IJARSCT

ISSN (Online) 2581-9429

International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal

Impact Factor: 7.53

Volume 5, Issue 1, January 2025

The Facile One–Pot Hydrothermal Synthesis and Characterizations of Heulandite/NiO Nanocomposite

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Abstract*: In this study, we report the synthesis and characterization of a Heulandite-Nickel oxide (Heu/NiO) nanocomposite using a facile hydrothermal route. Heulandite, a natural zeolite crystal, was firstly pre-treated and then combined with nickel oxide nanoparticles under hydrothermal conditions at 180˚C for 12h to form a nanocomposite. The hydrothermal process facilitated the combination of NiO nanoparticles onto the surface of Heulandite crystals, changing the structural and functional properties. The resulting Heu-NiO nanocomposite was characterized using a variety of techniques, including powder X-ray diffraction (PXRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM). XRD analysis confirmed the crystalline structure of both Heulandite and Heu-NiO nanocomposites, while SEM shown the uniform distribution of NiO nanoparticles on the surface of Heulandite. The FTIR spectra revealed characteristic bands associated with Heulandite aluminosilicate framework and NiO, demonstrating the presence of key functional groups and metal-oxygen bonds.The average crystalline sizes of the prepared NCs were calculated by the Debye-Scherrer equation. This work demonstrates the effective synthesis of a Heulandite-Nickel oxide nanocomposite and its characterizations.*

Keywords: Natural Zeolite, Heulandite, MOs (Metal Oxides), PXRD, FTIR, SEM

I. INTRODUCTION

Metal oxides play a very important role in many areas of chemistry, physics and materials science out of which Nickel oxide (NiO) is an important transition metal oxide with cubic lattice structure. It has attracted increasing attention owing to potential use in a variety of applications[1-7]. Recently, the development of novel, eco-friendly, and highly efficient catalytic systems for AOPs have garnered significant research interest. Among the various catalytic materials explored, zeolite-based Nano composites have shown remarkable potential due to their unique properties, including high surface area, tunable porosity, excellent thermal and chemical stability, and the ability to incorporate various active species within their framework [8–10]. Notably, the combination of transition metal oxides, such as NiO, with zeolite supports has been demonstrated to enhance the catalytic activity and selectivity for various oxidation reactions by promoting the generation of reactive oxygen species [11, 12]. Metal Oxides (MOs) nanoparticles such as; copper oxide (CuO) and zinc oxide (ZnO) have attracted a significant interest in the scientific research and varied scopes in the modern life due to their unique promising properties [13-15]. However, due to their fine size, the main drawback of nanoparticles that limits their wide applications is the agglomeration which reduces their surface area and hence their activity and efficiency [16]. To overcome the problems, attempts are being made by attachment hosts, supports and stabilizers materials with large surface area and porous structure to provide hybrid nanomaterials with surface functionalities for applications [17-20].

Zeolites, known also as a molecular sieve, are microporous, crystalline, hydrated aluminosilicates minerals of alkaline or alkaline earth metals. They are naturally occurring such as in volcanogenic sedimentary rock or synthetically produced. The framework structure of zeolites consists of three-dimensions of $[SiO4]^{4-}$ and $[A1O4]^{5-}$tetrahedral that are connected with each other by sharing oxygen atom to form cages or porous channels with diameters ranged between 0.3 and 1.2 nm. The replacement of Al^{3+} with Si^{4+} creates a negative charge in the lattice which can be neutralized by cations in the cavities such as; calcium, potassium, and sodium [21]. Furthermore, it is interesting to mention that in the last few years, several studies reported the use of Zeolite as a template support material to host and stabilize a variety of metals and metal oxides to control their nano size and distribution for the preparation of materials with hybrid properties and valuable applications [22, 23].Natural zeolite is a micro porous aluminosilicate mineral and recommended as promising catalyst carriers for its unique porous structure, surface area and environmental-friendly chemical composition [24-26]. Natural zeolites are environmentally and economically acceptable materials with exceptional ion exchange and adsorption properties. Their mechanical strength, chemical stability, and abrasion values make them one of the most promising materials in the water remediation applications (Barlokova, 2008).

Nanocomposites (NCs) are significant and promising materials of nanotechnology, which have attracted great attention due to their ability to merge the eligible properties of different Nanoscales with unique properties that are not found in conventional composites [27]. NCs introduce new technology and business opportunities for the majority of industrial sectors; further, they are environmentally friendly materials [28]. Moreover, NCs have been identified as appropriate alternatives to overcome the limitations of the agglomeration of nanoparticles [29-31].

