



Synthesis and full characterization of the phase-pure pyrochlore $\text{Ce}_2\text{Zr}_2\text{O}_7$ and the $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$ phases



Sven Urban^a, Paolo Dolcet^b, Maren Möller^a, Limei Chen^c, Peter J. Klar^c, Igor Djerdj^d, Silvia Gross^b, Bernd M. Smarsly^{a,*}, Herbert Over^{a,*}

^a Physikalisch-Chemisches Institut, Justus-Liebig-University, Heinrich-Buff-Ring 17, 35392 Giessen, Germany

^b Istituto per l'Energetica e le Interfasi, IENI-CNR, Dipartimento di Scienze Chimiche, Università degli Studi di Padova, via Francesco Marzolo, 1, I-35131 Padova, Italy

^c I. Physikalisches Institut, Justus Liebig University, Heinrich-Buff-Ring 16, 35392 Giessen, Germany

^d Department of Chemistry, J. J. Strossmayer University of Osijek, Ulica cara Hadrijana 8/a, HR-31000 Osijek, Croatia

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ABSTRACT

The $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$ phase has been synthesized starting from $t\text{-Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ solid solution which is reduced by hydrogen at high temperatures to form the pyrochlore $\text{Ce}_2\text{Zr}_2\text{O}_7$ phase ($\text{pyr-Ce}_2\text{Zr}_2\text{O}_7$) with high degree of ordering of the cationic sublattice. The final step in the synthesis of the $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$ phase includes a mild re-oxidation of $\text{pyr-Ce}_2\text{Zr}_2\text{O}_7$ at around 600 °C under atmospheric conditions. Yet, the synthesis of phase-pure $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$ phase (phase-pure and with highest ordering) is still not settled since most of the previous studies used reduction temperatures of 1300 °C and below. We show in this contribution that 1300 °C is not sufficient to warrant the preparation of phase-pure $\text{pyr-Ce}_2\text{Zr}_2\text{O}_7$ and $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$, but that rather temperatures as high as 1500 °C are required to assure phase purity of both phases. This conclusion is drawn from extended X-ray diffraction and X-ray absorption spectroscopy analyses together with Raman spectroscopy, providing in-depth details of the structure on the level of both, the evolution of the special periodic structure and the coordination of the metal atoms.

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1. Introduction

CeO_2 -based materials are employed in a variety of different applications in catalysis [1] acting as carrier for the active metal particles, as oxygen storage co-catalysts in exhaust gas post-treatment in automobiles, or even as a catalytically active component (with no noble metals being involved) such as in the catalyzed HCl oxidation reaction (Deacon reaction) [2–4]. One of the main challenges of CeO_2 -based materials in automotive catalysts is to balance the oxygen supply in the exhaust gas stream between lean and rich operation of the engine by buffering and releasing oxygen, respectively. This oxygen exchange of CeO_2 is best described by the so-called “oxygen storage capacity” (OSC). To further improve the thermal stability and the textural [5–7] as well as redox properties [8,9] of CeO_2 -based materials without deteriorating the OSC, $t\text{-Ce}_{1-x}\text{Zr}_x\text{O}_2$ solid solutions are employed in automotive catalysis [10]. It has been demonstrated that $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ solid solutions are also chemically much more stable against in-depth chlorination

than pure CeO_2 in the HCl oxidation. The solid solutions $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ are shown to be both catalytically active and chemically stable over a wide concentration range of Ce from 20 at.-% to 80 at.-% [11,12]. Solid solutions $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ are also used in other oxidation reactions [13].

In previous years, it was reported that the OSC can be dramatically enhanced by transforming a $t\text{-Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ solid solution featuring a statistical distribution of Zr and Ce atoms into a crystalline structure possessing an ordered cation sublattice, the so-called “kappa phase” $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$ [14–20]. The $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$ phase contains an ordered array of cations, and 1/8 of the oxygen anions can readily be removed leading to an extraordinarily high OSC. The $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$ phase has demonstrated high catalytic activity in the combustion of chlorinated compounds [21,22] due to the improved OSC properties.

