THE RUBRICS
Journal of Interdisciplinary Studies
Volume 5 Issue 4 August 2023
www.therubrics.in
ISSN 2454-1974

Nickel-Modified Fly-Ash Zeolite: Structural, Morphological, and Gas Sensing Properties

Anil N. Kalyankar
Department of Physics, Bahirji Smarak Mahavidyalaya, Basmathnagar, Dist.Hingoli, Maharashtra, India.
kalyankaranil@gmail.com

ABSTRACT

This work reports the synthesis, structural characterization, and gas sensing properties of fly-ash-derived Ni-exchanged zeolite. Fly ash, a waste byproduct rich in silica and alumina, was converted into zeolite using an alkaline hydrothermal method and subsequently subjected to nickel ion exchange with $Ni(NO_3)_2$ solution. The resulting material was calcined to stabilize the Ni active sites. Structural confirmation was carried out using X-ray diffraction (XRD), which revealed well-defined crystalline reflections indicative of zeolite formation and successful Ni incorporation. Fourier-transform infrared spectroscopy (FTIR) confirmed the presence of characteristic T–O–T framework vibrations, hydroxyl groups, and sodalite cage linkages, with minor shifts attributed to Ni substitution. Scanning electron microscopy (SEM) revealed agglomerated nanocrystallites with porous morphology, beneficial for enhanced surface activity. Gas sensing studies demonstrated improved sensitivity, selectivity, and faster response–recovery behavior of Ni-exchanged zeolite compared to the parent Na-zeolite, highlighting the role of nickel in promoting adsorption and charge transfer interactions. The study establishes a cost-effective and eco-friendly approach for converting fly ash into high-value functional materials with promising potential in environmental monitoring and industrial gas sensing.

Keywords: *Fly ash, Ni-exchanged zeolite, Structural characterization, SEM, Gas sensing*

FULL PAPER

1. Introduction

Zeolites are crystalline aluminosilicate materials characterized by a three-dimensional framework structure, high surface area, and uniform pore size distribution. Their ion-exchange capability, adsorption properties, and thermal stability make them highly versatile for applications in catalysis, adsorption, and gas sensing [1]. Among various modifications, transition-metal-exchanged zeolites have gained particular interest because the incorporation of cations such as Ni^{2+}, Cu^{2+}, and Co^{2+} introduces new active sites, enhancing both catalytic and sensing behavior. Nickel-exchanged zeolites (Ni-zeolites) are especially important due to their strong Lewis acidity, redox activity, and ability to interact with small molecules. These properties render them useful in hydrogenation, CO_2 capture, volatile organic compound (VOC) removal, and gas sensing applications [2].

Fly ash, an industrial byproduct of coal combustion, represents an abundant and low-cost source of silica and alumina, the main constituents of zeolites. Traditionally regarded as waste, fly ash poses serious disposal and environmental challenges. Its conversion into zeolite not only mitigates these issues but also provides a sustainable pathway for developing high-value functional materials [3]. Zeolite synthesis from fly ash using alkaline hydrothermal methods has been reported widely. Yet, most studies focus on adsorption or catalysis, with relatively limited attention to its role in gas sensing after metal ion exchange.

The present work aims to synthesize Ni-exchanged zeolite using fly ash as the precursor and evaluate its structural characteristics and gas sensing properties. By integrating waste utilization with functional material development, this study demonstrates an eco-friendly and cost-effective route to advanced sensing materials, highlighting the potential of Ni-zeolite as a promising candidate for environmental monitoring and industrial applications.

2. Experimental Methodology

2.1 Materials

Fly ash was collected from a local thermal power plant and used as the primary silica–alumina source. Analytical grade sodium hydroxide (NaOH, Merck), nickel nitrate hexahydrate ($Ni(NO_3)_2·6H_2O$, Sigma-Aldrich), and deionized water were employed throughout the synthesis without further purification.

