# FT-IR Studies of Cerium Oxide Nanoparticles and Natural Zeolite Materials

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## ABSTRACT

An emerging topic of our days is nanoscience and nanotechnology successfully applied in the food industry. Characteristics such as size, surface area and morphology can modify the basic properties and the chemical reactivity of the nanomaterials. The breakthrough of innovative materials, processes, and phenomena at the nanoscale, as well as the progress of new experimental and theoretical techniques for research, supply novel opportunities for the expansion of original nanosystems and nanostructured materials. These study examine two types of nanoparticles, namely cerium oxide nanoparticles ($CeO_2$ NP) and natural zeolites In view of the importance of $CeO_2$ NP in various biological applications, the primary objective of this study was to characterise four samples of $CeO_2$ NP in order to understand the role of the synthesis process in the final product. Nanocrystalline natural zeolites are materials with interesting properties which allows them to be used as adjuvant in many therapies. The characterisation of $CeO_2$ NP and two types of natural zeolites using FourierTransform Infrared (FT-IR) spectroscopy was described. Therefore, this study examined two types of nanomaterials, namely cerium oxide nanoparticles and zeolites, for further applications on microorganisms and living cells.

***Keywords****: nanomaterials, cerium oxide, natural zeolite, FT-IR, characterization.*

## INTRODUCTION

An emerging topic of our days is nanoscience and nanotechnology. Nanotechnology involves nearly any materials which are structured on the nanometer scale in order to fulfil functions or gain characteristics which could not be achieved in another way. Nano area is dealing with materials with dimension varying from 1 to 100 nanometers.

The nanodimensions of a material induce significant changes of its properties, namely optical absorption, electronic conductivity, chemical reactivity, biocompatibility, compared with the marco-dimensions of the same material. With reduction in particle size, the surface area increases outstandingly and the number of atoms situated on the surface of the particle is higher. The surface area grants a considerable change of surface properties (e.g. energy, morphology). All these factors modify the basic characteristics and the reactivity of the nanomaterials.

Even if nanotechnology is now sufficiently known, it remains in its pre-exploration phase; rising from basic research to the industrial practice. Many industries can benefit from further research in nanotechnology as the industry of materials, nanoelectronics, medicine and healthcare, energy, biotechnology and information. The breakthrough of inovative materials, pro-

cesses, and phenomena at the nanoscale, as well as the progress of new experimental and theoretical techniques for research supply novel opportunities for the expansion of original nanosystems and nanostructured materials. Nanosystems are wanted to find various distinct applications. Nanomaterials can be made with nonpareil nanostructures and properties. This area is awaited to open new venues in science and technology.

Cerium is a rare earth element belonging to the lanthanide series. Even if is a rare earth element, the earth crust is relatively rich in this element, being the most abundant from the lanthanides. After europium, cerium has the highest reactivity among the rare earth metals, passing easily into oxidized stage at room temperature. While most of the rare earths exist in trivalent state, cerium also occurs in $4^+$ state and may alternate between the two in a redox reaction (Gokon et al., 2013, Singh et al., 2011, Suzuki et al., 2001). Based on the results, it was theorized that cerium oxide nanoparticles prolong cellular longevity by scavenging free radicals generated during their lifetime (Estevez et al., 2011). The distinct structure of ceria nanoparticles, regarding the valence, support cell longevity as benefit of its antioxidant properties (Chigurupati et al., 2013). Antioxidant behaviour is strongly influenced by the co-existence of both $Ce^{3+}$ and $Ce^{4+}$ oxidation states in $CeO_2$ nanoparticles. Concerning the fact that a transition in the oxidation state occurs in the biological environment, a basic principle was pronounce sustaining the therapeutic benefit of $CeO_2$ nanoparticles, (Chigurupati et al., 2013, Estevez et al., 2011, Diebold et al., 2010).

