



**UNIVERSIDADE DE BRASÍLIA
INSTITUTO DE QUÍMICA
PROGRAMA DE PÓS GRADUAÇÃO EM
QUÍMICA
LABORATÓRIO DE MATERIAIS
CERÂMICOS E NANOESTRUTURADOS**



DOCTORAL THESIS

Production of inorganic zeolite membranes with KFI Zeolite for
gas separation.

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Production of inorganic zeolite membranes with KFI Zeolite for gas separation.

(Produção de membranas inorgânicas de zeólita KFI para separação de gases)

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List of abbreviations and acronyms (in alphabetical order)

- 8MR:** Zeolite with 8-membered ring
- 10MR:** Zeolite with 10-membered ring
- 12MR:** Zeolite with 12-membered ring
- ASTM B962-13:** Standard
- BET:** Brunauer-Emmett-Teller
- CD:** β -Cyclodextrin
- CDTN:** Nuclear Technology Development Center
- CHA:** Chabazite
- DAS:** Structure-Directing Agent (SDA)
- DDR:** Deca-Dodecasil 3R Zeolite
- DRX:** X-ray Diffraction (XRD)
- EDS:** Energy-Dispersive X-ray Spectroscopy
- ERI:** Erionite
- ETD:** Everhart-Thornley Detector (secondary electron detector of ETD type)
- FAU:** Faujasite
- FTIR-ATR:** Fourier Transform Infrared Spectroscopy in Attenuated Total Reflectance mode
- FWHM:** Full Width at Half Maximum
- GN:** Natural Gas
- HAP:** Hydroxyapatite
- IAST:** Ideal Adsorbed Solution Theory
- Im3m:** Space group of KFI zeolite
- IZA:** International Zeolite Association
- LED:** Low Energy Detector
- LEGGA:** Laboratory of Geodynamic, Geochronological and Environmental Studies
- LFD:** Secondary Electron Detector
- LTA:** Linde Type A Zeolite
- LTL:** Linde Type L Zeolite
- MER:** Merlinoite

MEV: Scanning Electron Microscopy (SEM)
MOFs: Metal-Organic Frameworks
MPa: Pressure measurement unit
NIH: National Institutes of Health
NLDFT: Non-Local Density Functional Theory model
NO_x: Oxidation Number
PEG: Polyethylene Glycol
PLA: Polylactic Acid
PVA: Polyvinyl Alcohol
RMN-RAM: Solid-State Nuclear Magnetic Resonance Spectroscopy with Magic Angle Spinning
SBU: Secondary Building Units
SE: Secondary Electron Detector
TBA: Tert-Butyl Alcohol
TEOS: Tetraethyl Orthosilicate
UFMG: Federal University of Minas Gerais
UnB: University of Brasília
μCT: X-ray Microcomputed Tomography

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Resumo

O desenvolvimento econômico e industrial tem levado a uma série de crises ambientais, como o aquecimento global, a poluição grave e o esgotamento dos recursos naturais. Para mitigar esses problemas, é crucial adotar estratégias de conservação de energia, de redução de emissões de poluentes e de controle de danos ambientais. O uso crescente de gás natural como fonte de energia tem sido observado devido ao seu menor impacto ambiental em comparação com outros combustíveis fósseis. A presença de contaminantes como N_2 pode afetar a combustão e contribuir para a formação de óxidos de nitrogênio altamente poluentes. Portanto, processos eficientes para a remoção de N_2 do gás natural são necessários. A separação de gases por membranas emergiu como uma tecnologia eficaz devido ao seu baixo custo, operação simples e alta eficiência energética. Porém, a separação dessas misturas gasosas permanece desafiadora devido à semelhança de tamanho molecular. Nesse contexto, membranas inorgânicas com zeólitas surgem como uma alternativa promissora devido à sua alta seletividade e estabilidade térmica. A zeólita KFI demonstrou potencial para separação de gases devido ao seu pequeno tamanho de poros. Além disso, estudos prévios de adsorção mostraram que esta zeólita apresenta elevada seletividade para a separação de N_2 , CO_2 e CH_4 e entender o comportamento de adsorção e da capacidade de adsorção dos gases, especialmente do CO_2 (que interage de forma mais intensa com a estrutura da zeólita em comparação com N_2 e CH_4) destaca o potencial da zeólita KFI para aplicações de adsorção seletiva e separação de CO_2 . Entretanto, estudos sobre a fabricação de membranas inorgânicas utilizando zeólita KFI são escassos na literatura. Portanto, este estudo investigou a preparação de membranas inorgânicas incorporando zeólita KFI, com foco na síntese de suportes cerâmicos e na formação da zeólita. Os resultados mostraram que a técnica de *freeze-casting* influenciou significativamente as propriedades mecânicas e a estrutura dos suportes cerâmicos de alumina, produzindo materiais com alta resistência mecânica e conectividade, aspectos cruciais para o desenvolvimento de suportes cerâmicos para separação de gases. Além disso, a escolha das fontes de alumínio e sílica na síntese da zeólita afetou a pureza e a estrutura das amostras resultantes. Amostras com alta área superficial e microporosidade, medidas em 523,8 e 469,4 m²/g, respectivamente, indicam que quase 90% da área é composta por microporos de pequeno tamanho de partícula, tornando-as ideais para aplicação em membranas de zeólita. Esses achados ressaltam a eficácia da síntese de membranas inorgânicas sem o uso de templates orgânicos, fornecendo materiais com alto potencial para aplicações em membranas devido à sua baixa hidrofobicidade e eficiência na separação.

Palavras-chave: Separação de gases; *Freeze-casting*; Suporte cerâmico; Zeólita KFI; Membranas.

Abstract

The global increase in economic and industrial development has led to a series of environmental crises, such as global warming, severe pollution, and depletion of natural resources. To mitigate these issues, it is crucial to seek means of energy conservation, reduction of pollutant emissions, and environmental damage control. The growing use of natural gas as an energy source has been observed due to its lower environmental impact compared to other fossil fuels. However, its composition, which includes contaminating gases like N_2 , can affect combustion and contribute to the formation of highly polluting nitrogen oxides. Therefore, efficient processes for N_2 removal from natural gas are necessary. Gas separation by membranes has emerged as an effective technology due to its low cost, simple operation, and high energy efficiency. However, the separation of these gases mixtures has been challenging due to the similarity in size between these gases. In this context, inorganic membranes, especially those based on zeolites, emerge as a promising alternative due to their high selectivity and thermal stability. The KFI zeolite has shown potential for gas separation due to its small pores. Additionally, previous adsorption studies have revealed higher selectivity of this zeolite for N_2 , CO_2 and CH_4 separation compared to other commercial zeolites. Understanding the adsorption behavior and adsorption capacity of gases, particularly CO_2 , seeing that CO_2 exhibits stronger interactions with the zeolite framework compared to N_2 and CH_4 , highlighting the potential of KFI zeolite for selective CO_2 adsorption and separation applications. However, studies on the preparation of inorganic membranes with KFI zeolite are scarce in the literature. Therefore, this study investigated the preparation of inorganic membranes with KFI zeolite, focusing on the synthesis of ceramic supports and zeolite formation. The results showed that the freezing method used in the freeze-casting technique had a significant impact on the mechanical properties and structure of alumina ceramic supports with high mechanical strength and high connectivity, crucial aspects in the development of ceramic supports for gas separation. Furthermore, the study of different sources of aluminum and silica in zeolite synthesis affected the purity and structure of the samples. Samples with high surface area and micropore area with values of 523.8 and 469.4 m^2/g , respectively, indicate that almost 90% of their area is formed by micropores with small particle size, ideal for use in zeolite membranes. These findings highlight the effectiveness of inorganic membrane synthesis without the use of organic templates, offering materials with high potential for membrane applications due to their low hydrophilicity and separation efficiency.

Keywords: Gas separation; *Freeze-casting*; Ceramic support; KFI Zeolite; Membranes.

INTRODUCTION AND OBJECTIVES

1. Introduction

With the rapid development of the global economy and continuous industrial progress, the world faces a series of environmental crises such as global warming, severe pollution, and the depletion of natural resources [1]. These issues have increasingly affected human life, forcing society to seek ways to conserve energy, reduce pollutant emissions, and mitigate environmental damage. Over the years, the consumption of natural gas as an energy source has grown steadily, as it produces a significantly lower environmental impact compared to other fossil fuels [2].

Natural gas is predominantly composed of methane (CH_4) and small amounts of other hydrocarbons, such as ethane, propane, and butane. However, contaminants including carbon dioxide (CO_2), nitrogen (N_2), and sulfur compounds are also present in its composition [3]. The presence of N_2 contaminants affects the combustion process of natural gas contributing to the formation of nitrogen oxides (NO_x), which are highly polluting gases. From an environmental and industrial perspective, CO_2 is one of the most significant target gases for adsorption studies due to its major contribution to global warming and its relevance in natural gas upgrading, biogas purification, and carbon capture and storage (CCS) technologies. Therefore, developing efficient processes for the removal of these gases from natural gas is essential [3,4].

Membrane-based gas separation is considered an effective technology due to its advantages of low production cost, simple operation and maintenance, high energy efficiency, and lower environmental impact compared to traditional separation methods such as adsorption and distillation [1,4,5]. The separation of N_2 , CO_2 and CH_4 mixtures using polymeric and ceramic membranes has been extensively studied. However, this process remains challenging because the kinetic diameters of CO_2 , N_2 and CH_4 differ by less than 5% (0.3 nm for CO_2 , 0.36 nm for N_2 and 0.38 nm for CH_4), making size-based separation difficult. Moreover, both gases are weakly adsorbed, resulting in low adsorption-based selectivity [3,4].

Currently, polymeric membranes dominate the global membrane separation market due to their good processability, economic competitiveness, and scalability. Nevertheless, they suffer from several limitations, such as the trade-off between permeability and selectivity, as well as low thermal and chemical stability, which restrict their operational performance and conditions [3,4,6]. Inorganic membranes, on the other hand, are particularly attractive since these materials generally exhibit high temperature and pressure resistance, as well as excellent chemical and thermal stability [3,4,6]. The main advantages of dense inorganic membranes

include high selectivity (approaching infinity for high-quality membranes) and thermal stability; however, they often suffer from low permeability, sensitivity, and possible poisoning of active sites [4,7,8].

Improved performance of inorganic membranes can be achieved by using porous materials such as carbon nanotubes, zeolites, and metal–organic frameworks (MOFs) [7,9]. Zeolites are especially promising for gas separation membrane fabrication due to their uniform pore systems with molecular-scale dimensions, high porosity, excellent thermal and chemical stability, and superior adsorption and permeation properties. These characteristics make them suitable for gas separation under industrially relevant conditions [3,4,6,7].