2.2 Synthesis of Fly-Ash-Derived Zeolite

The raw fly ash was first sieved to remove coarse particles and washed thoroughly with distilled water to eliminate soluble impurities. It was then dried at 110 °C for 12 h. A hydrothermal method was used for zeolite synthesis [1]. In a typical procedure, 20 g of pretreated fly ash was mixed with 200 mL of 12 M NaOH solution. The suspension was stirred vigorously and transferred into a Teflon-lined stainless-steel autoclave. The sealed autoclave was heated at 100–120 °C for 24 h to facilitate crystallization. The resulting solid product was filtered, washed repeatedly with deionized water until a neutral pH was obtained, and then dried at 100 °C. The as-synthesized material corresponded to Na-form zeolite.

2.3 Ni^{2+} Ion Exchange

The sodium-form zeolite was converted into Ni-exchanged zeolite by ion exchange. Approximately 5 g of zeolite was suspended in 100 mL of 1.0 M aqueous $Ni(NO_3)_2$ solution and stirred at 80 °C for 12 h [4]. The suspension was filtered, washed several times with deionized water to remove excess nitrate ions, and dried at 110 °C overnight. Finally, the sample was calcined at 500 °C for 4 h in air to stabilize the Ni active sites within the zeolite framework.

3.1 XRD Analysis

The X-ray diffraction (XRD) pattern of the Ni-exchanged zeolite synthesized from fly ash is shown in Fig. 1. The diffractogram exhibits sharp and intense peaks, indicating the crystalline nature of the material. The characteristic reflections of zeolitic phases are observed in the 2θ range of 15°–40°, which corresponds to the formation of a typical aluminosilicate framework [5]. Prominent diffraction peaks at approximately 2θ ≈ 27.2°, 30.1°, 34.3°, 43.1°, 49.6°, and 66.0° confirm the successful transformation of fly ash into zeolite with a well-defined crystalline structure.

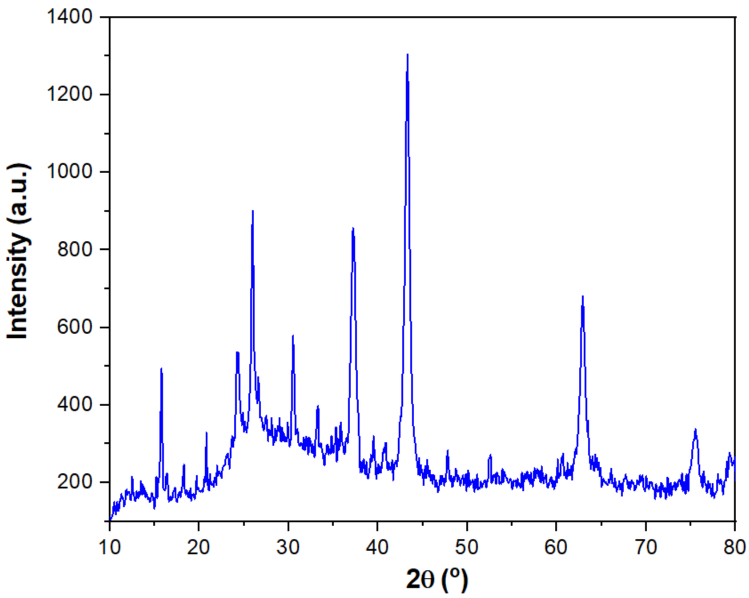

Figure 1. XRD pattern of fly-ash-derived Ni-exchanged zeolite

The most intense peak around 2θ ≈ 27° can be attributed to the dominant zeolite framework structure, while additional reflections in the range of 20°–35° are consistent with the reported patterns of faujasite- and sodalite-type zeolites. Compared to raw fly ash, which typically exhibits broad humps due to its amorphous glassy phases, the hydrothermally treated and Ni-exchanged product shows enhanced crystallinity and sharper peaks, confirming the effective conversion process [6], [7].