II. MATERIAL & CHEMICALS

All chemical materials were used without any further purification. Nickel Nitrate Hexahydrate (Ni $(NO_3)_2.6H_2O$) was purchased from SD Fine, $(NH_2)_2CO$ urea and ethylene glycol purchased from Loba chemicals. Heulandite a natural zeolite obtained from Chhatrapati Sambhaji Nagar, (Aurangabad) Maharashtra, India) and distilled water (DW) used thought out experiment as a solvent.

Preparation Heulandite/NiO NCs:

Pre-treatment on Heulandite crystal: Take naturally occurring Heulandite crystal. Using Top-down processes have been used for extracting macro material from heulandite crystal and making its fine powder using mortar pestle. Wash the fine powder of Heulandite with distilled water for one hour using a magnetic stirrer at room temperature and filter the pure heulandite powder and dry overnight at room temperature.

Synthesis of Heulandite/NiO NCs:

The facile one–pot hydrothermal method was used for synthesis of heulandite/NiO Nano-composite. In the typical synthesis, take 2mmole of Ni $(NO_3)_2.6H_2O$, 10mmole of $(NH_2)_2CO$, 5mL of ethylene glycol and mix in 35mL of distilled water using magnetic stirrer at room temperature for half hour after that add some naturally occurring heulandite perpetrated powder (0.47gm) and stir the solution for another half hour finally the mixture was placed in a 50mL stainless-steel autoclave and hydrothermal reaction was run at 180˚C for 12h. Cool the autoclave at room temperature filter and dry the product at 80˚C for 24h. The nickel oxide nanoparticles ware synthesised using the same method without addition natural heulandite powder. Calcinate Heu/NiO nanocomposite at 180˚C for 2 h in air while bare NiO calcinate at 450˚C fir 2 h in air.

Characterization

The crystalline structure of preparedNano composite were investigated using PXRD with table top XRD,Miniflex 600 RIGAKU instrument with the wide angle of 2θ(20-80^o). The FT-IR spectra were recorded in the range of 400 cm^{-1}–3500 cm^{-1} using FT-IR Spectrophotometer (FT-IR) -Shimadzu, Japan. The Micro images of the sample of heulandite type natural zeolite, Heu-NiO nanocomposite and bare nickel oxide were obtained on a JSM-IT500 scanning electron microscope (JEOL, Tokyo, Japan)

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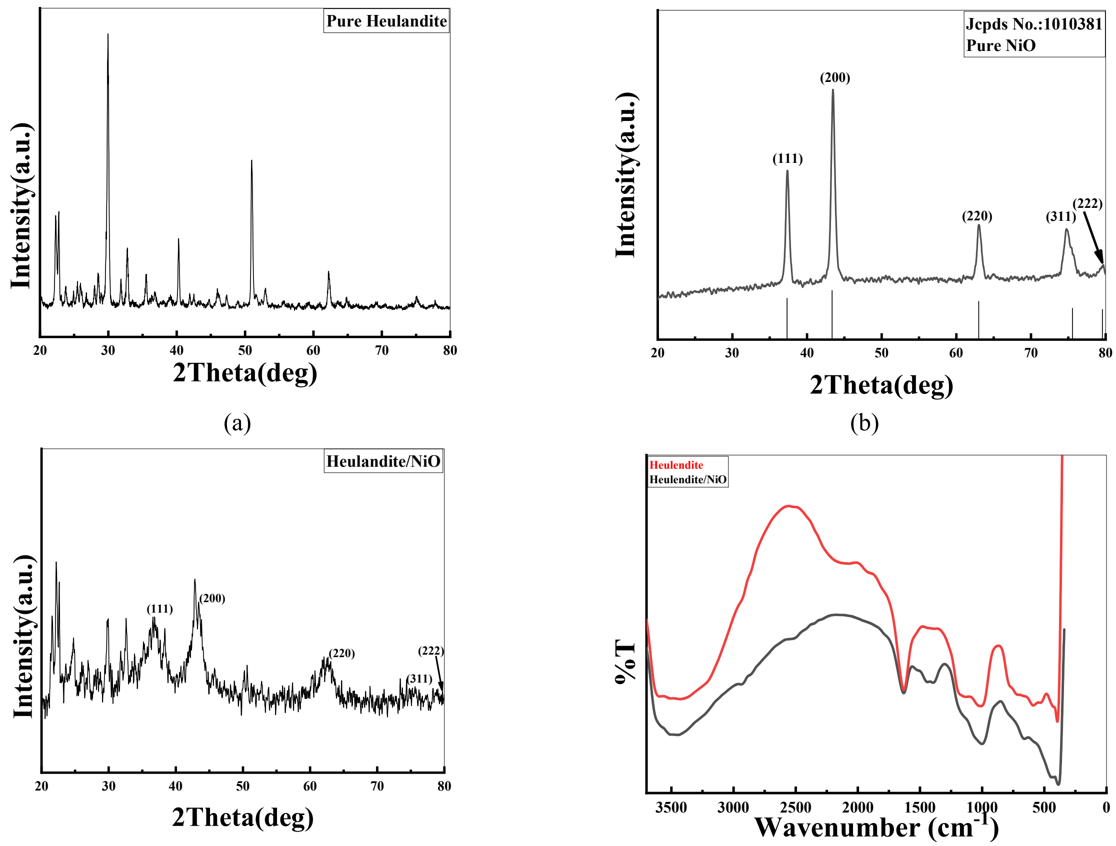
III. RESULTS AND DISCUSSION



