Original Paper



Effect of pre-treatments on analcime synthesis from abundant clay-rich illite

Abdellah Ait Baha¹, Kamal Tabit², Rachid Idouhli¹, Mohamed Hajjaji³, Burak Dikici⁴, Mohy Eddine Khadiri¹ and

Abdesselam Abouelfida¹

¹Laboratory of Physical Chemistry of Materials and Environment, Department of Chemistry, Faculty of Science Semlalia, Cadi Ayyad University, BP 2390, Marrakech, Morocco; ²LIPIM Laboratory, National School of Applied Sciences, Sultan Moulay Slimane University, PO Box 77, Khouribga, Morocco; ³Materials Science and Process Optimization Laboratory, Faculty of Science Semlalia, Cadi Ayyad University, BP 2390, Marrakech, Morocco and ⁴Department of Mechanical Engineering, Faculty of Engineering, Ataturk University, Istanbul, 25240 Erzurum, Turkey

Abstract

Analcime is an important nanomaterial in: heterogeneous catalysis, selective adsorption, stomatology, sensing, and nanoelectronics. Given its occurrence in limited regions worldwide, achieving low-cost, high-purity synthesis of this zeolite is crucial. The objective of the present study was to synthesize pure analcime from an abundant, naturally occurring clay-rich illite material without the use of an organic template. Various pretreatment methods - NaOH pre-fusion, sonication, and reflux - using 1.5 M NaOH were explored to enhance the material's reactivity at nanoscale. The resulting samples were annealed hydrothermally at 150°C for 36 h. The effect of the Si/Al mass ratio, ranging from 2 to 4, was examined by incorporating a fumed silica by-product into the optimally pre-treated sample. Characterization using X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), Fourier-transform infrared spectroscopy (FT-IR), and Brunauer-Emmett-Teller (BET) surface area measurement confirmed that all pre-treatment routes converted illite (Si/Al≈2) effectively into analcime, demonstrating nanoscale control and synthesis precision. The analcime content achieved 77.8% through hydrothermal synthesis without pre-treatment, while it increased to 80.2%, 83.4%, and 91.7% with sonochemical, reflux, and NaOH pre-fusion pre-treatments, respectively. Notably, high-purity analcime with superior crystallinity was attained using the NaOH pre-fusion pre-treatment of a blend of clay and fumed silica with a Si/Al ratio of 3.71. The zeolite synthesized exhibited a surface area of 23.76 m² g⁻¹ and a significant cation exchange capacity of 510 meq 100 g^{-1} . These results offer valuable insights into the synthesis of organic-template-free zeolites, emphasizing the importance of precise nanoscale methodology in enhancing clay-phase reactivity. Furthermore, this study distinguishes itself as one of the few in the literature to prepare pure analcime by innovatively combining low-cost precursor clay and fumed silica, contributing to the advancement of nanoscale material synthesis and its applications in technology.

Keywords: analcime; clay-rich illite; hydrothermal synthesis; NaOH pre-fusion; zeolite

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Introduction

Analcime $|Na(H_2O)|[AlSi_2O_6]$ is a crystalline aluminosilicate mineral with a mass ratio of 2<Si/Al<5, typically found in volcanic rocks and sedimentary environments (Dyer et al., 2004; Ma et al., 2015; Li et al., 2023a). It exhibits a unique cage-like structure with a three-dimensional framework of interconnected channels and voids, and crystallizes primarily in a cubic crystal structure belonging to the *Ia*-3*d* space group, allowing for various crystallization forms. This structure is characteristic of the most common analcime polymorph, which allows for significant ion exchange and adsorption properties (Sánchez-Hernández et al., 2016). Analcime can also exhibit orthorhombic and tetragonal

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polymorphs under specific synthesis conditions, with variations in framework tilt and distortion. These polymorphs, although less common, underscore the structural flexibility of analcime and contribute to its diverse crystallization forms, which are particularly beneficial in applications involving ion exchange and molecular sieving (Gatta et al., 2006). The name analcime-C refers specifically to its highly crystalline form, characterized by well-defined structural ordering and enhanced crystallinity, which is critical for applications that require a high thermal- and chemical-stability variant (Jamil and Youssef, 2016). Analcime is notable for its large cation exchange capacity (CEC; $1-5 \text{ meq } g^{-1}$), adsorptive capabilities, thermal stability up to 700°C, and relatively low silica-to-alumina ratio (2<Si/Al<4) compared with other zeolites (Geus et al., 1992; Jha and Singh, 2011). These properties render it suitable for various applications, including ion exchange, chemical sensing, catalysis, adsorption, electronics, dentistry, stomatology, desiccation, and molecular sieves (Tironi et al., 2012; Novembre and Gimeno, 2021;

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Corresponding author: Abdellah Ait Baha; Email: abdellah.aitbaha@ced.uca.ma

Sun et al., 2022). Given its good properties and potential networks, analcime remains a subject of significant interest in materials science and related fields (Osacký et al., 2017).