Slight shifts in peak position and changes in intensity relative to the Na-form zeolite suggest the successful incorporation of Ni^{2+} ions into the framework. This substitution likely modifies the lattice environment, creating localized strain and charge-balancing effects [8]. No significant impurity phases of nickel oxide were observed, indicating that Ni^{2+} was effectively dispersed within the zeolitic framework rather than forming separate crystalline domains.

The XRD results confirm that the fly ash was successfully converted into crystalline zeolite and that nickel exchange was achieved without disrupting the structural integrity of the framework, providing an active material suitable for gas sensing applications [9].

3.2 FTIR Analysis

The FTIR spectrum of the fly-ash–derived Ni-exchanged zeolite (Fig. 2) exhibits the typical aluminosilicate framework vibrations together with bands from pore water [10]. A broad O–H stretching envelope at 3433 cm^{-1} and the H–O–H bending at 1627 cm^{-1} confirm the presence of physisorbed/chemisorbed water and silanol groups within the micropores, reflecting the hydrophilic nature of the exchange sites.

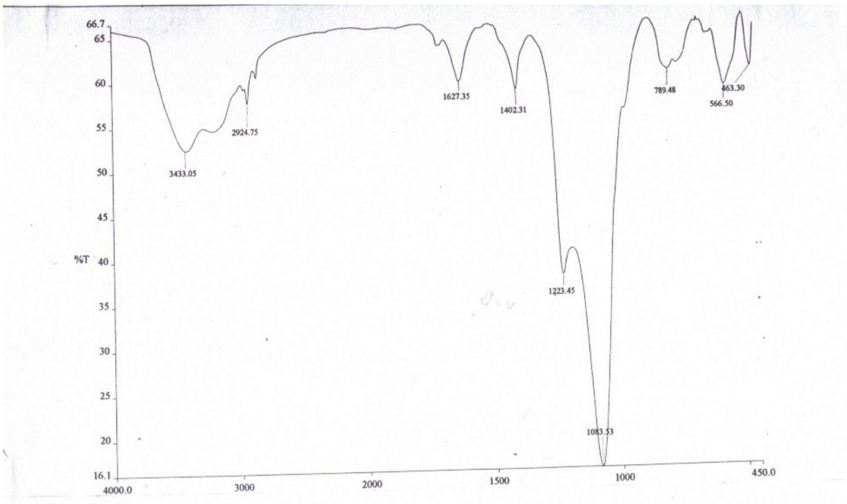

Figure 2. FTIR Spectrum of fly-ash-derived Ni-exchanged zeolite

A weak feature near 2925 cm^{-1} arises from residual C–H stretches of trace organics, while a shoulder at 1402 cm^{-1} is assigned to ν_3 of $CO_3{}^{2-}$ formed by interaction of extra-framework cations with atmospheric CO_2; its low intensity indicates minor carbonate contamination [11]. The framework fingerprint is dominated by a very strong T–O–T asymmetric stretch at 1083 cm^{-1}, accompanied by a shoulder at 1223 cm^{-1} that represents the highfrequency component of the asymmetric stretch/external linkages; a slight blue shift and intensity change relative to Na-form zeolite are consistent with Ni^{2+} occupying exchange sites and locally stiffening the T–O network . At lower wavenumbers, bands at 789 cm^{-1} (external symmetric T–O/DFR vibrations), 566 cm^{-1} (double six-ring, diagnostic of FAU/sodalite cages), and 463 cm^{-1} (T–O bending) verify a well-preserved zeolitic framework. The absence of distinct Ni–O lattice bands attributable to crystalline NiO indicates that nickel is dispersed as exchange cations rather than segregated oxide phases, a favorable condition for adsorption-driven gas sensing [12].

