

Tuning the mesoporosity and Lewis acidity in a beta zeolite by post-synthesis strategies: potential to be used as adsorbent of bulky organic molecules

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Abstract

Industrial operations, including the combustion of fossil fuels, have generated large amounts of CO₂ and others dangerous organic compounds that have led to serious environment problems affecting the human life and the flora and fauna. The adsorption of these organic contaminants on solids with appropriate physical and chemical properties is an effective and practical strategy to their abatement. In this regard, the adsorption of those compounds, the most having large kinetic diameters, could be promoted over zeolitic systems having intra and/or intercrystalline mesopores. The presence of intracrystalline mesoporous could diminish the diffusion constraints inside of the zeolite microporous, system then improving the diffusion and consequently favoring the molecules adsorption, which is also promoted on Lewis acid sites. With this objective in mind, we modified a beta zeolite (Si/Al=11.3) by post-synthesis treatments to generate mesoporosity by the removal of Al or Si atoms from the zeolite structure with subsequent isomorphic incorporation of Zr atoms to generate Lewis acidity. The obtained desilicated or dealuminated Zr-HBeta zeolites were characterized by X-ray diffraction, nitrogen physisorption measurements and FTIR of in situ adsorbed pyridine. The result showed that dealumination with further Zr incorporation was the most suitable procedure to obtain an acidic beta zeolite with potential properties to be used as an organic adsorbent.

Keywords: Beta zeolite, Mesoporous, Zirconium Incorporation, Lewis Acidity, Adsorption of Organic Molecules.

1. Introduction

As well known, the burning of fossil fuels or the industrial production of chemical and pharmaceutical products [1], have caused large emissions of anthropogenic pollutants such CO₂, NO, SO₂ and others dangerous organic contaminants with the consequent generation of serious environmental problems. Nowadays, there are several efficient proposed technologies for the abatement of these contaminants. Among them, adsorption stands out as a potential abatement technology due to its low operational cost and efficiency [2]. However, adsorption is directly influenced by the chemical and physical properties of the adsorbent [3]. In this sense, zeolites are increasingly being studied due to their versatile properties. Thermal and hydrothermal stability, high surface area, acidity and microporosity are some characteristics of zeolites. However, microporosity, despite being responsible for its shape selectivity

behavior, it hinders the diffusion of molecules to reach the internal active sites.

The adsorption of organic molecules with bulky structures or high kinetic diameters, could be favored with zeolites having microporous and mesoporous hierarchy following post-synthesis strategies [4].

In addition to porosity changes, chemical modifications in zeolites could allow to tune their acidic properties leading to improve the affinity with target molecules. Yu et al [5] found that the increase of silanol groups facilitates the formation of hydrogen bonding between benzene and MFI-type zeolites. The incorporation of tetravalent metals in zeolites allow that the hydrogen atoms of the organic molecule and oxygen atoms linked to metals incorporated in the zeolite structure form hydrogen bonds, increasing the adsorbate-adsorbent interaction [5]. In zeolites, in addition to hydrogen bonds, van der Waals forces and π complexation have a great influence on the interaction of organic molecules with the presence of Lewis acid sites in the zeolite structure [6], which can be generated by

the isomorphic incorporation of tetravalent metals, such as zirconium.

Using beta zeolites as adsorbents, Cosseron et al. [7] evaluated the adsorption of n-hexane, p-xylene and acetone and Khalid et al. [8] the adsorption of phenol. However, both studies revealed low adsorption capacity that was attributed besides to the zeolite chemical properties, also to diffusion constraints inside of the beta zeolite microporous system. Then, post-synthesis strategies in the design of zeolites, such as the generation of mesopores and incorporation of metals, such as zirconium, to generate Lewis acidity, could improve their adsorption capacity. With that objective, in this work, a commercial beta zeolite (Si/Al=11.3) was desilicated or dealuminated to generate intracrystalline mesoporosity, with subsequent Zr isomorphic incorporation. XRD, nitrogen adsorption measurements and FTIR of in situ adsorbed pyridine were used to determine the physic and chemical properties of the obtained modified Zr-HBeta zeolites.