Another material drew our attention because of its interesting properties due to which can be used as adjuvant in many therapies is zeolite. Natural zeolite materials are hydrated aluminosilicate minerals that encloses alkaline and alkaline-earth metals. Zeolites are well known because of their specific crystal structure, which allows them to serve as molecular sieves. Zeolites are noted by differences in their chemical compositions, the size and arrangement of their crystal configuration. The structure of the zeolites significantly influence their properties, so that it is absolutely necessary to characterize the structure of zeolites.

Nanocrystalline zeolites are zeolites with discrete, uniform crystals with dimensions of less than 100 nm that have distinct properties relative to conventional micrometer-sized zeolite crystals. Nanocrystalline zeolites have significantly higher external surface areas and reduced diffusion (Petushkov et al., 2011). Different characterization techniques have been used to obtain data about the structural, chemical and catalytic features of zeolite materials, as powder X-Ray diffraction (XRD) often used to assess the crystallinity and prove the identity of zeolites; electron microscopy is used to determine particle morphology and size (Song et al., 2004, Petushkov et al., 2011, Mastral et al., 2006).

Fourier transform infrared spectroscopy (FT-IR) is a technique widely used for the characterization of a large variety of materials (Kadir et al., 2011, Mitic et al., 2009, Campbell et al., 2014, Centeno et al., 2014, Thakur et al., 2014). Due to its non-destructively, relatively rapid analysis and accessibility, the usage of this technique is increasing.

In this study cerium oxide nanoparticles and zeolites are discussed. Consider the importance of cerium oxide nanoparticles in multiple biological proposals, the primary objective of this study is to characterise four samples of cerium oxide nanoparticles in order to understand the role of $CeO_2$ NP synthesis in the final product. The characterization of $CeO_2$ NP with Fourier Transform Infrared (FT-IR) spectroscopy is described. FT-IR spectroscopy is utilized to probe the structure of zeolites and monitor reactions in zeolite pores

## MATERIALS AND METHODS

Two types on natural zeolites were purchased from Melidava, Romania. The chemicals used in the synthesis of the $CeO_2$ nanoparticles: cerium nitrate hexahydrate, $Ce(NO_3)_3 \cdot 6H_2O$ (Aldrich) and cerium acetylacetonate $Ce(C_5H_7O_2)_3 \cdot xH_2O$ (Alfa Aesar) as cation sources, ammonia, $NH_4OH$ (Alfa Aesar) and oxalic acid dihydrate, $H_2C_2O_4 \cdot 2H_2O$ (LachNer) as precipitation agent and oleylamine, $C_{18}H_{37}N$ as solvent. All chemicals were reagent grade and used without further purification.

### $CeO_2$nps synthesis

**A1 –** The synthesis of $CeO_2$nps was achieved by precipitation method by using an aqueous cerium nitrate solution (0.2 M) as the cerium

precursor and excess of ammonia solution (0.2 M) as precipitating reagent. The reaction was carried out at room temperature under continuous magnetic stirring. A stream of $O_2$ was bubbled into the reactor to oxidize $Ce^{3+}$ to $Ce^{4+}$. Firstly, a white precipitate came out in the solution. Subsequently, the colour of precipitate turned into purple, and gradually became light yellow. The post-precipitation stage consisted in a 24 h aging, separation by filtering and drying.

**A1EtOH** – The A1 sample was washing with ethanol for three times.

The nanocrystalline**A2** -$CeO_2$ sample was prepared by the wet chemical synthesis route – simultaneous addition of reagents (WCS - SimAdd), using cerium nitrate hexahydrate, $Ce(NO_3)_3 \cdot 6H_2O$ as the corresponding starting salt and oxalic acid dihydrate, $H_2C_2O_4 \cdot 2H_2O$ as precipitating reagent. 0.5 M aqueous solutions of acetates and oxalic acid were prepared. The precipitation was carried out under continuous magnetic stirring and the pH value was adjusted to 8±0.2, by adding the ammonium hydroxide solution, $NH_4OH$. The post-precipitation stage consisted in a 24 h aging, separation by filtering and drying. The precursor thermal treatment was performed at 723 K, for 1 h, in air at a heating rate of 300 K/h.