The KFI-type zeolite was first synthesized by Kerr *et al.*, and is therefore often referred to as Kerr-5 or ZK-5. ZK-5 (KFI) is a small-pore, cage-based zeolite that can be synthesized with Si/Al ratios ranging from 2.0 to 5.0, with or without the presence of an organic structure-directing agent [10]. The KFI framework consists of double six-ring (d6r) units, *pau* cages, and *lta* cages interconnected through single six-ring (s6r) units in a body-centered cubic arrangement. The resulting three-dimensional pore network contains windows of approximately 3.9×3.9 Å in diameter (Figure 1) [10,11], which can accommodate CO₂, CH₄ and N₂ molecules with kinetic diameters of 3.3, 3.8 and 3.6 Å, respectively. Compared to N₂ and CH₄, CO₂ possesses a higher quadrupole moment and polarizability, resulting in stronger interactions with the negatively charged sites of aluminosilicate frameworks. Consequently, KFI zeolite is expected to exhibit a considerably higher adsorption capacity for CO₂ — often one to two orders of magnitude greater than that of N₂ under the same conditions — and enhanced CO₂/CH₄ and CO₂/N₂ selectivity at room temperature [12,13].

Beyond its structural potential for molecular sieving, understanding the adsorption behavior and adsorption capacity of KFI zeolite is of fundamental importance. The adsorption phenomenon provides insight into the interactions between gas molecules and the zeolite framework, revealing how factors such as pore size, cation distribution, and framework composition influence gas selectivity and capacity. These parameters are crucial for designing efficient separation processes and for evaluating the potential of KFI as both an adsorbent and as a component in membranes.

To the best of our knowledge, no studies have reported the use of KFI zeolite in the fabrication of inorganic membranes. These features highlight the potential of KFI-type zeolites

as promising materials for CO₂ separation and capture applications, contributing to both industrial efficiency and environmental sustainability.

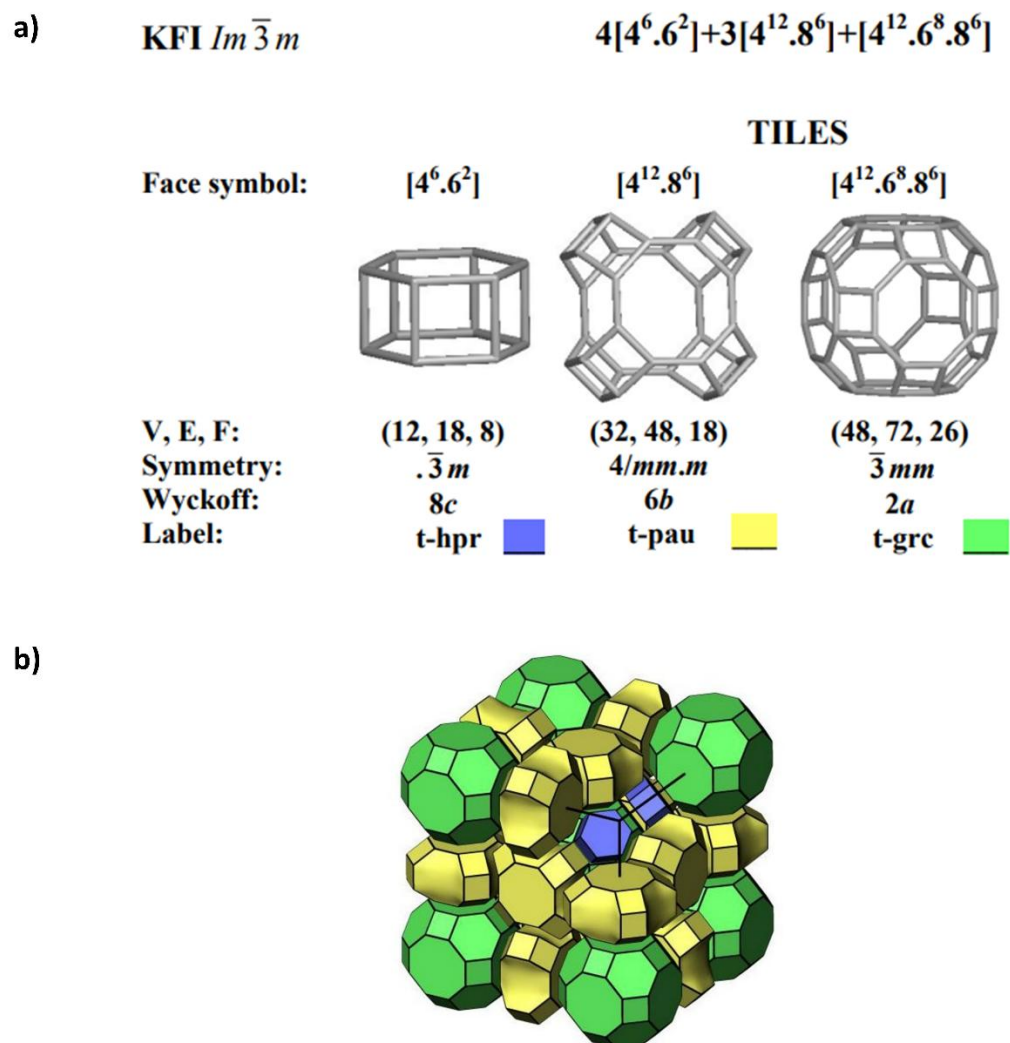


Figure 1. Structure of the KFI zeolite. (a) Structural view showing the different types of cages, which are connected by double six-ring units; (b) Image of the KFI.

2. Objectives

2.1 General Objective

The general objective of this project was to investigate the potential of KFI-type zeolite for application in inorganic membranes for gas separation, with particular emphasis on understanding the adsorption phenomena and determining the adsorption capacity of relevant gases such as CO₂, CH₄, and N₂.

2.2 Specific Objectives

The specific objectives were:

- To investigate the best fabrication conditions for alumina supports used in membrane production;
- To synthesize and characterize KFI zeolite, assessing its structural, textural, and chemical properties;
- To fabricate inorganic membranes incorporating KFI zeolite and evaluate their morphology and structural integrity;
- To evaluate the influence of the supports on the structure of the deposited films.
- To experimentally determine single-component adsorption isotherms of CO₂, CH₄, and N₂ at 298 K;
- To calculate the adsorption capacity and discuss the mechanisms of gas–zeolite interactions;
- To correlate the parameters of the N₂, CO₂ and CH₄ gas separation process with the structure of the zeolite membranes.
- To assess the prospects of KFI-based materials for CO₂ capture and natural gas purification processes.
- To evaluate the separation mechanism and the permselectivity of N₂, CO₂ and CH₄ gas in KFI zeolite membranes.

BIBLIOGRAPHIC REVIEW

3. Bibliographic review

This chapter presents the main concepts of gas separation using membranes, highlighting key applications and challenges, as well as the fundamental concepts of gas transport through membranes. Specifically, for inorganic membranes, the theoretical background and published studies that have contributed to the development of this field will be discussed, focusing on how they can overcome the limitations of conventional membranes for gas separation. Finally, a description of the ceramic materials used as supports and the zeolites employed in the experimental part of this work will be provided.

3.1. Membranes and Gas Separation

Among the available fossil fuels, natural gas (NG) has been considered the cleanest alternative and is increasingly used for energy supply [5]. Raw natural gas extracted from reservoirs presents a complex composition with many impurities, being composed predominantly of methane (approximately 90% or higher in most cases), along with small percentages of hydrocarbon gases such as ethane, propane, and butane, as well as small amounts of carbon dioxide, nitrogen, hydrogen sulfide, and trace amounts of water vapor. These impurities can negatively impact the application of this NG in industry; in particular, CO₂ and N₂ significantly reduce the calorific value of natural gas [3,14]. Therefore, the removal of CO₂ and N₂ from natural gas is essential to improve its calorific content and prevent pipeline erosion in the presence of moisture and CO₂.

To meet different separation demands, technologies such as distillation and extraction have been widely explored and are the most used in the current industry. However, the energy consumption of these technologies, especially in the case of cryogenic distillation, is remarkably high, accounting for 10 to 20% of total global energy consumption [15]. Therefore, economically viable separation alternatives are of utmost importance to reduce energy consumption and pollutant emissions. Due to their energy-saving characteristics and environmental friendliness, membrane separation techniques are commonly regarded as energy-efficient separation technologies and have gradually become the focus of research [5,9].

The use of membranes constitutes an increasingly important technology, as it is a versatile way to separate gas mixtures and has been widely used due to its advantages of simple operation, low cost, and high efficiency. It is also a technology that is easily scalable at the

industrial level [1,6]. Several important industries have processes that would benefit from the use of membranes, such as air separation (N_2/O_2) [9], hydrogen recovery from mixtures (H_2/N_2 , H_2/CO , H_2/CO_2 , $\text{H}_2/\text{hydrocarbons}$) [3,4,8,16], and CO_2 capture from natural gas [4], combustion gases, biogas, and synthesis gas (CO_2/air , CO_2/CH_4 , CO_2/H_2) [4,8,17].

After technological development in recent decades, membrane production has gained prominence, enabling numerous studies using different types of materials for membrane fabrication, including high molecular weight organic polymers [8,17,18], alumina [1,19], and natural minerals [3,4,7,20]. Membranes are generally categorized into three main groups based on the membrane material: polymeric, inorganic, and mixed matrix membranes.

However, polymeric membranes have raised some concerns about natural gas processing. For example, the low permeability and low selectivity [4] of polymeric membranes, as well as the challenge of achieving high selectivity without sacrificing gas permeability, remain significant limitations for this technology's use [5,6,16]. Additionally, long-term operation of these membranes for natural gas processing is problematic due to CO_2 -induced plasticization, low stability at high temperatures, and physical aging of the membranes [5,6].

Therefore, several research groups have recently begun exploring the use of membranes based on inorganic materials for natural gas processing, with a focus on producing thin, stable membranes that exhibit higher selectivity and permeability. These membranes can withstand high temperatures and pressures [6,7,20] and are better suited for harsh industrial conditions. Another significant advantage compared to polymeric membranes is the possibility of membrane recovery or cleaning with high temperatures and superheated steam, as well as the potential use of backflushing techniques to remove membrane fouling [1,5]. Furthermore, they are less susceptible to deterioration by bacteria, which are the main culprits in the biodegradation of most polymeric membranes [1].

Inorganic membranes are mainly based on dense structures [3,21], or porous structures, the latter offering higher fluxes and chemical stability compared to dense membranes [6]. Several porous inorganic membranes have recently been developed for natural gas processing [3,14], such as zeolites [7,16,17,20], ceramics [1,18,19], carbon [8] and MOFs (metal-organic frameworks) [9]. These membranes exhibit molecular sieving properties [3], enabling gas separation processes such as the removal of CO_2 and N_2 from raw natural gas.

Zeolite membranes are a subclass of inorganic membranes. Zeolites are ideal molecular sieving materials because they have well-defined nanometric pore sizes [6,7]. They are capable

of “discriminating” molecules of different sizes, shapes, and diffusivities, and due to the presence of uniform micropores, high surface area, adjustable acidity, hydrophobicity, as well as excellent thermal, chemical, and mechanical stability, zeolites have been widely used in various industrial applications such as catalysts, ion exchangers, and sorbents [5,6,20]. These properties are also highly desirable for gas separation membranes, which has driven research into zeolite membranes for many important separation processes.