Numerous studies have been conducted to synthesize analcime. aiming to surpass the properties exhibited by its natural counterpart. This was due primarily to the inherent limitations of natural zeolites, which often possess constrained pore diameters and channels contaminated by Fe²⁺, SO₄²⁻, SiO₂, or amorphous glass, rendering them unsuitable for widespread use (Yoldi et al., 2019). Analcime synthesis can be prepared via a hydrothermal route commonly in alkaline solutions from synthetic precursor materials rich in silica and alumina (Duan et al., 2011; Musyoka et al., 2014; Tabit et al., 2019; Azizi et al., 2021). In addition, analcime synthesis has conventionally relied on the use of organic templates (Joshi et al., 1991; Azizi and Yousefpour, 2009; Azizi and Yousefpour, 2010; Chouat et al., 2022; Fotouh et al., 2024). For instance, in a study by Al-Kadhi et al. (2024), the synthesis of analcime utilizing a polyvinylpyrrolidone template required subsequent calcination at elevated temperatures to remove the template (Al-Kadhi et al., 2024). Using organic templates in zeolite synthesis presents challenges such as rising energy consumption and the need for high-temperature calcination to remove them, posing environmental concerns and potential contamination (Meng and Xiao, 2014). Furthermore, free-organic template synthesis provides greater control over the purity, crystal size, and morphology of the resulting analcime (Bortolini et al., 2020; Sun et al., 2022). Nonetheless, restricted template options and expensive precursors hinder the process further, affecting reproducibility and scalability (Khaleque et al., 2020). As a result, the high price and limited availability of the precursor materials, along with issues related to the organic portion, prompted researchers to explore costeffective raw materials. This exploration also involved investigating alternative pretreatments and innovative environmentally freeorganic template synthesis techniques, driven by the increasing demand for zeolites.

Recent research on synthetic zeolites has largely focused on the utilization of inexpensive precursor materials or waste products, aligning with the principles of valorization and green chemistry (Khaleque et al., 2020; Ait Baha et al., 2024). Notably, the utilization of cost-effective silica-alumina sources, such as clay, has gained prominence as an economically viable procedure for zeolite synthesis (Belviso et al., 2015; Ait Baha et al., 2023). In addition, zeolite synthesis from clay is a valuable area of study due to its environmental and economic potential. Recent studies, including those by Gandhi et al. (2021), explored innovative clay modifications and zeolite-synthesis processes. Clays from different geographical regions offer different mineral compositions that can influence zeolite crystallization and properties, broadening potential applications (Ajayi et al., 2018; Gandhi et al., 2021). Among these clay materials are some of Earth's most abundant resources, including bentonite, smectites, illite, kaolinite, halloysite, and montmorillonite (Basaldella et al., 1990). Given that aluminosilicates constitute the majority of clay minerals, they have been suggested as suitable raw materials with the requisite Si-Al molar ratio for zeolite synthesis (Abdmeziem-Hamoudi and Siffert, 1989). Furthermore, recent research has focused on synthesizing analcime from kaolin, illite, and montmorillonite, leveraging their Si/Al ratio (McCaleb, 1962; Bentabol et al., 2006). Accordingly, the type of synthesized zeolite was significantly influenced by Si/Al ratio variation, playing a decisive role in zeolite crystallization (Joseph et al., 2021). Higher Si/Al ratios tend to favour the formation of analcime due to the abundance of silica, which acts as a framework builder, while lower Si/Al ratios may result in the

formation of other zeolite phases or amorphous materials (Sun et al., 2022). In this context, the *in situ* method has emerged as a primary means of transforming clay minerals into zeolites (Duan et al., 2011; Li et al., 2023b). This method typically involves two key steps: first, clays are subjected to dehydroxylation at high temperatures (500–1000°C) to create an amorphous phase that can be dissolved readily during zeolite production, ultimately yielding an active substance known as metaclay (García et al., 2015). The final zeolite was then produced through hydrothermal treatment of metaclay in the presence of an alkali metal cation. Furthermore, different pre-treatment methods, which can modify the composition of precursor particles and aid in the development of zeolite phases, could prove advantageous.

Several studies have investigated various pre-treatment methods, including NaOH pre-fusion (Mezni et al., 2011; Otieno et al., 2019; Murukutti and Jena, 2022), sonochemical treatment (Barata-Rodrigues et al., 2003; Sen et al., 2018), and reflux (Kloprogge et al., 2005; Gandhi et al., 2021), to activate clay minerals for zeolite synthesis via hydrothermal routes (Yoldi et al., 2019; Sun et al., 2022). Alkaline pre-fusion was found to dissolve clay minerals effectively, leading to increased silica and alumina availability and to significantly increased surface area and pore volume of clay minerals, resulting in improved zeolite yield and purity (Belviso et al., 2017). For instance, Pereira et al. (2018) reported an increase in specific surface area from 23 to 62 $m^2 g^{-1}$ after alkaline prefusion pre-treatment, leading to enhanced zeolite A crystallization and improved product quality (Pereira et al., 2018). Likewise, reflux and sonochemical pre-treatments further aid in breaking down mineral structures and promoting homogeneous nucleation (Carrado et al., 1997; Vaičiukynienė et al., 2021). For example, Sen et al. (2018) demonstrated that sono-assisted pre-treatment resulted in a twofold increase in LTA zeolite yield, attributed to the improved dispersion of clay particles and enhanced accessibility of reactive sites for H2-CO2 separation (Sen et al., 2018). Similarly, reflux pre-treatment, which has found use since the era as investigated by Baccouche et al. (1998), exhibited promising results in terms of illite-smectite dissolution and acceleration of the formation of sodalite zeolite with an increase of CEC from 167 to 367 meq 100 g^{-1} (Baccouche et al., 1998). These studies offer valuable insights into the potential of utilizing natural clay minerals for zeolite production, where the pretreatment methods offer effective strategies for activating clay minerals and enhancing their reactivity for zeolite synthesis. In the absence of an organic template, these pre-treatment methods would play a crucial role in controlling the crystallization process, optimizing reaction conditions, and ultimately enhancing the purity and crystallinity of the synthesized zeolite.

