engineering proceedings

Proceeding Paper

Mechanochemical Activation of CeO_2 in Order to Boost Physicochemical Properties for Catalytic Applications †

Matías G. Rinaudo *, Luis E. Cadús and Maria R. Morales

Facultad de Química, Bioquímica y Farmacia, Instituto de Investigación en Tecnología Química (INTEQUI-CONICET), Universidad Nacional de San Luis (UNSL), Almirante Brown 1455, 5700 San Luis, Argentina; luiscadus@gmail.com (L.E.C.); mrmorale14@gmail.com (M.R.M.)

* Correspondence: matirinaudo@gmail.com

† Presented at the 4th International Electronic Conference on Applied Sciences, 27 October–10 November 2023; Available online: https://asec2023.sciforum.net/.

Abstract: Mechanochemical activation, by means of high-energy ball milling, was applied to CeO_2 as a strategy to enhance its physicochemical properties. Different milling times were screened to evaluate their effect on ceria. Fluorite-type structure of cerianite was maintained in all cases, no matter the amount of energy introduced by milling process, as observed by X-ray Diffraction (XRD). A decrease in crystallite sizes along with a consequent increase in Specific Surface Area (S_{BET}) were observed by XRD and N_2 sorption (BET method). Pore diameters and total pore volumes were also in line with the duration of CeO_2 milling. Moreover, redox properties and oxygen mobility studied by H_2-Temperature Programmed Reduction (H_2- 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. Obtained features could play an essential role in terms of metal-support interaction, reactants adsorption and/or oxygen supply during catalytic reactions. Thus, high-energy ball milling becomes 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

Citation: Rinaudo, M.G.; Cadús, L.E.; Morales, M.R. Mechanochemical Activation of CeO_2 in Order to Boost Physicochemical Properties for Catalytic Applications. *Eng. Proc.* **2023**, *52*, x. https://doi.org/10.3390/xxxxx

Academic Editor(s): Name

Published: date

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 presence of noble and transition metals [1,2]. Among different uses, CeO_2 is employed as a primary component of three-way catalysts (TWC) for the remotion 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^{3+}/Ce^{4+}, acid-base surface properties and its well-known oxygen storage capacity (OSC) [4,5]. Furthermore, pure stoiquiometric CeO_2 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 nonstoiquiometric structures [1,3]. These defects are mainly composed of oxygen vacancies accompanied by the generation of Ce^{3+} 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, by 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) submitted to high-energy ball milling in a planetary ball mill (Fritsch Pulverisette 6), using an 80 cm^3 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 was varied between 1 and 8 h following the operational procedure described in the literature [8]. As-prepared materials were denoted CeX where X corresponds to milling time (h). Pristine CeO_2 was denoted 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 Kα 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 by nitrogen adsorption at 77 K in a Micromeritics Gemini V equipment. H_2-Temperature Programmed Reduction (H_2-TPR) was studied in a 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_2 (Figure 1). The presence of fluorite-type structure of cerianite patterns (PDF 00-34-0394) were detected in all the samples [9]. Moreover, 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_{BET} (m^2 g^{-1})	Pore Diameter (nm) [a]	Total Pore Volume (cm^3 g^{-1}) [b]	Crystallite Size (nm) [c]
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

[a] Average pore diameter from BJH method using adsorption branch; [b] Quantity of N_2 adsorbed at relative pressure of 0.98; [c] Average crystallite size from Scherrer equation.

In addition, particle refinement also occurred during milling process, obtaining a straightforward relationship between milling time and specific surface area (S_{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 to particle agglomeration and/or pore collapse due to excessive milling [8]. Textural changes during mechanochemical activation also affected average pore diameters, which located between 12.0 and 18.8 nm

(Table 1). Considering that catalytic reactions take place on the surface of solids, higher S_{BET} values could improve metal dispersion and/or reactants/products adsorption, enhancing overall reaction rate.

