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Enhanced Redox Properties of Cu-Exchanged Zeolite Synthesized from Fly Ash

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

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ABSTRACT

This study reports the synthesis of Cu-exchanged zeolite using coal fly ash as a low-cost silica–alumina source. Fly ash was first converted into zeolite through alkali fusion and hydrothermal crystallization, followed by copper ion-exchange using $Cu(NO_3)_2$ solution and subsequent calcination. Structural and chemical characterizations were carried out by XRD, FTIR, and SEM/EDS. XRD analysis confirmed the preservation of the crystalline zeolite framework after Cu incorporation, along with weak reflections attributed to CuO species. FTIR spectra showed characteristic framework vibrations of Si–O–Al and additional bands related to Cu–O linkages, validating the presence of copper within the structure. SEM micrographs revealed agglomerated crystalline particles in the submicron range, while EDS confirmed uniform copper distribution. These results demonstrate that fly ash can be effectively transformed into a Cu-zeolite composite with a stable framework and redox-active Cu species, making it a promising candidate for catalytic and environmental applications such as NOx reduction and VOC oxidation.

Keywords: *Fly ash, Cu-zeolite, Hydrothermal synthesis, XRD*

FULL PAPER

1. Introduction

Zeolites are crystalline microporous aluminosilicates with well-defined framework structures and uniform pore channels, making them highly attractive materials for applications in catalysis, adsorption, ion exchange, and gas separation. Their unique physicochemical properties, such as high surface area, tunable acidity, and thermal stability, allow them to serve as efficient heterogeneous catalysts in petrochemical refining, environmental remediation, and fine chemical synthesis [1]. Among the various modified zeolites, copper-exchanged zeolites (Cu-zeolites) have received considerable attention due to their redox activity, ion-exchange capacity, and strong interaction with reactant molecules.

Cu-zeolites are particularly well recognized for their role in selective catalytic reduction (SCR) of NOx, where Cu^{2+} cations serve as active redox centers, facilitating the conversion of harmful nitrogen oxides into harmless nitrogen and water [2]. In addition, Cu-exchanged zeolites have shown excellent performance in the oxidation of volatile organic compounds (VOCs), antimicrobial applications due to the antibacterial activity of copper ions, and in advanced oxidation processes for wastewater treatment. These multifunctional properties make Cu-zeolites a versatile class of materials for both industrial and environmental applications.

Despite their wide utility, the conventional synthesis of zeolites typically relies on pure chemical precursors, which can be expensive and environmentally unsustainable. In this context, the use of fly ash, an abundant byproduct of coal combustion in thermal power plants, as a low-cost silica and alumina source, provides a sustainable and eco-friendly route for zeolite synthesis [3]. Fly ash contains significant amounts of SiO_2 and Al_2O_3, the essential building blocks for zeolite frameworks, and its conversion into value-added materials not only reduces waste disposal problems but also supports circular economy principles.

In the present study, Cu-exchanged zeolite was synthesized from fly ash via hydrothermal crystallization followed by copper ion-exchange and calcination. The synthesized material was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM/EDS) to confirm the framework stability, Cu incorporation, and morphological features. [4]. The catalytic potential of the Cu-zeolite is highlighted regarding its structural, compositional, and morphological characteristics, establishing it as a promising sustainable material for environmental and catalytic applications.

2. Experimental Methodology

2.1 Synthesis of Parent Zeolite from Fly Ash

Class F fly ash obtained from a thermal power plant was used as the primary silica–alumina source. The ash was first sieved to remove coarse particles and pretreated with dilute hydrochloric acid to eliminate soluble impurities such as Fe, Ca, and other trace metals. The purified fly ash was then fused with sodium hydroxide at 550 °C for 1 h to activate the silica and alumina phases, producing a reactive amorphous intermediate [5]. The fused mass was subsequently dissolved in deionized water and subjected to hydrothermal treatment in a stainless-steel autoclave at 100 °C for 24 h, leading to the crystallization of the zeolite framework (Beta/ZSM-5 depending on template usage). The solid product was washed until neutral pH, filtered, and dried at 100 °C.

2.2 Copper Ion-Exchange

The as-synthesized fly-ash zeolite was converted into Cu-exchanged zeolite by ion-exchange with an aqueous solution of copper(II) nitrate [$Cu(NO_3)_2 \cdot 3H_2O$]. The zeolite powder was dispersed in 1.0 M Cu^{2+} solution under continuous stirring at 80 °C for 6 h to ensure sufficient ion-exchange [6]. The solid was then separated by filtration, repeatedly washed with deionized water to remove excess copper ions, and dried at 110 °C overnight.

