Surface Morphology and Stability Analysis of Ceria-based Nanoparticles for its Utilization as a Lubricant Additive

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Abstract: The lubricants added with nanoparticle additives have achieved a predominant position in the field of research on development of sustainable lubricating oils. The efficient physical and chemical properties of metal oxide nanoparticles as lubricant additives have widely extended its purview. The surface morphology and stability analysis of nano-sized Ceria (CeO_2)and Ceria-Zirconia (Ce-Zr) hybrid nanoparticles are carried out using High Resolution Transmission Electron Microscopy (HR-TEM), Fourier Transform Infrared Spectroscopy (FT-IR), X-Ray Diffraction (XRD) and Zeta Potential (ZP) analyses techniques. The ceria-based nanoparticles are synthesized through the bottom-up approach of chemical processing named Precipitation Method (PM). The better control on particle size of PM resulted in refined and spherically shaped nanoparticles. Further, to improve the dispersion stability of the prepared nanoparticles in the lubricant, a suitable surfactant namely Polysorbate 20 (Tween 20) was used. The characterization results proved that the ceria-based nanoparticles can play an important role in improving the lubricating properties of the base-oil, provided that proper measures are taken to compensate for its minimal undesirable effects.

Keywords:*Lubricant, Nanoparticles, Morphology, Precipitation Method, Surfactant*

1 Introduction

Nickel based alloys finds wide applications in different parts of gas turbines of aircraft, steam turbine power plants, reciprocating engines, tool & die industry, medical field, heat treatment equipments, nuclear power plants, The establishment of the concept of nanotechnology and its widespread acceptance has led to the study and development of materials at atomic scales. The positive change in physical and chemical properties of elements at nano/micrometre size has given a constructive leap in various fields of research such as chemistry, nano technology, material science and Engineering. The new challenges and demands in advanced technologies have forced the investigators to think and derive solutions to reduce or prevent the energy and material losses in various systems.

Diminishing fossil fuels and crude oil reserves along with its depleting effects on the environment has alarmed the need for establishment of new bio-degradable and sustainable energy sources. The central reason behind energy loss in mechanical systems viz., automobiles, industrial machineries etc. is recognized to be the phenomenon of friction. The most effective method derived so far for the reduction of friction and wear is the technique of lubrication. Recently, the addition of nanoparticles in lubricants and fuels to enhance its rheological, thermal and tribological properties is obtaining widespread attention due to its enhanced positive effects. The basic principle of nanolubrication is an inevitable factor needed for the field to advance and certain modifications done at accurate levels can impart effective surface protection [1]. Currently, many researches are being carried out in the field of nanolubrication to explore the possibilities in development of sustainable, eco-friendly and bio-degradable lubricants. Many investigators have identified that the addition of nanoparticles can magnify the required properties of lubricating oils, if properly mixed in definite ratios [2-6].

1.1 Nanoparticle Additives: State of Art

The synthesis of nanoparticles is achieved by two processes; viz., physical processes and chemical processes.

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The physical processes that are widely used include high energy ball milling, inert gas condensation, wire explosion, ion sputtering, arc discharge, laser ablation, etc. However, the need for large energy sources and ineffective control on particle size make the physical processes non-economical. In chemical methods, nanoparticles are developed starting from atoms. They include chemical reduction, sol-gel method, precipitation method, solvo-thermal synthesis, photo chemical synthesis, electro-chemical synthesis, etc. [7-11]. A wide range of nanoparticles such as MoS_2, CuO, TiO_2, ZnO_2, etc. have been tested as lubricant additives by many researchers in the past. The major reasons for the utilization of nanoparticles as lubricant additives are due to its shape, less chemical reactivity, non-volatility etc. Further, the size, shape, concentration and dispersion stability of the nanoparticles are the major factors which determine the friction reduction and anti-wear properties of the nanolubricants [12].

In this work, the nano-sized Ceria (CeO_2) and Ceria-Zirconia (Ce-Zr) hybrid nanoparticles are prepared by a bottom-up chemical process namely precipitation method. The synthesized nanoparticles are then subjected to various advanced characterization and stability analysis techniques to determine its size, shape and dispersion stability.

2 Experimental Work

2.1 Materials

The nano-sized Ceria (CeO2) and Ceria-Zirconia (Ce-Zr) hybrid nanoparticles are prepared chemically. The precursors used for the preparation of former include Cerium (III) Nitrate Hexahydrate, Iso-propanol and water. Further, the Ce-Zr hybrid nanoparticles are prepared from Cerium (III) Nitrate Hexahydrate, Zirconium Oxy Chloride and Water.