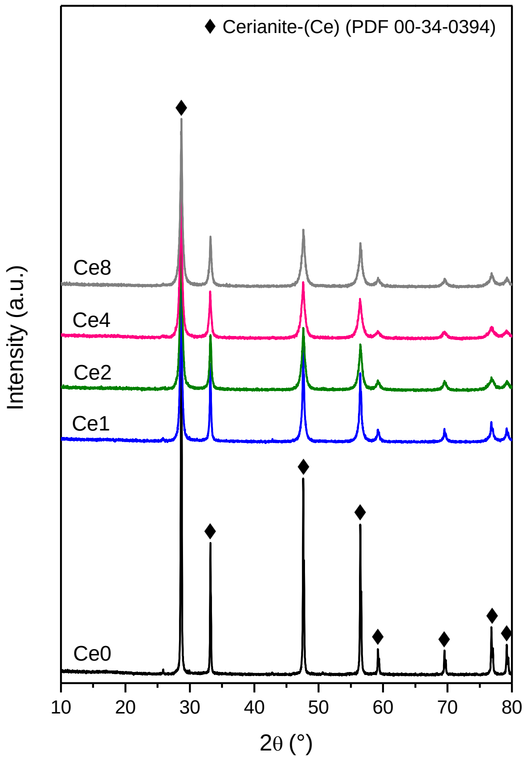

Figure 1. XRD spectra of samples.

Redox properties and oxygen mobility were studied by means of H_2-TPR (Figure 2). As reported by other authors [9,12], signals found between 250–550 °C are attributed to surface oxygen species while broader signals at higher temperatures are associated to lattice oxygen released from bulk cerium oxide during 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 CeO_2 [9]. Favored oxygen mobility observed in present materials would display a remarkable performance in oxidation reactions, acting as oxygen suppliers and surface regenerators through catalytic cycles [2,9]. Moreover, improved redox properties achieved could strengthen the interaction when adding a metal phase, preventing from sintering and/or leaching during reaction [7].

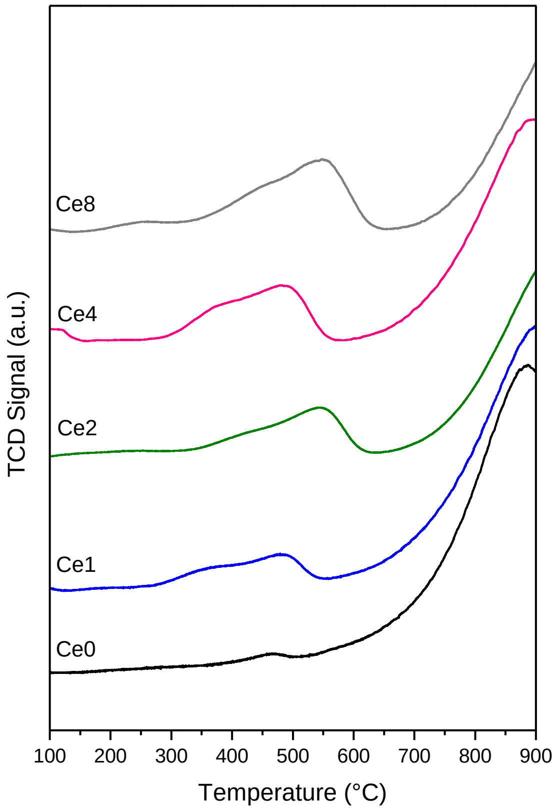

Figure 2. H_2-TPR of samples.

4. Conclusions

High-energy ball milling shows to be an outstanding, simple and green route for the synthesis and modification of materials. Intrinsic physicochemical properties of CeO_2 could be improved during mechanochemical activation, including S_{BET}, oxygen mobility and redox properties upgrade, enhancing its upcoming application in heterogeneous catalysis.

Author Contributions: Conceptualization, M.G.R., M.R.M. and L.E.C.; investigation, M.G.R..; visualization, M.G.R.; writing—original draft, M.G.R.; writing—review, M.G.R., L.E.C. and M.R.M.; writing—editing, M.G.R.; validation, M.G.R., L.E.C. and M.R.M.; supervision, L.E.C. and M.R.M.; resources, M.R.M. All authors have read and agreed to the published version of the manuscript.