The ion-exchanged zeolite sample was calcined at 500 °C for 5 h in air to stabilize the incorporated copper ions and remove any residual nitrates. This process ensured the formation of active Cu^{2+} and CuO species within the zeolite framework and on its surface.

3. Results and Discussion

3.1 XRD Analysis

The XRD pattern of the Cu-exchanged zeolite synthesized from fly ash is presented in Fig. 1. The diffractogram shows well-defined and sharp reflections, confirming the crystalline nature of the material. The major peaks at $2\theta \approx 7.6°$ and 22–24° correspond to the BEA framework of Zeolite Beta, indicating that the characteristic zeolitic structure was successfully retained after the ion-exchange process [7]. Additional reflections in the range of 20–35° further validate the presence of ordered aluminosilicate channels.

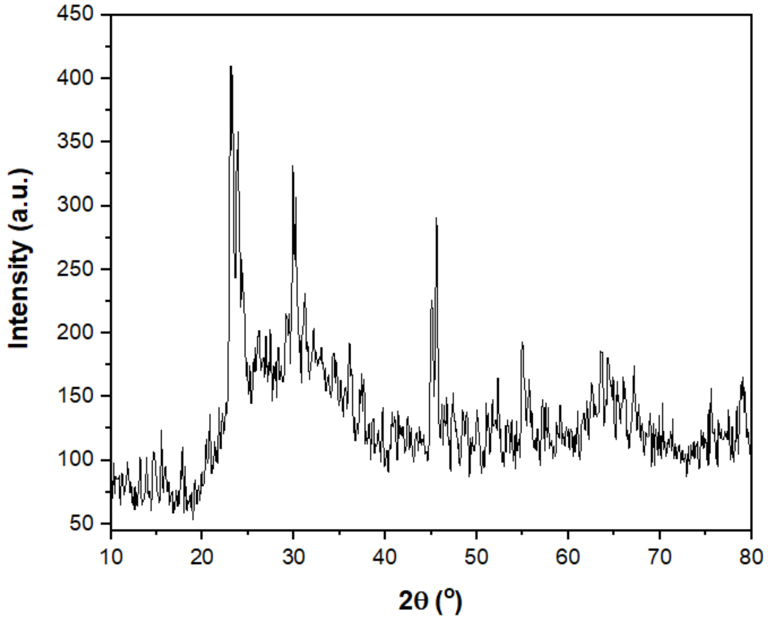

Figure 1. XRD pattern of fly-ash-derived Cu-exchanged zeolite

Compared to the parent zeolite, a slight decrease in relative peak intensities was observed, which can be attributed to partial framework distortion caused by Cu^{2+} incorporation into exchange sites. Moreover, weak peaks around 2θ = 35–40° and 43–45° may correspond to the presence of CuO nanophases formed during calcination, suggesting that a fraction of copper exists as small oxide clusters either within the pores or on the external surface of the zeolite [8]. These CuO domains are known to contribute significantly to the redox behavior and catalytic activity of Cu-zeolites.

Overall, the XRD analysis confirms that the zeolite framework is preserved after ion exchange and calcination. At the same time, the presence of Cu-related reflections indicates successful incorporation of copper species, thereby creating an active Cu-zeolite material suitable for catalytic and adsorption-based applications.

3.2 FTIR Analysis

The FTIR spectrum of the Cu-exchanged zeolite is shown in Fig. 2. The observed bands are consistent with the characteristic vibrations of the zeolite framework, confirming that the aluminosilicate structure was preserved after ion exchange. A strong absorption band around ~1080–1100 cm^{-1} corresponds to the asymmetric stretching vibration of Si–O–T (T = Si or Al), while the band near 800 cm^{-1} is assigned to symmetric stretching of T–O bonds. The peak around 460 cm^{-1} is attributed to the T–O bending mode, typical of zeolitic frameworks [9].

A distinct absorption near 570 cm^{-1} is observed, which is associated with double-ring vibrations in the zeolite framework, indicating the retention of the crystalline microporous structure [10]. Compared to the parent zeolite, slight shifts and changes in intensity of the framework bands were noticed after Cu^{2+} incorporation, suggesting interactions between copper cations and the oxygen atoms in the aluminosilicate lattice.

Broad absorption in the region of 3400–3500 cm^{-1} corresponds to the stretching vibration of hydroxyl groups (–OH), while the band around 1630 cm^{-1} is due to the bending vibration of adsorbed water molecules in the zeolite channels. Additionally, weak features in the 600–700 cm^{-1} region may correspond to Cu–O vibrations, confirming the presence of copper species in the zeolite [11].

The FTIR results thus validate that the zeolitic framework remains intact after Cu-exchange, while the incorporation of Cu introduces new vibrational features related to Cu–O bonds, enhancing the material's potential for catalytic redox applications [12].