(c) (d)

Fig.1 Powder XRD pattern (PXRD) of (a-c) of Heulandite, NiO and Heulandite/NiO Nanocomposite and (d) is the FT-IR of Heulandite and Heulandite/NiO Nanocomposite.

Powder XRD pattern (PXRD)

The XRD patterns of (a) natural Heulandite, (b)NiO, and (c) heulandite/NiOcomposite are depicted in fig.1. The structural properties and the changes in the crystalline phases were studied based on the XRD patterns. The natural zeolite mineral was defines as heulandite which obtained from its characteristic peaks correspondingat 2 θ = 22.33°, 26.06°, 28.21°, 30.06°and 35.83°[31]. Pure NiO exhibits peaks at 2θ = 37.32°, 43.36°, 63.00°, 75.56°, and 79.57° having miller indices (hkl) values (111), (200),(220), (311), and (222) which indicates that (JCPDS PDF Card No.:1010381). As illustrated in Fig. 1, the main core features of XRD patterns of NiO and Heulandite/NiO are very close, indicating that the introduction of Heulandite did not affect the structural properties of the NiO. However, the nanocomposite of Heulandite with NiO leads to an increase in the FWHM. In addition, the relative intensities of the diffraction peaks of Heulandite/NiO Nano-composite became weaker than the peaks of NiO, indicating a change in the crystallinity due to the distribution of NiO on the surface of the Heulandite (Zeolite).

The average crystalline sizesof the prepared NCs were calculated by the Debye-Scherrer equation,

$$D= \frac{k\lambda}{\beta Cos\theta}$$

Where, D is the average crystalline size, k represents the Scherrer constant (=0.98), λ denotes the wavelength (1.54), β denotes the full width at half maximum (FWHM), and Θ denotes Bragg's diffraction angle.The calculated average crystalline sizes of Pure Heulandite, NiO and Heulandite/NiO nanocomposite were found to be 38.87 nm, 12.39 nm and 44.44 nm respectively.

