



## Reactivity descriptors for ceria in catalysis

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### ABSTRACT

Ceria has been very successfully employed in oxidation catalysis, whereas its application in other reactions has been less intensively investigated. The catalytic activity of ceria can be further enhanced by the use of dopants, and it exhibits structure sensitivity for numerous processes. The rich chemistry of cerium oxide is gathered and discussed in the present work, where the nature of each step of the most common reactions performed on it is assessed. Chemically intuitive computational and experimental descriptors, namely acid-base, redox, and structural features, are put forward to correlate the observed trends among the different doped and undoped facets. We have attempted to generate a robust framework that maps the chemically sound descriptors to the experimental fingerprints and theoretically calculated parameters.

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### 1. Introduction

Ceria has reached an iconic status among binary oxides, as it keeps more secrets than any other due to the versatile chemical structure, in addition to the fact that although being a rare earth it is abundant and relatively cheap [1]. Ceria is an excellent playground to understand complex chemistry, as (i) it shows marked structure sensitive properties [2], which can be nowadays assessed through shape controlled synthesis [3–5]; (ii) it shows both acid-base and redox chemistry [6,7]; (iii) it presents oxygen transport properties [8,9]; (iv) it is stable under harsh conditions [10]; (v) it is relatively easy to modify by doping to improve its chemistry [11,12]; (vi) it presents interesting hydrophobic features [13,14]; and (vii) it also exhibits a complex electronic structure that makes modeling efforts challenging [15,16]. All these characteristics make ceria as a unique material with fascinating properties and a wide scope of applications in heterogeneous catalysis [1,17].

The exploitation of the catalytic and chemical properties of CeO<sub>2</sub> has been commonly based on its oxygen storage capacity, OSC

[11,15,18,19]. A good OSC material requires a few contributions: (i) the cycling between the oxidized and reduced forms is energetically not demanding (or, equivalently, it presents low vacancy formation energy); (ii) easy transport of the vacancies (O atoms) between the surface and the bulk and inside the bulk; and (iii) facile transformation between the crystal structures of the oxidized (CeO<sub>2</sub>) and reduced (Ce<sub>2</sub>O<sub>3</sub>) forms or, at least, facile alignment of vacancies through defect lines. The OSC has been instrumental to understand the chemistry, either as a catalyst or a support, in many oxidation processes [7,19]. Due to its OSC, ceria is also employed as a ceramic electrolyte in solid oxide fuel cells, typically doped with aliovalent cations [20–23].

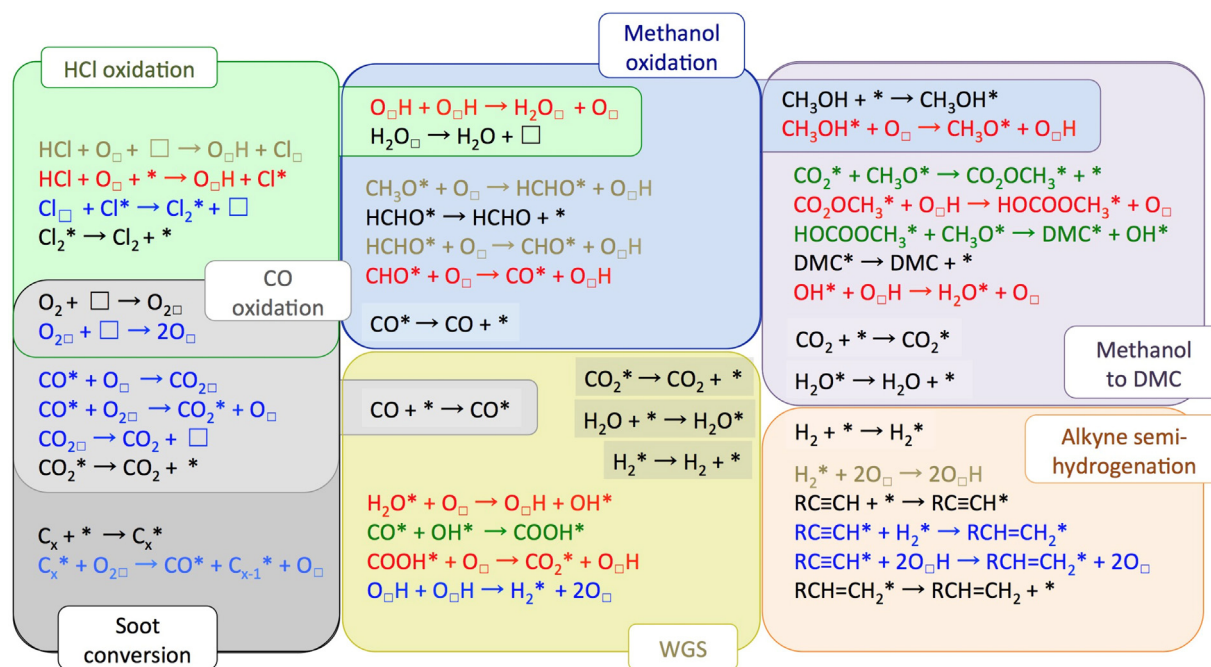
Since the identification of these properties, numerous reactions relying on the high oxidation ability of ceria-based materials have been put forward. For instance, CeO<sub>2</sub> can oxidize CO and soot, especially at medium temperatures, and thus it is incorporated in three-way catalysts in combination with metallic nanoparticles [7,19]. Ceria also performs nicely in the preferential oxidation (PROX) of CO in CO:H<sub>2</sub> mixtures [24–26]. This reaction is required to clean H<sub>2</sub> feeds from impurities that can damage fuel cells if H<sub>2</sub> is employed as an energy vector. In addition, it can also drive the water-gas shift reaction, i.e. the production of CO<sub>2</sub> and hydrogen from a mixture of CO and water, thus improving the hydrogen content in syngas mixtures [26–28]. Furthermore, oxidation properties can be extended to the application in the Deacon process [29]. This reaction aims at the recycling of hydrogen chloride by employing

