engineering proceedings

MDPI

Proceeding Paper

Eggshell Waste Valorization into $CaO/CaCO_3$ Solid Base Catalysts †

Matías G. Rinaudo [1,*], Sebastián E. Collins [2,3] and Maria R. Morales [1]

[1] Facultad de Química, Bioquímica y Farmacia, Instituto de Investigación en Tecnología Química (INTEQUI-CONICET), Universidad Nacional de San Luis (UNSL), Almirante Brown 1455, San Luis 5700, Argentina; mrmorale14@gmail.com
[2] Instituto de Desarrollo Tecnológico para la Industria Química (CONICET, UNL), Güemes 3450, Santa Fe 3000, Argentina; sebas.collins@gmail.com
[3] Facultad de Ingeniería Química, Universidad Nacional del Litoral (UNL), Santiago del Estero 2829, Santa Fe 3000, Argentina
* Correspondence: matirinaudo@gmail.com or mgrinaudo@unsl.edu.ar
† Presented at the 3rd International Electronic Conference on Processes—Green and Sustainable Process Engineering and Process Systems Engineering (ECP 2024), 29–31 May 2024; Available online: https://sciforum.net/event/ECP2024.

Abstract: Eggshell waste is a biodegradable residue composed of more than 90% $CaCO_3$, which makes it a great candidate to be converted into functional materials for diverse applications. Herein, domestic hen eggshell waste was dried and calcined in muffle under air at different temperatures (300 to 900 °C) and times (1 or 3 h) to achieve distinctive calcium species, compositions, and solid-phase transformations. The crystal structures achieved were characterized by X-ray diffraction (XRD), evidencing the transformation from $CaCO_3$ (calcite) to CaO (lime) at high temperatures and the formation of $Ca(OH)_2$ (slaked lime) due to the hydration of CaO facilitated by ambient water molecules. Considering this preliminary results, prepared solids could be useful as low-cost and metal-free (unsupported) catalysts for different heterogeneous reactions, such as the transesterification of vegetable oil and/or glycerol, where the presence of basic sites are needed.

Keywords: food waste valorization; eggshell; calcium carbonate; calcium oxide; solid base catalysts

Citation: Rinaudo, M.G.; Collins, S.E.; Morales, M.R. Eggshell Waste Valorization into $CaO/CaCO_3$ Solid Base Catalysts. *Eng. Proc.* **2024**, *67*, 36. https://doi.org/10.3390/engproc2024067036

Academic Editor: Juan Francisco García Martín

Published: 10 September 2024

1. Introduction

Food waste valorization has become an interesting and promising alternative for the production of new materials and the promotion of sustainable development and environmental protection [1–3]. For instance, the large amounts of eggshell residues from processing industries and domestic consumption are still disposed as waste in landfills without any pretreatment, being a source of organic pollution and contamination [4,5]. However, the synthesis of functional materials from thermo-treated eggshell residue has been increasing over the years, including its applications as a feed additive, dielectric material, fertilizer, bone substitute (hydroxyapatite), low-cost adsorbent for water pollutants removal, construction additive (limestone), and so on [1,4,6,7]. Since hen eggshells have an intrinsic pore structure composed of more than 90% $CaCO_3$ (calcite), with smaller amounts of magnesium carbonate, calcium phosphate, and organic matter (inner membrane), its transformation into CaO through calcination to obtain solid base catalysts becomes a fast, simple, and solvent-free alternative [4,6,8,9]. The aim of present work is the valorization of eggshell waste into $CaO/CaCO_3$ materials with the application as heterogeneous metal-free catalysts, particularly suitable for glycerol carboxylation (transesterification) to produce glycerol carbonate.

