Vol 6, Issue 4, April 2026 www.ijesti.com E-ISSN: 2582-9734
International Journal of Engineering, Science, Technology and Innovation (IJESTI)

Synthesis and Characterization of Ceria Zirconia Mixed Oxide Nanoparticles Using Microwave Combustion Method

Srikanth K [1]
[1] Research Scholar, Department of Chemistry, Mansarovar Global University, Sehore, M.P., India.

Dr. Pushpendra Tiwari [2]
[2] Supervisor, Department of Chemistry, Mansarovar Global University, Sehore, M.P., India.

ABSTRACT

The synthesis of ceria-zirconia mixed oxide nanoparticles was made through a microwave-assisted combustion process in which cerium nitrate and zirconyl nitrate were used as raw materials and ascorbic acid was used as a fuel. Different molar ratios were used to perform the synthesis to examine how zirconium doping affects the physicochemical characteristics of the ceria. The ready nanoparticles were systematically analyzed in the form of UV- visible spectroscopy, Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, and Raman spectroscopy. The UV- visible analysis demonstrated a significant change in absorption edge and progressive reduction in band gap energy with the increase in zirconium in the sample, which highlights strong electronic interaction and formation of defects in the lattice. The presence of CeO and ZrO bonds and hydroxyls was confirmed by the FT-IR spectra. XRDs showed a clearcut cubic fluorite structure that was nanocrystalline in nature and contracted the lattice with the addition of zirconium. The agglomerated particles were irregularly shaped flakes as observed through SEM analysis.

Keywords: *Ceria-Zirconia, Microwave, Ascorbic Acid, Nanoparticles, Crystal.*

I. Introduction

The reversible redox interaction between Ce3+ and Ce4+ ions inside the ceria crystal lattice gives ceria (CeO2) its oxygen storage and release capability. Other desirable properties of ceria include thermal and mechanical stability, acceptable pricing, and widespread application as a catalytic material. Doping, the process of substituting an atom of a different radius or valence for the cerium atom in ceria's crystal lattice, might further enhance the material's physicochemical qualities by introducing flaws. Zirconium is one of the most popular and well studied dopants, however there are many other transition and rare earth elements that may be used as dopants. An increased oxygen storage capacity, greater thermal stability, and higher catalytic activity are all seen in zirconium-doped ceria (CexZr1−xO2) solid solutions. Supercapacitors, sensors, anticorrosion pigments in aqueous epoxy-polymer coatings, and most significantly catalysis have all made use of Zr-doped ceria, which has been the subject of much investigation due to the fact that Zr doping improves the pseudocapacitive behaviour of ceria.

Some of the most common catalytic applications of CexZr1xO2 include promoting the formation of three-way catalytic converters, which remove pollutants caused by incomplete petrol combustion in car engines, and oxidising soot and reducing NOx in diesel engines. When considering new catalytic applications, it is crucial to focus on those that can safeguard both humans and the environment, such as the catalytic oxidation of volatile organic molecules. Mixed oxides or in conjunction with noble metals are the most common forms of ceria's use. For example, when it comes to the most challenging oxidiser, methane, pure ceria and mixed oxide systems like CeO2-ZrO2 showed good conversion in the mid to high temperature range. However, when noble metals were included, the conversion switched to lower temperatures. But we want to do away with noble metals altogether, or at least add very little of them, so we can get good

conversion at lower temperatures. Put another way, we want to make VOC abatement a low-cost and energy-efficient procedure in the end. Consequently, it is critical to select an appropriate catalyst that is thermally and mechanically stable, has a large specific surface area, and has strong catalytic activity. choose the optimal dopant, bringing the particle size down to the nanoscopic scale, and fine-tuning the morphology of the created catalyst—all of which are closely related to choose the right preparation method—are the keys to achieving the required attributes.