Funding: The authors acknowledge the Universidad Nacional de San Luis (UNSL), Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT) and Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) for their financial support.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Aneggi, E.; de Leitenburg, C.; Boaro, M.; Fornasiero, P.; Trovarelli, A. *Catalytic Applications of Cerium Dioxide*; Elsevier Inc.: Amsterdam, The Netherlands, 2020. https://doi.org/10.1016/b978-0-12-815661-2.00003-7.
2. Peng, R.; Li, S.; Sun, X.; Ren, Q.; Chen, L.; Fu, M.; Wu, J.; Ye, D. Size effect of Pt nanoparticles on the catalytic oxidation of toluene over Pt/CeO_2 catalysts. *Appl. Catal. B* **2018**, *220*, 462–470. https://doi.org/10.1016/j.apcatb.2017.07.048.
3. Ma, Y.; Gao, W.; Zhang, Z.; Zhang, S.; Tian, Z.; Liu, Y.; Ho, J.C.; Qu, Y. Regulating the surface of nanoceria and its applications in heterogeneous catalysis. *Surf. Sci. Rep.* **2018**, *73*, 1–36. https://doi.org/10.1016/j.surfrep.2018.02.001.

4. Tang, K.; Zeng, D.; Lin, F.; Yang, Y.; Wu, L. The contributions of distinct Pd surface sites in palladium-ceria catalysts to low-temperature CO oxidation, CrystEngComm. **2020**, *22*, 1251–1260. https://doi.org/10.1039/c9ce01916b.
5. Wang, F.; Yu, H.; Tian, Z.; Xue, H.; Feng, L. Active sites contribution from nanostructured interface of palladium and cerium oxide with enhanced catalytic performance for alcohols oxidation in alkaline solution. Journal of Energy Chemistry. **2018**, *27*, 395–403. https://doi.org/10.1016/j.jechem.2017.12.011.
6. Zhang, H.; Wu, C.; Wang, W.; Bu, J.; Zhou, F.; Zhang, B.; Zhang, Q. Effect of Ceria on redox-catalytic property in mild condition: A solvent-free route for imine synthesis at low temperature. *Appl. Catal. B* **2018**, *227*, 209–217. https://doi.org/10.1016/j.apcatb.2018.01.012.
7. Rinaudo, M.G.; Beltrán, A.M.; Fernández, A.; Cadús, L.E.; Morales, M.R. Pd supported on defective TiO_2 polymorphic mixtures: Effect of metal-support interactions upon glycerol selective oxidation. *Results Eng.* **2022**, *16*, 100737. https://doi.org/10.1016/j.rineng.2022.100737.
8. Rinaudo, M.G.; Beltrán, A.M.; Fernández, M.A.; Cadús, L.E.; Morales, M.R. Tailoring materials by high-energy ball milling: TiO_2 mixtures for catalyst support application. *Mater. Today Chem*. **2020**, *17*, 100340. https://doi.org/10.1016/j.mtchem.2020.100340.
9. Rinaudo, M.G.; Pecchi, G.; Cadús, L.E.; Morales, M.R. Is mechanochemical activation always an asset? The case of Pd/CeO_2 catalysts for glycerol selective oxidation. *Ceram. Int.* **2023**, *49*, 18614–18623. https://doi.org/10.1016/j.ceramint.2023.02.237.
10. Danielis, M.; Colussi, S.; De Leitenburg, C.; Soler, L.; Llorca, J.; Trovarelli, A. The effect of milling parameters on the mechanochemical synthesis of Pd-CeO_2 methane oxidation catalysts. *Catal. Sci. Technol.* **2019**, *9*, 4232–4238. https://doi.org/10.1039/c9cy01098j.
11. Sivakami, R.; Dhanuskodi, S.; Karvembu, R. Estimation of lattice strain in nanocrystalline RuO_2 by Williamson-Hall and size-strain plot methods. *Spectrochim. Acta A Mol. Biomol. Spectrosc*. **2016**, *152*, 43–50. https://doi.org/10.1016/j.saa.2015.07.008.
12. Lykaki, M.; Pachatouridou, E.; Carabineiro, S.A.C.; Iliopoulou, E.; Andriopoulou, C.; Kallithrakas-Kontos, N.; Boghosian, S.; Konsolakis, M. Ceria nanoparticles shape effects on the structural defects and surface chemistry: Implications in CO oxidation by Cu/CeO_2 catalysts. *Appl. Catal. B.* **2018**, *230*, 18–28. https://doi.org/10.1016/j.apcatb.2018.02.035.