2. Materials and Methods

2.1. Synthesis of Materials

Domestic hen eggshell waste was firstly washed with tap water to eliminate impurities and then the inner membrane was manually removed. The eggshells were dried in an oven at 80 °C for 24 h under air to eliminate moisture. Dried eggshells were then milled in an agate mortar and calcined in muffle at different temperatures (300 to 900 °C) and times (1 or 3 h) to achieve diverse compositions of calcium species. The obtained catalysts were labeled EG (corresponding to pristine dried eggshell), EG-300, EG-500, EG-700, EG-900, and EG-900-2 (calcined for 1 h instead of 3) according to the calcination temperature and time.

2.2. Characterization

Crystal structures achieved were characterized by X-ray diffraction (XRD) in a Rigaku Ultima IV diffractometer operated at 20 mA and 30 kV with a Cu Kα radiation lamp. Data were recorded at a scanning rate of 3° per minute in the range of 10–80°. Calcium species were identified and compared with the International Center for Diffraction Data Standard (JCPDS) patterns.

3. Results and Discussion

The XRD spectra of dried pristine eggshells (EGs) calcined at 300 °C (Figure 1) showed diffraction lines corresponding to $CaCO_3$ (limestone) with a crystal structure of calcite (PDF 00-005-0586), as expected due to the standard composition (more than 94% calcite) of raw eggshells [6,10]. Calcination at low to moderate temperatures (lower than 500 °C) only eliminates impurities, water, and organic matter with no phase transformation, as reported by the other authors [6,9].

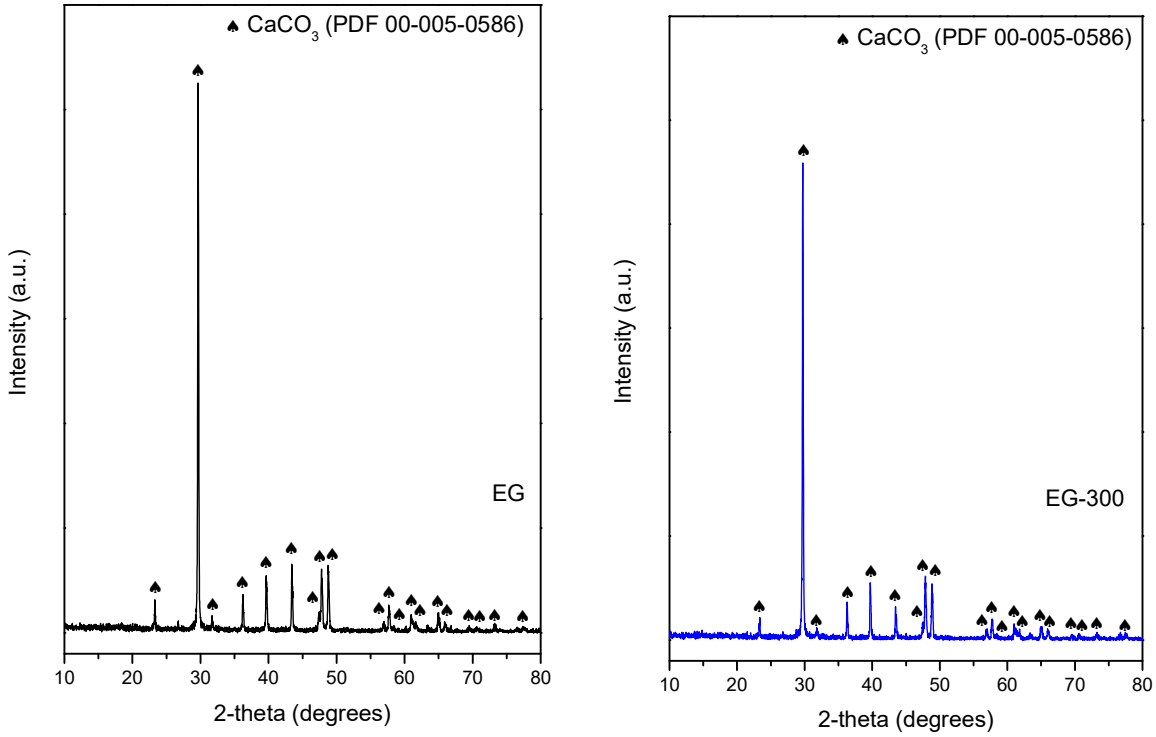

Figure 1. XRD spectra of EG and EG-300.