A crucial consideration in preparing of zeolite membranes is the selection of the support, as it serves as the foundation for the membrane preparation and overall application. To ensure membrane effectiveness, the support must have high flow permeability and excellent mechanical strength properties [1,5,6]. Defects in the support can lead to failures in both the intermediate layer and the overlying separation layer, highlighting the critical importance of support quality. It must maintain a uniform pore distribution and sufficient mechanical strength [1,19]. The choice of support material is largely determined by the compatibility of its thermal expansion with the zeolite. Zeolites tend to have negative thermal expansion coefficients, whereas most ceramic materials expand when heated [6]. The incompatibility between these coefficients is often responsible for defects observed in the zeolite layer after calcination, the conventional method for membrane activation and removal of the structure-directing agent (SDA) and other species occluded in the micropores. Therefore, the fabrication of zeolite membranes without organic directing agents is considered ideal to minimize these thermal stresses.

3.2. Ceramic Supports for Membranes

3.2.1. Properties of the Supports

Zeolite membranes generally consist of thin supported films, where the properties of the porous support play a crucial role in the success of membrane preparation. A rigid inorganic support is essential to provide mechanical stability to the thin membrane layer [5,6]. The primary requirements for support include high stability under hydrothermal and alkaline synthesis conditions, low permeation resistance, smooth surface without pores, and compatibility with the membrane active layer material [6,19,22]. Porous supports are predominantly composed of ceramic materials (such as α -alumina, titania, silica) or stainless steel.

Ceramic supports, generally thick and equipped with an internal macrochannel for flow along with a porous microstructure, have gained prominence as an emerging technology in liquid and gas filtration [19,23,24]. Although most research in this emerging field has focused on filtration behavior—permeability, selectivity, and fouling—and industrial scalability, which are fundamental aspects for their transformation and widespread implementation, a deeper study of their mechanical properties is also essential [25,26]. Ceramic membranes are expected to last at least a decade in service and, therefore, must possess sufficient long-term mechanical integrity. The study of the mechanical properties of ceramics, especially those related to fracture, is particularly important due to their inherently brittle nature, exacerbated by the abundance of macro- and microporosity in the supports [23,24].

Various scenarios may threaten the mechanical integrity of these supports in gas separation applications, such as shocks during handling, storage, and cleaning; stresses in membrane housings; service stresses; operating pressures; and stresses resulting from pressure differences [22,24,25]. Moreover, mechanical testing can be useful tool for quality control of membranes, as disparities in mechanical properties may reflect microstructural nonuniformities among nominally identical batches, causing issues in processing, modeling, and/or sintering [27].

Improving the mechanical properties of porous ceramics is essential to increase their wear resistance, and literature contains a variety of studies that extensively explore different approaches to achieve this. Some studies have highlighted that the inclusion of metal oxides such as TiO_2 [28,29], Fe_2O_3 [29,30], among others, as sintering additives can facilitate the sintering process (the final stage of ceramic material production) in the liquid phase and effectively modify the wettability between ceramic particles. This phenomenon contributes to the increased mechanical strength of porous ceramics by forming robust sintering necks during the initial stages of the sintering process. However, conventional sintering additives introduce a secondary phase in the intergranular region, compromising the ceramic membrane's resistance to strong acids and alkalis.

It is known that supports with high porosity, good mechanical strength, and well-aligned macropores are preferable for membrane production [6]. Moreover, to ensure the formation of a thin and defect-free zeolite layer, the support surface must be smooth and free of microscopic irregularities, as defects in the membrane's support often led to defects in the intermediate layer and the separation layer above it. Therefore, the quality of the membrane support is critical as it must maintain a narrow pore size distribution and sufficient mechanical strength for the

application, making the preparation of suitable supports for ceramic membrane applications a challenging task [22,24,31].

Thus, the choice of ceramic support production method has a significant impact on the support's properties. Currently, the preparation of these supports mainly involves the use of powders, pastes, and suspensions as precursors, which are shaped by various molding techniques such as extrusion, pressing, and the sol-gel method [1,22,30]. Porous supports obtained by conventional methods generally exhibit tortuous pore networks with many constrictions and dead-end pores, which can compromise their mass transport capacity [22]. For producing porous materials, *freeze-casting*, on the other hand, is an attractive shaping process offering the possibility to obtain customized pore structures that are aligned and interconnected [23,27,30]. The result is a material with high porosity, typically with high open porosity values. These characteristics of *freeze-casting* substrates make them an interesting alternative for applications requiring anisotropic pore structures, such as those demanding materials with high fluid flow through the pores [22,24]. For example, using this technique, fluid flow properties can be improved through pore connectivity and gradient structures by using camphene as a freezing vehicle, resulting in dendritic structures along the aligned channels produced [22,32]. More aspects of this technique will be discussed in the following sections.

3.3. Ceramic Supports Produced by *freeze-casting*

Ceramic materials have a wide range of applications, and typical processing methods such as foam or wood replication, direct foaming, or extrusion are common [22,27,33]. However, to reach their full potential, adequate control of porosity in terms of size, shape, and quantity is crucial. Although control over structure and properties has been improving, each method has intrinsic limitations, especially regarding pore characteristics [22,27]. The *freeze-casting* technique, as a recent innovation, stands out by providing highly porous ceramics with a well-defined pore structure [29,30]. This process involves freezing a liquid suspension, followed by sublimation and sintering to consolidate and densify the walls, resulting in a porous structure where the pores replicate the solvent crystals [24,27,32]. Additionally, it is a cost-effective and easy-to-implement approach, producing samples with ordered pore networks that facilitate gas permeation [22,23,31].

A variety of ceramic materials have been successfully prepared by this method in different configurations, such as flat plates [25], *hollow fiber* [34], disks [23,26], tubes [19,31,35] and monoliths [28,29,32,36]. This technique offers several advantages, including a simple production process without the need for burnable materials, a wide range of controllable porosity (30-99%) through suspension concentration, applicability to various types of materials, and cost-effective production with simple equipment requirements [27,32,37]. Moreover, the solvent removal process does not introduce impurities into the samples, eliminating the need for an additional purification step. Most importantly, the ability to adjust freezing parameters allows for the preparation of materials with various pore morphologies and nanostructures [27,32].

Currently, water [24,31], camphene [28,29,32], tert-butyl alcohol [23,36] (TBA), and naphthalene-camphor [37] have been successfully used as freezing solvents. Unique or complex porous structures can be achieved by modifying the freezing solvent, starting materials, and processing conditions (freezing temperature, solid loading/volume) [29,31,32]. The versatility of this technique enables the fabrication of materials with dense, cellular, lamellar, unidirectional, and complex microstructures [22,24,32].

Based on the final pore structure, porous ceramics produced by the *freeze-casting* technique show great promise for a variety of applications, including thermal and acoustic insulation [22,27], membranes for gas and liquid separation [23,31,32], dye separation [38], and bone tissue production [39], due to their high permeability, high specific strength, large surface area, excellent adsorption capacity, and good chemical and thermal resistance.

3.3.1 Process Principles

As shown in Figure 2, the freezing process begins with the preparation of a stable colloidal suspension, which is poured into a mold. The liquid suspension is then frozen, followed by sublimation of the frozen phase and subsequent sintering. This results in a porous structure with unidirectional channels in the case of directional freezing, where the pores replicate the shape of ice crystals [22,30,32,40]. During this process, the solidification of the suspension is critical, as crystal morphology influences the resulting porous microstructure, and the volume change associated with the phase transformation impacts the material's integrity. Various freezing conditions, such as temperature, time, freezing rate, solid content, particle size, type of solvent, and freezing direction, can affect the pore structure of the materials [23,27,31].

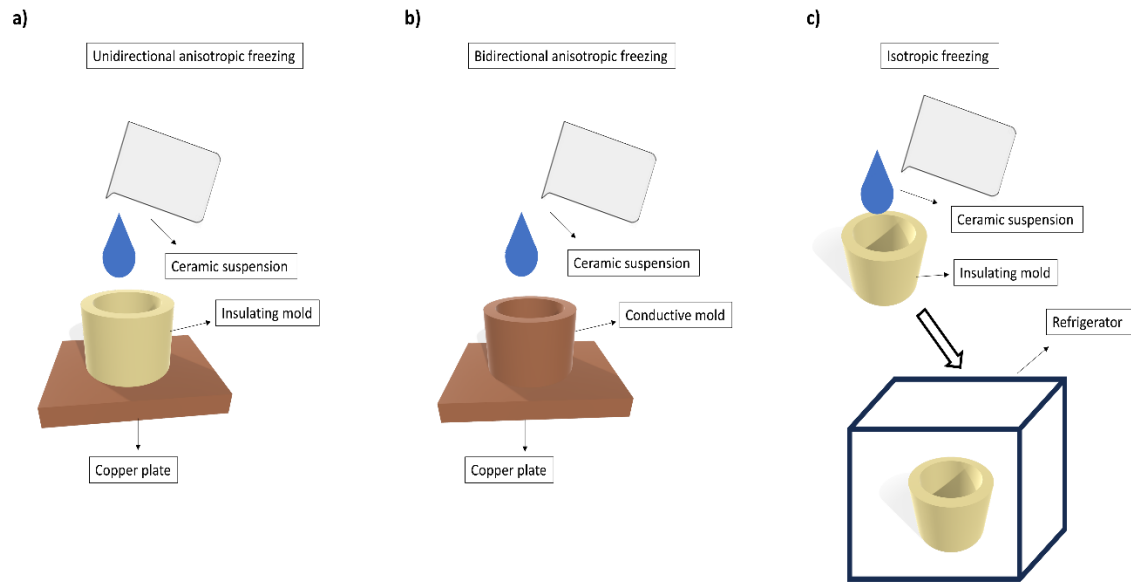


Figure 2. Representation of the different forms of freezing in the freeze-casting process.

As the ceramic suspension freezes, ice crystals expel the ceramic particles, creating a microstructure oriented in the direction parallel to the movement of the freezing front [32,40]. For suspensions with high solid loading, particle interactions are critical, and some particles may become trapped within the ice crystals, forming bridges between adjacent walls. Controlling the size and morphology of the pores is crucial for the final properties and various applications of porous ceramics. Since the porosity of the sintered porous ceramic replicates the original ice structure, manufacturing parameters can be adjusted to control the final pore structure. Porosity can be modified by varying the solid content in the suspension, pore size is influenced by freezing kinetics, and pore morphology can be controlled by selecting different solvents and additives in the suspension [28–30].

The process can be divided into four stages, and the experimental conditions will determine the properties of the final material:

- 1. Suspension Preparation:** This is the stage where the solid is poured into the liquid solvent. To ensure proper dispersion of the ceramic powder in the liquid medium, it is common to use a dispersant to promote a more efficient interaction between the solvent and the solid [27]. The suspension temperature must be within the range where the

solvent remains liquid—room temperature is generally sufficient in the case of water, but different temperatures are required for camphene-based slurries (60°C) and tert-butyl alcohol (30°C), respectively [23,29,32,36]. The solid loading typically ranges from 10 to 40 vol.%, depending on the desired total porosity. Carefully controlling the stability of the suspension is crucial to avoid segregation phenomena that may occur in the second stage, resulting in density and porosity gradients in the final materials, which can be especially problematic at low solid loadings [22,31,32]. Finally, the presence of an organic binder (commonly PVA, PEG, or PLA) is necessary to provide strength to the green body (the ceramic material before sintering) after sublimation. Although the solvent acts as the structuring agent, it is removed during the sublimation phase, meaning that green bodies would collapse in the absence of an organic binder [27,29,32].