2.2 Synthesis Procedure

The 0.1M aqueous solution of precursors, were mixed thoroughly in the desired ratio. The prepared solution was stirred for 30 minutes at 60ºC, by using a magnetic stirrer with heating arrangement. The temperature and the pH of the solution were checked repeatedly using a pH meter. Aqueous ammonia was added drop wise to vigorously stirring solution, and the pH was maintained above the value of 10 to keep the solution basic so that the particles formed will be of nanometre size. On the addition of aqueous ammonia, solution turned pale yellow and mixture was stirred for about 2 hours. The precipitates were collected by filtration and washed repeatedly with distilled water to remove excess ammonia .The slurry was then dried for 4 hours at 500°C in a muffle furnace. A porous yellow powder was obtained which was crushed to get fine powder and calcinated at 500°C for 1 hour to obtain nano-sized Ceria (CeO2) particles. Similar procedure was followed for the synthesis of Ceria-Zirconia (Ce-Zr) hybrid nanoparticles; except that Zirconium Oxy Chloride was used in place of Iso-propanol as precursor and the solution turns dark red on addition of ammonium hydroxide solution. A deep yellow powder was obtained in case of Ceria-Zirconia (Ce-Zr) hybrid nanoparticles.

2.3 Characterization of Nanoparticles

The surface morphology and stability analysis of the synthesized nanoparticles were carried out using advanced characterization techniques. HR-TEM using the Jeol/JEM 2100 model with resolution details; Point: 0.23 nm and Lattice: 0.14 nm was used to determine the exact size and morphology of the nanoparticles. FT-IR analysis to obtain the absorption spectra was conducted using the Model: Thermo Nicolet, Avatar 370, having a spectral range of 4000-400 cm-1 and maximum resolution of 4 cm-1. XRD plot for interpretation of crystal lattice structure, atomic spacing and to confirm the formation of the desired nanoparticles was performed using the Model: Bruker AXS D8 Advance, with Copper as the X-ray source which produce rays of wavelength: 1.5406 A°. The Zeta potential value which determines the dispersion stability of the nanoparticles was found out using the Zetasizer Nano ZS model. Hexane is used as the base fluid to perform the testing to obtain the ZP value in mV of the different type of nanoparticles.

3 Results and Discussion

3.1 Surface Morphology and Stability Analysis

The various advanced characterization techniques viz. HR-TEM, FT-IR, XRD and ZP analyses were carried out on the synthesized Ceria (CeO2) and Ceria-Zirconia (Ce-Zr) hybrid nanoparticles.

A. High Resolution Transmission Electron Microscopy (HR-TEM)

HR-TEM is an advanced characterization equipment used to determine the surface topography and morphology of materials and particles. To be specific, this ideal equipment is one of the recent developments in the field of microscopic studies for high resolution requirements in researches. Fig. 1 and Fig. 2 show the HR-TEM images of nano-sized Ceria (CeO2) and Ceria-Zirconia (Ce-Zr) hybrid nanoparticles. The results proved that the size of the both type of nanoparticles were much less than 50nm and majority of particles seem to have size of nearly 10nm.