Hydrothermal and solvothermal synthesis, the sol-gel technique, mechanochemical synthesis, the precipitation method, spray pyrolysis, and many more ways are at your disposal for the manufacture of ceria nanoparticles. Due to its rapid processing time, lack of complexity in the necessary equipment, and inexpensive chemicals, solution combustion synthesis (SCS) has recently gained popularity as a means of nanomaterial creation. When oxidants (often metal nitrates) and fuels (such as urea, citric acid, various amino acids, etc.) are mixed in water to create a saturated solution, and then heated until the water evaporates and the combination self-ignites, the process is known as SCS. By controlling the fuel-to-oxidant ratio (F/O), which greatly affects the characteristics (crystallite size, morphology, specific surface area, etc.) of the end product, this method allows for the preparation of nanosized metal oxide materials—often without the need for subsequent thermal treatment—while uniformly adding small amounts of the doping agent. By balancing reducing elements, which have positive valences, with oxidising elements, which have negative valences, the fuel to oxidant ratio may be determined.

II. Review of Literature

Dziembaj, Roman et al., (2023) Redox processes are particularly facilitated by non-stoichiometric CeO2−y, particularly when it is aggregated into nanocrystals. Not only does it function as an oxygen buffer, but it also greatly enhances the activity of transition metals and their oxides that are scattered on or in it. In particular, the interface between the M/CeO2−y nanoparticles and the surface layer of their solid-state solutions, MxCe1−xO2−y, are sites of generation of active oxygen species ($O_2^{n\cdot}$, O^-). We talk about the crystal structure and flaws of CeO2, ZrO2, and (Ce, Zr)O2 in relation to the particular catalytic activity that results. This article provides a thorough overview of all the methods that have been used to synthesise these nanomaterials. These methods include sol-gel methods, hydrothermal and solvothermal techniques, combustion and flame spray pyrolysis, methods that use molecular and solid-state matrices for precipitation, 3D printing, and mechanochemical methods. The rules of individual procedures and preparation details are also detailed. Also included were techniques including impregnation, washcoating, and precipitation deposition for coating CeO2 nanoparticles with metal catalysts and their oxides. Detailed information on specific synthesis of efficient ceria-based catalysts for redox processes may be found in the more than 160 cited exemplary studies that make up this review.

E, Kumar. (2019) The authors of this study used a microwave-assisted solution approach to create ZrO2 metal oxide nanoparticles. A variety of analytical tools were used to characterise the prepared sample, including XRD, HRTEM, Particle size analyser, PL, and Zeta potential. The XRD pattern unveils the monoclinic structure of the synthesised ZrO2 nanoparticles, with an average crystallographic size of around 25 nm. The TEM scan also confirmed this. By employing PL spectroscopy, one may examine surface flaws and the manufactured material's electrical structure. The majority of the particles are aggregates, according to the particle size analyser. The surface electric charge and particle stability are inferred from the Zeta potential study.

Ayanwale, Ayodeji et al., (2018) Synthesis of zirconia mixed metal oxide nanoparticles has been accomplished by various synthetic routes. Zirconia mixed metal oxide nanoparticles with varying physicochemical characteristics can be synthesised by a variety of processes, taking into account variables

such as concentration, pH, precursor type, etc. The synthetic routes of zirconia mixed metal oxide nanoparticles, including sol-gel, hydrothermal, and coprecipitation methods, are discussed in this paper. The physicochemical properties, characterisation, and applications of these synthesised nanoparticles are also covered.

Reddy, Benjaram et al., (2009) A nanosized ceria-zirconia solid solution (MW) was created by utilising a straightforward and inexpensive microwave-assisted synthesis technique. A coprecipitation (CP) approach was also used to synthesise a ceria-zirconia solid solution with the same composition, which was then calcined at 773 K for comparative purposes. The CO oxidation activity of both materials was assessed using a variety of characterisation techniques, including transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, Raman spectroscopy, BET surface area, and others. A solid solution of Ce0.5, Zr0.5, and O2 was seen in the MW sample according to XRD analysis, while in the CP sample a solid solution of Ce0.75, Zr0.25, and O2 was observed. The sample generated using the microwave approach had nanometre sized particles with a broad particle size distribution, according to TEM examinations. Lattice flaws and oxygen vacancies were found to be more prevalent in the MW sample, according to Raman spectroscopy and studies of oxygen storage capacity. The MW sample was found to have a high reducibility and a surface enrichment of Ce 3+ ions, according to XPS tests. In contrast to the coprecipitated sample, the one synthesised by microwave had a lower light-off temperature and higher CO oxidation activity.