For the **C4 -** $CeO_2$ NPs synthesis, the solvothermal decomposition (heating-up process) of cerium acetylacetonate (2 mmol) dispersed in 50 ml oleylamine (OLA) was used. The solution was directly added into a three-neck round bottomed flask equipped with a condenser, a magnetic stirrer, and thermograph and heating mantle. The mixture was slowly heated-up to reflux at around 320°C and kept at reflux for 2 hours. A brown homogeneous colloidal suspension containing ceria NPs dispersed in OLA has been obtained. It has been noticed that these colloids are stable at room temperature. The addition of a 4:1 volume ratio mixture of ethyl acetate and ethanol to the final solution resulted in the separation of the $CeO_2$ NPs. Eventually, the cerium oxide powder was obtained by drying the precipitate under vacuum.

**FT-IR measurement**

The measurements were conducted using an IR Prestige 21 FTIR 8400S (Shimazu) spectrometer with a single reflection horizontal ATR accessory**.** The absorption FT-IR spectrum of the pellet in the range between 700 and 2000 $cm^{-1}$ was recorded at room temperature. The codification for each sample are shown in Table 1.

## RESULTS AND DISCUSSIONS

**$CeO_2$ NP FT-IR characterization**

The FT-IR spectrums (Fig. 1) for the four samples of $CeO_2$ NP shown characteristic frequency bands of Ce-O bound stretching.

It can be observed that the bands corresponding to characteristic of Ce-O stretching vibrations are at approximately 800 $cm^{-1}$, fact confirmed by the literature (Thakur et al., 2014, Sharma et al., 2012). The samples A1 and A1EtOH shows similar spectra, noting the fact that the intensity of the signal is higher for the sample where the $CeO_2$ NP were not washed with ethanol. Band near 1620 $cm^{-1}$ may be due to single H-O-H bending vibrational mode due to absorption of water in air. Bands around 1100 $cm^{-1}$ is assigned to C-O bond stretching mode.

**Natural zeolite material FT-IR characterization**

The framework of the zeolite is composed of the network formed by $TO_4$ (T = Si or Al) with tetrahedral corners. Vibrations of the zeolites frameworks create representative bands in the mid-IR and far-IR regions. A difference is made between external and internal vibrations of the

**Tab. 1.** Samples codification

| | |
|---|---|
| $CeO_2$NP obtained by precipitation method in $O_2$ flow | A1 |
| $CeO_2$NP obtained by precipitation method in $O_2$ flow, washed with ethanol | A1EtOH |
| $CeO_2$NP obtained by precipitation method - SimAdd | A2 |
| $CeO_2$NP obtained by solvothermal synthesis | C4 |
| Natural Zeolite 1 | Z1 |
| Natural Zeolite 2 | Z2 |

$TO_4$ tetrahedral. The expressions internal and external have been used in the IR spectroscopy of zeolite materials to describe the vibrations in the tetrahedral building units and between them (e.g., double rings as in A-, X-, Y-type and pore openings as in mordenite),respectively.

The most predominant bands occur in the ranges from 1250 to 950, from 790 to 650, and from 500 to 450 $cm^{-1}$, assigned tentatively to the asymmetrical stretching mode, the symmetrical stretching mode, and the T-O bending mode of the $TO_4$ tetrahedral, respectively. Similarly, bands around 650–500 $cm^{-1}$ and 420–300 $cm^{-1}$ are due to external linkage vibrations, namely, vibrations of double four-membered rings, double five-membered rings, or double six-membered rings, and pore opening vibrations, respectively. For example, structural information can be easily identified by IR spectroscopy for zeolites containing five-membered rings (Can et al., 2003). The absorption bands near 550 $cm^{-1}$ have been assigned to the presence of five-membered rings in the structure.