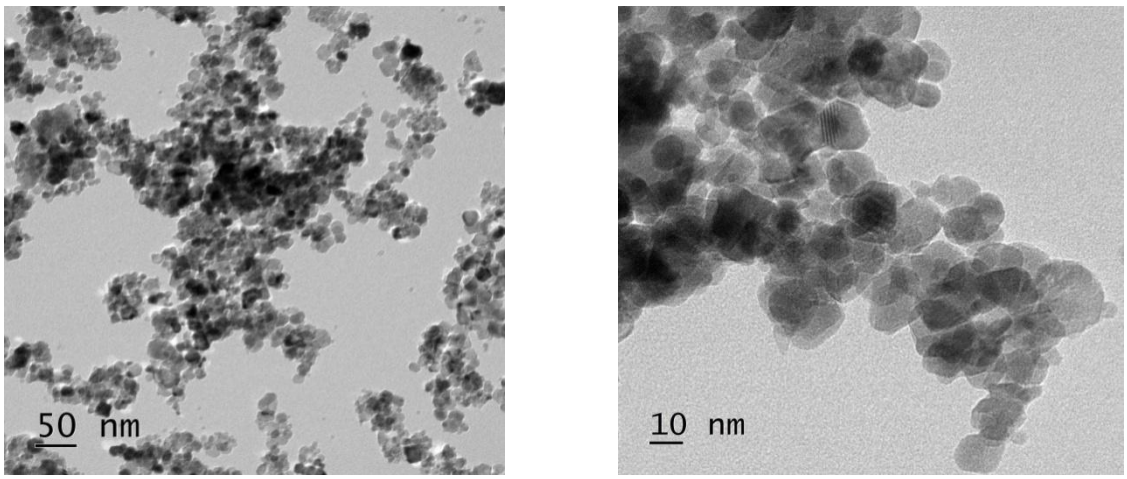

Fig. 1. HR-TEM images of CeO_2 nanoparticles

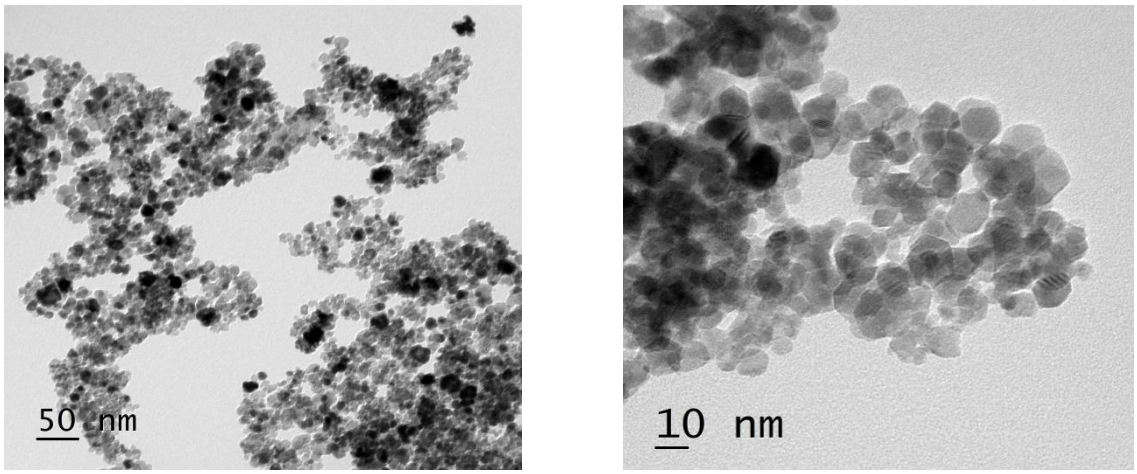

Fig. 2. HR-TEM images of Ce-Zr hybrid nanoparticles

The nearly spherical morphology and polycrystalline nature of both the nano-sized Ceria (CeO2) and Ceria-Zirconia (Ce-Zr) hybrid nanoparticles can be clearly identified from Fig. 3 obtained using HRTEM. These characteristics are found to be critical in the use of these nanoparticles as lubricant additives.

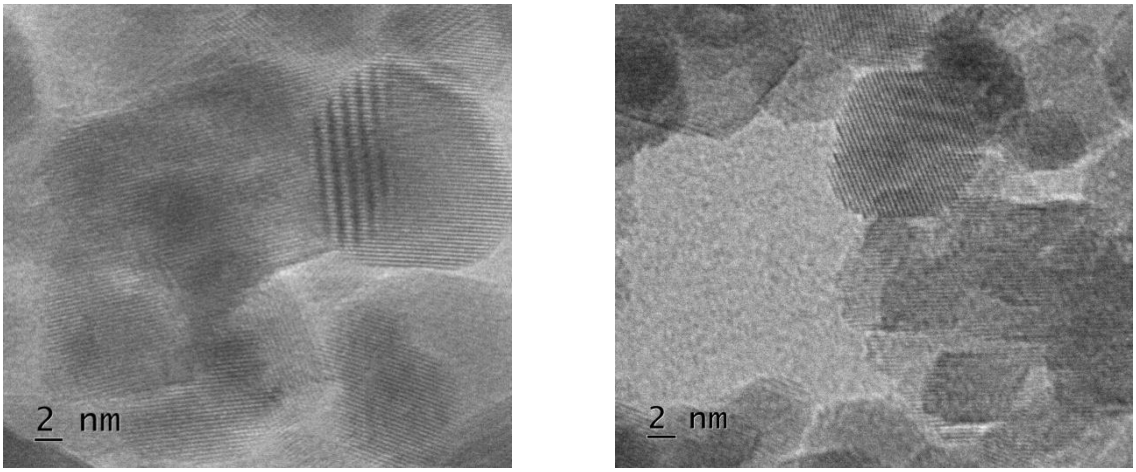

Fig. 3. HR-TEM images showing crystalline nature of both nanoparticles

The Scanning Electron Microscopy (SEM) images of agglomerated nanometer sized Ceria (CeO2) and Ceria-Zirconia (Ce-Zr) hybrid nanoparticles due to exposure to moisture and improper calcination resulting in larger particles is as shown in Fig. 4.