Zawadzki, Mirosław. (2008) Using a diethylene glycol solution with metal nitrate and hexamine as a precipitating agent, nanocrystalline ceria particles were effectively produced at mild temperature and pressure conditions using a microwave-assisted approach. Through the use of X-ray diffraction, transmission electron microscopy, electron diffraction, FTIR, Raman spectroscopy, textural analysis (surface area and porosity), and thermal (DTA-TG) testing, the crystalline structure and phase purity, particle shape and size distribution, and other properties of the as-prepared powder and samples subjected to additional thermal treatment were examined. The powder's as-prepared shape is characterised by a narrow size distribution and spherical-like particle size (average: 3 nm). The microporous structure and high specific surface area (180m2/g) of the as-prepared CeO2 were shown by the textural examination. A change in the distribution of pore sizes towards the mesoporous area and an increase in the degree of crystallinity were found after heat treatment. Ceria produced by microwave-assisted solvothermal techniques are state-of-the-art materials with several potential uses in optics, catalysis, and high-tech ceramics.

III. Experimental Setup

The raw materials cerium nitrate and zirconyl nitrate were selected since nitrates are known to aid combustion processes. We dissolved the cerium(III) nitrate [Ce(NO3)3•6H2O] (Merck, 99%) and zirconyl(IV) nitrate [ZrO(NO3)2•2H2O] (Aldrich, 99%) in deionised water to the appropriate concentrations for the present study. In five separate pyrex glass plates, the mixture was added in five different molar ratios: 1:1, 0.8:0.2, 0.6:0.4, 0.4:0.6, and 0.2:0.8. It was necessary to add ascorbic acid (AR grade) in a stoichiometric ratio to the produced solutions while stirring until well mixed in order to get the clear solutions. Next, the plates that have been treated with the solution are placed in the modified common microwave oven. The solution begins to boil and dehydrate at the outset. Lightly yellow residues were the end product of the reaction's breakdown, which released gases such as N2, CO2, H2O, and trace amounts of NO2. It has taken around 10 minutes for the liquid to evaporate and for a considerable amount of ceria-zirconia powder to be produced. By carrying out the method under the same conditions and obtaining the same results, we can establish that the experiment is reproducible.

A twin beam UV-Vis was used to get the UV-visible spectra, while an FT-IR spectrophotometer was used to collect the IR spectra. UV-Probe software is installed on the spectrophotometer. To capture X-ray diffraction patterns, the Shimadzu lab X-6000 diffractometer was utilised, which emits CuKα radiation with a wavelength of 1.54 Å. The JEOL model JSM 6390 SEM, equipped with an accelerating voltage of 20 kV, was used to take the SEM pictures. A Raman spectrometer ranging from 50 to 3000 cm-1 was used to gather the Raman spectra, with He-Ne (632 nm) and argon (514 nm) serving as the sources.

IV. Results and Discussion

Ultraviolet-Visible Studies

Fig. 1 shows the spectra and results of the ultraviolet-visible (UV-VIS) analysis that was utilised to quantify the five generated ceria-zirconia nanoparticles (CZAA-0, CZAA-1, CZAA-2, CZAA-3, and CZAA-4). Crystalline cerium oxide has an absorbance threshold in the ultraviolet-visible range of around 400 nm and a band gap of 3.0 eV. Compared to other compounds, ZrO2's UV-visible absorption wavelength of 240 nm was very long. The band gap of the ceria crystal lattice changes to blue and a single peak at 252 nm is attributed to cerium oxide as a result of zirconium oxide doping. It has been shown that the wavelength of UV-visible absorption is highly dependent on particle size, especially for zirconium and cerium.