2. **Solvent Solidification:** This step is critical, as it is during solidification that the structure is formed and the characteristics of the future porosity are established. During this process, continuous solvent crystals are generated and, under certain conditions, grow along the suspension. The ceramic particles in suspension are repelled by the freezing front, becoming concentrated and trapped between the growing crystals. To induce this natural segregation phenomenon, the suspension is poured into a mold, which undergoes isotropic or anisotropic freezing to promote homogeneous or directional solidification [22,27,30]. The freezing conditions play a fundamental role in determining the characteristics of the growing solvent crystals and, consequently, the final pore characteristics.
3. **Solvent Sublimation:** After completing solidification of the ceramic material, the sample is subjected to low temperature and reduced pressure conditions, determined by the physical properties of the solvent. Under these sublimation conditions, the solidified solvent transitions directly from solid to gas [22,27]. Several studies indicate that porosity develops in the regions formerly occupied by the solvent crystals, resulting in the formation of a porous structure known as the green body [27,33,39]. This porosity is a direct replication of the structure of the solidified solvent.
4. **Sintering or Densification of the Green Body:** After completing solvent removal, the resulting green body can be sintered using a conventional furnace. Due to the low strength of the green body, pressure-assisted sintering is not a feasible option.

Additionally, the low amount of organic binder (usually <5%) eliminates the need for a special and often problematic binder burnout process [27–29]. During the sintering stage, it is possible to remove microporosity from the ceramic walls while preserving the macroporosity generated by the solvent crystals.

3.3.2 Anisotropic and Isotropic Freezing

The main stage of the freeze-casting process involves freezing, which can be classified as *anisotropic* or *isotropic*, with most of the literature focusing on anisotropic techniques, also known as *unidirectional* freezing [29,32,35]. Initially, the particle suspension is placed in a mold with a thermally conductive base and thermally insulating side walls. The base is cooled, inducing nucleation and directional propagation of a solidification front [27,32,40]. At the start of the process, the solidification rate is high, and the suspended particles are initially engulfed by the solidification front, forming a dense layer at the bottom of the sample. The latent heat released during this initial freezing stage reduces the solidification rate, causing the particles to be pushed ahead of the advancing solidification front rather than being engulfed by it. This results in a particle/solute accumulation zone ahead of the front, as illustrated in Figure 3 [27,29,40].

As solidification progresses, the particles continue to be pushed by the freezing front, creating an accumulation region in front of it. Once solidification is complete, the solidified fluid is removed by sublimation, and the resulting structure is sintered to densify the compacted particle walls. The pore morphology of the final material reflects that of the solidified fluid, displaying an elongated structure aligned vertically with horizontal orientation within the colonies [23,27,32]. Under anisotropic conditions, solidification typically occurs vertically, from bottom to top.

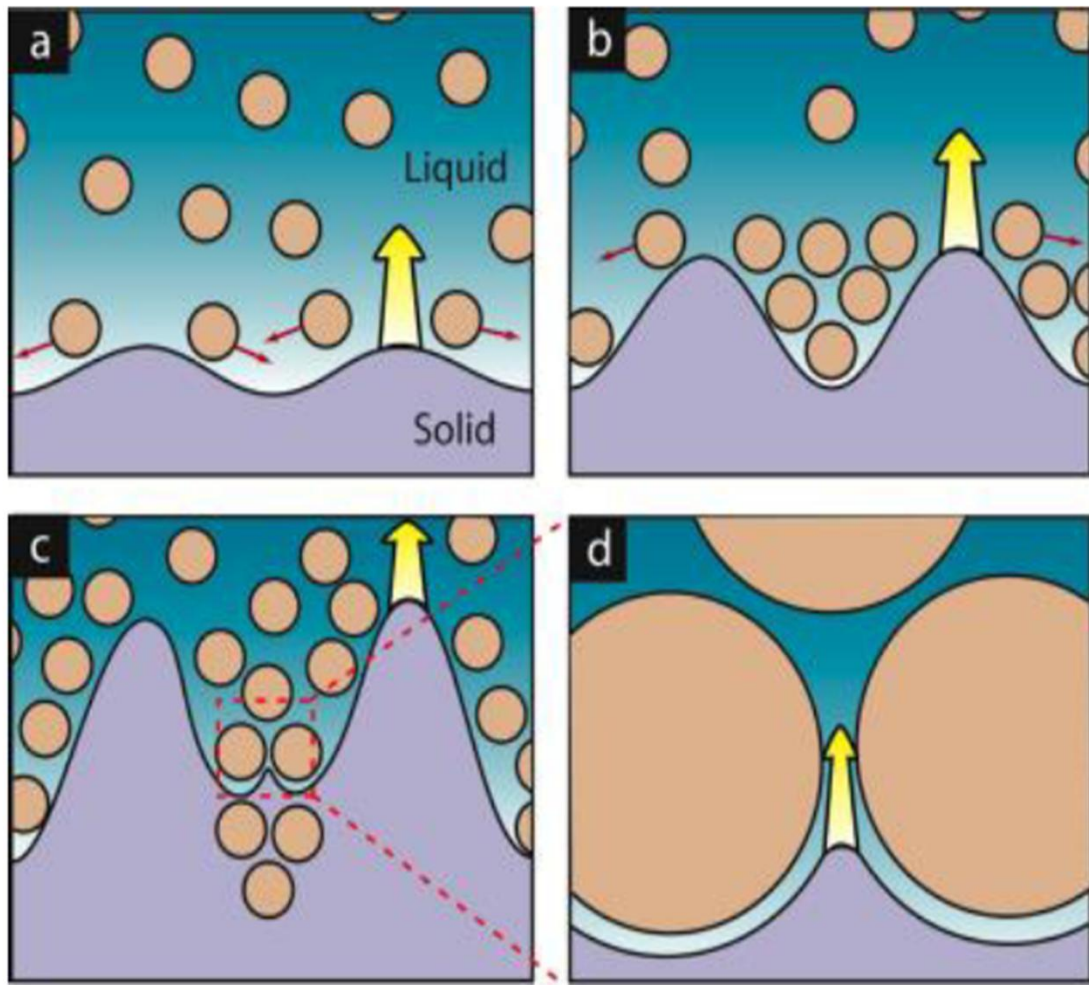


Figure 3. Particle redistribution during solidification. (a-b) Particles are packed together among the frozen crystals until (c) capillary pressure exceeds osmotic pressure, at which point (d) the solid/liquid interface shifts into the space between the particles. Adapted from [41].

Anisotropic freezing in radial and bidirectional forms is also used to produce ceramic materials [31,32,42,43]. In the case of radial freezing, the top and bottom of the mold are made of thermally insulating material, while the side walls and a rod placed in the center of the mold are thermally conductive. During cooling, solidification begins at the perimeter or at the center of the suspension and propagates horizontally in a radial manner [31,40,42]. On the other hand, in bidirectional freezing, the base and side walls are made of thermally conductive materials, resulting in solidification that progresses from the bottom to the top and from the sides to the center of the suspension, generating a two-dimensional solidification front [32,40,43].

Isotropic freezing techniques were developed as early as 1954 and are still used today to produce non-homogeneous porosity. In this process, a suspension contained in a thermally insulating mold is placed in a freezer, where random solid nucleation occurs throughout the

suspension [27,33,40]. After nucleation, solid crystal growth proceeds in random orientations, with no preferred growth direction. Following sublimation and sintering, the resulting pore structures are nearly isotropic. In some cases, thermally conductive molds are used, and freezing progresses directionally from the bottom and radially from the sides. Although some microstructural directionality is often observed in the resulting material, especially radially and at the bottom, the overall structure remains nearly isotropic [27,40]. A schematic representation of these freezing phenomena is illustrated in Figure 2, discussed in the previous section.

3.3.3. Formation, Control of Structures, and Properties

The parameters that affect the final structure can be identified in all processing stages: formulation and preparation of the suspension (including the characteristics and properties of the starting powders), solidification, and sintering. Some parameters are very specific and are related to the core of the process: the freezing of the suspension. The solidification step is the most critical for the final porous structure, as most of the porosity characteristics are created during this phase.

3.3.3.1 Freezing Parameters

Factors such as freezing temperature, freezing rate, and freezing time have a significant influence on the nucleation of solvent crystals and, subsequently, on the morphology and microstructures of porous ceramics produced by the *freeze-casting* technique [22,32,44–46]. Although different systems are affected differently by these factors, the general trend in microstructure formation is shared by most materials.

The freezing temperature affects how solvent crystal nucleation and growth occur. Crystal nucleation requires supercooling. Under high supercooling, i.e., at low temperatures, the nucleation rate exceeds the crystal growth rate, favoring solvent crystal nucleation overgrowth [32,35,40,44]. At these freezing temperatures, many small solvent crystals are formed, resulting in a porous microstructure with uniform and small pores. Conversely, if supercooling is low, i.e., at higher temperatures, the growth of solvent crystals is favored, leading to the formation of fewer but larger solvent crystals during freezing, which in turn results in larger pores after solvent sublimation [22,32,43,46]. In summary, different freezing temperatures result in different solidification behaviors of the solvent and, ultimately leading to varied pore sizes and

morphologies [32,43]. Since particles do not have time to reorganize under high supercooling conditions, lower freezing temperatures produce greater porosity in the materials. The typical freezing temperature range for aqueous systems is from -18 to -196 °C [27,44,45].

The velocity of the solidification front, i.e., the freezing rate, also greatly influences the morphology of the porous microstructures. For aqueous systems, the typical freezing rate ranges from 0.05 °C min⁻¹ to rapid immersion in liquid nitrogen, resulting in an abrupt change from room temperature to -196 °C [32,43,44,47]. At high freezing rates, solvent crystal nucleation is kinetically more favorable than crystal growth, thereby increasing the likelihood of forming smaller pores. Additionally, suspension dispersion is more likely to be maintained at high freezing rates since there is less time for particles to reorganize [32,44].

Figure 4 shows the effect of the freezing rate on the microstructure. Wang *et al.*[43] investigated how the freezing type, as well as the cooling rate, could affect SiC ceramic samples produced by *freeze-casting*. In his work, Wang froze his samples in three different ways using isotropic (or homogeneous), unidirectional anisotropic, and bidirectional freezing, with freezing rates of 0.25 °C/min, 0.35 °C/min, and 0.47 °C/min, respectively. Wang concluded that the pore size and wall thickness of the samples prepared by bidirectional freezing were smaller compared to those prepared by homogeneous and unidirectional freezing. A lower freezing rate allows ceramic particles for more time to reorganize, leading to denser particle packing, larger pore sizes, and lower overall porosity. Moreover, the freezing rate depends on the heat transfer within the sample. When the temperature gradient is large, heat transfer efficiency is high, allowing solvent crystals to grow continuously and form more interconnected porous structures. When heat transfer is low, solvent molecule diffusion and crystal growth are hindered, leading to larger pores with an oval appearance [32,43,44]. To minimize these effects, Deville emphasizes the importance of a system capable of precisely controlling the freezing temperature with the most constant cooling rate possible, thus enabling the formation of a more ordered pore structure.