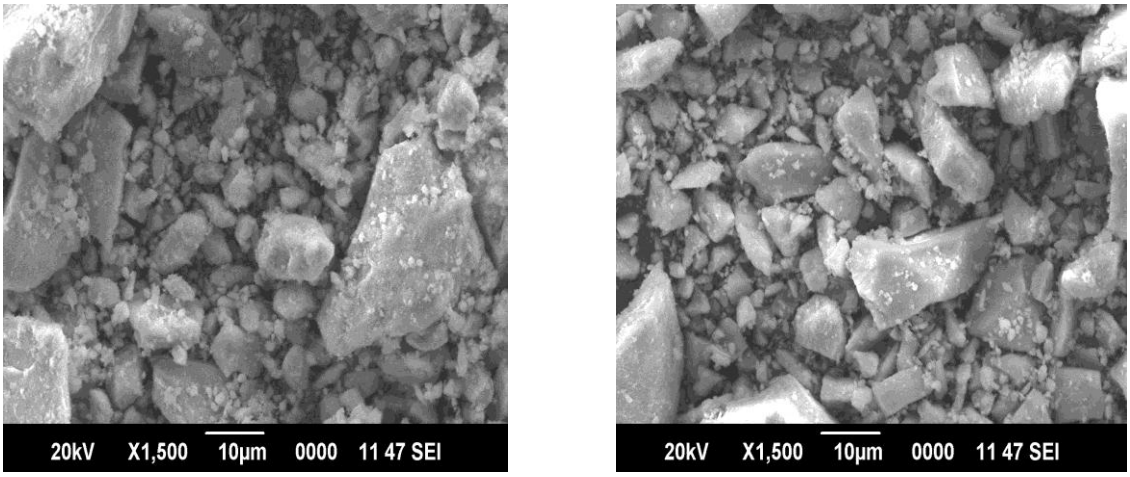

Fig. 4. SEM images of agglomerated CeO_2 and Ce-Zr nanoparticles to form larger sized particles

The particle size variation is too large which can be undesirable. Further, it can be seen that the shape of the particles get changed to irregular than spherical and measures should be taken to prevent the same to achieve the required spherical nanometer sized particles.

B. Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR analysis is used to derive the qualitative and quantitative information about the samples being tested. The purity of the synthesized nanoparticles can be verified and the presence of any impurities can be identified by this technique. The FTIR spectra of CeO2 and surfactant modified CeO2 nanoparticles is as shown in Fig. 5. The absorption peaks recorded between the wavenumbers of 4000 to 400cm-1 has a number of significant peaks which are considered.