In case of EG-500 and EG-700 (Figure 2), once again, a temperature of 500 °C was not high enough to trigger the thermal decomposition of $CaCO_3$ to form CaO (lime) and release CO_2 [6,9]. On the other hand, at a calcination temperature of 700 °C, some diffraction lines

attributed to CaO (PDF-00-037-1497) and $Ca(OH)_2$ (slaked lime) (PDF 00-044-1481) could be observed. This behavior would indicate some extent of mineralization of $CaCO_3$ into CaO (ash) [11]. The presence of $Ca(OH)_2$ could be associated with the reaction of CaO (easy to hydrate) with ambient moisture, promoted by the high temperature, as was observed by other authors [6,12].

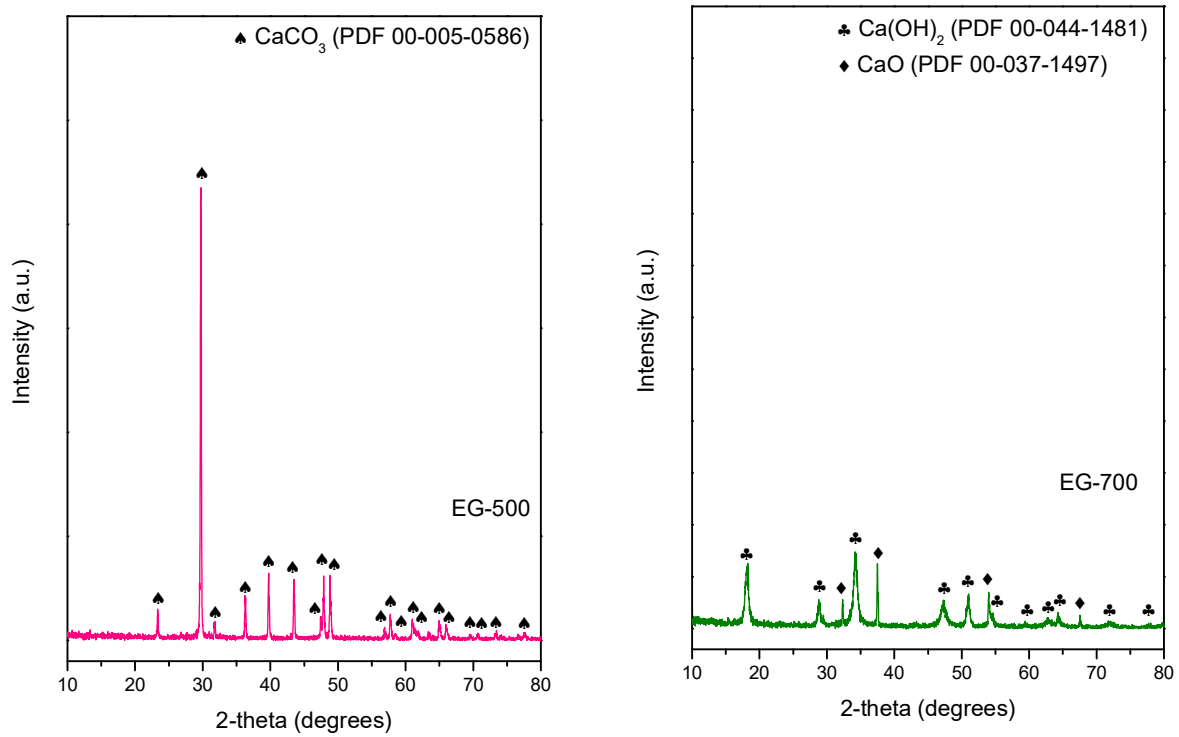

Figure 2. XRD spectra of EG-500 and EG-700.