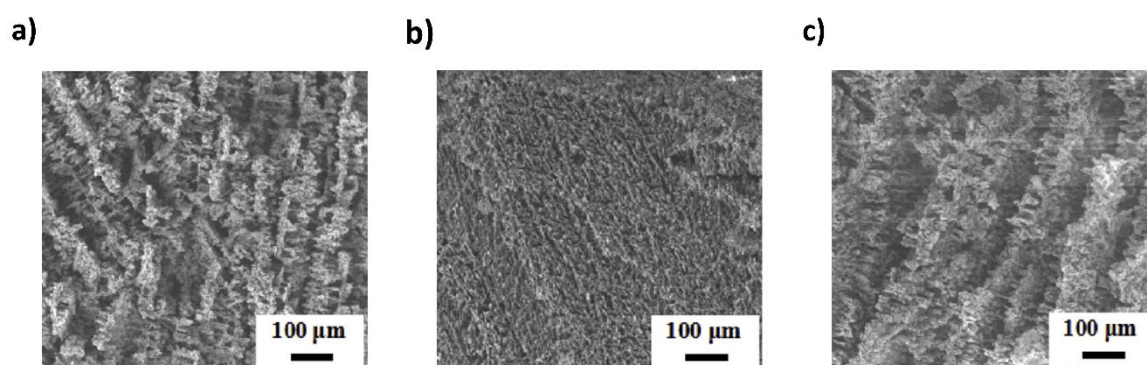


Figure 4. SEM of samples with SiC as solid with freezing a) homogeneous; b) unidirectional and c) bidirectional. Taken from [43].

The freezing time also influences the pore structure of the final material produced. When a sample remains at a specific freezing temperature, solvent crystals continue to grow, and small crystals may merge to form larger ones. This phenomenon (as shown in Figure 5 and discussed in the previous section) is influenced by the hindrance faced by solid particles as they are rejected by the solidification front, resulting in the formation of walls and continuous growth of solvent crystals, leading to finer structures. Consequently, this results in more elongated pores with small branches in the final material [28,32,40,44,47,48]. Samples subjected to long freezing periods tend to favor the formation of fine, columnar microstructures [45]. Therefore, adjusting the freezing time enables control over the porous structure [32].

In combination, the use of low freezing temperatures and high freezing rates leads to the formation of numerous small pores. On the other hand, the homogeneity of the microstructure is favored by shorter freezing periods and low heat transfer efficiency. Although the literature contains few studies analyzing these freezing conditions' effects on microstructures [32,36,42–45,47], the fundamental physical principles are applicable to most studied materials. Given that the effects of freezing conditions are independent of the *freeze-casting* systems, it is possible to predict the evolution of the porous microstructure when these factors are properly controlled.

3.3.3.2 Solid Loading in the Suspension and Particle Size Effect

The solid-to-liquid ratio (solid loading) in the suspension is another factor that affects the characteristics of samples produced by the *freeze-casting* technique. Suspensions with higher solid loading contain less solvent and, therefore, produce a final material with lower porosity

[27,29,31,35,41]. Additionally, solid loading in the suspension can also influence the homogeneity of the microstructure in the final material.

When the solid loading is low, particles are effectively repelled by the advancing solidification front of the solvent. The frozen crystals become elongated along the direction of the thermal gradient and grow into large sizes with highly interconnected microstructures [27,31,32,41,44]. With higher solid loading, particles are less efficiently “rejected,” and the movement of the solidification front is not powerful enough compared to the growth of pore walls. Eventually, the redistribution of these particles ceases, and the solid-liquid interface advances through the interparticle spaces, hindering further solvent crystal growth [32,44]. This phenomenon, known as “breakthrough” [27,49] occurs as the solid-liquid interface penetrates the suspension. A simple yet effective model was developed by Shanti *et al.*[49] illustrated in Figure 3, where particles accumulate at the solid-liquid interface as the solidification front advances through the suspension (Figures 3 (a) and (b)). The local particle packing density continues to increase until the capillary force becomes sufficient to counterbalance the osmotic pressure. Then, the solid-liquid interface progresses into the interparticle spaces, trapping some particles within the newly formed crystals (Figures 3 (c) and (d)). This defines the maximum packing density of particles and sets the limit for the final sample’s porosity [27,44,49].

The reduction in porosity resulting from increased solid loading contributes to the production of stronger solid samples. The finer microstructure resulting from higher solid loading further enhances the mechanical strength of the material, improving its suitability for applications involving high applied loads [31,32,35,44]. Although the specific effects of solid loading on microstructure evolution may vary between different systems, the fundamental principles of particle hindrance and rejection remain consistent.

The uniformity of the porous structure is also affected when the particle size becomes comparable to that of the solvent crystals. Since solvent nucleation occurs via a heterogeneous process, the nucleation of solvent crystals is controlled by particle size, where particle surfaces act as nucleation sites. Apparently, smaller particles provide a larger surface area and more branching in the structure, leading to an increase in nucleation sites and consequently generating smaller pores [22,49,50]. The reduced particle size results in a lower dependence on supercooling, as nucleation and growth can occur at higher temperatures compared to larger particles. In contrast, larger particles generate fewer, larger pores. Additionally, larger particles result in more significant supercooling effects compared to smaller ones, as they provide fewer

nucleation sites that reach the required nucleation temperature [22,44]. Consequently, a more pronounced structural gradient is observed in systems with larger particles due to the corresponding advancement of the solidification front.

Choosing the appropriate particle size is crucial to accurately replicate the morphological characteristics of the crystals in the final structure [44,50]. Larger particles tend to become trapped by the solidification front, while smaller particles are rejected by it, resulting in more elongated crystals or oval-shaped pores depending on the freezing rate [32,44,50]. To create porous structures with pore sizes below one hundred microns, it is preferable to use powders with submicron average particle sizes and ensure a homogeneous particle distribution in the suspension [32,50]. There is a critical velocity for a given particle size, above which the particles cannot be ejected by the advancing solidification front, thereby affecting processing conditions [48]. Particle size also influences the final mechanical properties and ceramic densification, with smaller powders resulting in lower porosity [22,27,44,48,50].

3.3.3.3. Properties for Gas Separation

The appropriate selection of solvent and solute is essential to ensure the production of porous ceramic supports with the desired characteristics in terms of structure, porosity, and mechanical properties, thereby creating a material with ideal properties for gas separation. The microstructures of materials produced by the *freeze-casting* technique are qualitatively described based on their pore structure, where this structure and its properties are directly linked to the choice of solvent and solute.

The most reported anisotropic pore structures include lamellar [24,31], dendritic [28,29,32], honeycomb-shaped [40] and prismatic structures [23,35]. These pore structures are categorized as shown in Figure 5 and defined as follows: Anisotropic lamellar structures (Fig. 5 (a)) exhibit plate-like walls aligned parallel to the freezing direction, which are typically observed when water is used as the solvent. Dendritic structures (Fig. 5 (b)) display primary trunks (or "primary arms") and branching structures resembling tree branches, known as secondary arms. These structures are commonly associated with the use of camphene as a solvent. Honeycomb-like structures (Fig. 5 (c)) present elongated hexagonal shapes and may also appear as elongated tubes. Lastly, prismatic structures are generally associated with the use of TBA (tert-butyl alcohol) as a solvent. Each of these structures imparts distinct properties to the final material, making different applications favorable depending on the obtained structure.

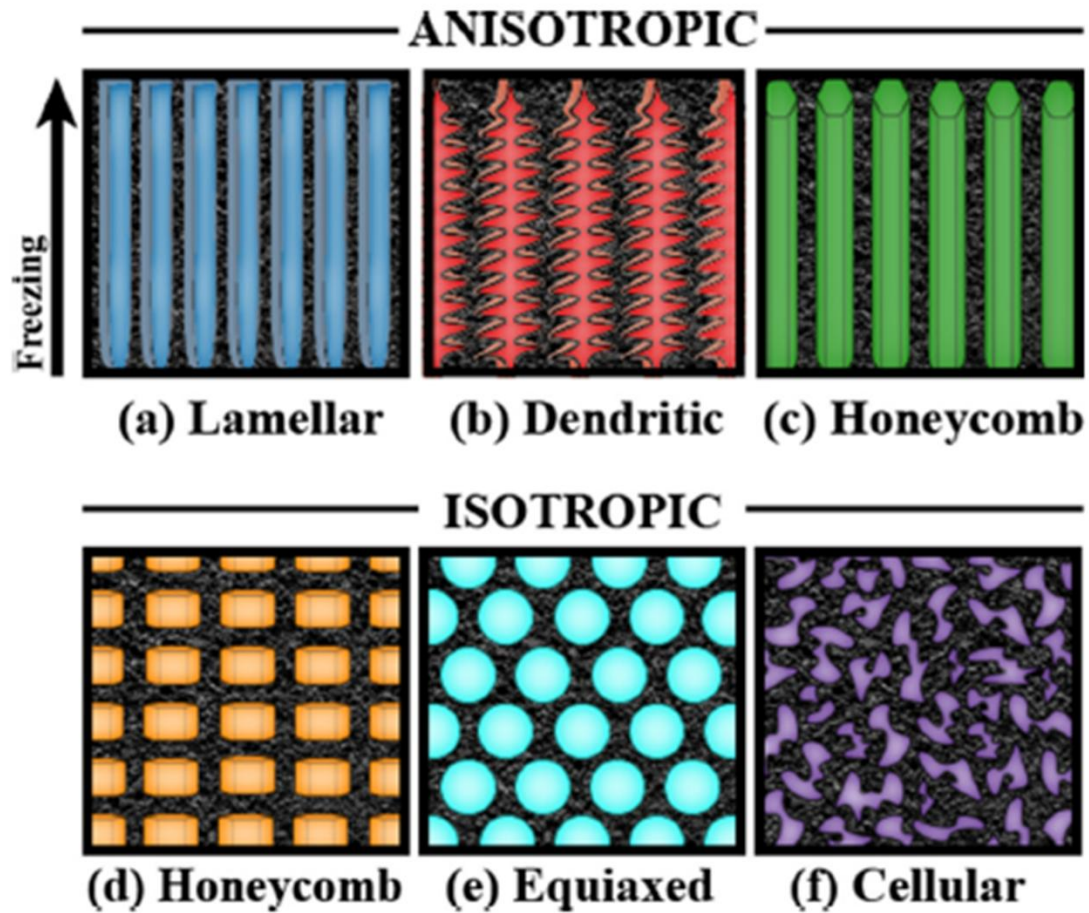


Figure 5. Schematic representation of the most commonly observed pore structures in freeze-cast materials, including anisotropic (a) lamellar, (b) dendritic and (c) elongated honeycomb and (d) cellular honeycomb, (e) equiaxed and (f) cellular structure. Adapted from [40].