In general, the $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$ phase is synthesized starting from $t\text{-Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ solid solution which is reduced by hydrogen at high temperatures to form the pyrochlore $\text{Ce}_2\text{Zr}_2\text{O}_7$ phase ($\text{pyr-Ce}_2\text{Zr}_2\text{O}_7$). In this way oxygen vacancies are generated, which facilitate the mobility of the cations and therefore the ordering of the cationic sublattice. The synthesis of $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$ is achieved by a mild re-oxidation of $\text{pyr-Ce}_2\text{Zr}_2\text{O}_7$ at 600 °C under atmospheric conditions.

* Corresponding authors.

E-mail addresses: Bernd.Smarsly@phys.Chemie.uni-giessen.de (B.M. Smarsly), Herbert.Over@phys.Chemie.uni-giessen.de (H. Over).

In literature most of the studies employed reduction temperatures of 1300 °C and below for the synthesis of the *pyr*-Ce₂Zr₂O₇ phase [17,23–28]. Hence, the single steps in the synthesis of κ -Ce₂Zr₂O₈ seem to be straightforward and well established. However, the reduction of *t*-Ce_{0.5}Zr_{0.5}O₂ at quite elevated temperatures represents a critical issue. In this contribution we will report on the synthesis of the κ -Ce₂Zr₂O₈ phase by varying the reduction temperature from 1300 °C to 1500 °C at which the *t*-Ce_{0.5}Zr_{0.5}O₂ solid solution is chemically reduced by hydrogen to form *pyr*-Ce₂Zr₂O₇. The structural evolution resulting in the pyrochlore and kappa phases (*pyr*-Ce₂Zr₂O₇ and κ -Ce₂Zr₂O₈, respectively) is subjected to in-depth characterization, employing a variety of different experimental techniques, including X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS) and Raman spectroscopy. We show as a main outcome of these studies that reduction at 1300 °C is not sufficient to produce phase-pure *pyr*-Ce₂Zr₂O₇ and κ -Ce₂Zr₂O₈, rather reduction temperatures as high as 1500 °C are required.

2. Experimental

2.1. Synthesis

For the preparation of the *t*-Ce_{0.5}Zr_{0.5}O₂ solid solution, 2.5 mmol Ce(NO₃)₃·6H₂O and 2.5 mmol Zr(NO₃)₂·xH₂O were dissolved in 40 mL H₂O, using an ultrasonic bath (60 °C, 240 W power, 37 Hz) for 120 min and shaking it every 30 min to stir up the sediment. We added 30 ml of glacial acetic acid to the slightly opaque solution, and treated this solution in an ultrasonic bath (60 °C, 240 W power, 37 Hz) for 60 min. The solution was then heated in an open beaker at 130 °C for 24 h, resulting in a xerogel-like foam. After grinding the sample and heating up to 500 °C for 4 h (heating rate 3 K min⁻¹ in air) in a ceramic crucible with a non-airtight cover, we obtained a faint yellow/white powder of *t*-Ce_{0.5}Zr_{0.5}O₂ (cf. Fig. 1, top left).

t-Ce_{0.5}Zr_{0.5}O₂ was then reduced by hydrogen at various high temperatures (1300, 1400, or 1500 °C). In this way oxygen vacancies were generated, which promoted the mobility of cations and thus the ordering of the cationic sublattice [17,23–26]. This ordering of the cationic sublattice has been visualized in a previous high resolution TEM (transmission electron microscopy) study employing atomic-resolved chemical mapping. [27] The resulting so-called pyrochlore phase *pyr*-Ce₂Zr₂O_{7+δ} was a black powder (cf. Fig. 1, top center). The synthesis of the κ -Ce₂Zr₂O₈ phase was based on a mild re-oxidation of pyrochlore phase Ce₂Zr₂O_{7+δ} at 600 °C under ambient atmosphere, yielding a yellow powder (cf. Fig. 1, top right). Using TEM it could be proven that the ordered cation arrangement is maintained after mild oxidation up to 600 °C [28]. In Fig. 1 the temperature protocol and the used composition of the reaction feeds are summarized.