The aims of the present study were: (1) to synthesize the freeorganic template analcime zeolite hydrothermally using clay-rich illite; (2) to investigate thoroughly the influence of pre-treatment methods, specifically NaOH pre-fusion, sonochemical, and reflux, along with variations in Si/Al ratio, on the content and the crystallinity of analcime; (3) to carry out a comprehensive, detailed evaluation of the as-received clay and the microstructural evolution of the synthesized samples using X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopyenergy dispersive X-ray spectroscopy (SEM-EDX), Fouriertransform infrared spectroscopy (FT-IR); and (4) to carry out complementary investigations into textural properties via Brunauer-Emmett-Teller (BET) measurements, along with a determination of cation exchange capacity.

Materials and methods

Zeolite synthesis

The raw clay material was sourced from a deposit near Benguerir, located in the Marrakech-Safi region of Morocco. The clay consisted of illite, pyrophyllite, kaolinite, and quartz. For the current investigations, the clay underwent crushing, milling, and air-drying and the particle-size distribution was controlled using a two-step process. The material was initially sieved through a 100-mesh sieve, followed by a 50-mesh sieve to isolate particles within the 50–100 μ m range. To verify the particle-size distribution, laser diffraction analysis was conducted, confirming that only particles falling within the desired size range (50–100 μ m) were selected for synthesis purposes. Fumed silica, an abundant industrial by-product, was procured from local plant production of ferrosilicon. Analytical-grade sodium hydroxide (99%) was purchased from Sigma Aldrich.

The synthesis of zeolites was carried out using a variety of pretreatment methods, and the following procedures were employed to prepare the clay samples and promote the crystallization of analcime zeolite (Fig.1).

Initially, raw clay samples were calcined at 800°C for 1 h (PROTHERM furnace, STF 12/60/250 model, Turkey) to remove moisture and organic impurities, thus increasing the reactivity of the clay. This process was necessary to facilitate the subsequent interactions between the clay and sodium hydroxide (NaOH) solution. After calcination, the clay was mixed with a 1.5 M NaOH solution in a liquid-to-solid mass ratio of 10 (Ait Baha et al., 2023). The mixture was then stirred (S/N 85215 device, Velp Scientifica, Europe) at room temperature for 30 min to ensure a homogeneous distribution of the NaOH solution and to promote the dissolution of the clay structure.

For hydrothermal treatment without pre-treatment, the clay-NaOH slurry was placed in a 100 mL Teflon^{*} stainless steel autoclave, designed to withstand high temperatures and pressures, and treated at 200°C for 12 h. Following this, the temperature was reduced to 150°C and maintained for 24 h to promote the crystallization of analcime zeolite. The cooling step was necessary to allow for optimal zeolite growth and phase formation. This process was aimed at observing the effect of the hydrothermal treatment without any prior modification of the clay.

In the reflux pre-treatment method, the clay-NaOH slurry was refluxed at 120°C for 5 h. Refluxing serves to enhance the dissolution of the clay and improve the availability of silicon and aluminum ions for zeolite formation. After refluxing, the slurry was treated hydrothermally at 150°C for 24 h, as described in the previous step, to allow for zeolite crystallization.

For the sonochemical-assisted pre-treatment (model 021187, JP Selecta Ultrasons, Spain), the calcined clay was added gradually to the 1.5 M NaOH solution while stirring for 1 h. The mixture was then sonicated for 24 h at a frequency of 50 Hz and an intensity of 110 W. Sonication enhances the dispersion and dissolution of the clay particles by applying acoustic energy, which facilitates the formation of finer zeolite crystals. After sonication, the slurry was treated hydrothermally at 150°C for 24 h, as per the previous steps.

The alkaline pre-fusion method involved mixing the raw clay with NaOH solution in a 1.5 M NaOH concentration. This mixture was fused at 800°C for 1 h to alter the structural framework of the clay minerals, resulting in their decomposition and promoting amorphization. This high-temperature fusion step enhances the reactivity of the clay and facilitates the formation of a more suitable precursor for zeolite synthesis. Following fusion, the sample obtained was subjected to hydrothermal treatment at 200°C for 2 h to allow the initial phase of zeolite formation. The temperature was then reduced to 150°C for 36 h to promote the crystallization of analcime zeolite.

To study the influence of the Si/Al ratio, fumed silica was added to the raw clay prior to the pre-fusion process. The amount of fumed silica added was controlled carefully to maintain a favourable Si/Al ratio for the formation of analcime. This step aimed to enhance the crystallization process and improve the properties of the resulting zeolite, particularly its surface area and cation exchange capacity.

After synthesis, the products from all treatments were filtered, washed with distilled water to remove any residual alkali, and then dried at 80°C for 24 h. This final step ensures the removal of excess water and any soluble by-products, leaving behind a clean zeolite solid phase.

The degree of purity of the analcime was quantified carefully using XRD analysis, specifically through the Rietveld method, implemented with *HighScore* software. This method is widely regarded for its precision in phase quantification, structural refinement, and the ability to model complex diffraction data (Hillier, 2000; Novembre et al., 2011; Zhou et al., 2018). Additionally, the XRD patterns were evaluated for the calculation of the relative crystallinity index, employing the reference intensity ratio (RIR) method, comparing the intensity of diffraction peaks from the zeolite phase with that of an internal standard, in this case, quartz, which serves as well-established reference material and designated as 100% (Rayalu et al., 2005; Li et al., 2010; Tabit et al., 2019; Ranjbar Toroghi et al., 2023).