2. Materials and methods

A commercial HBeta zeolite (Si/Al=11.3) was desilicated using a NaOH solution (0.37 mol.L⁻¹) [9] or dealuminated with HNO₃ solution (7.3 mol.L⁻¹) [10]. 1 g of zeolite was added to 6.3 mL of NaOH (0.37 mol.L⁻¹). The mixture was stirred at room temperature for 20 minutes, transferred to a Teflon bottle and maintained in an oven at 80°C for 6 h. Subsequently, the suspension was cooled, separated by centrifugation and the solid dried at 80 °C. The desilicated beta zeolite was ion exchanged with a solution of NH₄NO₃ (1.0 mol.L⁻¹), at 80°C for 4 h, using a proportion of 100 mL.g⁻¹ of zeolite. To obtain the beta zeolite in the proton form, the NH₄⁺ beta zeolite was subsequently calcined at 550°C (10°C.min⁻¹) under air atmosphere for 6 h. The resultant sample was denoted as HDeSiBeta. A dealuminated beta zeolite was also prepared as follows, 1 g of the HBeta zeolite was added to 55 mL of HNO₃ (7.3 mol.L⁻¹), with the suspension being kept under stirring for 6 h at 80°C. Then, the solids were recovered by centrifugation, washed with distilled water, dried at 80°C. The resultant sample was denoted as HDeAlBeta.

For the isomorphic incorporation of Zr into the precursor HBeta and into the desilicated and dealuminated HBeta zeolites, ZrCl₄ (Sigma Aldrich, 99.5%) was used as a Zr precursor following the 2-

propanol impregnation method [11]. The experiments were carried out in a glove box to avoid the formation of Zr oxides. Before Zr incorporation, the zeolites were previously dried at 200°C under vacuum for 1 hour. Then, 2 wt% Zr/g of zeolite was dissolved into 5 mL of 2-propanol. Subsequently, the zeolite was added, and the mixture was subjected to a stirring at 50°C until complete evaporation of the alcohol. Finally, the solids were calcined under air at 550°C for 5 h. (2°C. min⁻¹). The resultant samples were denoted as ZrH-beta, Zr-HDeSiBeta and Zr-HDeAlBeta.

The studied zeolites were analyzed by XRD in the range of 5 to 40° (2θ) at a scanning speed of 10°.min⁻¹ using a Rigaku MiniFlex 600 diffractometer with a Cu Kα radiation (λ=0.1542 nm) operating at 40 kV and 30 mA. The textural properties were determined by N₂ physisorption measurements, using a Micromeritic ASAP 2420 equipment. The Brønsted and Lewis acidity quantification was evaluated by FTIR of in situ adsorbed pyridine at 150°C, as a probe molecule. It was used a Bruker spectrometer model Vertex 70, equipped with an MCT detector and a transmission cell with CaF₂ windows. The background was determined at 150 °C under argon flow (100 mL.min⁻¹) after 30 min of heating. For the analyses, a self-supporting tablet of the sample was pretreated at 350 °C under an argon atmosphere (100 mL.min⁻¹) for 60 min. Then, the system was cooled to 150 °C and then the sample was saturated with pyridine vapor. The excess and physically adsorbed pyridine were purged with argon (100 mL.min⁻¹). FTIR spectra were collected at 150 °C with a resolution of 4 cm⁻¹ in the region of 4000 to 1000 cm⁻¹. The spectra of the samples without and with adsorbed pyridine were subtracted. The quantification of the Brønsted (C_B) and Lewis (C_L) acid sites was estimated through the integrated areas of the band referring to the Brønsted (1545 cm⁻¹) and Lewis (1450 cm⁻¹) acid sites. The molar absorption coefficients used for the quantification of Bronsted and Lewis acid sites were ε (B) = 1.12 cm.μmol⁻¹ and ε (L) = 1.71 cm.μmol⁻¹[12].

3. Results and discussion

Fig. 1 shows the X-ray diffractograms of the HBeta and their derived modified HDeSiBeta and HDeAlBeta. The observed peaks are characteristic of the BEA structure, the same observed for the precursor HBeta zeolite, evidencing that the BEA

structure was preserved after the applied treatments [13].

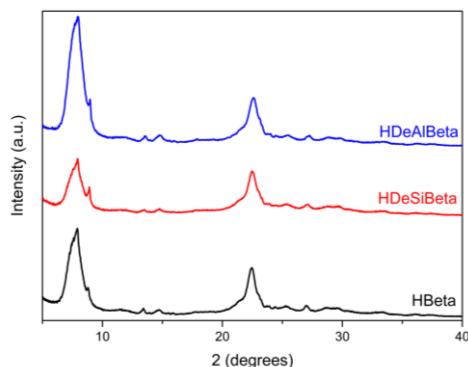


Figure 1 – X-ray diffraction patterns of the HBeta and their derived.

