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Zinc concentration evaluation in zeolite-A4 with possible Np-ZnO synthesis application
Evaluación de la concentración de zinc en zeolita-A4 con posible aplicación en síntesis de Np-ZnO

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Abstract

Zeolites have been shown to have a large number of technological applications, especially in the formation of nanostructures inside them. In this work evaluates the Zn concentration in an A4 zeolite for the formation of nanoparticles by ion exchange, by controlling the temperature parameters. XRD and FT-IR analysis was carried out to verify that the zeolite structure was not affected and by UV-vis and SEM-EDS we analyzed which of the concentrations would be the most convenient. Taking as criteria the optimum ion exchange and the stability of zeolite A4).

Keywords: Zeolite A4, Ion exchanged, Zn.

Resumen

Las zeolitas han demostrado tener una gran cantidad de aplicaciones tecnológicas, especialmente en la formación de nanoestructuras en su interior. En este trabajo se evalúa la concentración de Zn en una zeolita A4 para la formación de nanopartículas, mediante el intercambio iónico, controlando los parámetros de temperatura. Se realizo análisis de XRD y FT-IR para comprobar que la estructura de la zeolita no se alterara y por medio de UV-vis y SEM-EDS se analizó cuál de las concentraciones es la más adecuada. Tomando como criterio el óptimo intercambio iónico y la estabilidad de la zeolita A4.

Palabras Clave: Zeolita A4, Intercambio Iónico, Zn

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1. Introduction

Zeolites are hydrated crystalline aluminosilicates, with elements of groups I and II as exchange ions. They consist of a framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra connected at the vertices by oxygen atoms, whose main characteristic is the great capacity for selective adsorption of ions (Eroglu et al., 2017; Leal-Perez et al., 2022). Among the zeolite family are the so-called synthetic zeolites, of which 67% of those produced worldwide are consumed as Linde Type A (LTA, Zeolite A), which were first synthesized in 1656 (Breck et al., 1956). These have perfectly defined cavities compared to natural zeolites and therefore have a much higher economic value. These have perfectly defined cavities compared to natural zeolites and therefore have a much higher economic value (Król, 2020).

Zeolite A is commonly divided into zeolite A3 when the exchange ion is potassium, zeolite A4 (ZA4) for sodium ion and zeolite A5 for calcium ion (Melo et al., 2012). The general formula of ZA4 is $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}].27H_2O$ with a silicon/aluminum (Si/Al) ratio equal to 1 according to Lowenstein's rule (Mozgawa et al., 2011; Mumpton, 1978). On the other hand, the zeolite A structure is formed by substructures, the four-double ring structure (D4R) and the six-single ring structure (S6R). In addition, among them the one comprising two types of cages: the β-cage (sodalite cage), and the α-cage (Brouwer et al., 2020; Mozgawa et al., 2011). Zeolites have extensive applications in technology: water

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treatment (Millar et al., 2016; Wen et al., 2018), gas adsorption (Lin et al., 2012), green chemistry (Adebajo, 2007), ion exchanged (Hedström, 2001), among others. Zinc is a very attractive ion-exchange for zeolite functionalization, because its ion-exchange occurs in a simple way. In which the concentration can significantly influence the formation and growth of ZnO nanoparticles (Np-ZnO) (Cerri et al., 2021). Studies have been reported where Zn concentration has been a determinant factor in formation of ZnO (Amooaghaie et al., 2017; Ismail et al., 2005; Lee et al., 2008). On the other hand, in zeolites, work has been reported on a natural zeolite observing this effect (Sanatgar-Delshade et al., 2011). However, similar work for zeolite A4 has not been found.

In this work different concentrations of Zn in zeolite A4 are studied in order to determine the most suitable for the formation of Np-ZnO. Using XRD and FT-IR techniques to verify the structural and molecular stability of the zeolite in ion-exchange, as well as SEM-EDS and UV-vis for the analysis of the concentrations.

