

# Mechanochemical Activation of CeO<sub>2</sub> in Order to Boost Physicochemical Properties for Catalytic Applications <sup>†</sup>

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**Abstract:** Mechanochemical activation, by means of high-energy ball milling, was applied to CeO<sub>2</sub> as a strategy to enhance its physicochemical properties. Different milling times were screened to evaluate their effect on ceria. The fluorite-type structure of cerianite was maintained in all cases, no matter the amount of energy introduced by the milling process, as observed via X-ray diffraction (XRD). A decrease in crystallite sizes and a consequent increase in specific surface area ( $S_{\text{BET}}$ ) were observed through XRD and N<sub>2</sub> sorption (BET method). Pore diameters and total pore volumes were also in line with the duration of CeO<sub>2</sub> milling. Moreover, redox properties and oxygen mobility studied through H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) showed an increase in reducibility with milling time, including signals of both bulk and surface ceria, due to the greater number of defects and/or oxygen vacancies achieved by mechanochemical activation. The obtained features could play an essential role in terms of metal–support interaction, reactant adsorption and/or oxygen supply during catalytic reactions. Thus, high-energy ball milling is a useful, simple and green method for the design of materials with catalytic applications.

**Keywords:** cerium oxide; high-energy ball milling; physicochemical properties; redox features; materials design



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## 1. Introduction

Cerium oxide is a ceramic extensively used in heterogeneous catalysis since it can act as a support, stabilizer, promoter or co-catalyst in the presence of noble and transition metals [1,2]. Among different uses, CeO<sub>2</sub> is employed as a primary component of three-way catalysts (TWCs) for the removal of volatile organic compounds (VOCs) and, in combination with metals, in several oxidation and hydrogenation reactions [1,3].

The origin of its wide range of industrial applications comes from a series of distinctive features, including the reversible redox couple Ce<sup>3+</sup>/Ce<sup>4+</sup>, acid–base surface properties and its well-known oxygen storage capacity (OSC) [4,5]. Furthermore, pure stoichiometric CeO<sub>2</sub> presents a fluorite-type structure with atoms ordered in a unique face-centered cubic cell (space group Fm3m), where the introduction of defects into the lattice could lead to nonstoichiometric structures [1,3]. These defects are mainly composed of oxygen vacancies accompanied by the generation of Ce<sup>3+</sup> species, which determine the key role of cerium oxide as a support and/or catalyst [3,4,6].

In this line, high-energy ball milling has become an excellent way to increase the number of bulk and surface defects in a solid matrix [7,8]. Based on the principles of mechanochemistry, this eco-friendly and versatile technique has been extensively used to modify the properties of solids, including particle refinement, specific surface area increase, mechanochemical activation of compounds, oxygen mobility and so on [8–10].

Thus, the aim of present work is to improve physicochemical properties of cerium oxide via high-energy ball milling in order to enhance the suitability of obtained materials for catalytic applications.

## 2. Materials and Methods

### 2.1. Preparation of Catalytic Materials

Catalytic materials were obtained from Cerium oxide (IV) (99%, Sigma-Aldrich, St. Louis, MO, USA) submitted to high-energy ball milling in a planetary ball mill (Fritsch Pulverisette 6), using an 80 cm<sup>3</sup> vial made of WC and 5 balls with a diameter of 15 mm made of the same material. Milling parameters were selected according to a previous work [9]: ball to powder mass ratio (BPR) was fixed at 43:1 with a milling rotational speed of 350 rpm under air. Milling time varied between 1 and 8 h following the operational procedure described in the literature [8]. As-prepared materials were denoted as CeX, where X corresponds to milling time (h). Pristine CeO<sub>2</sub> was denoted as Ce0.

### 2.2. Characterization

X-ray diffraction (XRD) was measured in a Rigaku Ultima IV diffractometer operated at 20 mA and 30 kV with a Cu K $\alpha$  radiation lamp. Step scan data were recorded at a step width of 0.02° and a counting time of 2 s. Brunauer–Emmet–Teller (BET) method was performed with nitrogen adsorption at 77 K using Micromeritics Gemini V equipment. H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) was studied using homemade equipment by means of a quartz tubular reactor and a Thermal Conductivity Detector (TCD) under the same conditions reported in a previous work [8].