The removal of silica from the HBeta zeolite led to a slightly reduction of the intensity of the peak at 22.5 °2θ of its X-ray diffractogram, attributed to the generation of silanol groups and mesoporosity, as it is shown for the HDeSiBeta in Fig. 2. The removal of aluminum from the HBeta zeolite, despite the generation of silanol groups, did not reduce the intensity of the above-mentioned peak, however under the applied conditions the dealumination treatment was not efficient to generate mesoporosity, as it is shown in Fig. 2c.

According to the IUPAC classification, the isotherms shown in Fig. 2 can be classified as type I for the precursor HBeta and HDeAlBeta zeolites and of type I and IV for the HDeSiBeta, characteristic of zeolites having microporous and intracrystalline mesoporous [14].

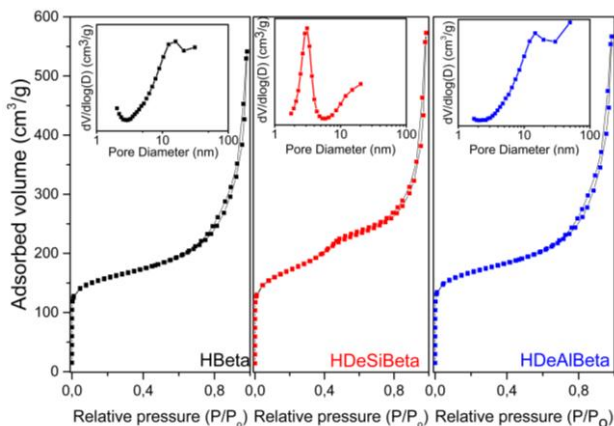


Figure 2 – N₂ adsorption/desorption isotherms of the HBeta zeolite and after its desilication or dealumination.

The textural parameters (Table 1) confirm the generation of intracrystalline mesopores in the HDeSiBeta with a mean pore size of around 3 nm, while the mesopores for the HBeta and HDeAlBeta zeolites can mainly be attributed to interparticle mesoporosity, because the beta zeolite particles are nanometric, consequently their agglomeration will generate mesopores between them. As just discussed, bulky compounds having high kinetic diameters, including aromatic and halogenated hydrocarbons, will better diffuse and adsorb in zeolites having mesopores [2].

Table 1 – Textural properties of the precursor HBeta and their derived.

Sample	V _{micro} cm ³ .g ⁻¹	V _{meso} cm ³ .g ⁻¹	V _{total} cm ³ .g ⁻¹	D _p nm
HBeta	0.17	0.67	0.84	16.18*
HDeSiBeta	0.08	0.78	0.86	3.03
HDeAlBeta	0.19	0.69	0.88	14.74*

*Interparticle pore diameter.

The X-ray diffractograms of the precursor HBeta and their derived desilicated or dealuminated zeolites after incorporation of Zr are shown in Fig. 3. The observed peaks refer to the precursor HBeta zeolite, with no peaks related to ZrO₂, suggesting that Zr was isomorphically incorporated into the BEA crystalline structure [11].

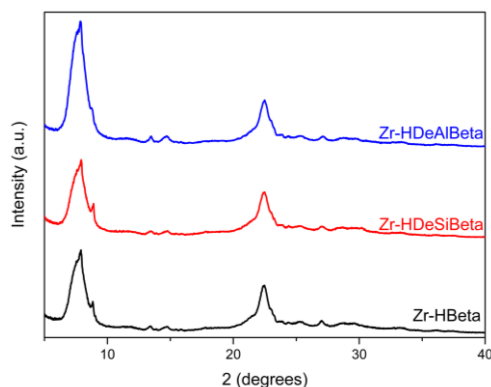


Figure 3 – X-ray diffraction patterns of the Zr incorporated HBeta zeolites.

Brønsted and Lewis acidity of the precursor HBeta and their derived Zr incorporated zeolites were analyzed by FTIR spectroscopy of an in situ adsorbed pyridine. As can be seen in Fig. 4, the bands at 1543 and 1446 cm⁻¹ are related to the Brønsted (B) and Lewis (L) acid sites, respectively. It is possible to observe that in comparison with the HBeta zeolite all the Zr incorporated zeolites

presented a slight decrease of the intensity corresponding to the Brønsted acid sites., Excepting the Zr-HDeAlBeta zeolite, the other ones show a very close intensity of the Lewis band that indicates that Zr was not enough incorporated. The generation of substantial Lewis acidity is clearly seen in the spectrum of the Zr-HDeAlBeta, thus evidencing the isomorphically Zr incorporation.