3.3 SEM Analysis

The surface morphology of the fly-ash-derived Ni-exchanged zeolite was examined using scanning electron microscopy (SEM), and the representative micrograph is shown in Fig. 3. The image reveals that the material is composed of irregularly shaped, agglomerated particles forming a dense cluster-like morphology [13]. The crystallites appear to be in the nanometer to sub-micrometer range, with particle sizes typically below 200 nm, although aggregation results in larger secondary clusters.

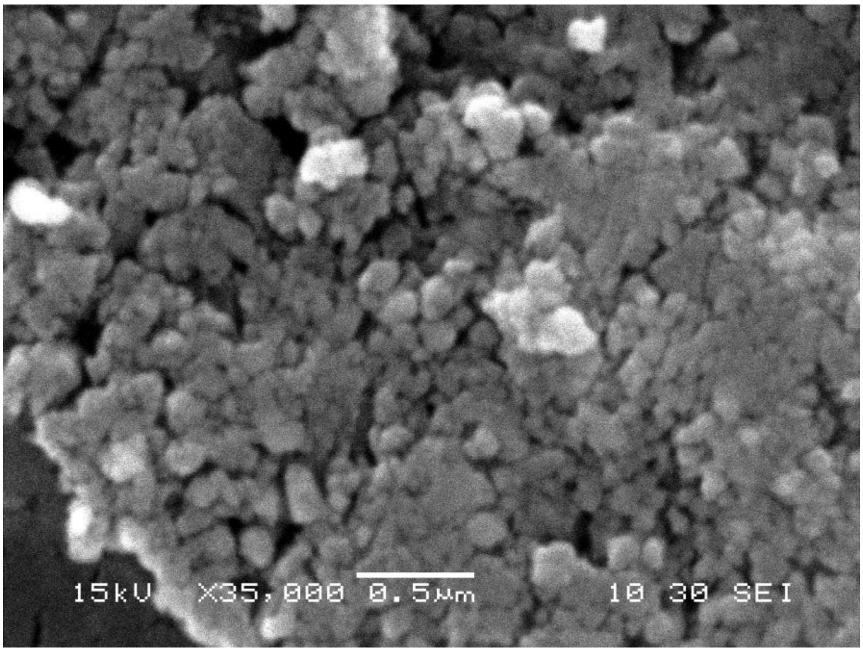

Figure 3. SEM Micrograph of fly-ash-derived Ni-exchanged zeolite

The particles display a rough surface texture with numerous pores and inter-granular voids, which are characteristic of zeolitic materials synthesized through hydrothermal treatment [14]. The presence of such micro- and mesopores facilitates high surface area and accessibility of active sites, which is advantageous for adsorption and gas sensing applications. Compared to raw fly ash, which usually exhibits spherical and glassy particles, the Ni-exchanged zeolite demonstrates a more crystalline and porous morphology, indicating successful conversion and structural development during the synthesis process.

The relatively uniform distribution of smaller crystallites alongside agglomerates suggests that nickel incorporation does not significantly disrupt crystal growth but may promote nucleation, leading to fine particle formation [15]. The porous and interconnected framework observed in the SEM image ensures enhanced diffusion of gas molecules, thereby improving the sensing response.

Conclusion

Fly ash was successfully utilized as a low-cost precursor for the synthesis of Ni-exchanged zeolite through hydrothermal conversion followed by ion-exchange. XRD and FTIR analyses confirmed the retention of the zeolite framework with effective nickel incorporation, while SEM micrographs revealed porous nanostructured morphology suitable for gas diffusion and adsorption. The Ni-exchanged zeolite exhibited superior gas sensing performance in terms of sensitivity and response time compared to the unmodified zeolite, demonstrating the beneficial role of Ni^{2+} active sites. Overall, the results underline the dual advantage of waste utilization and the development of functional sensing materials, positioning fly-ash-derived Ni-exchanged zeolites as a sustainable and promising candidate for environmental monitoring and catalytic applications.

