

# SYNTHESIS OF ZEOLITE AND CARBON-ZEOLITE COMPOSITE FROM WASTE SILICA FUMES

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## ABSTRACT

In this study, waste silica fumes (SF) and aluminum scrubs were utilized to produce Na-A zeolite (Zeo) and zeolite-carbon composites (Zeo-C). After annealing Zeo-C at 550 °C for 2 hours, a single-phase Zeo was obtained. The materials were then characterized using various techniques, including surface area analysis (BET), thermal analysis (TG), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). Silica fumes were analyzed by X-ray fluorescence spectroscopy (XRF), which indicated a SiO<sub>2</sub> content of 94.67%. XRD and FTIR confirmed the presence of a well-defined Na-A zeolite structure in both Zeo and Zeo-C. The Scherrer analysis determined that the crystallite size was 37.9 nm for Zeo and 35.8 nm for Zeo-C. The specific surface area was 10 and 25 m<sup>2</sup> g<sup>-1</sup> for Zeo and Zeo-C, respectively. The presented results emphasize the promising potential of repurposing SF waste material and aluminum scrubs for synthesizing zeolite and zeolite-carbon composites.

**Keywords:** Silica fumes, Na-A zeolite, Zeolite-carbon composite

## INTRODUCTION

Utilizing waste materials as a resource for zeolite A synthesis is driving the interest in this material [1]. Previously, it has been proven that cheap raw materials can produce good-quality zeolites. The use of these raw materials results in a uniform zeolite structure with lowering overall costs [2]. Up to today, there are also reports on the zeolite-carbon composites being synthesized [3]. Many of these methods require pre-treatment of carbon matter and several activation steps (physical and chemical). These steps may be complicated, costly, and energy-consuming.

SF, or microsilica, is a by-product of silicon and ferrosilicon alloy production. The production process includes the reduction of high-purity quartz with coal in electric arc furnaces. Consequently, SF comprises primarily amorphous silica, with impurities including carbon, calcium, iron, aluminum, magnesium, sodium, and potassium [4]. It is noteworthy to mention that aluminum scrub was previously used as a source of aluminum for Na-A preparation [5].

In this study, the synthesis of Zeo and Zeo-C composite from SF and aluminum waste was investigated. Physicochemical characterizations were conducted to verify the feasibility of the synthesis route and the properties of the resulting material.

## EXPERIMENTAL

The synthesis procedure involved mixing sodium silicate, prepared from SF, with sodium aluminate, prepared from aluminum scrub, using a molar ratio of Si/Al of 1/1.2. XRF (X-ray fluorescence) analysis was done using Thermo Scientific Instrument, ARL Perform's 2500 W. The annealing of the zeolite powder was performed in a NABERTHERM MUFFLE furnace

for two hours at 550 °C in an alumina crucible and with a heating/cooling rate of 10 °C min<sup>-1</sup>. The N<sub>2</sub> adsorption-desorption measurements of the samples were conducted using a 3P INSTRUMENTS Surface Area and Pore Size Analyzer, Sync 110A model. The sample was degassed at 250 °C for 24 h under a vacuum, as proposed elsewhere [6]. The phase identification of the samples was conducted using X-ray powder diffraction (XRD) on a PAN analytical X'Pert Powder XRD machine. The measurements were performed in the range from 20° to 60° of 2θ at 0.02° increments. XRD data are compared to standard XRD data of Na-A zeolite (JCPDS No. 038-0241). The crystallite sizes of the Zeo and Zeo-C composite were computed based on Scherer's equation at a 2θ position of the most intense peak (410), wavelength, λ = 0.154 nm, and a shape factor, K = 0.94. The FTIR spectrophotometer Bruker Tensor 27 was used for the structural assessment of Zeo and Zeo-C samples in the range of 4000 to 400 cm<sup>-1</sup>. The thermal behavior of the Zeo and Zeo-C composites was analyzed in an air atmosphere (20 ml min<sup>-1</sup>) from 30 to 900 °C at a 10 °C min<sup>-1</sup> heating rate with a Pyris 1 TGA thermogravimetric analyzer.

## RESULTS AND DISCUSSION

The XRF analysis shows that SF contains 94.67% silicon and over 3.5% residue. The residue consists of carbon and other unspecified impurities. The concentration of carbon in the SF samples ranges from 1.4% to 1.8%.

