



## Kinetics of hydrogen activation on ceria–zirconia



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### ARTICLE INFO

#### Article history:

Received 12 March 2015

Revised 4 May 2015

Accepted 26 May 2015

Available online 20 June 2015

#### Keywords:

Deuterium

Isotopic exchange

Hydrogenation

Dissociative adsorption

Hydrodeoxygenation

Oxygen storage capacity

### ABSTRACT

Ceria–zirconias are popular catalysts and supports for metal particles. Even without supported metal particles, these materials are active for hydrogenation and hydrodeoxygenation reactions, where oxygen vacancies serve as the active site. To gain a detailed understanding of the ability of ceria-based catalysts to dissociatively adsorb hydrogen, H<sub>2</sub>–D<sub>2</sub> exchange is studied as a test reaction. The density of exchangeable hydrogen per surface area approaches the values for typical metal surfaces. Below 250 °C, H<sub>2</sub>–D<sub>2</sub> exchange occurs at oxygen vacancies with an activation energy of ca. 24 kJ mol<sup>−1</sup>. At higher temperatures, additional sites at the edges of ceria–zirconia crystallites contribute to the reaction. The kinetics and the density of active sites for dissociative adsorption of hydrogen are correlated with physicochemical properties of the catalysts. Specifically, the crystallite size has a strong influence on the reactivity of different samples.

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## 1. Introduction

Ceria can be used for a variety of catalytic reactions that involve Lewis acid–base sites, redox sites, or a combination of these functionalities [1]. Acid–base reactions, such as ketonization, can be performed with pure ceria or with ceria supported on metal oxides such as silica or titania [2–4]. In addition to acid–base sites, redox sites are necessary for reactions such as the dehydrogenation of ethylbenzene to produce styrene [1,2]. The facile interconversion between Ce<sup>4+</sup> and Ce<sup>3+</sup> in cerium-based oxides is also leveraged in three-way catalysts for automotive pollution control and fluid catalytic cracking, where the high affinity of ceria to oxygen and sulfur is beneficial [1,2,5,6]. Other applications of pure or supported ceria for redox reactions include selective hydrogenation, oxidation of CO and toluene, as well as catalytic wet oxidation of methane [7–9]. Ceria combined with gadolinium, copper, or yttrium-stabilized zirconia has been extensively studied for alternative solid oxide fuel cells [10–13]. Often, ceria is utilized as a promoter or co-catalyst but not as the component responsible for the primary functionality. Many of these reactions involve supported metals

such as platinum, ruthenium, palladium, gold, nickel, or cobalt as well as a dopant such as zirconia or praseodymia to increase oxygen storage capacity and thermal stability and to promote hydrogen dissociation and spillover [5,7–18].

Pure ceria can also perform reactions with dissociated hydrogen in the absence of reduced metal particles. Selective hydrogenation of propyne to propene was observed on pure ceria at 1 bar and 250 °C [19]. The limiting factor in this reaction was suggested to be the availability of hydrogen on the surface, and the most effective catalyst in this study was oxidized CeO<sub>2</sub> without reductive pretreatment. It was proposed that some surface oxygen vacancies are necessary to stabilize dissociatively adsorbed hydrogen, but too many oxygen vacancies may result in complete hydrogenation of the reactant and reduce selectivity toward the desired product. Adsorbed hydrogen is also necessary for the reduction of ceria and the creation of oxygen vacancies [20]. These sites are relevant in three-way catalysis, where oxygen is removed from NO<sub>x</sub> to produce N<sub>2</sub> and CO<sub>2</sub> [6].

Recently, our group and others showed that oxides with vacancies can catalyze hydrodeoxygenation of biomass-derived oxygenates [21–23]. To design a highly efficient ceria-based catalyst for this reaction, it is important to gain quantitative insight into the amount of reactive hydrogen present on the surface under reaction conditions as well as the kinetics and types of active sites necessary for dissociative adsorption of hydrogen.