Characterization techniques

The chemical composition of the clay, as received, as well as of the resulting materials, was determined using the RIX 3000 X-ray



Figure 1. Experimental protocols for zeolite synthesis.

fluorescence spectrometer (Rigaku Industrial Corporation, Japan) where samples were prepared by pressing the material into discs. X-ray powder diffraction (XRD) was employed to analyze the different materials, utilizing a Rigaku D/Max-IIIB diffractometer with copper radiation at 40 kV and 50 mA power. Data collection utilized a step size of $0.02^{\circ}2\theta$ with a scanning speed of $5^{\circ}2\theta$ min⁻¹ within the range 5–60°2 θ and the relative crystallinity of analcime was calculated based on the intensity of the peaks at $10-40^{\circ}2\theta$. Infrared spectroscopy was conducted on the various products using a DTGS detector (Bruker Corporation, Germany), covering the spectral range between 2000 and 400 cm⁻¹. The samples were ground with KBr as a diluent and then pressed into 100 mg pellets with a 1:100 weight ratio of the sample. For morphological and compositional examinations, a Tescan Vega 3 SEM with an electron beam acceleration voltage of 10 kV, equipped with a secondary electrons detector (Czech), and energy dispersive spectroscopy (EDAX) were employed. To prevent surface charging, the samples were carbon-sputtered. The particle size of the various materials was computed using ImageJ software. The total loss on ignition (LOI) was determined gravimetrically after heating the samples to 1000°C. The CEC of the zeolites obtained was determined using the sodium ammonium acetate method (Tabit et al., 2019). The amount of sodium ions extracted, representing the CEC of the product, was measured through a titration method. Surface area values were measured through gas isothermal sorption analysis using a multiple-point method (typically in the range of 0.35 to 0.7 P/P_0). The samples were degassed under vacuum at 200°C for 7 h, and measurements were performed using a Micromeritics 3Flex 5.00 instrument (Norcross, Georgia, USA).

Results

Analysis of raw materials

The XRD patterns of the raw and calcined clays are shown in Fig. 2a,b. For the raw clay, the main crystalline phases are quartz (PDF#83-2465) and illite (PDF#2-0056). Peaks observed at 9.64, 19.32, and 29.14°2 θ correspond to the pyrophyllite phase (PDF#46-1308),

Table 1. Chemical composition of raw clay (wt.%)

	SiO ₂	Al_2O_3	K ₂ 0	Na ₂ O	Fe_2O_3	CaO	MgO	TiO ₂	
Raw clay	48.73	22.31	3.12	1.47	0.42	0.18	1.26	0.92	

while those at 12.36, 23.14, and 24.92°2 θ are the characteristic peaks of kaolinite (PDF#5-0143). Some of these peaks were masked or their intensity was reduced following calcination corresponding to the transformation of illite to muscovite (PDF#2-0055). The elemental analysis (Table 1) revealed that silica (48.73%) and alumina (22.31%) were the major constituents of the clay, with a SiO₂/Al₂O₃ mass ratio of 2.18, along with traces of titanium, iron, potassium, calcium, and potassium oxides. Notably, calcination of the clay enhanced its hydrophobicity by altering its chemical composition, probably due to the elimination of residual water and the organic portion (Han et al., 2019), as shown by LOI of 6%. The BET surface area and the CEC of the sample were determined as 8.99 m² g⁻¹ and 17 meq 100 g⁻¹, respectively.

Infrared characteristic vibration bands for illite and quartz (Fig. 3) were located in the regions 420-540 cm⁻¹ and 900-1200 cm⁻¹, respectively (Mezni et al., 2011). The bands between 1200 and 400 cm⁻¹ were attributed to OH bending vibrations, Si-O vibrations, and Al-O vibrations (Belviso et al., 2017). In the first region (420-500 cm⁻¹), the bands at 475 cm⁻¹ and 538 cm⁻¹ were related to the bending mode of Si-O-Al vibration and have been assigned as T-O bending mode (where T=Si or Al) (Jiang et al., 2008). In the second region, the observed band at 1025 cm⁻¹ was attributed to the asymmetric stretching mode of Si-O-Si vibration and is assigned as the T-O stretching mode (Kloprogge et al., 2005; Moneim and Ahmed, 2015). Additional infrared (IR) bands such as those at 694 cm^{-1} and 780 cm⁻¹ corresponded to OH-stretching vibrations (Mezni et al., 2011). Quartz was characterized by the bands of Si-O-Si vibrations located at 797 cm⁻¹, while the band characteristic of carbonate appeared at 1418 cm⁻¹. Bands located in the range 1600–3700 cm⁻¹ were attributed to water (Efimov et al., 2003), as was the band at ~1620 cm^{-1} . The band located at 3458 cm^{-1} was due to the hydrogen bonding of water molecules to surface oxygen (Perraki and Orfanoudaki, 2004). The intensity of the band at 3632 cm^{-1} was



Figure 2. XRD patterns of (a) raw and (b) calcined clay.



Figure 3. FT-IR spectra of raw and calcined clay minerals.