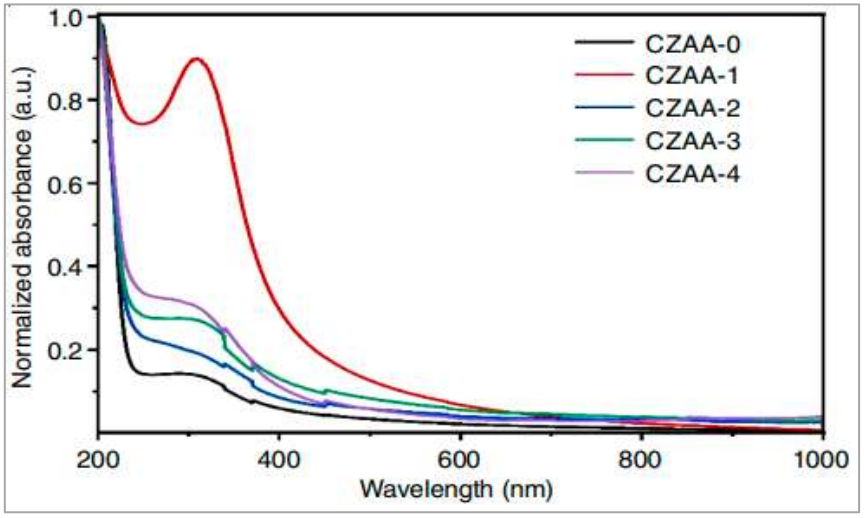

Figure 1: UV-Visible Spectra of Ceria-Zirconia Nanoparticles

A prominent absorption band below 400 nm is observed in the absorption spectra of all synthesised ceria-zirconia mixed oxides, which is caused by the charge-transfer transition from O - (2p) to Ce4+ (4f) orbitals in cerium oxide. Because of the interface polar on effect generated by electron-phonon coupling, the absorption spectra undergo a red shift as the concentration of zirconium dopants increases. A red shift occurs in the UV-visible spectra of nanoparticles as the concentration of zirconium dopant increases, as seen in Fig. 1. Due to the observed charge transfer transition, the band gaps in CZAA-0, CZAA-1, CZAA-2, CZAA-3, and CZAA-4 were found to be 4.92, 4.27, 4.11, 4.02, and 3.95 nm, respectively. So, the band gap is reduced as Zr content increases because Ce3+ is more readily formed from Ce4+ when Zr4+ ions are replaced in the cerium lattice, which leads to an increase in oxygen vacancies.

FT-IR Studies

The FT-IR spectra of all four nanoparticles—CZAA-0, CZAA-1, CZAA-2, and CZAA-3—are shown in Figure 2. There was a wide band at 3395 cm-1, which corresponds to the stretching vibration of hydroxyl groups. The vibrations at 1628 cm-1 are associated with water bending vibrations while the oscillations at 1381 cm-1 are associated with ce-OH stretching vibrations. For zirconium-oxygen bonds (Zr-O) and cerium-oxygen bonds (Ce-O), the bands at around 540 cm-1 and 740 cm-1, respectively, were identified.

