



## Structure and reactivity of ceria–zirconia catalysts for bromine and chlorine production via the oxidation of hydrogen halides



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### ARTICLE INFO

#### Article history:

Received 12 June 2015

Revised 14 August 2015

Accepted 22 August 2015

Available online 27 September 2015

#### Keywords:

Hydrogen halide oxidation

Bromine

Chlorine

CeO<sub>2</sub>–ZrO<sub>2</sub>

Mixed oxide

Prompt-gamma activation analysis

### ABSTRACT

The impact of zirconia on the activity and stability of ceria has been investigated in the gas-phase oxidation of HBr and HCl to the corresponding halogens. Homogeneous and non-homogeneous ceria–zirconia catalysts with a Ce:Zr ratio of 75:25 were prepared and characterized by X-ray diffraction, temperature-programmed reduction in hydrogen, transmission electron microscopy, and X-ray photoelectron spectroscopy. Catalytic tests demonstrated that ZrO<sub>2</sub> promotes the activity of CeO<sub>2</sub> independently of the metal homogeneity in the mixed oxide. Upon cycling of the temperature and feed composition, no differences with respect to chlorine formation were observed. On the other hand, a hysteresis of the reaction rate was measured in HBr oxidation, which was more pronounced over the non-homogeneous mixed oxide due to the higher extent of bromination. A moderate degree of bromination was attained in the homogeneous mixed oxide, leading to an improved long-term stability. The impact of phase homogeneity on the halogenation properties of the catalysts, and thus on the lifetime, was further rationalized by the determination of the halogen uptake by *operando* prompt-gamma activation analysis. While the chlorine uptake under different reaction conditions was comparable over both materials, the bromine uptake on the non-homogeneous sample was up to 50% higher compared to the homogeneous counterpart. This indicates not only that the catalysts are more prone to bromination than chlorination, but also that their robustness depends on the intermixing of the Ce and Zr phases, suggesting that the mixed oxides are more stable than supported ceria catalysts. The degree of halogenation of the homogeneous ceria–zirconia catalysts can be controlled by tuning their Ce:Zr ratio, minimizing the halogen uptake at a Zr content in the range of 70–90 mol.%.

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### 1. Introduction

Ceria (CeO<sub>2</sub>) is a key ingredient of many heterogeneous catalysts for a variety of reactions [1–6], including the oxidation of HCl, a key step to recover Cl<sub>2</sub> in the polyurethane and polycarbonate industries [7–9]. In this reaction, the success of CeO<sub>2</sub> can be attributed to its unique structural and electronic properties associated with the ability to switch easily between the Ce<sup>4+</sup> and Ce<sup>3+</sup> oxidation states, forming and annihilating oxygen vacancies which function as active sites [10–15]. However, under oxygen-lean conditions, ceria tends to form chlorinated species at the surface and the bulk,

which leads to the deactivation of the catalyst [9]. In an attempt to enhance the stability of CeO<sub>2</sub>, it has been shown that the use of ZrO<sub>2</sub> as a carrier could significantly promote the performance of ceria compared to Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, due to the improved redox properties of the CeO<sub>2</sub>/ZrO<sub>2</sub> catalyst [16]. The latter catalyst also exhibited lower chlorine uptake during reaction compared to CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, as shown by *operando* prompt-gamma activation analysis. This resulted in an increase of the stability of ceria, which was verified in a 700 h stability test over a technical CeO<sub>2</sub>/ZrO<sub>2</sub> catalyst at pilot scale [16].

The successful demonstration of CeO<sub>2</sub>/ZrO<sub>2</sub> triggered further investigations that focused on the effect of intermixing ceria and zirconia by doping strategies. In fact, the doping of CeO<sub>2</sub> with iso- and aliovalent elements is an attractive methodology to lower

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the formation energy of oxygen vacancies [13,17–20], as shown for the automotive three-way catalyst where the incorporation of  $Zr^{4+}$  into  $CeO_2$  with a Ce:Zr ratio of 75:25 enhances its catalytic performance [21–23]. The incorporation of 20 mol.% of  $Zr^{4+}$  into bulk ceria promotes the HCl oxidation activity in contrast to trivalent ions such as  $La^{3+}$  [24]. Theoretical calculations suggested that the balanced reduction between the formation energies of both oxygen and chlorine vacancies enhanced the activity [24]. These results were supported by studies on the structural stability of electrospun ceria–zirconia nanofibers, observing that the incorporation of at least 20 mol.%  $ZrO_2$  into  $CeO_2$  increased the stability against sintering and lowered the likelihood of bulk cerium chloride formation compared to pure ceria [25,26].