Few studies in the literature on the *freeze-casting* technique correlate the properties with a specific final property, as most of the focus has been on structural control and processing conditions. However, recent works [32,35,42,43] have emerged discussing more critical ceramic properties, such as compressive strength. Strength is of particular importance for ceramics, especially considering the various applications these materials can have. For example, Deville [51] in his early work using hydroxyapatite (HAP), achieved compressive strength values of 65 MPa with 56% porosity and 145 MPa with 47% porosity by simply using a controlled temperature system and water as the solvent. These values exceeded typical results found in the literature, even with higher porosity levels, highlighting that by adjusting the structure through solvent selection and controlling the cooling rate, it was possible to obtain materials with enhanced strength.

More recently, Liu [35] produced porous tubular supports using mullite, obtaining materials with unidirectionally aligned pores by employing TBA as a solvent. He investigated the effects of freezing temperature, solid loading, and particle size distribution of mullite powders on the microstructure and properties of the supports. He observed that pore size, porosity, and compressive strength could be effectively tuned by controlling these parameters. Specifically, pore size increased along with the freezing direction, while it significantly decreased with higher solid loading, lower freezing temperatures, and reduced particle sizes. Porosity also decreased with increasing solid content and freezing temperature, as well as with smaller particle sizes, whereas compressive strength increased accordingly.

The properties of the chosen ceramic powder can affect the final structure and properties of the produced material. However, it is consistently discussed in the literature that the primary mechanism is based on the interaction between these particles and the solidification front. Several parameters can modify these interactions, including particle size, size distribution, shape, surface roughness, and surface tension. The most significant influence reported is particle size [27,41], affecting the relationship between solidification kinetics and the final structure's thickness. It is well known that the production of ceramic materials using $\alpha\text{-Al}_2\text{O}_3$ not only reduces costs but also results in materials with high mechanical strength [19,24,29,31,36].

The chosen solvent has a significant impact on the shape of the formed ice crystals and, consequently, on the pore structure, which can influence the application of the produced material. For instance, since fluid flow properties can be enhanced by pore connectivity and support structure, dendritic structures formed along aligned channels—prepared using camphene as a structuring vehicle—make this solvent particularly attractive for separation applications [22,27,38]. Additionally, the hierarchical pore structure and the variation in channel size along the height of the channels during the freezing process grant porous ceramics prepared by *freeze-casting* the ability to filter a wide range of particle sizes, thus increasing the effectiveness and efficiency of ceramics produced by this method [22].

Therefore, the microstructure and properties of ceramics produced by the *freeze-casting* technique can be influenced by the manufacturing parameters. Factors such as solvent selection, solid loading, freezing temperature, and starting material particle size directly influence porosity and, consequently, mechanical strength. Adjusting these parameters allows to produce support materials for zeolite membranes with ideal properties.

3.4. Zeolites

The history of zeolites originates in the far north of Europe, with the first known mention of the term “zeolites” made by the Swedish mineralogist Axel Fredrik Crönstedt in 1756. He reported the discovery of a new class of natural minerals that, when heated with a blowtorch flame, released vapor—something he associated at the time with the loss of water. For this reason, he coined the term “zeolite,” derived from two Greek words: *zeo* = to boil and *lithos* = stone, meaning “boiling stones” [52,53].

From their discovery until the mid-1930s, zeolites underwent significant advancements in research, during which new species were identified, and hydrothermal synthesis methods were explored to reproduce the structures and properties of these minerals [52–54]. The first definition of the crystalline structure of zeolite was provided through studies by researchers Taylor and Pauling, who used X-ray crystallography techniques to elucidate the structures of the zeolites analcime, natrolite, and cancrinite. This discovery led to a better understanding and prediction of zeolitic structures, which was of great importance for the development of zeolite synthesis studies over the years [53,54]. It was only in 1963 that J. V. Smith proposed the first formal definition of a zeolite as “an aluminosilicate with a structure that contains cavities occupied by large ions and water molecules, both of which have considerable freedom of movement, allowing ion exchange and reversible dehydration” [54].

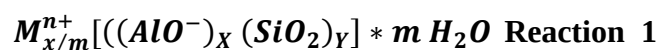
The properties of these synthetically produced zeolites were then enhanced, especially in terms of acidity and hydrophobicity, compared to natural zeolites, which had limitations due to impurities and structural defects. In addition to structural improvements, the development of synthetic zeolites also became possible [52–54]. These characteristics have made zeolites one of the most widely applied classes of materials in industry, enabling their use in several specific applications such as catalytic cracking of petroleum [55], catalysts for propane dehydrogenation [56], catalytic reduction [57], catalytic dehydration of ethanol [58], methanol dehydration [59] adsorption [11–13], adsorption [4,7,16,20].

3.4.1. Structure and Properties

All zeolites are composed of a fundamental aluminosilicate framework, which consists of a tetrahedral arrangement of silicon (Si^{4+}) and aluminum (Al^{3+}) cations, each surrounded by four oxygen anions (O^{2-}) [13,52,60,61]. Each oxygen ion in the Si–O and Al–O bonds connect

two cations and is shared between two tetrahedra (as illustrated in Figure 6), resulting in a three-dimensional macromolecular structure composed of SiO₂ and tetrahedral AlO₂ building blocks. Since the oxygen atoms are shared among the tetrahedra, the aluminum tetrahedron contributes to a net negative charge, while the silicon tetrahedron is electrically neutral. This negative framework charge is balanced by compensating cations, which do not occupy framework positions and act solely as charge-balancing species within the structure [52,60].

A representative formula for the unit cell of a zeolite can be written as:



Where **M** is a cation with valence **n** ($x > 0$); these may be metal or non-metal cations (such as protons in the case of Brønsted acidic zeolites), or organic cations. These cations are introduced either during crystallization or via ion exchange [52,61,62]. The **y/x** ratio represents the Si/Al ratio, which is equal to or greater than 1, due to Al³⁺ ions not occupying adjacent tetrahedral sites, in accordance with Loewenstein's rule (this rule prohibits the existence of Al–O–Al linkages in the crystal lattice; therefore, only up to 50% of the Si atoms in the crystalline structure can be replaced by Al atoms) [54]. The sum of **x** + **y** represents the number of T atoms (T = tetrahedrally coordinated atom, i.e., Al or Si), and **m** corresponds to the number of water molecules per unit cell.

Currently, the term “zeolite” applies to a wide variety of both natural and synthetic minerals formed by a three-dimensional network composed of TO₄ tetrahedra (where T = Si, Al, B, Ga, Ge, Fe, P, Co, etc.), with a framework density ranging from 12.1 to 20.6 tetrahedrally coordinated atoms per 1000 Å³ [52,59,61]. These tetrahedra are connected via shared oxygen atoms, forming the fundamental structural units known as Secondary Building Units (SBUs) [52,61]. These SBUs are likely precursors to crystal growth, and upon completion, they give rise to a variety of channels and cavities, endowing the material with high porosity. This high porosity increases the surface area of the material, ultimately resulting in zeolite formation [60,61]. The microporosity of these materials is accessible, enabling transfer between the internal crystalline space and the external medium, which is limited by the pore diameter of the zeolitic structures [52–54]. This broadened definition extends beyond the previous classification of zeolites solely as crystalline aluminosilicates and now encompasses a wide range of natural and synthetic minerals containing various chemical elements.

To understand the unit cell structure of zeolites, it is essential to examine the organization of these tetrahedra as small building blocks, which results in the characteristic topology of

zeolitic crystalline structures. The tetrahedra may connect linearly to form simple chains (Figure 6 (a)), simple rings (Figure 6 (b)), or more complex building units such as polyhedral structures or double rings, resulting in cage-like frameworks (Figure 6 (c)) [5,52,61].

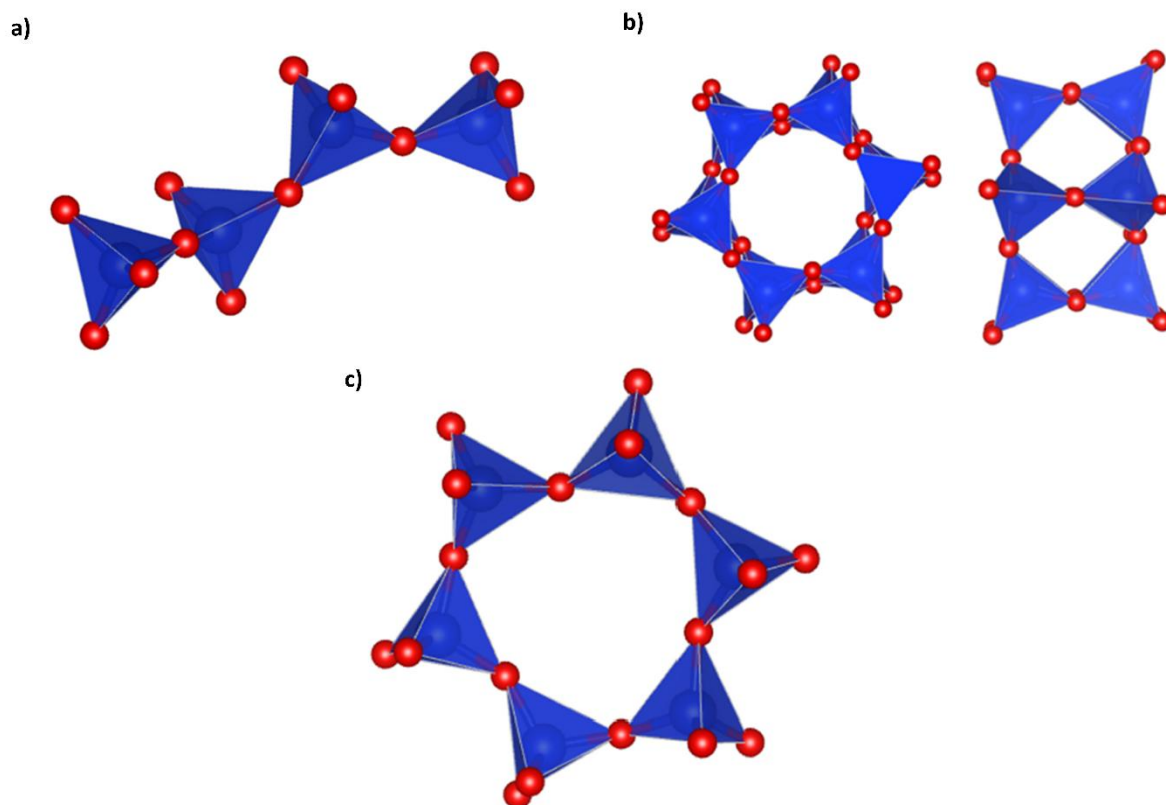


Figure 6. Tetrahedra linked to form (a) a single chain; (b) a single ring of six central atoms; and (c) a double ring of six central atoms (front view and side view). Adapted from [5]

As these tetrahedra connect, they form secondary building units in the shape of rings known as *n-rings*, where *n* represents the number of central atoms that make up the ring—for example, in the case of the KFI zeolite, which features an 8-membered ring structure (8MR) [5,10,11,59]. Polyhedral or double rings, as composite building units, are designated as [*nm*], where *n* is the number of central atoms in each face, and *m* is the number of times that face is repeated within the polyhedron. These indices are repeated as necessary to complete the geometry of the solid [5,52,61]. The combination of these small building blocks gives rise to the unique framework structure of each type of zeolite, such as KFI, CHA, FAU (illustrated in Figure 7), among many others.

