Optimization of the selective effect of zeolite in the synthesis of Cu2O Nanoparticles

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Abstract

In this study, we exhibit a novel method for synthesizing Cu$_2$O nanoparticles by employing ion exchange within the synthetic nanozeolite 4A matrix. The nanoparticles showed a consistent particle size, predominantly around 6 nm, with a narrow distribution. Nanosizing of the zeolite was achieved through high-energy milling treatments, thereby enhancing the surface-to-volume ratio. A band close to 700 cm$^{-1}$ was observed in the FTIR spectrum, potentially indicating an aspect of zeolite downsizing related to symmetric stretching of the Si-O bond post-milling. Furthermore, a distinctive band corresponding to Cu(I)-O stretching vibrations was identified around 600 cm$^{-1}$. Additionally, optical absorption analyses in the UV-Vis spectrum revealed two characteristic bands attributable to Cu$_2$O nanoparticles, positioned at 370 nm and 470 nm, respectively. These findings lead to advancements in resource use and promote sustainable and environmentally friendly production practices.

Introduction

In recent decades, nanotechnology has emerged as a focal point of scientific research, fostering the development of innovative materials with unique properties and diverse applications. [1, 2] Among these materials, nanozeolites have captured the attention of the scientific community due to their exceptional versatility and promising characteristics at the nanoscale. [3] Nanozeolites represent a significant advancement in the synthesis, stabilization, and adaptation of materials at the nanometer scale. These crystalline structures, primarily composed of aluminosilicates, exhibit a three-dimensional porous network, with a higher surface-to-volume ratio that increases the number of active sites. Additionally, nanozeolites are characterized by uniform channels and cavities that can possess molecular sizes with effective ion exchange capacity. This ability allows them to stabilize species of atom units in their cavities or surface and enhance molecular manipulation. [4] Regarding the synthesis of nanozeolites, various strategies have been successfully implemented. [5]. Commonly employed synthesis methods include hydrothermal processes, microemulsion, among others, providing precise control over the nucleation and formation of nanozeolites. [6] The incorporation of high-energy milling processes has ensured the downsizing of the zeolite, reaching nanodimensional regions using specific conditions and parameters. [7] The ability to adjust experimental parameters during such processes opens up the possibility of creating nanozeolites suitable for selective applications. In this regard, ion exchange and/or adsorption processes in nanozeolites can be modified, achieving diverse effects on the selectivity and synthesis of molecular species. [8, 9] Recently, natural clinoptilolite nanozeolite has been used for the synthesis of Cu$_2$O and NiO particles for catalytic applications. [10] However, this is not an isolated phenomenon, as various types of zeolites have been successfully employed in similar studies. Among them are zeolites such as clinoptilolite, mordenite, and ZSM-5, which have proven to be effective in obtaining nanomaterials with well-defined optical properties. [11, 12] Other authors have synthesized nanozeolites using silicon and aluminum precursors combined with Cu$_2$O nanoparticles (previously synthesized). Finally, they have been used for pollutants separation in aqueous solutions. [13]
Additionally, Jampa and co-workers were able to synthesize zeolite nanoparticles to stabilize Cu$_2$O for antibacterial purposes. [14] Despite the diversity of results obtained when synthesizing copper particles using conventional zeolites (whether in the form of oxides or metals), [15, 16] there is the possibility of developing a new research area by considering the specific impact of nanozeolites on this process. In this context, the distinctive adsorption capability of nanozeolites, combined with their unique structural parameters and modification of active sites, raises questions about the potential influence of these characteristics on the formation process of copper particles at the nanoscale.

In this regard, the present study focuses on obtaining Cu$_2$O nanoparticles, exploring the structural downsizing of synthetic zeolite 4A. The results obtained provide options and strategies for synthesizing copper nanomaterials using nanozeolites, promoting the design of efficient and selective systems.

**Materials and methods**

In the initial stage of the proposed synthesis process, we subjected synthetic zeolite 4A (Z4) to the milling process to obtain nanozeolite 4A (NZ4). This procedure involved milling 10 g of zeolite for 1 hour at 400 rpm, using a ball-to-charge ratio of 5:1 (by weight). Copper sulfate (CuSO$_4$) was used as the precursor for copper ions. The samples were hydrated, and the ion exchange with CuSO$_4$ was carried out following the methodology previously established by our group. [17, 18] In this stage, a light gray hue was observed. In the final phase, the solution was kept under magnetic stirring at 90°C, and 30 ml of rongalite (HOCH$_2$SO$_2$Na$_2$H$_2$O) at a concentration of 0.1 mM was added. Gradually, the solution underwent a color change from gray to yellow.