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Incorporation of zirconia into ceria is known to increase the oxygen storage capacity and to lower the temperature of surface and bulk reduction because the distortion of the crystal lattice increases the mobility of oxygen ions therein [24,25]. During surface reduction with hydrogen, an oxygen atom is removed from the surface, and water is formed. When oxygen defect sites are present, hydrogen engages in interactions that are not observed without oxygen vacancies [26]. Thus, it is possible that the availability of hydrogen on reduced ceria–zirconia will exceed that on pure ceria in the same environment. Theoretical studies on oxygen vacancies in reduced ceria are not comprehensive, and the added complexity of an additional metal in ceria–zirconia makes computational research much more difficult, resulting in a large deviation between computational and experimental data [27]. In an effort to quantify the density of oxygen vacancies, oxygen uptake has been studied. However, as most studies are motivated by automotive exhaust catalysis, they typically do not contain experiments below 500 °C [17].

The ability of ceria to dissociate hydrogen has been attributed to the strength and concentration of its Lewis acid sites. A study found that ceria was much more active for the hydrogenation of acetylene than  $\text{La}_2\text{O}_3$  due to differences in acidity [6]. It was shown that oxygen vacancies on the surface of ceria have Lewis acidic character [28]. The strength of Lewis acid sites in ceria–zirconia was reported to be between that of pure ceria and pure zirconia [29].

The purpose of this study was to provide a comprehensive picture of hydrogen dissociation on ceria–zirconia catalysts and to elucidate the influence of the composition and structure of these materials on their reactivity. The effects of composition and calcination temperature of the catalysts on their performance are studied. The ability to dissociate hydrogen is described by the activation energies for isotopic hydrogen exchange and the amount of exchangeable hydrogen on the surface of each catalyst. Based on a detailed kinetic study, the presence of different types of sites is established. Temperature-programmed reduction (TPR) and oxygen storage capacity (OSC) measurements are performed to quantify oxygen vacancies that are formed below 450 °C. Finally, infrared spectroscopy is used to probe sites that are contributing to hydrogen exchange activity at different temperatures.

## 2. Experimental

### 2.1. Chemicals

Cerium (III) nitrate hexahydrate (99% trace metals basis), zirconyl (IV) oxynitrate hydrate (99% trace metals basis) and ammonium hydroxide (A.C.S. reagent grade, 28–30%  $\text{NH}_3$  content) were purchased from Sigma Aldrich. Gases (hydrogen, argon, helium and oxygen) with ultra-high purity (UHP Grade 5) were purchased from Airgas. Deuterium was purchased from Cambridge Isotope Laboratories, and the dry air was generated in house using a Parker Balston Gas Generator 1000. Deionized water was obtained from a Barnstead NANOpure ultrapure water system which was purified to 18.2 M $\Omega$ /cm.

### 2.2. Catalyst synthesis

All catalysts were prepared by coprecipitation or precipitation of the precursors [30]. Cerium nitrate hexahydrate and zirconyl nitrate hydrate were dissolved in deionized water to form a 0.1 M solution. The coprecipitation or precipitation was performed by adding the 0.1 M precursor solution drop-wise to an aqueous ammonium hydroxide solution while stirring continuously. The precipitate was filtered, rinsed with deionized water, and dried

in an oven overnight at 100 °C. With one exception, the catalysts were calcined for 4 h in 200 mL  $\text{min}^{-1}$  zero grade air at 500 °C with a heating rate of 5 °C  $\text{min}^{-1}$ . The Ce60-700 sample was calcined for 4 h at 700 °C using the same heating rate and flow rate.