Finally, at a calcination temperature of 900 °C (Figure 3), an increase in CaO formation was observed. In the case of EG-900, the thermal treatment for 3 h would lead to an excess of $Ca(OH)_2$ due to the combination of moisture, amount of CaO produced, high temperature, and long residence time [6,12]. Therefore, a new calcination process at 900 °C for only 1 h was performed (EG-900-2) in order to restrain $Ca(OH)_2$ formation. In this case, CaO was achieved as the major phase and some remaining $CaCO_3$ as the minor phase.

The several crystal phases achieved herein serve as a starting point for their performance evaluation as metal-free base catalysts in transesterification reactions, including glycerol valorization into glycerol carbonate and biodiesel production [1,4,12].

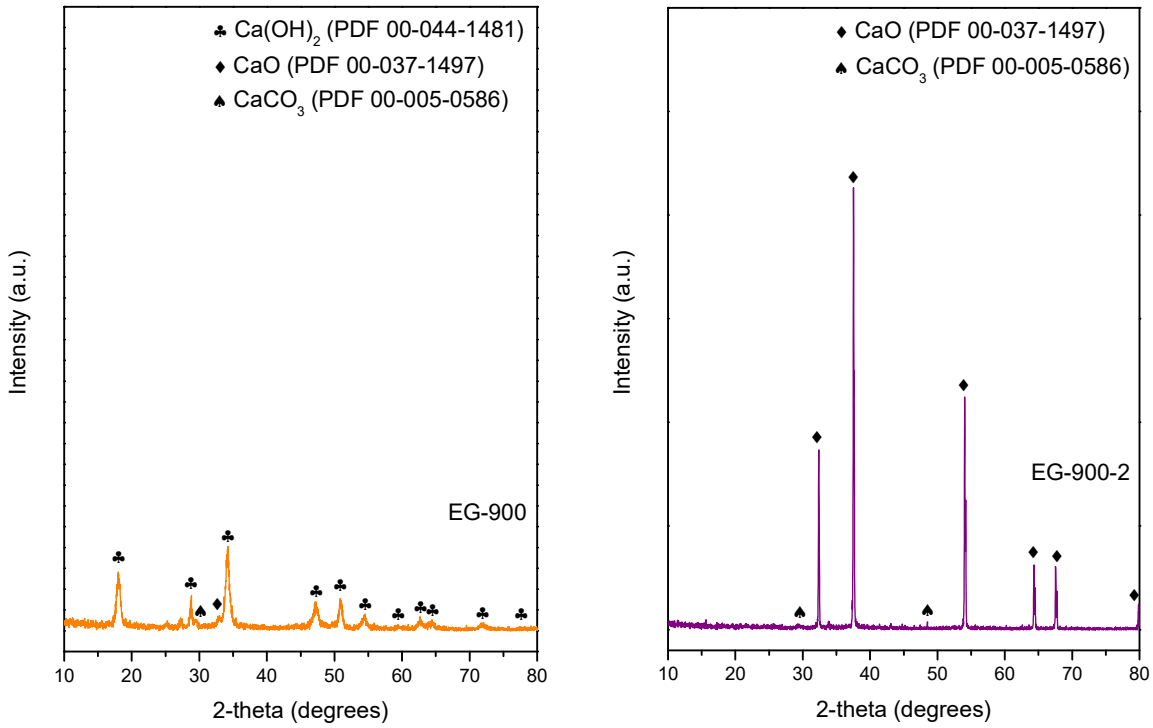

Figure 3. XRD spectra of EG-900 and EG-900-2.