The main drawback of this high temperature synthesis route (1500 °C) is the sintering of the material, resulting in an active surface area of below 1 m² g⁻¹. The SEM image (cf. Fig. 2) nicely shows that the grains possess sizes in the sub-micrometer range,

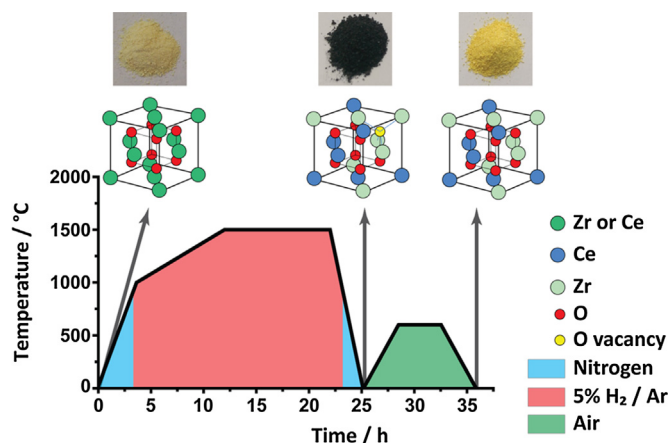


Fig. 1. Temperature profile and reaction conditions for the synthesis of the κ -Ce₂Zr₂O₈ phase. The starting material is a solid solution (almost white powder) *t*-Ce_{0.5}Zr_{0.5}O₂, possessing a statistical spatial distribution of Zr and Ce. High-temperature reduction at 1300, 1400, 1500 °C in 5% H₂/Ar (noxal) leads to black powder. Up to 800 °C heating was performed under nitrogen atmosphere and subsequently switched to noxal. As temperature ramp we used 4.5 K min⁻¹ up to 1000 °C and subsequently a temperature ramp of 1 K min⁻¹ was applied. The final temperature of either 1300, 1400, or 1500 °C was kept for 10 h before cooling the sample down to room temperature. The resulting pyrochlore phase is mildly re-oxidized at 600 °C in air for 4 h leading to the desired κ -Ce₂Zr₂O₈ phase. Shown are also the reduced unit cells of *t*-Ce_{0.5}Zr_{0.5}O₂, *pyr*-Ce₂Zr₂O_{7+δ} and κ -Ce₂Zr₂O₈. Actually, the unit cells of the pyrochlore and κ -Ce₂Zr₂O₈ are twice as large in all three directions compared to the tetragonal starting phase. The unit cells shown are adopted from Ref. [9].

thus being compatible with the small active surface area. At lower reduction temperatures of 1000 °C, the active surface area of the resulting κ -Ce₂Zr₂O₈ phase (not phase-pure as shown later) can be maintained to be 20–40 m² g⁻¹ [29].

2.2. Characterization

2.2.1. X-ray diffraction

X-ray diffraction measurements were performed on a PANalytical Empyrean diffractometer with a Cu K α X-ray source (1.54060 Å, Ni filter for filtering the Cu K β -radiation). The Rietveld refinement of powder XRD patterns has been performed using the software FULLPROF. The modified Thompson-Cox-Hastings pseudo-Voigt method, which is known to allow for facile size analysis, was chosen as profile function. In this approach, we assumed that line broadening of the deconvoluted profile is a result of the small crystallite size and lattice microstrain. The values of the half-width parameters, V, W, and X, were kept constant at values determined by using LaB₆. The quality of the refinement was assessed by the values of the discrepancy factor (profile weighted residual error), R_{wp}, and the goodness-of-fit, χ^2 .

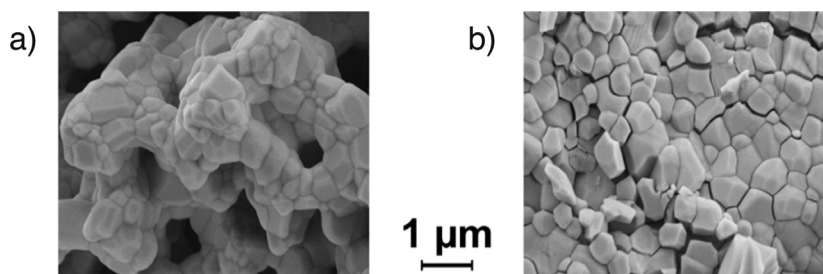


Fig. 2. Scanning electron microscopy (SEM) images of the pyrochlore phase *pyr*-Ce₂Zr₂O₇ (left) and the κ -Ce₂Zr₂O₈ phase (right) when the solid solution *t*-Ce_{0.5}Zr_{0.5}O₂, possessing a statistical spatial distribution of Zr and Ce is reduced at 1500 °C in 5% H₂/Ar (noxal).

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