The structure-sensitive vibrations near 1200 and 550 $cm^{-1}$ provide information on the differentiation of the zeolite types and are also useful for identifying some framework features of zeolites of undetermined crystal structures. The FT-IR spectrums for the two samples of natural zeolites shown in Fig 2.

Particularly, structural information can be acquire from the vibrational frequencies of the zeolite material observed in the range between 400 and 4000 $cm^{-1}$. In the O-H stretching zone, infrared spectra of natural zeolite materials give plenty of information on hydroxyl groups attached

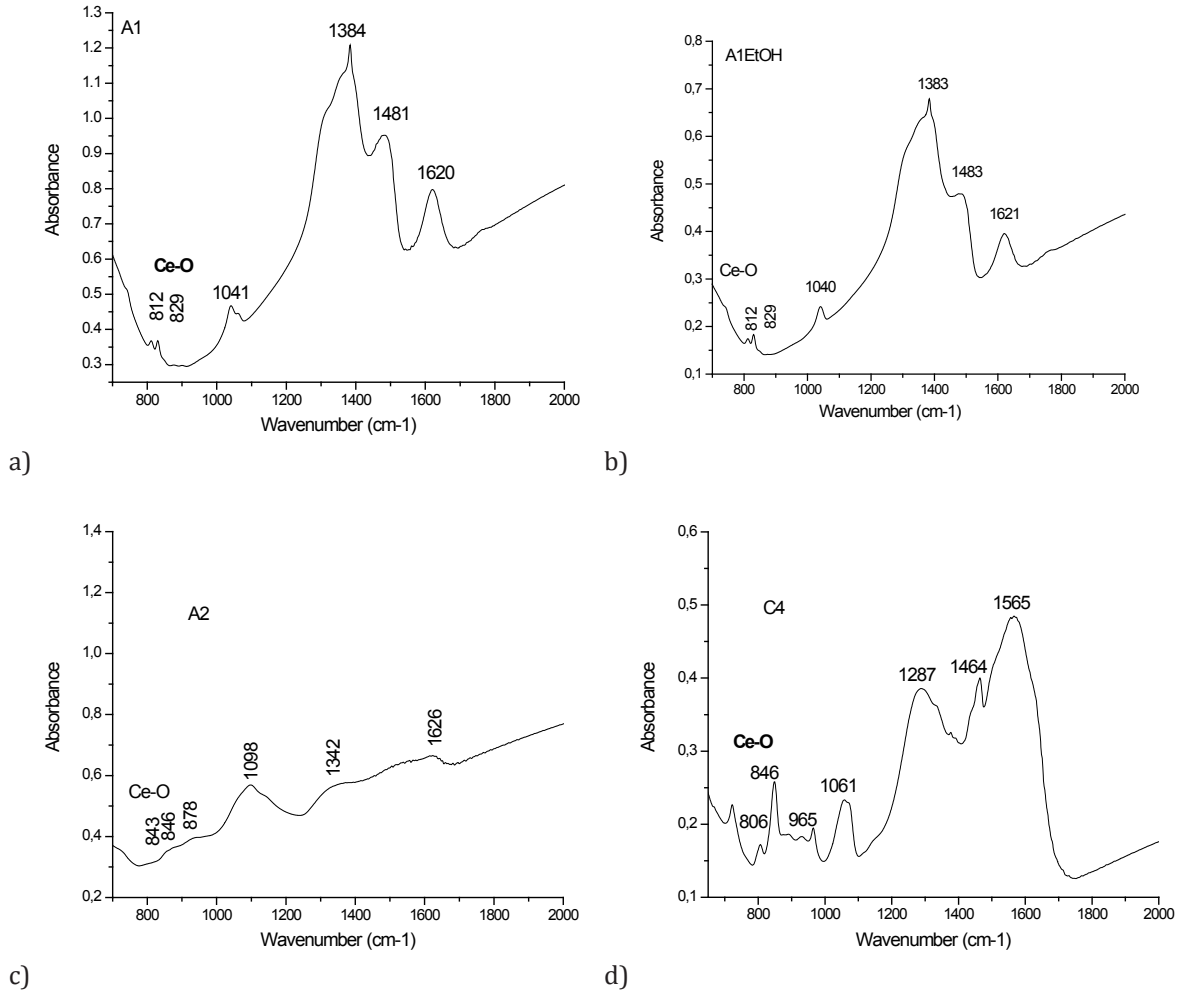
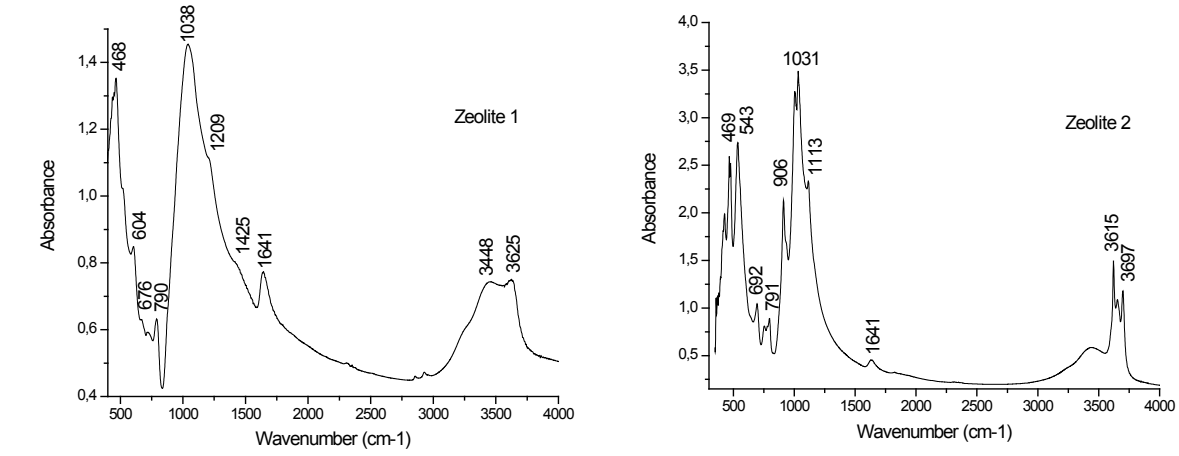