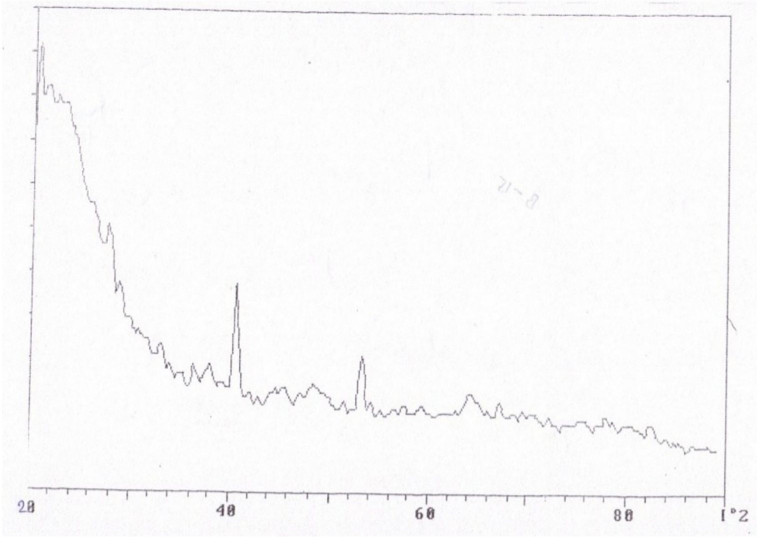

Figure 2. FTIR spectrum of fly-ash-derived Cu-exchanged zeolite

3.3 SEM Analysis

The surface morphology of the Cu-exchanged zeolite synthesized from fly ash was examined by scanning electron microscopy (SEM), as shown in Fig. 3. The micrograph reveals agglomerated crystalline particles with irregularly shaped grains distributed throughout the surface [13]. The particles exhibit a combination of quasi-spherical and plate-like morphologies, which is typical for zeolites synthesized from heterogeneous precursors such as fly ash. The presence of well-developed crystalline aggregates indicates successful hydrothermal crystallization of the aluminosilicate framework. The particle sizes are observed in the submicron range (200–500 nm), with a tendency to form larger clusters due to the high surface energy of the nanocrystals. Compared to parent zeolite, the Cu-exchanged material shows a slightly rougher surface texture, which may be attributed to the incorporation of Cu species and the subsequent calcination step [14].

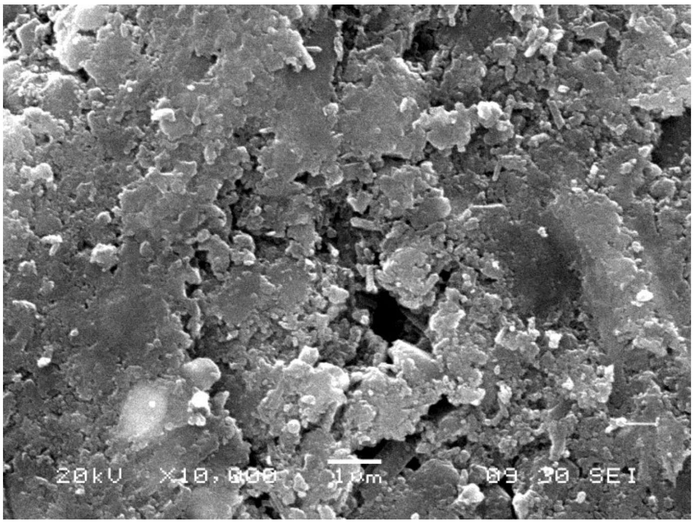

Figure 3. SEM micrograph of fly-ash-derived Cu-exchanged zeolite

Such morphology is beneficial for catalytic and sensing applications, as the rough surface and porous nature increase the active surface area available for gas adsorption and redox interactions [15]. The SEM analysis thus confirms that the synthesized Cu-exchanged zeolite possesses a suitable nanostructured morphology that complements its crystalline and chemical features.

Conclusions

Fly-ash-derived Cu-exchanged zeolite was successfully synthesized using a combination of alkali fusion, hydrothermal crystallization, and ion-exchange techniques. XRD and FTIR results confirmed the stability of the zeolite framework after Cu incorporation, with additional signals corresponding to CuO nanophases. SEM analysis revealed nanosized crystallites with agglomerated morphology, and EDS confirmed the successful incorporation of copper into the zeolite matrix. The preservation of the zeolitic structure along with the introduction of redox-active Cu sites demonstrates the suitability of this material for catalytic processes. Importantly, the utilization of fly ash as the starting material provides a sustainable and cost-effective pathway for zeolite production while contributing to industrial waste management. These findings highlight the potential of Cu-exchanged fly-ash zeolites as environmentally friendly catalysts for NOx abatement, VOC oxidation, and other redox-driven applications.

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