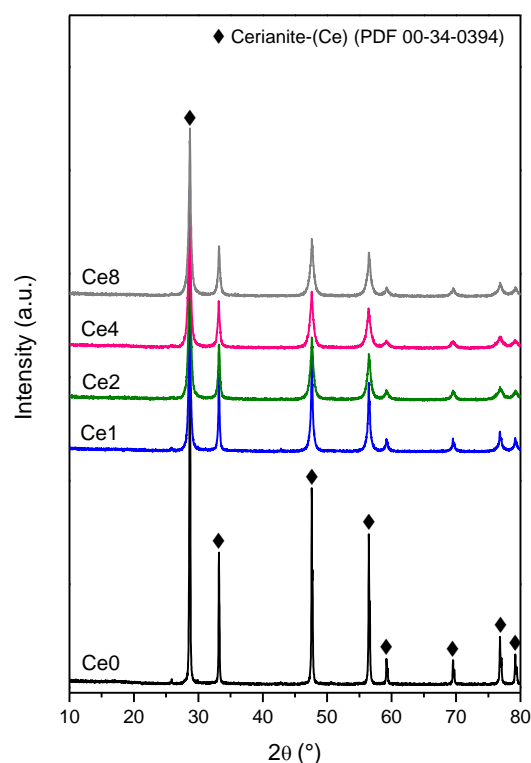
## 3. Results and Discussion

XRD was used to analyze the impact of mechanochemical activation on the crystal structure of pristine CeO<sub>2</sub> (Figure 1). The presence of the fluorite-type structure of cerianite patterns (PDF 00-34-0394) was detected in all the samples [9]. Moreover, the narrow and clear signals observed indicated a high degree of crystallinity, even after a few hours of milling. A broadening of diffraction lines with milling time was also observed due to particle and crystallite refinement caused by high-energy ball milling [8]. The most intense reflection line (111) and Scherrer equation were used to estimate the average crystallite size of each sample (Table 1), displaying a downtrend from 0 to 4 h and remaining the same afterwards [11].

**Table 1.** Textural properties and crystallite sizes of the samples.

Sample	S <sub>BET</sub> (m <sup>2</sup> g <sup>−1</sup> )	Pore Diameter (nm) <sup>a</sup>	Total Pore Volume (cm <sup>3</sup> g <sup>−1</sup> ) <sup>b</sup>	Crystallite Size (nm) <sup>c</sup>
Ce0	3	15.7	0.01	51
Ce1	7	12.0	0.02	29
Ce2	15	17.4	0.06	19
Ce4	17	18.8	0.08	17
Ce8	16	13.7	0.05	17

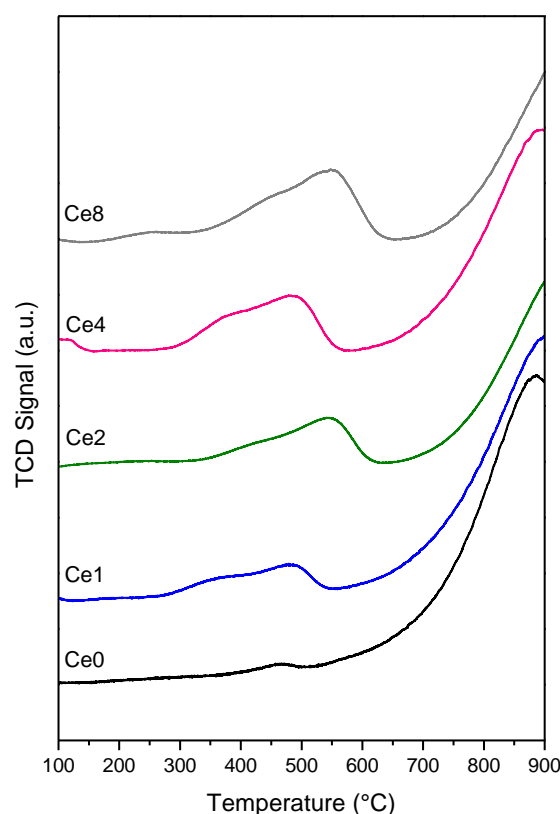
<sup>a</sup> Average pore diameter from BJH method using adsorption branch; <sup>b</sup> quantity of N<sub>2</sub> adsorbed at relative pressure of 0.98; <sup>c</sup> average crystallite size from Scherrer equation.



**Figure 1.** XRD spectra of samples.

In addition, particle refinement also occurred during the milling process, obtaining a straightforward relationship between milling time and specific surface area ( $S_{\text{BET}}$ ) (Table 1) [9]. Total pore volume also showed an increase with milling time up to 4 h (Table 1), with a slight decrease at 8 h, which could be associated with particle agglomeration and/or pore collapse due to excessive milling [8]. Textural changes during mechanochemical activation also affected average pore diameters, which were located between 12.0 and 18.8 nm (Table 1). Considering that catalytic reactions take place on the surface of solids, higher  $S_{\text{BET}}$  values could improve metal dispersion and/or reactant/product adsorption, enhancing the overall reaction rate.

Redox properties and oxygen mobility were studied by means of  $\text{H}_2$ -TPR (Figure 2). As reported by other authors [9,12], signals found between 250 and 550 °C are attributed to surface oxygen species, while broader signals at higher temperatures are associated with lattice oxygen released from bulk cerium oxide during the reduction process. Mechanochemical activation showed an increase in reducibility with milling hours, indicating a promotion of oxygen mobility, particularly from surface-chemisorbed species. This behavior could be a consequence of the defective structures generated during high-energy ball milling, increasing the number of oxygen vacancies, both in the surface and bulk of  $\text{CeO}_2$  [9]. Favored oxygen mobility observed in the present materials would display a remarkable performance in oxidation reactions, acting as oxygen suppliers and surface regenerators through catalytic cycles [2,9]. Moreover, the improved redox properties achieved could strengthen the interaction when adding a metal phase, preventing them from sintering and/or leaching during the reaction [7].



**Figure 2.** H<sub>2</sub>-TPR of samples.

#### 4. Conclusions

High-energy ball milling is an outstanding, simple and green route for the synthesis and modification of materials. The intrinsic physicochemical properties of CeO<sub>2</sub> could be improved during mechanochemical activation, including  $S_{\text{BET}}$ , oxygen mobility and redox properties upgrade, enhancing its upcoming application in heterogeneous catalysis.

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