2. Methodology

Synthetic ZA4 (Sigma Aldrich, 98%), zinc Acetate $(CH_3COO)_2Zn.2H_2O$ (Sigma Aldrich, 99%), and deionized water were used as solvent to hydrate.

We followed the methodology reported by Flores-Valenzuela et al (Flores-Valenzuela et al., 2015). 5 g of ZA4 was hydrated with 50 ml of deionized water for a period of 48 hours. Then, 100 ml solutions of deionized water were prepared with zinc acetate at molar concentrations of 0.01, 0.02, 0.03, 0.05, 0.075, 0.1 M. Then, hydrated ZA4 samples and zinc acetate solutions were placed in culture tubes inside a thermal bath vessel to adjust the temperature parameter to 50 °C. Once the conditions were obtained, the zinc acetate solution was added into the hydrated ZA4 growth tube and kept under magnetic stirring for 60 minutes. Subsequently, the product (ZA4+XZn, where X corresponds to each of the zinc acetate concentrations) is recovered by the filtration equipment carrying out the necessary washes to remove residues from the precursor solutions. Once the ion exchange is carried out, the obtained sample of Zeolite A4+XZn is dried at room temperature. This process was carried out in the same way for each of the concentrations. Only the analyses carried out on samples ZA4+0.01Zn, ZA4+0.05Zn, and ZA4+0.1Zn are shown.

XRD analysis was carried out with PHI5100 Bruker AXS D8 Advance diffractometer. The vibrational energy of bonds present in structures of different samples was determined by IRAffinity 1-S Shimadzu Infrared Spectrometer. Optical absorption spectra were taken whit UV Visible Spectrophotometer Evolution 220 Thermo. Micrographs and EDS were measured with the JEOL JSM-7401F field emission scanning electron microscope (FESEM).

3. Results and discussion

Figure 1 shows the FTIR analysis corresponding to ZA4, ZA4+0.01Zn, ZA4+0.05Zn, and ZA4+0.1Zn. The specific bands of ZA4, at 1642 and 3444 cm^{-1}, are observed, assigned to the vibrational bending and stretching modes of the -OH bonds of chemical and physical water. At 1000 cm^{-1}, the band characteristic of the asymmetric stretching vibrations of Si-O-Si and Si-O-Al. The band observed at 554 cm^{-1} corresponds to the symmetric stretching vibrations of the Si-O-Si and O-Si-O bonds, and the signal at 665 cm^{-1} corresponds to the asymmetric stretching vibrations of the Si-O-Al bonds (Mozgawa et al., 2011; Şen et al., 2008). The samples where the ion exchange with Zn was applied, show a similar behavior to the pure ZA4.

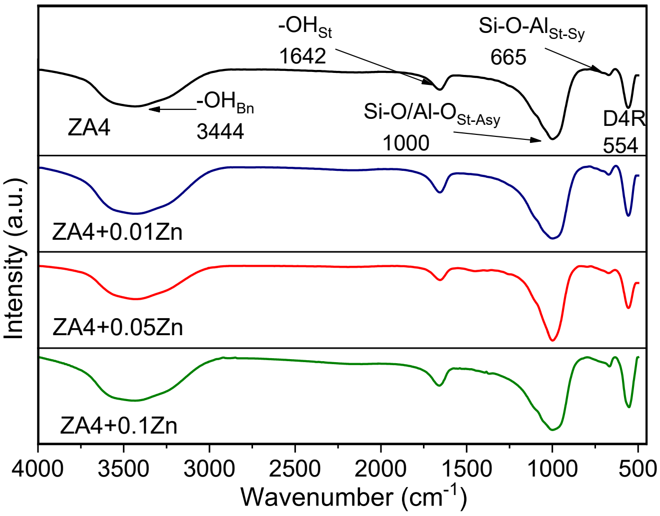

Figure 1. FTIR of ZA4, ZA4+0.01Zn, ZA4+0.05Zn, and ZA4+0.1Zn.