The developments in catalytic HCl oxidation additionally envisaged new studies on HBr oxidation, an attractive route to recover  $Br_2$  from bromine-mediated alkane functionalization processes [27]. Ceria has been reported as potential catalyst for this reaction besides  $RuO_2$  and  $TiO_2$  [28,29]. However, apart from preliminary activity tests, no work has been dedicated to investigate the differences of ceria-catalyzed HBr and HCl oxidation, the role of an additional metal (such as  $Zr^{4+}$ ) on the performance of ceria, as well as the robustness of ceria-based systems for HBr oxidation.

Herein, we have studied the effect of the phase homogeneity and composition of ceria–zirconia catalysts for HBr and HCl oxidation. The materials were prepared by co-precipitation and thermal decomposition and characterized by bulk and surface techniques to determine structural and chemical features. The activity and stability of the catalysts were evaluated in the gas-phase oxidation of HBr and HCl at different temperatures and oxygen partial pressures. *Operando* prompt-gamma activation analysis was essential as it enabled to determine and compare the bromine and chlorine uptake at different conditions over the homogeneous and non-homogeneous ceria–zirconia catalysts. Our results underscore the necessity to maximize the homogeneity of the ceria–zirconia mixed oxide and to individually optimize the Ce:Zr ratio in order to obtain a stable and active catalytic system for HBr and HCl oxidation.

## 2. Experimental

### 2.1. Catalyst preparation

Ceria–zirconia mixed oxides with different Ce:Zr ratios were synthesized by following two different preparation routes. The samples are coded as ‘CZXX’, where C represents Ce, Z represents Zr, and XX indicates the Ce content (0–100 mol.%) in the mixed oxide (see Table 1). Homogeneous mixed oxides (coded with the suffix ‘-h’) were prepared by co-precipitation of the precursor salts in the presence of  $H_2O_2$ . The addition of  $H_2O_2$  during co-precipitation improves the morphological, redox, and thermal stability properties of the mixed oxide.  $H_2O_2$ , in fact, oxidizes the precursor  $Ce^{3+}$  species into the more easily hydrolysable  $Ce^{4+}$  and forms cerium hydroperoxide complexes. This disrupts the formation of a compact Ce–O–Ce network during the crystallization process, favoring the formation of highly-dispersed nanocrystallites of cerium oxide [30,31]. The desired amount of cerium nitrate ( $Ce(NO_3)_2 \cdot 6H_2O$ , Treibacher Industrie AG) was dissolved in deionized water and kept under stirring while the corresponding amount of aqueous zirconyl nitrate ( $ZrO(NO_3)_2$ , Treibacher Industrie AG, 0.4 M) was added. Hydrogen peroxide ( $H_2O_2$ , Aldrich, 35%) was poured into the solution to obtain a molar  $H_2O_2:(Ce + Zr)$  ratio of 3. The precipitation of the ceria–zirconia precursor was obtained by addition of aqueous ammonium hydroxide ( $NH_4OH$ , Aldrich, 30%) until a pH of 10.5 was reached. The slurry was stirred for 4 h, washed with deionized water, and filtered. The precipitate was dried overnight at 373 K and calcined in an oven with circulating air at 773 K for 3 h. The non-homogeneous mixed oxide (coded with the suffix ‘-nh’) was

prepared by thermal decomposition of the precursor salts. In this case, cerium and zirconyl nitrates were dissolved in deionized water and the obtained solution was heated in an oil bath kept at 423 K under magnetic stirring, until complete evaporation of the solvent and precipitation of the solid. The catalyst was filtered, washed, dried overnight at 373 K, and calcined in an oven with circulating air at 773 K for 3 h. Pure  $CeO_2$  and  $ZrO_2$  were obtained by precipitation of the corresponding precursors in the presence of  $H_2O_2$ , following the same preparation procedure of the homogeneous mixed oxides.