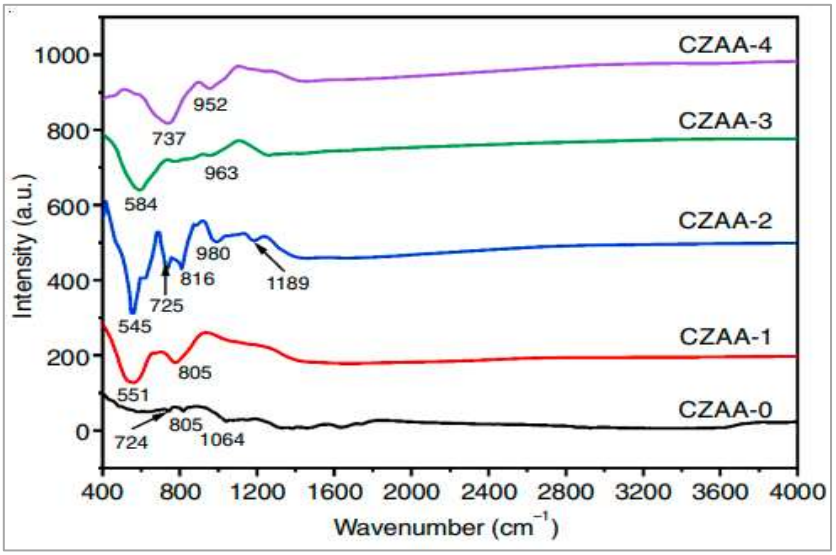

Figure 2: FT-IR Spectra of Ceria-Zirconia Nanoparticles

XRD Studies

Figure 3 shows that the produced nanoparticles have a well defined crystalline structure. A crystallite usually measures 67.29 nm in size. Based on the cubic phase structure of CeO2, the diffraction peaks were located using the following crystallographic planes: (111), (200), (220), (311), (400), and (331). The diffraction peaks at 2θ = 29.19º, 33.50º, 48.50º, and 57.49º reveal that the ceria-zirconia nanoparticles are uniformly distributed throughout the structure, indicating the presence of a solid solution. High 2θ values from XRD, in comparison to pure ceria, suggest the existence of a small amount of zirconia-rich phase. Compared to Ce4+, whose ionic radius is 0.97, Zr4+ produces a peak shift towards larger 2θ values. Zirconium ions, when added to ceria unit cells, cause a contraction of the lattice and a decrease in cell characteristics. The fact that the synthesised ceria-zirconia nanoparticles exhibit large peaks in all diffraction patterns suggests that they are nanocrystalline.

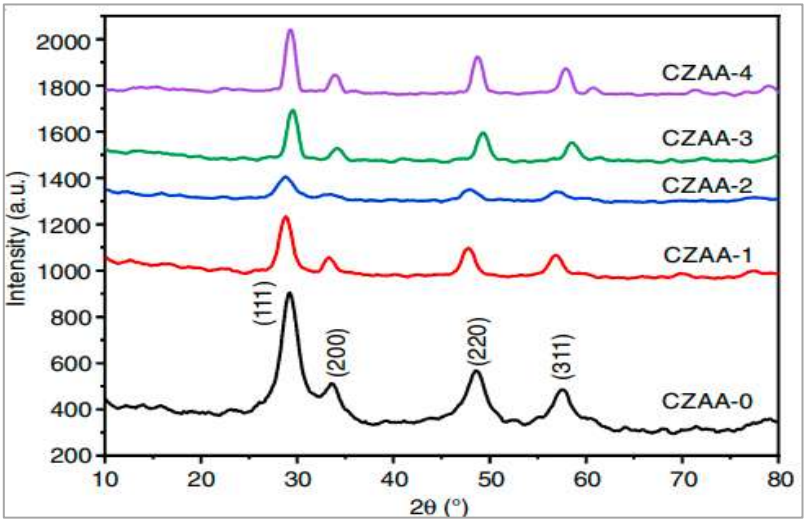

Figure 3: XRD Pattern of Ceria-Zirconia Nanoparticles

SEM Studies

The scanning electron micrographs (SEM) (Fig. 4a-b) reveal that the particles aggregate, revealing agglomerated crystallites that are tightly packed. The particles are larger and have an irregularly formed flake structure as a result of the structural breakdown that occurs during microwave heating (Fig. 4c).