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**Fig. 1.** Schematic representation of the sets of frequent applications of CeO<sub>2</sub> in catalysis, manifesting common steps in the reaction networks. The related inverse steps are also highlighted. The colors of the reactions correspond to Brønsted acid-base (red), Lewis acid-base (black), redox (blue), combined acid-base redox (brown), and condensation (green) steps. For more details see the corresponding sections below. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

the following process  $4\text{HCl} + \text{O}_2 \rightarrow 2\text{Cl}_2 + 2\text{H}_2\text{O}$ . The reaction can be seen as an oxidation and thus close to the traditional uses of CeO<sub>2</sub>, but at the same time the competition of Cl and O for the same type of sites limits the application of the common descriptors for oxidation processes [10,30–33]. Still, limiting the catalytic properties of ceria to its use in oxidation is far a simplistic identification, as it was recently shown to drive the semi-hydrogenation of alkynes to alkenes under hydrogen-rich conditions [34–36]. The description of this catalytic versatility sets a new landmark in the research of these materials.

Perhaps not so widespread but still largely studied are other reactions performed over ceria, mostly involving simple or polyfunctional organic molecules. The conversion of alcohols, e.g. methanol [37–41], ethanol [42,43], or polyols [44–46], has been carried out on ceria, as well as other organic compounds [47–51]. Methanol is also used in the conversion of CO<sub>2</sub> to dimethyl carbonate (DMC) catalyzed by ceria [52–55]. Finally, NO<sub>x</sub> [56–58], SO<sub>x</sub> [59–64], and H<sub>2</sub>S [65–67] react on ceria leading to either oxidized or reduced products depending on the reactant and the exposed ceria facet.

Fig. 1 illustrates the intricate map of the most common reactions catalyzed by CeO<sub>2</sub>. The links between the different steps and the identification of the chemical nature of each step are also shown. A coherent systematization of the catalytic properties of ceria has not been yet undertaken, although many authors have pointed out the need of separating the different terms as acid/base, redox, or condensation [68–73]. We herein aim at revising these applications and to identify the principles that guide the performance of CeO<sub>2</sub> in catalysis. For this purpose, a set of activity and selectivity descriptors both for oxidations and hydrogenations are presented, and the detailed analysis is then applied to describe: (i) a set of relevant reactions; (ii) several facets that account for the strong structure sensitivity observed; and (iii) the effect of introducing dopant cations on the different properties. This integrative perspective identifies the descriptors and maps them to direct observables accessible from experiments.

## 2. Descriptors for ceria

### 2.1. Previous descriptor-based oxidative chemistry

Structure–performance relationships are crucial to rationalize catalytic phenomena [74–76]. Typically, if the rate, selectivity, or stability correlate with a single parameter or a group of parameters these are taken as descriptors, as they can express the activity summarizing all the information for a class of materials. Energy descriptors have been extensively used since the work of Sabatier [77], and are nowadays accepted as the most robust theoretical tools in high-throughput computational screening of materials. Reactions become more complex on oxides, and thus the assessment of their catalytic performance requires complex descriptors. In particular, to describe the activity and selectivity of oxides, especially in oxidation processes, seven pillars were postulated in the pioneering work by Grasselli [78]: host structure, redox, metal–oxygen bond, lattice oxygen, phase cooperation, multifunctionality of active sites, and site isolation, as illustrated in Fig. 2. These pillars, despite providing clear conceptual guidelines, are described in a qualitative manner and can hardly be mapped directly to particular fingerprints in experiments. Thus, this list may be considered as a set of general principles, rather than quantitative parameters that can be adjusted to reach the desired reactivity. Furthermore, some pillars are not orthogonal and hence they cannot be individually tailored, hindering the direct interpretation of the described chemical process.

The oxygen vacancy formation energy has been commonly taken as the primary, and sometimes single, descriptor for reactivity in computational approaches, restricting the pillars into a single property. However, not all reaction schemes involving vacancy formation can be described with this magnitude, especially for reaction environments where the surface structure differs significantly from the pristine surface [31]. Moreover, hydrogenation reactions do not entail vacancy formation, presenting a complementary set

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