### 2.3. Catalyst characterization

To determine the composition of each catalyst, proton induced X-ray emission (PIXE) analysis was performed by Elemental Analysis Inc. with a 95% confidence interval. Powder X-ray diffraction (XRD) patterns were measured on a Philips X'pert diffractometer equipped with an X'celerator module using  $\text{Cu K}\alpha$  radiation. Diffractograms were obtained for the range  $2\theta = 10\text{--}90^\circ$  with a step size of 0.0083556°. The inter-planar spacing was calculated using the Bragg equation with a wavelength of 1.54 Å. The crystallite size was calculated using the Scherrer equation for the (111), (200), (220) and (311) planes and averaged to reduce the experimental error [31–33]. Nitrogen physisorption was performed on a Micromeritics ASAP 2020 physisorption analyzer. For each sample, a quantity of ca. 0.150 g was degassed under vacuum at 200 °C for 4 h. The Brunauer–Emmet–Teller (BET) surface area was calculated from the adsorption isotherm of nitrogen in the  $0.05 \leq P/P_0 \leq 0.3$  pressure range [34]. Pore volumes were calculated from the adsorption branch using the Barrett–Joyner–Halenda (BJH) method [35]. Temperature programmed reduction (TPR) measurements were performed on a Micromeritics Autochem II 2920 using 0.19 g ( $\pm 0.05$  g) of each catalyst. The catalysts were heated to 450 °C in flowing a 10 vol% oxygen blend (helium balance) at 10 °C  $\text{min}^{-1}$  and held at 450 °C for 60 min before cooling to 0 °C at 15 °C  $\text{min}^{-1}$ . Using a heating rate of 10 °C  $\text{min}^{-1}$ , the catalysts were heated to 1000 °C in a 10 vol% hydrogen blend (argon balance), and the gas exiting the reactor was monitored using a thermal conductivity detector (TCD). A reference experiment with a pure helium flow over ceria–zirconia with a ceria content of 82 mol% was performed to ensure that no desorbing contaminants contributed to the TCD signal over the entire temperature range. Oxygen storage capacity measurements were also performed on a Micromeritics Autochem II 2920 using ca. 0.21 g ( $\pm 0.08$  g) of catalyst. The catalyst was heated to 450 °C while flowing a 10 vol% oxygen blend (helium balance). The sample was held at this temperature for 60 min before being cooled to the analysis temperature of 200, 300, or 450 °C. A 10 vol% hydrogen blend (argon balance) was used to reduce the sample for 30 minutes. The sample temperature was held at 200, 300, or 450 °C for 30 min after which 10 vol%  $\text{O}_2/\text{He}$  was pulsed over the sample until saturation (3 consecutive peaks of approximately equal area).

The acidity of the samples was characterized by adsorption of pyridine followed by IR spectroscopy and temperature-programmed desorption (TPD) of  $\text{NH}_3$ . Pyridine adsorption followed by FTIR spectroscopy was performed using a Nicolet 8700 FTIR spectrometer with an MCT/A detector. The sample was pressed into a self-supported wafer, loaded into a custom built vacuum chamber, and activated at  $<10^{-6}$  mbar and 450 °C. Pyridine was adsorbed after cooling the sample to 150 °C. The cell was evacuated for 30 min before the relevant spectrum was taken. For each spectrum, 128 scans were recorded with a resolution of 4  $\text{cm}^{-1}$ . For TPD of  $\text{NH}_3$ , 50 mg of catalyst held in place by quartz wool inside of a quartz, U-tube reactor and a gas flow rate of 50  $\text{cm}^3 \text{min}^{-1}$  was used. The catalysts were heated in 100%  $\text{H}_2$  to 450 °C at 10 °C  $\text{min}^{-1}$  and held for 60 min and then cooled to 120 °C in  $\text{H}_2$  flow. At 120 °C, the catalysts were purged of  $\text{H}_2$  with He for  $\geq 15$  min, and then  $\text{NH}_3$  adsorption was conducted in 10 mol%  $\text{NH}_3/\text{He}$  for 30 min, prior to purging with He for  $\geq 15$  min. The TPD was performed by ramping in He from 120 °C to 550 °C at 20 °C  $\text{min}^{-1}$ , followed by a 15 min hold. Stainless steel gas lines downstream of the catalyst were heated to 150 °C. An MKS

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