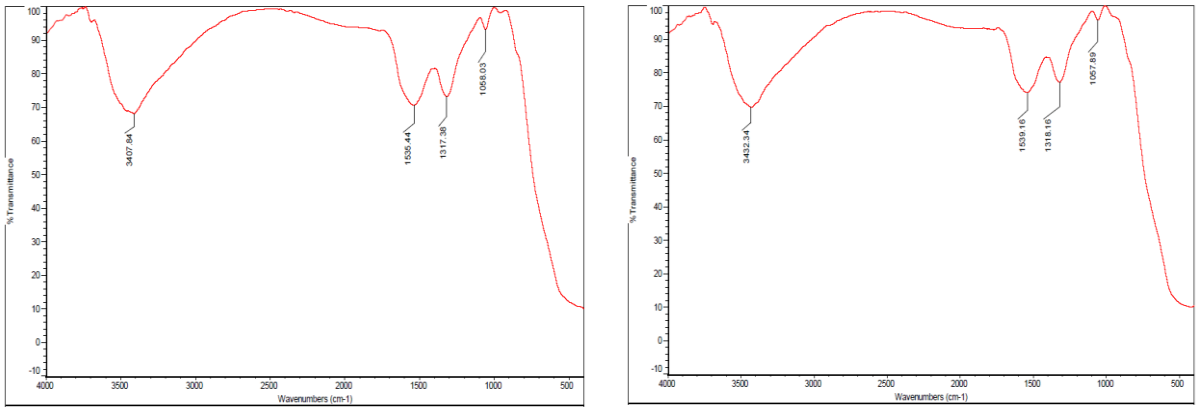

Fig. 5. FT-IR spectra of CeO_2 and surfactant modified CeO_2 nanoparticles

The absorption peak from 2700-3500 cm-1 is due to the vibrations caused by O-H stretching of H2O in the sample. The water molecules absorbed physically resulted in the absorption bands at 1525.44 and 1317.38 cm^{-1}. Moreover, the typical peak for Ce-O stretching vibrations is featured by the absorption bands at 840 and 540 cm^{-1} [13].

The FT-IR spectra of Ce-Zr hybrid and surfactant modified hybrid nanoparticles are shown in Fig. 6. Again, the peak at 3425.29 and 1623.73 cm^{-1} in the spectra is due to the O-H stretching vibrations and externally absorbed water molecules. Further, the absorption peaks at 540 and 400 cm-1 is due to the Ce-O and Zr-O stretching vibrations respectively [13-15]. These adsorption spectra have proved the formation of the desired metal oxide particles to some extend.

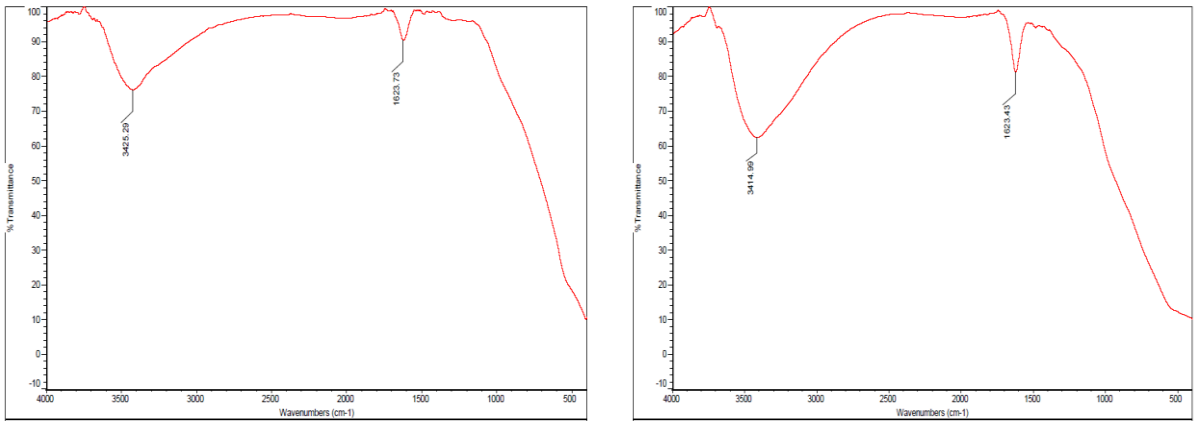

Fig. 6. FT-IR spectra of Ce-Zr hybrid and surfactant modified Ce-Zr hybrid nanoparticles

The FT-IR spectra of surfactant modified Ceria (CeO2) and Ceria-Zirconia (Ce-Zr) hybrid nanoparticles does not show much variations form the spectra's related to their respective bare particles, which can be considered as the evidence for absence of chemical reaction of surfactants with- the nanoparticles.

C X-Ray Diffraction (XRD)

Fig. 7 and shows the XRD patterns of Ceria (CeO2) and Ceria-Zirconia (Ce-Zr) hybrid nanoparticles respectively. Sharp peaks are obtained for the former and broader peaks for the latter with a shift in all diffraction peaks towards higher 2θ angles.