4. Conclusions

Eggshell waste transformation into valuable materials could be an excellent way to promote sustainable processes and circular economy. Apart from the environmental benefits, suitable metal-free (unsupported) $CaO/CaCO_3$ catalysts for different reactions can be achieved by means of simple and green methods of synthesis. This preliminary study provides a foundation for this final objective. The base catalysts presented herein are being thoroughly characterized by different techniques and will be compared with the high-energy ball-milled catalysts also obtained from hen eggshell waste as a starting material. Finally, catalysts of both series selected according to their physicochemical properties, will be tested under glycerol carboxylation (transesterification) with dimethyl carbonate to form glycerol carbonate.

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

Funding: This research was funded by Universidad Nacional de San Luis (UNSL), Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT) and Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

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

Acknowledgments: 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.

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

References

1. Wei, Z.; Xu, C.; Li, B. Application of waste eggshell as low-cost solid catalyst for biodiesel production. *Bioresour. Technol.* **2009**, *100*, 2883–2885. [CrossRef] [PubMed]
2. Vandeginste, V. Food waste eggshell valorization through development of new composites: A review. *Sustain. Mater. Technol.* **2021**, *29*, e00317. [CrossRef]
3. Boechat, C.L.; Arauco, A.M.d.; Duda, R.M.; Sena, A.F.S.d.; Souza, M.E.L.d.; Brito, A.C.C. Solid Waste in Agricultural Soils: An Approach Based on Environmental Principles, Human Health, and Food Security. In *Solid Waste Management in Rural Areas*; InTech: Penang, Malaysia, 2017. [CrossRef]
4. Laca, A.; Laca, A.; Díaz, M. Eggshell waste as catalyst: A review. *J. Environ. Manag.* **2017**, *197*, 351–359. [CrossRef] [PubMed]
5. Waheed, M.; Yousaf, M.; Shehzad, A.; Inam-Ur-Raheem, M.; Khan, M.K.I.; Khan, M.R.; Ahmad, N.; Abdullah; Aadil, R.M. Channelling eggshell waste to valuable and utilizable products: A comprehensive review. *Trends Food Sci. Technol.* **2020**, *106*, 78–90. [CrossRef]
6. Tangboriboon, N.; Kunanuruksapong, R.; Sirivat, A.; Kunanuruksapong, R.; Sirivat, A. Preparation and properties of calcium oxide from eggshells via calcination. *Mater. Sci.* **2012**, *30*, 313–322. [CrossRef]
7. Kirubakaran, M.; Selvan, V.A.M. Experimental investigation on the effects of micro eggshell and nano-eggshell catalysts on biodiesel optimization from waste chicken fat. *Bioresour. Technol. Rep.* **2021**, *14*, 100658. [CrossRef]
8. Quina, M.J.; Soares, M.A.R.; Quinta-Ferreira, R. Applications of industrial eggshell as a valuable anthropogenic resource. *Resour. Conserv. Recycl.* **2017**, *123*, 176–186. [CrossRef]
9. Cree, D.; Pliya, P. Effect of elevated temperature on eggshell, eggshell powder and eggshell powder mortars for masonry applications. *J. Build. Eng.* **2019**, *26*, 100852. [CrossRef]
10. Correia, L.M.; Saboya, R.M.A.; Campelo, N.d.; Cecilia, J.A.; Rodríguez-Castellón, E.; Cavalcante, C.L.; Vieira, R.S. Characterization of calcium oxide catalysts from natural sources and their application in the transesterification of sunflower oil. *Bioresour. Technol.* **2014**, *151*, 207–213. [CrossRef] [PubMed]
11. Jo, Y.H.; Jeong, W.G.; Park, J.; Baek, K. Partially calcined $CaCO_3$ for remediating multi-heavy metals-contaminated groundwater. *Chem. Eng. J.* **2023**, *471*, 144652. [CrossRef]
12. Tan, Y.H.; Abdullah, M.O.; Nolasco-Hipolito, C.; Taufiq-Yap, Y.H. Waste ostrich- and chicken-eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil: Catalyst characterization and biodiesel yield performance. *Appl. Energy* **2015**, *160*, 58–70. [CrossRef]