Figure 2, the Miller indices of ZA4, ZA4+0.01Zn, ZA4+0.05Zn, and ZA4+0.1Zn are shown. For ZA4, the Miller indices were indexed with the JCP2:01-089-5423 card, which shows the characteristic peaks. For samples ZA4+0.01Zn, ZA4+0.05Zn, and ZA4+0.1Zn, an evident decrease in the relative intensity of the peaks exists, mainly at (220), (420), (640) and (664), as well as, the absence of the peak at (440). In addition, two new peaks are observed around 15° and 25°, not identified for possible Zn precursor species. Therefore, these peaks are referred to as forbidden planes. Which could be originated by defects in ZA4 structure at atomic substitutions (ion exchange, this work*)*, an interstitial or a vacancy. Causing rearrangement of neighboring atoms, as well as change in valence electron states. This phenomenon is extensively reported as "defects in non-resonant X-ray scattering". (Dmitrienko & Ovchinnikova, 2000; He et al., 2015; Williams & Carter, 1996; Yan et al., 2012). These results indicate the presence and interaction of Zn^{2+} ion with the structure of ZA4 causing the described effects. On the other hand, no ZnO characteristic peaks are observed at 36° and 42° for a cubic structure indexed with pdf 96-153-4837.

Figure 3 shows the optical absorption spectra of ZA4, ZA4+0.01Zn, ZA4+0.05Zn, and ZA4+0.1Zn. ZA4 shows poor absorption bands, it could be considered invisible in the UV-vis range. In ZA4+0.01Zn, ZA4+0.05Zn, and ZA4+0.1Zn we observed an absorption band at 216 to 240 nm with a maximum at 227 nm and a second band is observed from 256 nm associated with Zn^{2+} ions (Dapurkar et al., 2001; Xu et al., 2012). On the other hand, at 370 nm a small band is observed, which has been reported for ZnO structures (Santhoshkumar et al., 2017; Singh & Gopal, 2007), possibly formed on the zeolite surface, when Zn ions are exposed to the environment.

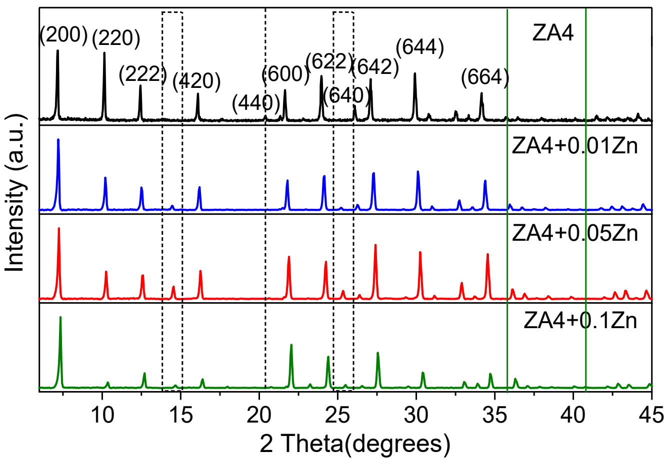

Figure 2. XRD of ZA4, ZA4+0.01Zn, ZA4+0.05Zn, and ZA4+0.1Zn.

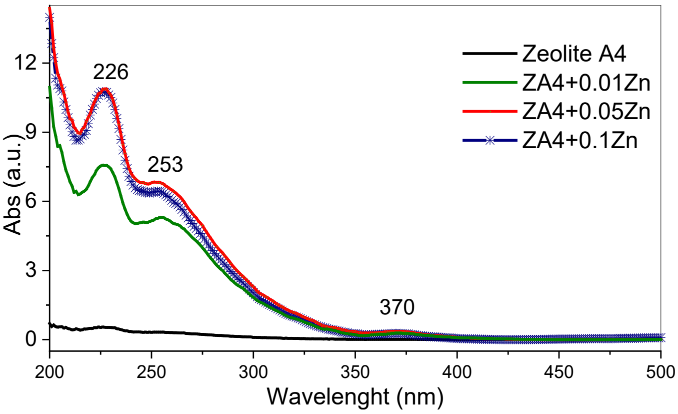

Figure 3. Optical absorption spectra of ZA4, ZA4+0.01Zn, ZA4+0.05Zn, and ZA4+0.1Zn.