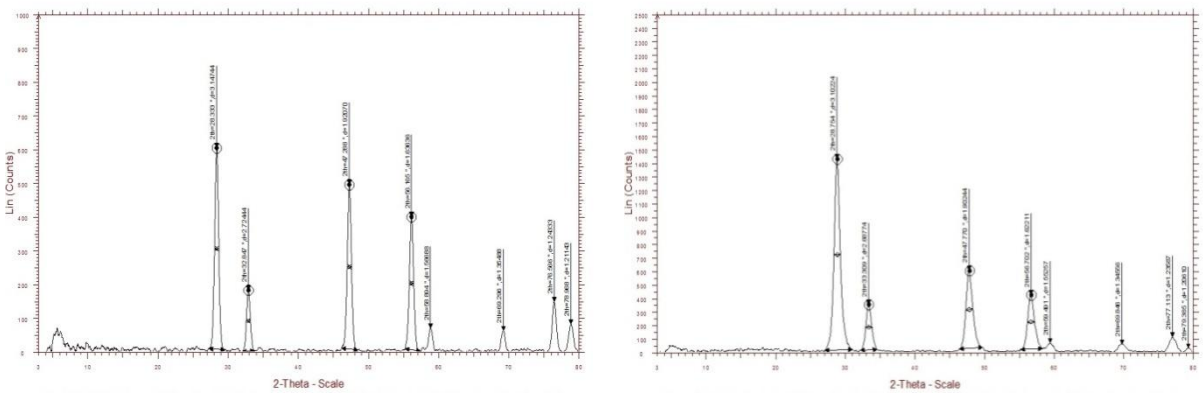

Fig. 7. XRD pattern of CeO_2 and Ce-Zr hybrid nanoparticles

The peaks obtained for Ceria (CeO2) and Ceria-Zirconia (Ce-Zr) hybrid nanoparticles corresponding to the planes (111), (200), (220), (311) which are similar to that of a face centered cubic fluorite structure. The average particle size of both types of nanoparticles can be obtained using Scherrer's equation:

$$Dhkl = 0.9\lambda / \beta\cos\theta$$

Where Dhkl is the average particle size, λ the wavelength of radiation (0.15406 nm), β the full width at half maximum (FWHM) and θ the Bragg's angle of the peak. The average particle size and FWHM values of different planes of both type of nanoparticles is summarized in Table 1 and Table 2.

Table 1 Crystalline size and FWHM of CeO_2nanoparticles

Plane	FWHM	Average Particle Size (nm)
111	0.614°	13.352
200	0.595°	13.939
220	0.650°	13.870
311	0.637°	13.636

Table 2 Crystalline size and FWHM of Ce-Zr hybrid nanoparticles

Plane	FWHM	Average Particle Size (nm)
111	0.921°	8.9128
200	0.892°	9.3073
220	1.048°	8.3006
311	1.022°	8.8414

Further, comparing the average particle size of both type of particles from HR-TEM images and XRD obtained values we can see that both are in agreement which proves that the results are true. Moreover, the broadening of peaks and their shift towards higher angles of Ce-Zr hybrid nanoparticles compared to nanosized Ceria (CeO2) can be due to the reduction in size of the particles.

C. Zeta Potential Analysis (ZP)

Zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. The magnitude of the zeta potential is a measure of stability of the nano-lubricants. The ZP value of nanosized Ceria (CeO2) and Ceria-Zirconia (Ce-Zr) hybrid nanoparticles dispersed separately in a standard liquid medium of hexane at 30°C is as shown in Table 3. It can be seen that the surfactant modified Ceria-Zirconia (Ce-Zr) hybrid nanoparticles have the highest ZP value of 40.5 mV; hence it is the most dispersion stable among all other nanoparticles considered.

Table 3 ZP values of various nanoparticles considered

Sample No.	Description	Zeta Potential (mV)
1	Hexane + CeO_2	28.92
2	Hexane + Ce-Zr hybrid	31.70
3	Hexane + Surfactant modified CeO_2	38.58
4	Hexane + Surfactant modified Ce-Zr	40.50

4 Conclusions

The following conclusions are derived on the basis of the characterization process carried out on the nanosized Ceria (CeO_2) and Ceria-Zirconia (Ce-Zr) hybrid nanoparticles.

- HR-TEM results proved that both type of nanoparticles have spherical morphology with the majority of particle size ranging from 10 nm to 20 nm. Further, the crystalline nature of CeO2 nanoparticles is not lost after doping with Zr. SEM images of the agglomerates nanoparticles proved the need for securing the synthesized particle from atmospheric interactions.
- FT-IR results confirmed the formation of the required metal oxide nanoparticles by PM. Moreover, the absence of chemical interaction of the added surfactant with the nanoparticles can be clearly noted.
- XRD analysis gave an insight into the average particle size of the synthesized nanoparticles, which are compared with the HR-TEM results for confirmation. The reduction in particle size of the Zr doped nanoparticles can be seen from the data derived of the XRD patterns.
- Finally, the dispersion stability of the surfactant modified nanoparticles over the bare nanoparticles is confirmed from the ZP analysis data.

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