UV-vis spectroscopy was measured using the VELAB 5100 UV spectrophotometer. For this, the wavelength spectrum ranged from 200 to 900 nm. A spectroscopic resolution of 0.5 nm was considered. The atomic resolution TEM/STEM ARM200F microscope was utilized with an acceleration voltage of 120–200 kV to obtain high-resolution images of copper nanostructured systems. Equipped with an X-ray spectrometer incorporating EELS (Ultrafast electron energy-loss spectroscopy), it enabled mapping to be performed.

**Results and discussions**

In previous research by our group, rongalite has been highlighted as a highly effective reducing agent, and its combination with other stabilizers has been previously documented as a successful strategy for obtaining copper metal nanoparticles (CuNPs). [19]. However, this study proposes a different effect when attempting to interact rongalite with the NZ4-Cu$_{x^+}$ system. In an initial stage of interaction following the milling process, we assume that due to its higher surface-to-volume ratio, the zeolite facilitated the reduction of Cu$^{+2} \rightarrow$ Cu$^+$. Finally, upon adding rongalite, the formation of Cu$_2$O occurred. Although rongalite is considered an effective reducer, other authors have previously reported conditions where rongalite has acted as a catalyst or facilitated the production of oxidized species. [20, 21]
Zeolite 4A underwent milling processes to reduce size, promote a more significant surface-to-volume ratio, and increase the number of active sites. We analyzed the vibrational behavior and the emergence of bands in the vicinity of 700 cm$^{-1}$, offering potential indicators of the downsizing properties of zeolite 4A. In this context, FTIR studies were conducted for a more detailed analysis (Fig. 1a). The FTIR spectra visually depict the vibrational behavior of the zeolite during different milling periods, ranging from 0.5 to 3.0 hours, as illustrated in Fig. 1 (the spectra were vertically shifted for better qualitative analysis). The band around 950 cm$^{-1}$ is associated with the asymmetric stretching (Si-O-T, T = Si or Al) in zeolite. [22]

Other authors have indicated a band centered around 716 cm$^{-1}$ after prolonged milling processes in different synthetic zeolites, which is related to the symmetric stretching of the Si-O bond. [23, 24] In addition, recent findings on the formation of amorphous zeolites report a band at 690 cm$^{-1}$ associated with O-T-O symmetric stretching vibrations. [25] Consequently, we could deduce from the results obtained from the amorphization and undersizing in zeolite 4A the appearance of a band located around 690 cm$^{-1}$ in the FTIR spectrum. The copper(I) oxide, Cu$_2$O, detection by FTIR spectroscopy is supported by discernible vibrational band in the proximity of 600 cm$^{-1}$. This band is associated to the Cu(I)-O stretching phenomenon in the structure of Cu$_2$O. [26] The specific position of this band can provide some information about the structure and arrangement of the chemical bonds in the resulting material.

Figure 1. FTIR spectra: a) zeolite 4A exposed to different milling periods and b) Cu$_2$O nanoparticles stabilized in the undersizing zeolite 4A matrix.

However, this location often experiences minor shifts, displacing either slightly to the left or right. The positional variability of this band can be directly attributed to the interaction between Cu$_2$O and its environment, particularly with the stabilizing medium or the environment matrix. Therefore, the response in the FTIR spectrum of Cu$_2$O is influenced by the specific conditions of the medium in which it is found. In this sense, Kumar and coworkers detected a band at 596 cm$^{-1}$ associated with Cu$_2$O, which was synthesized using the sol-gel method. [27] In addition, Shelar and coworkers detected the band associated with Cu(I)-O vibrations, located at 618 cm$^{-1}$. [28] They used the green synthesis method and detected particle sizes ranging from 5–20 nm. This phenomenon is interesting from the point of view of the vibrational sensitivity of Cu$_2$O according to the conditions of its molecular environment.