Figure 4 shows the SEM-EDS of ZA4, ZA4+0.01Zn, ZA4+0.05Zn, and ZA4+0.1Zn. For ZA4, well-defined cubic crystals are observed, as well as the elements O, Al, Si, and Na in characteristic atomic ratios (Mumpton, 1978). In ZA4+0.01Zn, ZA4+0.05Zn, and ZA4+0.1Zn, besides the Zn signal, evidence of ion exchange can be observed. In samples ZA4+0.05Zn and ZA4+0.1Zn, the Zn ratio is very similar. Therefore, it can be suggested that the concentration of 0.05 M is more suitable in the formation of nanoparticles. Because the use of reagents would be optimized. On the other hand, it is possible to observe a stronger deformation in the zeolite structure with the 0.05 M concentration in comparison with 0.1 M. For each of the samples, 4-point EDS and 1 large area EDS measurements were carried out, where the same results were obtained, therefore, only one EDS analysis is shown for each sample.

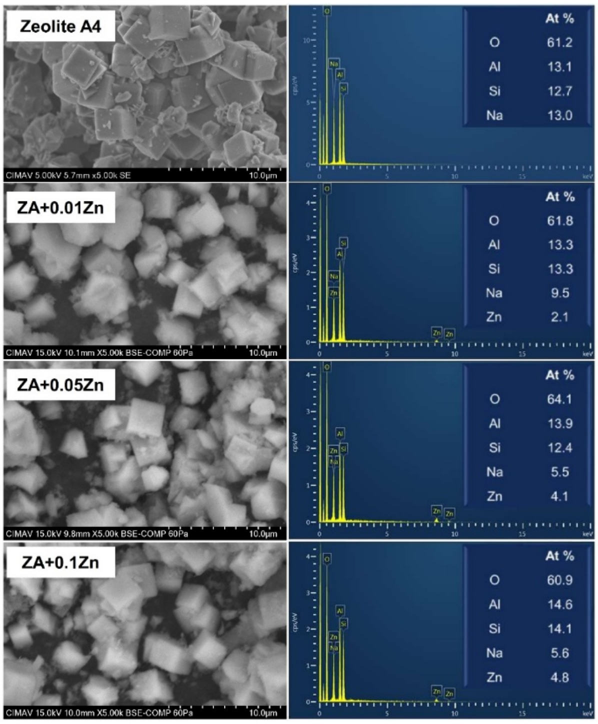

Figure 4 shows the SEM-EDS of ZA4, ZA4+0.01Zn, ZA4+0.05Zn, and ZA4+0.1Zn.

4. Conclusion

XRD and FT-IR analysis suggests that the zeolitic structure is not significantly affected during Zn ion exchange. In addition, no evidence of other species formation is shown. On the other hand, optical absorption spectra analysis shows a tendency in the identification of ionic species, as well as a small signal at 370 nm, which could be attributed to the formation of oxides on the zeolite surface due to environmental exposition. Also, SEM-EDS analysis showed that the atomic content of Zn in the 0.05 and 0.1 M samples were very similar. Furthermore, the zeolite structure for 0.05 M concentration is less affected by chemical attack in ion exchange. Determining that the concentration of 0.05 M could be the most suitable for formation of nanoparticles, because it allows an optimal ion exchange and preserves the structure of ZA4 significantly.

Declaration of competing interest.

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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