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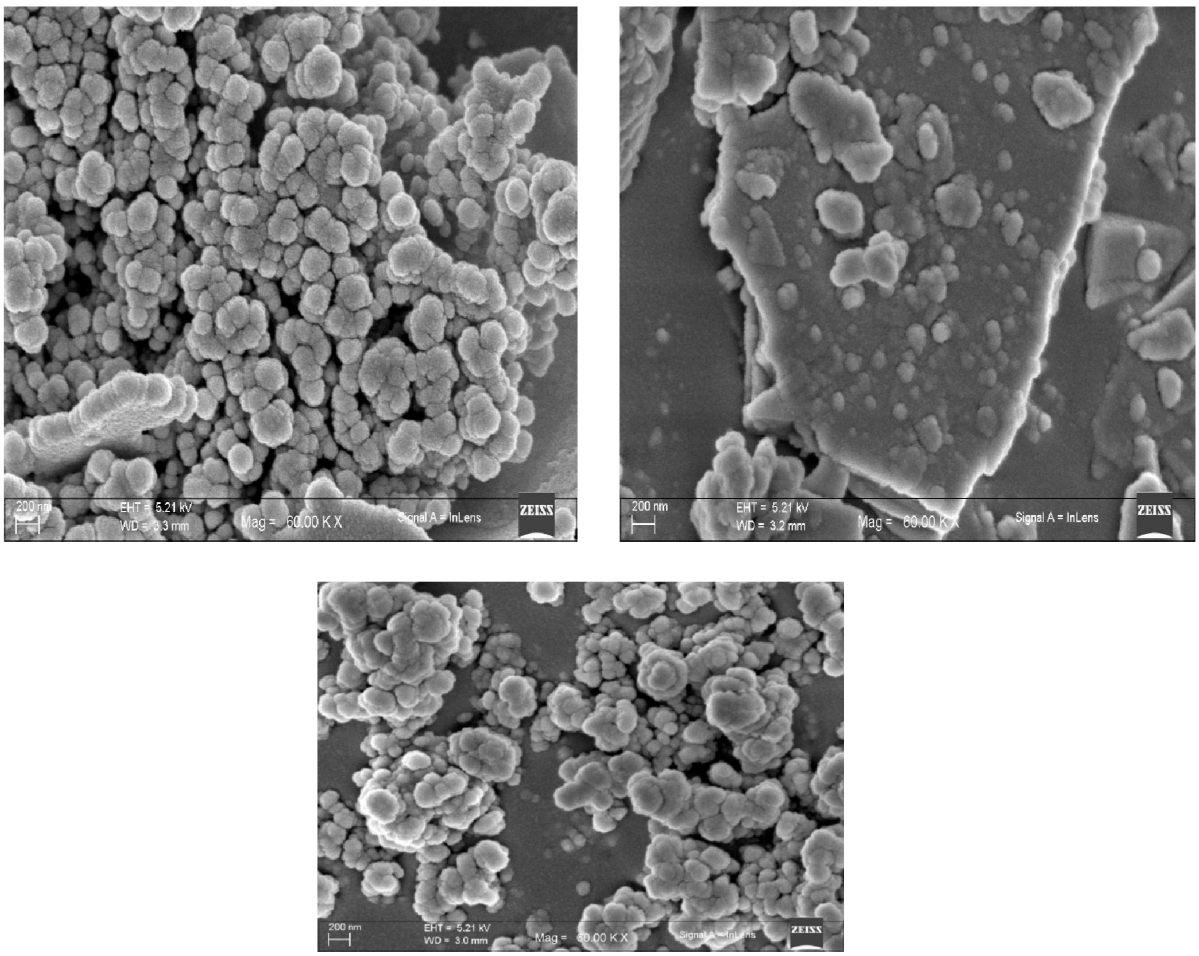
Fourier Transform-Infrared Spectroscopy (FTIR)

The FT-IR analysis of synthesized nanomaterial within the spectral range of 400 cm^{-1} to 3500 cm^{-1}. The FT-IR results, as illustrated in fig.1 (d). Provided insights into the structural composition and bonding interactions among the various components, including NiO, and Heulandite/NiO. The findings from this study confirmed the molecular properties and interactions of the generated nanomaterial. In the FT-IR spectra of Heulandite/NiO, the surface acidity is confirmed by a broad peak at 3433 cm^{-1} which represented by O-H stretching. Moreover distinct bands observed in Heulandite/NiO at 2829 cm^{-1} (C-H stretching), 1645 cm^{-1} (C=O stretching), 1385 cm^{-1} (C-H, H-O-H bending), 1004 cm^{-1} (Si-O-Al stretching), and 423 cm^{-1}, 552 cm^{-1} (Ni-O, Si-O, Si-O-Na stretching).

Scanning electron microscopy (SEM)



(c)

Fig.2 (a) pure heulandite, (b) Pure NiO (c) Heulandite/NiO Nanocomposite

The morphological properties of the (a)pure heulandite, (b)Bare NiO (c)Heulandite/NiO composite were investigated using scanning electron microscopy (SEM) as presented in Fig.2The appearance and structure of nanoparticles may be clearly seen using a scanning electron microscope (SEM). The studied natural heulandite zeolite appeared in the SEM images as micro aggregates of uniform shapes but without the definite crystalline habit. Investigation of the surficial morphological properties of heulandite after compositing with NiO revels the precipitated nickel oxide covered the surface of the prepared composite and appeared as well developed regular grains of flaky to columnar habits. The

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crystal growth of nickel oxide resulted in the formation of separated individual nickel oxide grains or twinned grains interlocked with each other in the same or different growth directions.

IV. CONCLUSION

In this study, a Heulandite/NiO nanocomposite was successfully synthesized via a facile one-pot hydrothermal method, demonstrating an efficient and eco-friendly approach for composite material fabrication. The structural and morphological characterizations confirmed the synthesis of Heulandite- Nickel oxide nanocomposite, with Fourier Transform Infrared Spectroscopy (FTIR) identifying the characteristic functional groups and metal-oxygen bonds. XRD analysis verified the phase, crystalline nature of the nanocomposite and average crystalline size of heulandite, Nickel Oxide and Heulandite- Nickel oxide nanocomposite measures using Debye-Scherrer formula were found 38.87 nm, 12.39 nm and 44.44 nm respectively. SEM provided detailed insights into its morphology. This work highlights the synergy between natural zeolites and metal oxides in developing advanced nanocomposites and provides a foundation for further exploration of their multifunctional applications.

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