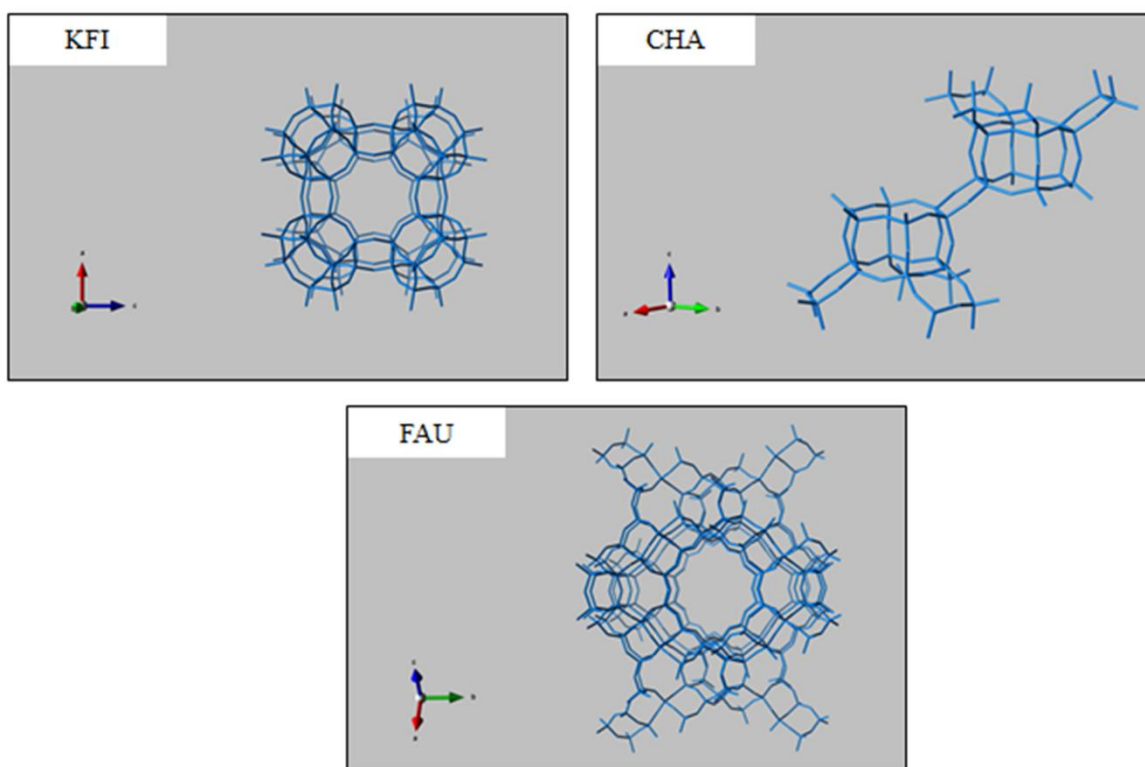


Figure 7. Structures of KFI, CHA and FAU zeolites. Taken from [5].

The pore size (i.e., channel opening) of zeolites falls within the microporous range (<2 nm) [60,61]. To date, approximately 300 unique zeolite structures have been documented by the International Zeolite Association (IZA), each assigned a three-letter framework code [52,53]. Depending on the application of zeolitic material, zeolites are classified based on the pore size of their crystalline structure. The pore opening is associated with the number of silicon and aluminum atoms forming the framework. According to the size of these micropores, zeolites are categorized as small-pore (8-membered ring/8MR), medium-pore (10MR), large-pore (12MR), and extra-large pore (>12 MR) zeolites [52,60,61].

The entire process of forming this three-dimensional network, including the generation of pores, channels, and cages, means that the structural characteristics of zeolites play a fundamental role in their properties. The main features include:

- i) **Porosity and surface area:** The pores formed by the regular arrangement of silica and alumina tetrahedra in the structure result in high porosity and, consequently, a large surface area, which is critical for molecular adsorption applications [11,12,52,61].

- ii) **Selectivity:** The porous structure confers specific molecular selectivity, enabled by the presence of pores with well-defined shapes and sizes. This allows for the selective adsorption of molecules based on their size and polarity [61,63,64].
- iii) **Thermal and chemical stability:** The crystalline structure of zeolites is highly stable, providing resistance to high temperatures and chemically aggressive environments. This is particularly advantageous in catalytic applications, where long-term stability is crucial for maintaining catalytic activity [52,57–59].

These properties open a broad range of possible applications. For example, due to their porous structure and ion exchange capabilities, zeolites are widely used as catalysts in industrial chemical reactions [55,58,59]. The ordered pore structure enables controlled access of reactants to active sites on the catalytic surface, thereby increasing reaction efficiency [57,58]. In addition, their selective adsorption capabilities are exploited in gas and liquid purification processes [11,12,16,20,60,61].

With the advancement of synthesis techniques, it has become feasible to tune various zeolite properties, including acidity, microporosity, pore size, hydrophobicity, hydrophilicity, and the size and morphology of zeolite crystals. The selection of the ideal zeolite is closely tied to the specific nature of the desired application. Zeolitic membranes, for instance, are an excellent choice for gas separation. Figure 8 (a), adapted from Ref. [61] illustrates the annual number of studies published on zeolite membranes for this purpose, highlighting that approximately one-quarter of these studies focused on CO and CO₂ separation as well as carbon capture processes. Figure 8 (b), adapted from Ref. [6], shows the number of publications indexed in Scopus that include the term “XXX zeolite membranes” (where XXX is the zeolite framework code) in the article title, abstract, or keywords. The data reveal that small-pore zeolites (8MR) are the most frequently studied for this application.

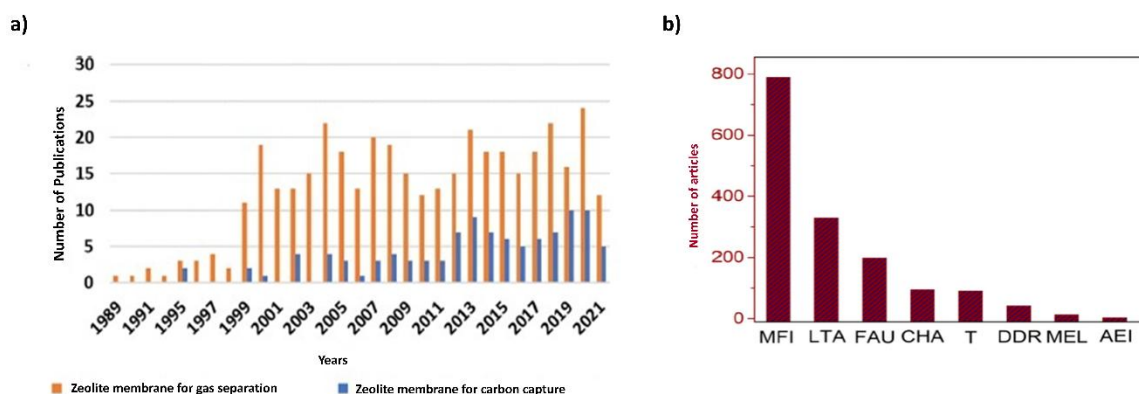


Figure 8. (a) Publications on zeolite membranes for gas separation adapted from [61] ; (b) number of publications indexed in Scopus containing the term “XXX zeolite membranes” adapted from [6].

3.4.2. KFI

The KFI zeolite, also known as ZK-5 or Kerr-5 zeolite, was first synthesized by Kerr and collaborators in the 1960s and is considered the first synthetic zeolite that does not occur naturally [65,66]. This zeolite features a three-dimensional network composed of 8-membered rings [4^66^2], double six-membered rings (d6rs), larger α -cages (ita) with 26 members [$4^{12}6^88^6$] (diameter of 11.6 Å), and smaller γ -cages (pau) with 18 members [$4^{12}8^6$] (6.6 Å x 10.8 Å), as illustrated in Figure 9 [67]. Each α -cage connects to six γ -cages (one above, one below, and four in the plane), while each γ -cage links to two α -cages (either one above and one below or two in the plane) and four additional γ -cages. These α and γ cages are interconnected by flat 8-membered rings with pore sizes of $3.9 \times 3.9 \times 3.9$ Å, consisting of d6r, pau, and lta cages. An additional 8-membered ring with a smaller diameter of 3.0 Å connects the γ -cages [11,12,59].

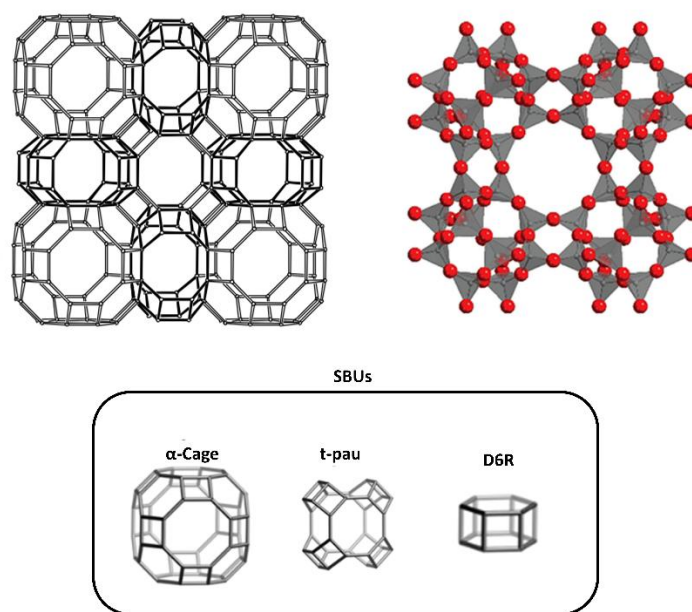


Figure 9. KFI zeolite structure along [100] and its building blocks. Taken from [66]

The KFI zeolite has a body-centered cubic structure with a lattice parameter of $a = 18.72$ Å and a Si/Al ratio ranging from 2 to 5. It was originally synthesized without the use of organic structure-directing agents (OSDAs) organic molecules typically added during synthesis to direct the final structure, which are usually removed by calcination. This makes its synthesis more environmentally friendly [12,65,66]. However, the absence of an OSDA makes the synthesis highly sensitive to small variations in parameters. To improve reproducibility, organic templates such as 18-crown-6 ether have been used to direct KFI formation (in some cases, achieving Si/Al ratios above 5), although this increases production cost and reduces environmental sustainability [68].

Due to the drawbacks of organic templates, alternative techniques have been employed to improve the reproducibility of KFI zeolite synthesis. Kim *et al.* [57] successfully developed an interzeolite transformation route to synthesize KFI (Si/Al ratio of 4) from high-silica FAU zeolite, exploiting the shared presence of the d6r building unit.

Another increasingly refined strategy involves the use of structure-directing inorganic cations such as K^+ , Sr^{2+} , and Cs^+ [10,12,69] Kamimura *et al.* reported a seed-assisted synthesis of KFI (Si/Al = 4) in the presence of Sr^{2+} [70]. Madalena *et al.* [71] synthesized KFI with a Si/Al ratio near 5 using a dual-template method involving inorganic cations and anions. They observed that KFI formation only occurred in the presence of K^+/Cs^+ ; substitution of these cations with Na^+ alone prevented KFI formation. In current conventional syntheses, only a

small amount of K^+ ions is required, primarily to occupy the pores of the resulting zeolite structure [11–13,69,70].