### 2.2. Catalyst characterization

The Ce and Zr content of the samples were determined by X-ray fluorescence (XRF) spectrometry, using an Orbis Micro-EDXRF analyzer equipped with a 35 kV Rh anode and a silicon drift detector. The Br and Cl content in the catalysts were determined by elemental analysis in a LECO CHN 900 combustion furnace. X-ray diffraction (XRD) patterns were recorded on a Philips X’Pert diffractometer equipped with an X’Celerator detector, using Ni-filtered  $CuK\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ). Rietveld refinement was carried out by using the GSAS-EXPGUI software package [32]. X-ray photoelectron spectroscopy (XPS) was conducted in a Physical Electronics Instruments Quantum 2000 spectrometer using monochromatic  $AlK\alpha$  radiation generated from an electron beam operated at 15 kV and 32.3 W. The spectra were collected under ultra-high vacuum conditions (residual pressure =  $5 \times 10^{-8} \text{ Pa}$ ) at a pass energy of 50 eV. For chemical identification, the spectra were referenced to Zr 3d at 182.2 eV.  $N_2$  sorption at 77 K was measured in a Micromeritics TriStar II unit after evacuation of the samples at 423 K for 90 min. Temperature-programmed reduction in hydrogen ( $H_2$ -TPR) was conducted in a Micromeritics Autochem 2920 unit equipped with a thermal conductivity detector. The catalyst (ca. 50 mg) was loaded into a U-shaped quartz micro-reactor and pretreated in air ( $35 \text{ cm}^3 \text{ min}^{-1}$ ) at 623 K for 1 h. The analysis was performed in 5 vol.%  $H_2/N_2$  ( $35 \text{ cm}^3 \text{ min}^{-1}$ ), ramping the temperature from 323 to 1273 K at  $10 \text{ K min}^{-1}$ . Temperature-programmed desorption (TPD) of water and bromine was performed in the same setup, using a Balzers Omnistar QMS mass spectrometer for the chemical analysis of the gases. The catalyst (ca. 50 mg) was loaded into a U-shaped quartz micro-reactor and the analysis was conducted in air ( $35 \text{ cm}^3 \text{ min}^{-1}$ ), ramping the temperature from 323 to 623 K at  $10 \text{ K min}^{-1}$ . High-resolution transmission electron microscopy (HRTEM) was undertaken in a FEI Tecnai F30 microscope operated at 300 kV. Scanning transmission electron microscopy (STEM) analysis with elemental mapping using energy-dispersive X-ray spectroscopy (EDS) was conducted in a FEI Talos microscope operated at 200 kV. Prior to microscopic analysis, the solids were dispersed in ethanol; a few droplets of the suspension were poured onto a holey carbon-coated copper grid and dried completely.

### 2.3. Catalyst testing

The gas-phase oxidation of hydrogen halides was studied in a quartz continuous-flow fixed-bed micro-reactor (8 mm internal diameter) at ambient pressure and in the temperature range of 450–750 K. The reactor was loaded with 0.25 g of catalyst (particle size = 0.2–0.4 mm). A total volumetric flow of  $166 \text{ cm}^3 \text{ STP min}^{-1}$  consisting of 10 vol.% HBr or HCl (Air Liquide, anhydrous) and 7.5–90 vol.%  $O_2$  (PanGas, purity 4.5) balanced in  $N_2$  (PanGas, purity 5.0) was continuously fed. After stabilizing the catalysts for 1 h under each condition, the halogen formation was quantified by iodometric titration using a Mettler Toledo G20 Compact Titrator. The iodometric titration is an off-line method to quantify  $Br_2$  and  $Cl_2$  ( $X_2$ ) contents in gas streams [33]. The gas at the reactor outlet

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