Figure 4. SEM image of (a) raw clay and (b) calcined clay minerals.

assigned to stretching vibrations of octahedral OH groups of inner Al₂OH, which is characteristic of the kaolinite phase (Brantley and Mellott, 2000). After calcination, some bands in the raw clay spectrum disappeared or were greatly reduced in intensity, except for those of quartz and aluminosilicates, which remained discernible, indicating compositional changes. Although the calcination process at 800°C was expected to remove a significant amount of hydroxyl groups, it is often insufficient for complete dehydroxylation. According to previous studies (Bohor, 1963; Murad and Wagner, 1996; Csáki et al., 2022), higher temperatures (typically >1000°C) were required for the full removal of hydroxyl groups which would promote complete dehydroxylation as it could also cause the mineral structure to become more disordered, leading to possible phase transformation or excessive sintering, which may impact the

desired zeolite synthesis. In many cases, calcining at 800°C is sufficient to remove most of the hydroxyl groups without compromising the structural integrity of the material (Cheng et al., 2019).

The SEM images of the raw and calcined clays (Fig. 4a,b) revealed irregular platelets, poorly defined flakes with an illitic layered crystalline structure, and pseudohexagonal platy morphology characteristics of the kaolinite phase while muscovite exhibited a smooth and flat surface in the metaclay. This description is consistent with previous works. For instance, in an analysis conducted by Sengupta et al. (2008), SEM characterization of kaolinite clay presented a pseudohexagonal morphology arranged in a face-to-face pattern. Similarly, the flaky habit and the sheeted structure of muscovite were confirmed in a study by Selim et al. (2018). In contrast, quartz exhibited aggregated, microsphere-like, ragged-edged particles, sub-rounded with observed



Figure 5. Composition of calcined clay minerals.

particle size fractions ranging from 2 to 10 μ m (Mezni et al., 2011; Martín et al., 2022). EDX analysis (Fig. 5) illustrated an increase in the quartz content compared with alumina. The prevalence of quartz among clay minerals is probably due to the formation of clay minerals through the slow chemical weathering of silicate-bearing rocks (Belviso et al., 2013).

TG-DTA examination of the raw clay minerals was conducted between ambient temperature (22°C) and 700°C under atmospheric pressure (Fig. 6), revealing two distinct mass losses on the TGA thermograms corresponding to various physicochemical transformations. For raw clay, a prominent endothermic peak at 35° C (accounting for ~96% of the weight) was observed, attributable to the loss of adsorbed moisture (Al-Nahari et al., 2023). This peak diminished significantly when the clay was calcined, where the residual weight stabilized at ~99%. The TG curve for raw clay showed a gradual mass loss with notable transitions: an exothermic peak at 107°C, probably linked to the removal of interlayer water and minor organic volatiles (Ayele et al., 2016). Upon calcination, this peak decreased, reflecting the removal of volatile phases. This behavior was attributed to the hygroscopic nature of the clay minerals, such as kaolinite and illite, which are known to retain surface and interlayer water. Furthermore, the raw clay exhibited three additional mass-loss events at 437, 518, and 597°C, corresponding to key transformations linked to the presence of quartz and the transformation of illitic phases to muscovite (van de Kamp, 2008; Marsh et al., 2018).

According to the literature, subjecting illite to high temperatures and pressures during metamorphism transforms it into muscovite (Rosenberg, 2002; Verdel et al., 2011; Den Hartog et al., 2013; Zhang et al., 2015). In detail, at 437°C, dehydroxylation of structural hydroxyl groups in kaolinite and/or illite begins, releasing water and forming amorphous metaclays. At 518°C, dehydroxylation continues and approaches completion, marking the primary transition of the clay structure into an amorphous phase. The event at 597°C was attributed to structural rearrangements, including the incipient formation of intermediate aluminosilicate phases or reactions in impurities, such as quartz restructuring. In calcined clay, these distinct peaks were replaced by a broad endothermic band between 400 and 500°C, indicative of residual structural rearrangements and possible final adjustments in the amorphous metakaolinite network (Labaied et al., 2023). The TG curve continued to diminish beyond 600°C while the DTA curve stabilized, suggesting ongoing mass loss without significant heatflow changes. This indicates that the processes responsible for the mass loss were energy-neutral or involved minimal heat absorption or release, hence not appearing as distinct thermal events on the DTA curve. Potential contributors to this behavior included residual dehydroxylation, where any remaining structural hydroxyl groups were gradually removed, and minor transformations of impurities such as quartz or feldspar (Dehmani et al., 2023). By calcining the clay to 800°C, structural hydroxyl groups were fully



Figure 6. TG-DTA curves of raw clay.



Figure 7. XRD patterns of the synthesized products by (a) hydrothermal, (b) sonication-mediated hydrothermal, and (c) reflux-mediated hydrothermal processes.

removed, leading to the formation of amorphous metakaolinite. Beyond this temperature, recrystallization into mullite or other hightemperature phases may have occurred, along with transformations in accessory minerals, such as the decomposition of carbonates or the recrystallization of silica. These findings align with previous research (Novembre et al., 2011; Mourak et al., 2021), as supported by XRD and FT-IR analysis data.