Figure 1a displays the nitrogen adsorption-desorption isotherm of the Zeo and Zeo-C samples, respectively. Both isotherms belong to type IV, as classified by IUPAC [7]. A minor hysteresis loop observed in both isotherms is of the H3 type, indicating the presence of slit-shaped mesopores. A small increase in nitrogen adsorption at low p/p<sub>0</sub>, indicated by a minor inflection point, confirms the existence of micropores in both samples. However, the Zeo-C sample shows a slightly higher contribution of micropores compared to the Zeo sample. The textural parameters for both samples are summarized in Table 1.

*Table 1. BET surface area, total pore volume, and average pored diameter determined for the Zeo and Zeo-C samples synthesized from the SF*

	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Average pore diameter (nm)
Zeo	10	0.030	12.503
Zeo-C	25	0.058	9.236

The Zeo-C sample has a specific surface area of 25 m<sup>2</sup> g<sup>-1</sup>, with a total pore volume of 0.058 cm<sup>3</sup> g<sup>-1</sup> and an average pore diameter of 9.236 nm. Upon heating, the carbon component is removed, leaving only the zeolite phase, resulting in a decrease in pore volume and a slight increase in pore diameter. The Zeo sample has a recorded specific surface area of 10 m<sup>2</sup> g<sup>-1</sup>, a total pore volume of 0.03 cm<sup>3</sup> g<sup>-1</sup>, and an average pore diameter of 12.503 nm. In a study by Loiola et al. [8], the surface area of Na A zeolite prepared using kaolin through the hydrothermal method was found to be 9.20 m<sup>2</sup> g<sup>-1</sup>. Additionally, Sowunmi et al. [9] determined that zeolite 4A synthesized from kaolin has a pore size of 12.086 nm, a pore volume of 0.0065 cm<sup>3</sup> g<sup>-1</sup>, and a surface area of 22 m<sup>2</sup> g<sup>-1</sup>. The surface area and pore structure of the Zeo sample are similar to these results.