**Fig. 1.** FT-IR spectra of samples that revealed the characteristic peaks related to cerium oxide nanoparticles: a) sample A1; b) sample A1EtOH; c) sample A2; d) sample C4;




a) b)

**Fig. 2.** FT-IR spectra of the natural zeolite material that revealed the characteristic peaks
a) sample Z1; b) sample Z2;

to zeolite structures. Significant groups for the chemistry of natural zeolite materials are the hydroxyl groups (Flores-Lopez et al., 2012).

At least two types of hydroxyl groups are present in samples namely OH groups attached to cations which compensate the negative charge of the framework, at 3697 $cm^{-1}$ and OH groups attached to extra framework aluminium species, at 3625 $cm^{-1}$.

Adsorbed water (bending mode at 1641 $cm^{-1}$) was observed in both zeolite samples.

Quantitative and qualitative information regarding the adsorption/desorption of hydrocarbons and other adsorbents in zeolites can be obtained with FT-IR spectroscopy.

## CONCLUSION

This study has presented analyses of four types of cerium oxide nanoparticles and two types of natural zeolite materials. The analysis was conducted using the FT-IR spectroscopy.

This study has shown that the differences induced by the type of synthesis method of $CeO_2$ NP, can be indicated in the FT-IR spectra.

The same technique, FT-IR spectroscopy showed valuable information about the composition of the natural zeolite material.

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