Influence of sonication and reflux pretreatments

XRD analysis was conducted to classify the composition of the resulting materials by hydrothermal curing after sonication-reflux pre-treatment variations of the calcined clay (Fig. 7). The XRD patterns revealed sharp and intense peaks at 20 angles of 16.08, 18.28, 24.38, 25.95, 30.65, 33.31, 35.82, 40.60, and 52.61°20. These peaks were attributed to the formation of analcime-C (PDF#41-1478). Unreacted muscovite peaks derived from the source clay were detected in all treatments. The analcime content reached

77.8% after hydrothermal synthesis without prior treatment while the muscovite content was 22.8%, which increased to 80.2% and 83.4% after sonochemical and reflux pre-treatments, respectively. The increase in analcime content with sonication and reflux pretreatments was attributed to the enhanced diffusion of reactants in solution, which promoted crystal nucleation and growth. This led to greater analcime content compared with untreated samples (Baccouche et al., 1998; Sen et al., 2018).

The band at 3631 cm⁻¹ in the FT-IR spectra (Fig. 8) is associated with the asymmetric stretching mode of water coordinated to the edges of the channels, while the band at 1639 cm⁻¹ is assigned to the zeolitic water in the zeolite channels (Frost et al., 2000). Concurrently, the absorption peak intensity of bound water strengthened with the gradual formation of analcime, affirming the improved degree of crystallization of the synthesized product with prolonged synthesis time (Ward, 1967). As crystalline Si-O-Al, Si-O-Si, O-Na-O, and Al-O-Al bonds developed, the broad band at 1200–900 cm⁻¹, arising from aluminosilicates, shifted to lower wavenumbers (Yusuf, 2023).



Figure 8. FT-IR spectra of the synthesized products using various hydrothermal routes.



Figure 9. SEM-EDX of the synthesized products by (a) hydrothermal, (b) sonication-mediated hydrothermal, and (c) reflux-mediated hydrothermal processes.

This shift suggests a restructuring or reorganization of the aluminosilicate network due to the development of crystalline phases. In addition, symmetric stretching and bending vibration of the T-O bonds in the TO₄ tetrahedral structure produced peaks at 722 cm⁻¹ and 500 cm⁻¹. In addition, the double-membered rings D4R and D6R, providing characteristic markers for the presence of analcime in the sample, were identified by the band centered on 567 cm⁻¹ (Jin et al., 2022). The band at 432 cm⁻¹ is characteristic of O-Si-O bonding mode, i.e. typical of the bending vibrations of 4-membered rings (Novembre and Gimeno, 2021).

SEM images (Fig. 9) show the dissolution of clay minerals and the crystallization process. The final material consisted mainly of a visible-channel analcime system, smooth-rough microcrystals, or crystals resembling clean-faceted octahedra, while some exhibit intergrowths and fractures. In addition, remnants of a nearly fully dissolved flat and smooth, layered structure, typical of original muscovite, were observed, with the beginnings of the formation of crystals of the same diameter as analcime (Ma et al., 2015; Bortolini et al., 2020). These observations are reliable based on information from several previous studies (Dyer et al., 2004; Azizi and Ehsani Tilami, 2013; Ma et al., 2015; Osacký et al., 2017). In addition, EDX analysis of the sample-mediated hydrothermal process (Fig. 9) showed similar quartz and alumina rates, indicating comparable solubility kinetics under these hydrothermal conditions. This intriguing feature suggests the potential use of these unprocessed clay minerals not only as a precursor for silicon and aluminum but also as a hard co-template that shapes the growth geometry of zeolite crystals.

Influence of NaOH pre-fusion pre-treatment on zeolite crystallization

The resulting materials from the various experiments were identified by XRD. These experiments included NaOH pre-fusion alone, NaOH pre-fusion-mediated hydrothermal treatment, and variations involving the addition of fumed silica during pre-fusion (Fig. 10). First, the XRD pattern of the NaOH pre-fusion treatment (Fig. 10a) revealed sharp peaks attributed to the nepheline phase (PDF#76-2469). Under these conditions, sodalite (PDF#82-1812), a secondary product, was formed. No peaks associated with illite, pyrophyllite, or kaolinite were detected, as they underwent dissolution upon pre-fusion with NaOH, resulting in structural changes.



Figure 10. XRD patterns illustrating the effect of NaOH perfusion (a) only, (b) mediated hydrothermal, (c) with fumed silica addition only, and (d) with addition of fumed silica and mediated hydrothermal treatment.

Upon subsequent hydrothermal treatment, the composition (Fig. 10b) revealed a mixture of analcime-C and nepheline, with the amounts reaching 91.7% and 8.3%, respectively. In addition, the crystallinity of the analcime attained 167% and the Si/Al mass ratio of the resulting sample was determined to be 2.20 according to XRF analysis. The crystallinity value exceeding 100% suggests a high degree of structural order within the analcime crystal lattice, as verified by quantitative XRD measurements. This elevated value was attributed to the effectiveness of the NaOH pre-fusion pretreatment in promoting crystallization from high-purity sources, namely clay and fumed silica. These sources, when pre-treated, provided an optimal balance of silica and alumina, facilitating the growth of highly ordered analcime crystals. Consequently, this treatment enhanced nucleation density and crystal growth, leading to the observed high crystallinity. Throughout the hydrothermal curing, the peaks associated with the sodalite phase exhibited recrystallization tendencies, acting as precursor materials; sodalite provided essential components for analcime formation under heightened heat and pressure conditions. These findings are corroborated by various studies in the field (García-Villén et al., 2018; Zhang et al., 2022). Notably, the pre-fusion method significantly contributed to the formation of analcime compared with other routes. It is worth mentioning that the reaction time and temperature influenced the crystallinity of analcime, with a gradual increase in diffraction peak intensity as starting materials pre-fused entirely (Atta et al., 2012).