Moreover, rongalite sometimes plays a selective role in chemical processes by leading to partial reduction of ions, e.g., for iron salts the reduction Fe$^{3+}$→Fe$^{2+}$ has been observed. [29] In this study, we obtained copper nanoparticles (CuNPs), as evidenced by the UV-Vis spectra in the Supplemental information, without adding zeolites. In this spectrum, the absorption band corresponding to the surface plasmon resonance of the CuNPs, as well as the hue of the solution, agree with the typical characteristics associated with colloidal CuNPs. The Uv-Vis spectra of Cu$_2$O nanoparticles are shown in Fig. 2.

Figure 2. UV-Vis spectra of Cu$_2$O stabilized on undersizing zeolite 4A.
Usually, the source and shifts of the absorption bands are closely related to the size and morphology of the particles, as well as their crystalline phase. In relation to Cu$_2$O, other authors have indicated the presence of an absorption band located approximately between 460–490 nm, associated with species of nanoparticles. [30–32] In addition, Yongsong and co-workers have associated different morphological behaviors of Cu$_2$O particles with an absorption band located at 370 nm. [33] Similarly, Yokhebed and co-workers have identified the presence of two distinct bands in the visible spectrum related to Cu$_2$O nanoparticles. These bands are located at wavelengths of approximately 360 and 460 nm, revealing an optical behavior characteristic of nanoparticles with dimensions close to 100 nm. [34] Overall, the spectra in Fig. 1 suggest a distinctive role of conventional zeolite and nanozeolites in the morphology and composition of the nanoparticles generated in these matrices.

Figure 3. a) TEM image of Cu$_2$O nanoparticles stabilized in zeolite matrix 4A, b) Particle size histogram of Fig. 2a and c) Elemental mapping on a Cu$_2$O nanoparticle.

Regarding the structural behavior of the Cu$_2$O particles, they exhibited a narrow distribution, as shown in Fig. 3a. The TEM image revealed the presence of particles with a spherical morphology featuring a uniform dispersion. A quantitative particle size analysis has shown that the predominant size, considering the diameter, lies in the order of 6 nm, as represented in the particle size histogram in Fig. 3b. It emphasizes the homogeneity in the particle formation through the proposed method, resulting in competitive and low cost about previously reported. In addition, elemental mapping on these particles, as evidenced in Fig. 3c, reveals the presence of copper and oxygen. This elemental analysis confirms the expected chemical composition of Cu$_2$O and provides information on the spatial location of the constituent elements, highlighting the homogeneity in the component at the nanometer level. The structural results reveal a feature in Cu$_2$O nanoparticles with uniform and narrow distribution. This attribute has fundamental implications that can significantly expand the potential of these particles in various applications. [35] Uniformity in the size and narrow distribution of Cu$_2$O nanoparticles can facilitate precise control over various properties. As well as contribute significantly to the development of innovative and sustainable technologies. [36–38]

**Conclusions**

The undersizing of zeolite through high-energy milling methods has proven to be an effective strategy for modifying ion exchange properties and increasing the number of available active sites. The inclusion of rongalite in this synthesis process promotes the creation of Cu$_2$O nanoparticles, benefiting from the enhanced availability of nucleation sites facilitated by the undersizing zeolite. FTIR spectroscopy has been fundamental to analyzing the behavior of the zeolite, highlighting the vibrational band around 700 cm$^{-1}$ as a preliminary pointer of this structural behavior. This advance represents a potentially applicable tool for identifying other types of undersizing zeolites.
The uniformity in size and narrow distribution of the nanoparticles obtained through this process is suitable for innovative development and sustainable technologies, where matching the characteristics of nanoscale materials can lead to significant advances in catalysis, energy, and environmental mitigation. Finally, this research promotes the more efficient use of resources and the creation of cleaner and less environmentally impactful processes.

Declarations

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Compliance with ethical standards

Conflict of interest. The authors declare that they have no conflict of interest.

Data availability statement

The raw/processed data required to reproduce these findings are available on request to corresponding author M. Cortez-Valadez.

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Figures

![Figure 1](image)

**Figure 1**

FTIR spectra: a) zeolite 4A exposed to different milling periods and b) Cu$_2$O nanoparticles stabilized in the undersizing zeolite 4A matrix.
Figure 2

UV-Vis spectra of Cu$_2$O stabilized on undersizing zeolite 4A.
Figure 3

a) TEM image of Cu$_2$O nanoparticles stabilized in zeolite matrix 4A, b) Particle size histogram of Fig.2a and c) Elemental mapping on a Cu$_2$O nanoparticle.

Supplementary Files

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