.

2.3. Procedure

A known mass of CeO_2 was placed into a high purity alumina boat with a target of ~20 mg unless stated otherwise. The alumina