A thorough morphological analysis was conducted as part of the comprehensive investigation. SEM images of the nepheline phase (Fig. 11a) were represented by small, jagged particles slightly colored, consistent with published data on this phase (Jena et al., 2014), while analcime appeared as large, angular spheres of rough microcrystals with some fractures (Bortolini et al., 2020). In terms of EDX analysis, the pre-fusion-mediated hydrothermal process demonstrated greater solubility kinetics for alumina. This phenomenon contributed to the prevalence of sodium in the formation of the nepheline phase (Azizi and Yousefpour, 2010). SEM-EDX images further corroborated the XRD results, validating the effectiveness of the pre-fusion process in extracting silicon and aluminum species from the clay. This extraction enhanced the

hydrothermal reactivity of the clay. Overall, the alkaline fusion process promoted interaction between crystalline mineral phases successfully within the clay and the alkaline activator.

In order to assess the impact of the Si/Al mass ratio, additional experiments were conducted where fumed silica was added to the raw clay to be prefused. A literature survey, incorporating additional silicon, resulted in greater Si/Al ratios, thus enhancing catalytic activity (Mintova and Valtchev, 2002; Otieno et al., 2019), and the observed peaks (Fig. 10c) corresponded to nepheline (Si-rich) (PDF#79-0993). However, no zeolite formation occurred when extra silicon was added without hydrothermal curing, indicating an amorphization step as manifested by lower peak intensities of Si-rich nepheline and the high background signal (Cundy and Cox, 2005; Li et al., 2018; Zhang et al., 2024b). In contrast, all XRD peaks (Fig. 10d) in the resulting material corresponded to pure analcime-C (highly crystalline form), indicating the formation of high-purity crystalline analcime when followed by hydrothermal curing. While the XRD patterns confirmed the complete crystallization of pure analcime-C and the absence of peaks from precursor materials, it is acknowledged that trace amounts of amorphous material, inherent in the synthesis process, may have existed but were below the detection limit of XRD techniques (Chiang et al., 2010; Akinbodunse et al., 2024). The Si/Al mass ratio of the synthesized sample was determined to be 3.71, based on XRF analysis, which led to an estimated normalized chemical formula of NaAlSi₄O₁₀. Although this differs slightly from the ideal formula of analcime, in NaAlSi₂O₆·H₂O, which typically contains two silicon atoms per formula unit, the presence of four silicon atoms in the formula can be explained by the structural flexibility inherent in zeolites, especially analcime (Ma et al., 2021). Zeolitic frameworks are known to exhibit some variability in their Si/Al ratio, with the silicon content occasionally being greater than the ideal stoichiometric ratio due to variations in the local structure or synthesis conditions (Mattioli and Cenni, 2020; Novembre and Gimeno, 2021). The 10 oxygen atoms observed can also be accounted for, as analcime and other zeolites exhibit flexible silicate frameworks where oxygen atoms are involved in bridging between silicon and aluminum, which may slightly alter the overall

stoichiometry, particularly in partially hydrated forms or suboptimal synthesis conditions (Henderson et al., 2014; O'Keeffe, 2014). These variations are common in the synthesis of zeolites under various temperature and pressure conditions. referring to the inherent variability in synthesis conditions leading to deviations from the ideal stoichiometric composition (Zhang and Ostraat, 2016; Asselman et al., 2022). Thus, despite the differences in the Si/Al ratio, the synthesized material can still be classified as analcime due to its structural and chemical similarities, including its framework structure and cation exchange properties, which are characteristic of analcime and its close relatives in the tectosilicate group (Samantray et al., 2022; Kropáč et al., 2024). In addition, the formation of analcime and the effectiveness of fumed silica during the pre-fusion and hydrothermal stages is further supported by SEM-EDX data (Fig. 11b), confirming analcime crystallization. The shapes of globules were related to analcime, representing rounded, cleanfaceted crystals with an average diameter of ~7 µm computed using ImageJ software. This result is very satisfactory when compared with the size of the crystals obtained by other authors in the past; for example, Jamil and Youssef (2016), synthesized analcime from kaolinite, reaching crystal sizes of 5-7 µm, while Hegazy et al. (2010) observed average dimensions of 10 µm. Based on the XRD and SEM results, this adjustment of the Si/Al ratio with more silicon led to the production of pure analcime, in line with evidence from the literature (Rubtsova et al., 2022).

A comparative study using a variation of CEC and BET analysis

An overview of CEC and BET values obtained from the raw clay before and after various hydrothermal pretreatments (Table 2) revealed a marked increase in CEC values in the products, ranging from ~100 to 510 meq 100 g^{-1} , compared with 17 meq 100 g^{-1} in the raw material. While maintaining the Si/Al mass ratio as in the raw clay, a noteworthy value of 447 meq 100 g^{-1} was obtained when utilizing the NaOH pre-fusion mediated hydrothermal method, surpassing the other routes. This variance can be attributed to the muscovite mineral composition among the other products, as shown by XRD patterns, which constrained the porosity of the resulting analcime. In addition, the pre-fusionmediated process yielded a product rich in nepheline. The adsorptive behavior of nepheline along with analcime was quite beneficial, promoting retention capabilities (Wang et al., 2017; Tahmasebipour et al., 2023). In terms of specific surface area (Fig. 12), the greater value of ~19.62 $m^2 g^{-1}$ was similarly achieved for the NaOH pre-fusion mediated hydrothermal sample, followed by reflux-mediated hydrothermal treatment (17.88 m² g⁻¹), hydrothermal treatment (12.39 m² g⁻¹), and sonochemical-mediated hydrothermal treatment (8.14 m² g⁻¹). This result may be attributed to enhanced crystal growth facilitated by sonication, leading to larger, well-formed crystals, which in turn may reduce the overall surface area by decreasing porosity and potentially promoting crystal aggregation (Zhang et al., 2024a).