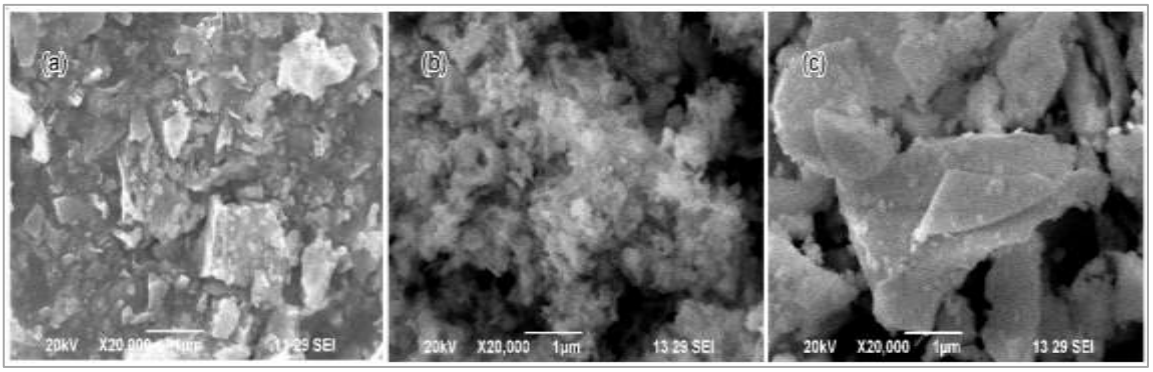

Figure 4: SEM Images of Ceria-Zirconia Nanoparticles

V. Conclusion

Various characterization methods ensured the successful incorporation of zirconium ions into the ceria lattice as they indicated that structural, optical and morphological properties changed significantly. Reduction of the band gap energy as a function of the concentration of zirconium suggests the formation of more defects and formation of oxygen vacancies, which are essential in the catalytic activity. The XRD data indicated the stabilization of a cubic phase with a nanocrystalline structure, and SEM analysis provided evidence of agglomerated and irregular shapes of the particles. In general, the results indicate that controllable zirconium doping is important in the modification of ceria-based ceramics nanomaterials. Such materials have significant potential in applications to catalysis, sensors, and energy storage systems, as they have better physicochemical properties.

References

1. Mužina, K., Kurajica, S., Biljanić, H., Brleković, F., and Duplančić, M., "Combustion synthesis of zirconium-doped ceria nanocatalyst," *Crystals*, vol. 14, no. 2, p. 108, 2024.
2. Dziembaj, R., Molenda, M., and Chmielarz, L., "Synthesis and specific properties of the ceria and ceria-zirconia nanocrystals and their aggregates showing outstanding catalytic activity in redox reactions," *Catalysts*, vol. 13, no. 8, pp. 1–21, 2023.
3. E. Kumar, "Synthesis and characterization of ZrO2 nanoparticles using microwave assisted method and its antimicrobial activity," *Journal of Nanoscience and Nanotechnology*, vol. 5, no. 1, pp. 642–644, 2019.
4. Shah, P., Burnett, J., Morgan, D., Davies, T., and Taylor, S., "Ceria–zirconia mixed metal oxides prepared via mechanochemical grinding of carbonates for the total oxidation of propane and naphthalene," *Catalysts*, vol. 9, no. 5, pp. 1–15, 2019.
5. Ayanwale, A., Cornejo, A., González, J., Espinosa Cristóbal, L., and Reyes-López, S., "Review of the synthesis, characterization and application of zirconia mixed metal oxide nanoparticles," *International Journal of Research GRANTHAALAYAH*, vol. 6, no. 8, pp. 136–145, 2018.
6. Damma, D., Reddy, L., Park, S.-E., and Reddy, B., "Ceria–zirconia mixed oxides: Synthetic methods and applications," *Catalysis Reviews*, vol. 60, no. 5, pp. 1–101, 2018.
7. Sultana, S. S. P., Kishore, D. H. V., Kuniyil, M., Khan, M., Alwarthan, A., Prasad, K. R. S., Labis, J., and Syed, F., "Ceria doped mixed metal oxide nanoparticles as oxidation catalysts: Synthesis and their characterization," *Arabian Journal of Chemistry*, vol. 10, no. 6, pp. 1–5, 2015.
8. Das, D., Thrimurthulu, G., Lakshmi, K., and Reddy, B., "Microwave-assisted synthesis of highly active nanosized ceria-zirconia solid solutions for CO oxidation," *International Journal of Nanotechnology*, vol. 7, no. 9, pp. 1166–1177, 2010.

9. Reddy, B., Reddy, L., and Ibram, G., "Synthesis of nanosized ceria-zirconia solid solutions by a rapid microwave-assisted combustion method," *The Open Physical Chemistry Journal*, vol. 3, no. 1, pp. 24–29, 2009.
10. Zawadzki, M., "Preparation and characterization of ceria nanoparticles by microwave-assisted solvothermal process," *Journal of Alloys and Compounds*, vol. 454, no. 1, pp. 347–351, 2008.
11. Yang, H., Huang, C., Tang, A., Zhang, X., and Yang, W., "Microwave-assisted synthesis of ceria nanoparticles," *Materials Research Bulletin*, vol. 40, no. 10, pp. 1690–1695, 2005.
12. Chung, D. and Lee, E., "Microwave-induced combustion synthesis of Ce1−xSmxO2−x/2 powder and its characterization," *Solid State Ionics*, vol. 374, no. 1, pp. 69–73, 2004.