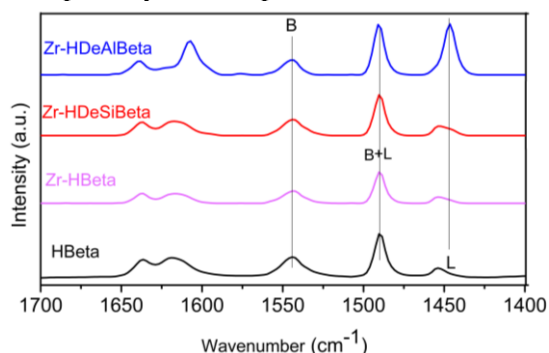


Figure 4 – FTIR spectra of in situ adsorbed pyridine on the HBeta and on the Zr incorporated HBeta zeolites.

As commented, the presence of tetrahedrally coordinated Zr in the beta zeolite structure generates acidic sites with Lewis character [11]. The electronic deficiency of these acid sites favors the interaction with organic compounds, improving their adsorption [2]. That makes the Zr-HDeAlBeta zeolite a promising material to be applied in the adsorption of organic contaminant.

4. Conclusions

The desilication of the HBeta zeolite, despite generation of intracrystalline mesopores, was not efficient to Zr incorporation. On the other hand, the Al removal, without observable generation of intracrystalline mesoporosity, significantly favored the incorporation of tetrahedrally coordinated Zr, consequently generating Lewis acidity, then gaining an important potential to be applied as an adsorbent of organic contaminants.

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References

- [1] C. Zheng et al., “Quantitative assessment of industrial VOC emissions in China: Historical trend, spatial distribution, uncertainties, and projection,” *Atmos Environ*, vol. 150, pp. 116–125, Feb. 2017.
- [2] S. Zhang et al., L. “Recent advances in zeolite-based materials for volatile organic compounds adsorption,” *Sep Purif Technol*, vol. 350, p. 127742, Dec. 2024.
- [3] S.-W. Baek et al., “Design of dual functional adsorbent/catalyst system for the control of VOC’s by using metal-loaded hydrophobic Y-zeolites,” *Catal Today*, vol. 93–95, pp. 575–581, Sep. 2004.
- [4] Y. Shen, “Biomass-derived porous carbons for sorption of Volatile organic compounds (VOCs),” *Fuel*, vol. 336, p. 126801, Mar. 2023.
- [5] W. Yu, L. et al., “Preparation of hierarchically porous diatomite/MFI-type zeolite composites and their performance for benzene adsorption: The effects of desilication,” *Chemical Engineering Journal*, vol. 270, pp. 450–458, Jun. 2015.
- [6] R. M. Serra et al., “Experimental and theoretical studies about the adsorption of toluene on ZSM5 and mordenite zeolites modified with Cs,” *Microporous and Mesoporous Materials*, vol. 147, no. 1, pp. 17–29, Jan. 2012.
- [7] A.-F. Cosseron et al., “Adsorption of volatile organic compounds in pure silica CHA, *BEA, MFI and STT-type zeolites,” *Microporous and Mesoporous Materials*, vol. 173, pp. 147–154, Jun. 2013.
- [8] M. Khalid, G. Joly, A. Renaud, and P. Magnoux, “Removal of Phenol from Water by Adsorption Using Zeolites,” *Ind Eng Chem Res*, vol. 43, no. 17, pp. 5275–5280, Aug. 2004.
- [9] N. Suárez, J. Pérez-Pariente, F. Mondragón, and A. Moreno, “Generation of hierarchical porosity in beta zeolite by post-synthesis treatment with the cetyltrimethylammonium cationic surfactant under alkaline conditions,” *Microporous and Mesoporous Materials*, vol. 280, pp. 144–150, May 2019.
- [10] J. Dijkmans et al., “Post-synthesis Sn β : An exploration of synthesis parameters and catalysis,” *J Catal*, vol. 330, pp. 545–557, Oct. 2015.
- [11] R. Barakov et al., “Optimization of Zr-Al-USY and Zr-Al-Beta zeolites catalysts for a one-pot cascade transformation of furfural to γ -valerolactone,” *Catal Today*, vol. 426, p. 114406, Jan. 2024.
- [12] V. Zholobenko, et al., “Probing the acid sites of zeolites with pyridine: Quantitative AGIR measurements of the molar absorption coefficients,” *J Catal*, vol. 385, pp. 52–60, May 2020.
- [13] R. Baran et al., “Influence of the nitric acid treatment on Al removal, framework composition and acidity of BEA zeolite investigated by XRD, FTIR and NMR,” *Microporous and Mesoporous Materials*, vol. 163, pp. 122–130, Nov. 2012.
- [14] M. Thommes et al., “Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report),” *Pure and Applied Chemistry*, vol. 87, no. 9–10, pp. 1051–1069, Oct. 2015.