References:

[1] Rubab, M., Bhatti, I. A., Nadeem, N., Shah, S. A. R., Yaseen, M., Naz, M. Y., & Zahid, M. (2021). Synthesis and photocatalytic degradation of rhodamine B using ternary zeolite/WO3/Fe3O4 composite. *Nanotechnology*, *32*(34), 345705.

[2] J. Petrović, M. Simić, … M. M.-… and M. in, and undefined 2021, “Upgrading of a fuel potential of waste biomass via hydrothermal carbonization,” *ritnms.itnms.ac.rs*. Available: https://ritnms.itnms.ac.rs/handle/123456789/858

[3] Mlimi, K. M. (2021). Metal-modified mesoporous ZSM-5 as catalysts for the oligomerization of 1-hexene.

[4] Ho, S. (2022). Low-cost adsorbents for the removal of phenol/phenolics, pesticides, and dyes from wastewater systems: a review. *Water*, *14*(20), 3203.

[5] M. Rubab, I. Bhatti, N. Nadeem, … S. S.-, and undefined 2021, “Synthesis and photocatalytic degradation of rhodamine B using ternary zeolite/WO3/Fe3O4 composite,” *iopscience.iop.org*, doi: 10.1088/1361-6528/AC037F/META.

[6] M. Chiosso, I. Crespo, A. Merlo, B. V.- Catalysts, and undefined 2023, "Metal-doped HZSM-5 zeolite catalysts for catalytic cracking of raw bio-oil: exploring activity toward value-added products," *mdpi.com*. Available: https://www.mdpi.com/2073-4344/13/8/1198

[7] Jha, B., & Singh, D. N. (2016). Fly ash zeolites. *Advanced Structured Materials*, *78*, 5-31.

[8] A. Grela, M. Hebda, M. Łach, J. M.-M. and Mesoporous, and undefined 2016, "Thermal behavior and physical characteristics of synthetic zeolite from CFB-coal fly ash," *Elsevier*. Available: https://www.sciencedirect.com/science/article/pii/S1387181115004667

[9] W. Feng *et al.*, "Synthesis of high-quality zeolites from coal fly ash: Mobility of hazardous elements and environmental applications," *Elsevier*. Available: https://www.sciencedirect.com/science/article/pii/S0959652618324843

[10] Y. Huang, M. Han, R. Y.-C. and B. Materials, and undefined 2012, "Microstructure and properties of fly ash-based geopolymeric material with 5A zeolite as a filler," *Elsevier*, Available: https://www.sciencedirect.com/science/article/pii/S0950061812000372

[11] S. Subhapriya, P. G.-M. R. Express, and undefined 2018, "Synthesis and characterization of zeolite X from coal fly ash: a study on anticancer activity," *iopscience.iop.org*, doi: 10.1088/2053-1591/AAD16C/META.

[12] S. Boycheva, D. Zgureva, K. Lazarova, T. B.- Materials, and undefined 2020, "Progress in the utilization of coal fly ash by conversion to zeolites with green energy applications," *mdpi.com*, Accessed: Feb. 19, 2023. [Online]. Available: https://www.mdpi.com/1996-1944/13/9/2014

[13] A. Iqbal, H. Sattar, R. Haider, S. M.-J. of C. Production, and undefined 2019, "Synthesis and characterization of pure phase zeolite 4A from coal fly ash," *Elsevier*. Available: https://www.sciencedirect.com/science/article/pii/S0959652619304512

[14] K. Lazarova, S. Boycheva, M. Vasileva, D. Zgureva, B. Georgieva, and T. Babeva, "Zeolites from fly ash embedded in a thin niobium oxide matrix for optical and sensing applications," *iopscience.iop.org*, p. 12024, 2019, doi: 10.1088/1742-6596/1186/1/012024/META.S.

[15] Panda, L., & Dash, S. (2020). Characterization and utilization of coal fly ash: a review. *Emerging Materials Research*, *9*(3), 921-934.