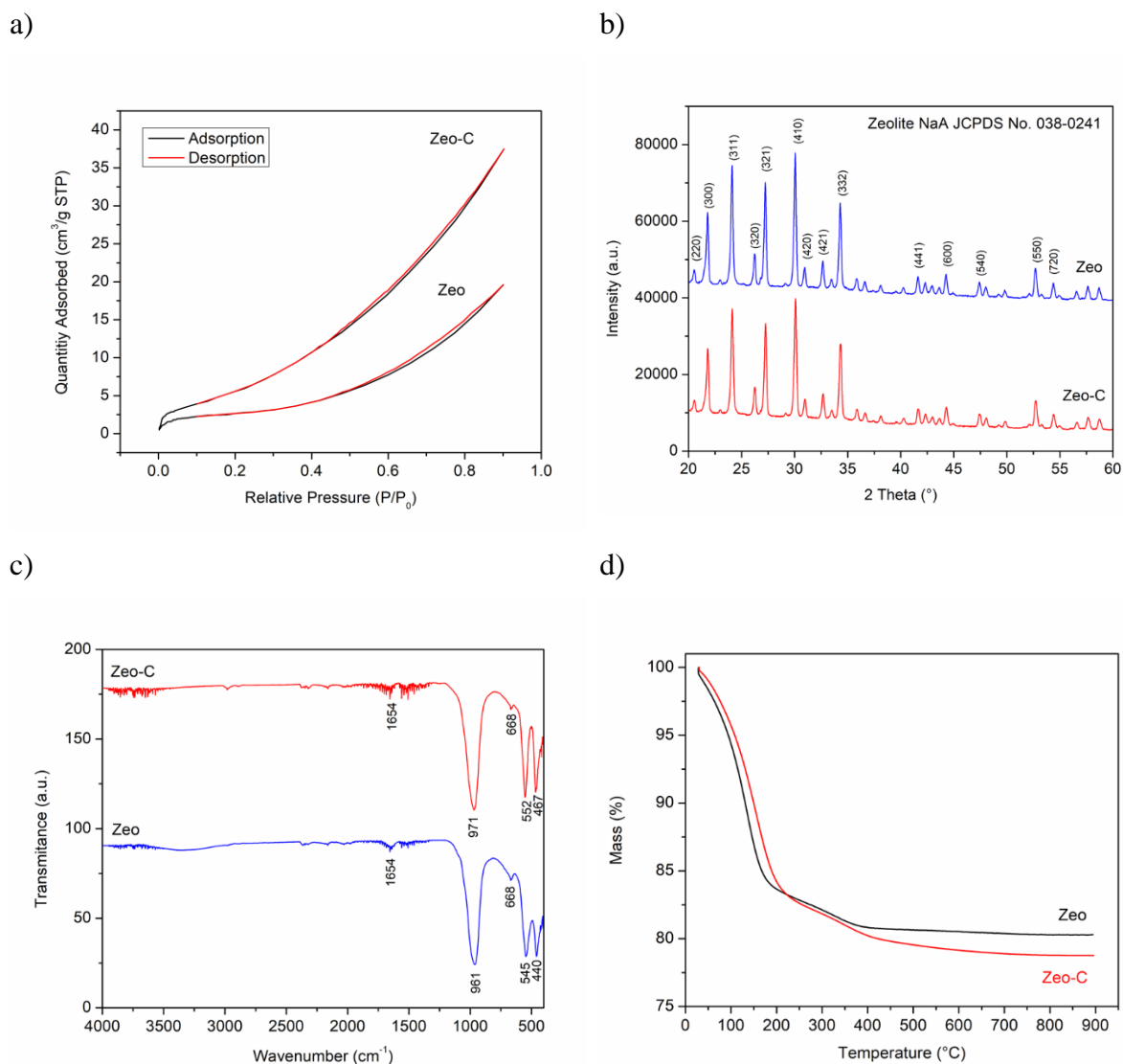


Figure 1. (a) The N<sub>2</sub> adsorption-desorption isotherm, (b) XRD, (c) FTIR, and (d) TG of synthesized Zeo and Zeo-C composite

X-ray diffraction (XRD) analysis confirms the presence of single-phase zeolite-A in both the Zeo and Zeo-C samples (Figure 1b). However, the intensity of the peaks after calcination is higher in the Zeo sample, indicating increased crystallinity. The crystallite size of Zeo and Zeo-C samples was determined to be 37.9 and 35.8 nm, respectively, using Scherrer's equation. The introduction of carbon into the composite did not alter the zeolite crystallite size.

FTIR spectra of Zeo-C and Zeo samples are given in Figure 1c. The band at around 440 cm<sup>-1</sup> is related to vibrations of O-Si and O-Al bonds, while the band at 545 cm<sup>-1</sup> corresponds to the vibration of the double ring and O-Si-O bonds. The 668 cm<sup>-1</sup> band is also associated with vibrations of the double ring, while the 961 cm<sup>-1</sup> band is a characteristic infrared spectrum band of zeolite, resulting from asymmetric stretching in the Si-O-Si and Si-O-Al planes [10]. Additionally, the band at 1654 cm<sup>-1</sup> is due to the presence of OH groups. The predominance of the 545 cm<sup>-1</sup> band over the 668 cm<sup>-1</sup> band suggests the presence of the Na-A phase in the synthesized zeolite. After annealing, slight peak shifts and noise reductions are observed in comparison to the Zeo-C composite before annealing.

The mass change during heating up to 900 °C differs for the Zeo-C and ZeO samples (Figure 1d). However, both samples exhibit three distinct stages of mass loss. During the first stage, both samples experience a mass loss due to the removal of surface water up to a temperature of around 200°C. However, the Zeo-C sample exhibits increased thermal stability for adsorbed water, likely due to the presence of carbon. The same effect is observed in the second stage, where both samples lose zeolite water in the temperature range of 200-400°C. The most significant difference between the two samples was observed in the third stage, which can be attributed to decarbonization.

## CONCLUSION

In conclusion, this study demonstrates the successful utilization of SF and aluminum scrubs to synthesize Na-A zeolite (Zeo) and zeolite-carbon composites (Zeo-C). Through annealing Zeo-C at 550°C for 2 hours, a single-phase Zeo was achieved, as confirmed by various characterization techniques. Both Zeo and Zeo-C exhibited a well-defined Na-A zeolite structure, as evidenced by XRD and FTIR. Additionally, Scherrer analysis indicated crystallite sizes of 37.9 nm for Zeo and 35.8 nm for Zeo-C. These findings underscore the promising potential of repurposing SF and aluminum scrubs for the synthesis of zeolite and zeolite-carbon composites, offering sustainable solutions and contributing to the circular economy.

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