Figure 11. SEM images and EDX analysis of the effect of NaOH pre-fusion: (a) NaOH pre-fusion mediated hydrothermal, and (b) NaOH pre-fusion with the addition of fumed silica and mediated hydrothermal treatment.

Table 2. CEC and BET measurements

Route	Raw clay	Hydro*	Sonication-mediated hydro*	Reflux-mediated hydro*	NaOH pre-fusion mediated hydro*	NaOH pre-fusion mediated hydro* + Si
CEC (meq 100 g ⁻¹)	17	376	140	240	447	510
Specific area (m ² g ⁻¹)	8.99	12.39	8.14	17.88	19.62	23.76

Hydro* = hydrothermal.



Figure 12. BET analysis of the resulting powders.

These results underscore the significant positive impact of the pre-fusion method on the synthesis process where others have emphasized that the most substantial zeolitization occurs through the reaction between NaOH and the raw material at elevated temperatures, facilitating the dissolution of species in water (Tironi et al., 2012; Belviso et al., 2017).

In addition, a distinct synthesis pathway was evaluated for the NaOH pre-fusion mediated hydrothermal method where the impact of introducing additional silicon during pre-fusion was explored. This finding explicitly affirms the supremacy of the NaOH prefusion mediated hydrothermal method in the realm of zeolite synthesis when adding fumed silica. Not only did this method yield analcime samples with the largest CEC values (510 meq 100 g^{-1}), but it also exhibited remarkable enhancements in BET surface area $(23.76 \text{ m}^2 \text{ g}^{-1})$ compared with its counterparts. This can be attributed to fumed silica that acts as an additional, highly reactive source of silicon that readily integrates into the zeolite framework, promoting uniform and dense crystal growth with well-defined pore structures (Otieno et al., 2019). This additional silica not only increases the nucleation sites, leading to more extensive crystal formation but also optimizes the Si/Al ratio, which is essential for forming an open and accessible aluminosilicate framework (Barthel et al., 2005). The result is a zeolite structure with increased porosity and a greater number of exchange sites, thereby maximizing both the BET surface area and the CEC. The notable increase in CEC values associated with the introduction of extra silicon is pivotal, showcasing the enhanced ion-exchange capacity achievable through this method. This result bears profound implications for applications in water treatment, catalysis, and environmental remediation, where superior ion exchange properties are essential (Smyth and Caporuscio, 1981; Yuan et al., 2016; Tsitsishvili et al., 2021). Moreover, the BET analysis underscores the substantial gains in surface area and porosity achieved by incorporating extra silicon. This augmented surface area holds paramount importance in catalysis and adsorption processes, illustrating the method's potential for advanced material engineering (Cundy and Cox, 2003; Sharma et al., 2023).

This comprehensive comparative study firmly establishes the NaOH pre-fusion mediated hydrothermal process as the method of choice for producing zeolites with exceptional CEC and BET values. These results underscore the importance of alkaline pre-fusion in enhancing clay reactivity and optimizing zeolite properties. The purity of the analcime synthesized was quantified at 100%, aligning with the threshold for industrial standards, which typically require \geq 90% purity, and the exceptional surface area and cation exchange capacity of the zeolites synthesized highlight their potential for various applications, promising advances in fields such as ion exchange and catalysis (Zhang et al., 2024c). Put simply, the protocol's efficacy in achieving this level of purity supports its potential scalability and adaptation for industrial processes.

Conclusions

The present study aimed to hydrothermally synthesize analcime from Moroccan clays at 150°C for 36 h, employing various nanoscale synthesis pre-treatments including NaOH pre-fusion, sonication, and reflux, all using a 1.5 M NaOH solution. The experiments further explored the role of fumed silica in the synthesis process. The results demonstrated that each method impacted the chemical breakdown and nanoscale reconfiguration of the clavs differently, with the NaOH pre-fusion method proving most effective in disrupting the clay structure and advancing the amorphization process. Analcime-C emerged as the primary zeolite phase across all methods, with high-purity crystals predominantly formed through the hydrothermal pre-fusion process, especially when enhanced with fumed silica. Traditional nanoscale synthesis techniques such as sonication or reflux yielded zeolites of lower purity primarily because these methods did not achieve the same degree of structural breakdown and amorphization as the NaOH pre-fusion approach. While sonication and reflux introduced nanoscale modifications, they failed to disrupt the silicate framework of the clay minerals significantly, which is necessary for the structural reorganization that forms high-purity zeolite phases. The synthesized zeolite showcased a remarkable surface area of 23.76 m² g⁻¹ and an impressive CEC of 510 meq 100 g⁻¹, underscoring the effectiveness of innovative zeolite synthesis methods in optimizing clay reactivity at nanoscale. This research highlights the critical role of alkaline pre-fusion in enhancing feedstock reactivity, leading to the synthesis of high-purity zeolites. It provides valuable insights into zeolite synthesis and its applications, laving the foundation for further nanoscale research and development in this field.

Data availability statement. The data used to support the findings of this study are included in the article.

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