The larger ionic radius of K^+ (0.133 nm) compared to Na^+ (0.098 nm) and Sr^{2+} (0.118 nm) is advantageous for balancing fewer negative charges in the zeolite unit cell, resulting in a product with lower aluminum content. High-silica KFI zeolites are desirable because Al-rich forms tend to exhibit poor hydrothermal stability, which significantly limits their practical applications [66].

Numerous studies have demonstrated that pore size, metallic cation distribution, and varying Si/Al ratios—enabled by the incorporation of Al^{3+} —play a significant role in tuning pore diameters and, consequently, the adsorption capacity of zeolites [11–13,72,73]. Yang [74] *et al.* synthesized K-KFI with a Si/Al ratio of 4.59 and demonstrated superior performance in CO_2/CH_4 separation compared to commercial zeolite sorbents such as 5A and 13X under the same conditions. In another study, Yang [13] prepared nanosized KFI zeolite (50–100 nm) using β -cyclodextrin as a crystal growth inhibitor. The sample with the lowest β -cyclodextrin concentration showed the highest BET surface area ($370\text{ m}^2/\text{g}$), pore volume ($0.22\text{ cm}^3/\text{g}$), and CH_4 uptake of 1.34 mmol/g at 298 K, with the second-highest CH_4/N_2 IAST selectivity (4.3) among all reported zeolites.

In a related study, Kencana [67], synthesized KFI zeolite using β -cyclodextrin and incorporated Ag^+ through ion exchange into the final structure. The resulting material showed CH_4 adsorption capacity of 1.6 mmol/g at 298 K and 1.0 bar, along with an IAST CH_4/N_2 selectivity of 11.8—values significantly higher than those of conventional zeolites. These results highlight the benefits of nanocrystallinity in KFI structures for selective CH_4/N_2 separation.

The synthesis of KFI zeolite typically involves four main steps [11,13,65,72,73,75]:

- i) **Precursor gel preparation:** A gel is prepared from silica sources (commonly colloidal silica) and alumina sources (e.g., aluminum hydroxide) in an aqueous medium containing alkaline salts such as KOH and $Sr(NO_3)_2$. The Sr^{2+} and K^+ ions act as structure-directing agents and charge-compensating cations, while OH^- serves as the mineralizing agent, dissolving reactive species (silicates) and facilitating their incorporation into the crystalline structure.

- ii) **Crystallization:** The precursor gel is subjected to hydrothermal crystallization at an appropriate temperature (typically $\sim 150\text{ }^{\circ}\text{C}$) and controlled pressure, usually below 20 bar.
- iii) **Crystal growth:** During this stage, ions in solution react with gel components to form zeolite nuclei. These nuclei grow over time into larger crystals, forming the characteristic pores and channels.
- iv) **Washing and drying:** After crystallization, the zeolite crystals are washed to remove residual impurities and then dried at an appropriate temperature to eliminate any remaining solvent.

For KFI zeolite, the calcination or activation step—commonly required in zeolite synthesis to remove organic templates—is not necessary. This makes KFI particularly attractive for membrane fabrication, since membrane calcination is reported to be the most critical step in producing defect-free materials [64,73,74,76].

It is important to note that zeolite synthesis is highly influenced by factors such as gel composition, temperature, pH, reaction time, reagent concentration, and purity. Fine-tuning these parameters allows control over the crystal size, chemical composition, and morphology of the resulting zeolite [69,71,75]. In the case of KFI, which can be synthesized without organic templates, such refinements are essential for producing a pure, defect-free crystalline structure with properties suitable for various industrial applications.

3.5. Zeolitic Membranes

Zeolitic membranes are produced by depositing a thin layer of zeolite onto porous supports, providing greater mechanical strength to the inherently fragile zeolite structure. Various materials such as metallic fiber, aluminum, silica, and alumina are used as supports, along with different geometries including flat sheets, single-channel, and multichannel formats [5,63,73]. So far, several zeolite structures such as CHA, DDR, MER, BEA, and LEV, have been developed in membrane form [4,20,61,77–79].

In these membranes, the zeolitic separation layer must be homogeneous and defect-free, as structural flaws can compromise selectivity by allowing undesired gas diffusion through non-selective pathways [6,80,81]. Studies have shown that secondary growth technique is effective in producing high-quality zeolite membranes. This method involves depositing pre-synthesized

zeolite crystals onto the porous support, followed by hydrothermal synthesis in which the seeded support is immersed in a precursor gel [5,76,82].

To achieve high permeances, the zeolite film on the substrate must be extremely thin, typically ranging from a few micrometers to nanometers [80,81]. However, there is a trade-off between permeance and selectivity: thinner films increase gas flux through the membrane but may reduce selectivity [80]. Developing optimal conditions that combine high permeance with efficient gas separation remains one of the main challenges in zeolite membrane research for natural gas processing.

3.5.1 Membrane Preparation

Significant efforts have been devoted to preparing high-quality zeolitic membranes by adapting the general methodology of zeolite synthesis. In the context of porous supports, two main strategies are recognized for membrane fabrication: in situ synthesis and secondary growth [15,63].

The in-situ synthesis approach is based on the nucleation of zeolite crystals on the surface of the support, followed by integrated crystallization. Although this process is simple and straightforward, it presents challenges in controlling membrane uniformity and quality [6]. In this method, the support is immersed in a synthesis of gel solution, and the zeolite layer is formed during hydrothermal treatment. Nucleation and crystal growth occur simultaneously and are influenced by factors such as the chemical composition and molar ratios of the gel components, solution pH, and crystallization temperature [6,15,63,76]. One of the main advantages of in situ synthesis is the reduction in the number of preparation steps. Additionally, the various in situ conditions enable zeolite infiltration into the support, resulting in thick zeolite layers. However, the reproducibility of this method is limited, and the resulting membranes often exhibit low permeance due to the potentially high effective thickness of the zeolite layer [6,63].

The secondary growth method, currently the most widely adopted, offers greater control over the formation of the zeolite structure due to the decoupling of nucleation and crystal growth steps. This method, illustrated in Figure 10, involves three distinct stages: (i) preparation of zeolite seeds or nanocrystals (typically 50–100 nm in size); (ii) deposition of these seeds as a thin layer on the surface of the support;

(iii) growth and stabilization of the zeolite layer via hydrothermal treatment, which promotes the formation of chemical bonds between the support and the zeolite crystals [3,15,63].

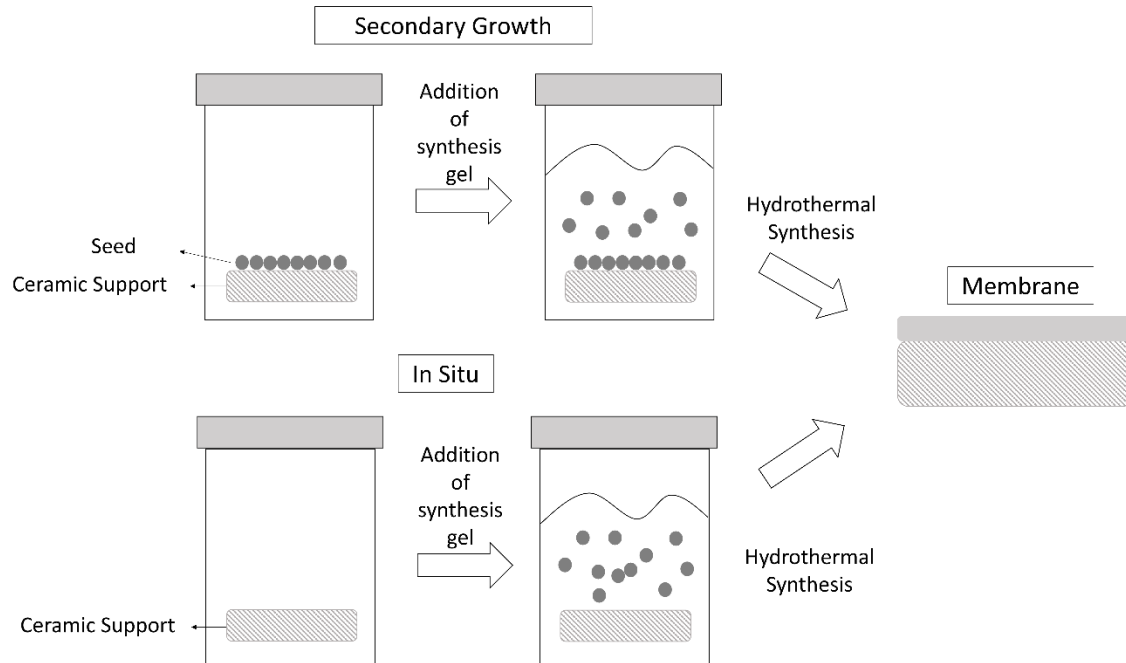


Figure 10. Representation of different membrane production methodologies.

Given the potential for effective regulation of all these steps, the secondary growth strategy is considered a viable approach for large-scale synthesis of zeolite membranes. Various methods can be employed for zeolite deposition in membrane fabrication, each with specific characteristics that influence the final quality and performance.

The rubbing technique [4,15] involves the mechanical application of zeolite particles onto the support through friction forces, promoting effective initial adhesion before secondary synthesis. Covalent chemical deposition [63,64], on the other hand, uses chemical reactions to bond zeolite crystals to the support via covalent bonds, enhancing the stability and adhesion of the active layer. The filtration method [7,64] relies on the flow of a zeolite crystal suspension through the support, enabling selective deposition of particles within the pores or on the surface, resulting in a homogeneous layer.

Finally, dip-coating [20,77,83–85] is a widely used method for depositing zeolites in membrane production, as it allows control over the thickness and uniformity of the deposited layer. The process involves immersing the porous support into a zeolite crystal suspension,

followed by the controlled withdrawal of the support, allowing a thin layer of material to adhere to the surface. After this step, the membrane is typically subjected to a drying process and then hydrothermal treatment for membrane growth.

Several factors influence the quality and performance of the membrane produced by dip-coating, including:

(1) **Immersion and Withdrawal Speed:** Generally, slower withdrawal results in a thicker deposited layer, as there is more time for partial drying of the suspension. Rapid withdrawal can lead to thinner and less homogeneous films.

(2) **Zeolite Suspension Concentration:** More concentrated suspensions tend to form thicker layers due to the greater number of crystals adhering to the support, which increases mechanical strength. However, they may lead to cracking. Diluted suspensions produce thinner, more homogeneous films but may not fully cover the support.

(3) **Ambient Temperature and Humidity:** These affect the solvent evaporation rate in the suspension, impacting the adhesion and final structure of the deposited layer.

(4) **Immersion Time:** Longer immersion times can increase the layer thickness, while very short times may result in insufficient deposition.

(5) **Support Properties:** More porous supports favor zeolite anchoring, whereas very smooth surfaces may reduce adhesion of the deposited layer.

(6) **Number of Layers:** Applying multiple layers can improve coverage and minimize defects, but it requires precise control to avoid excessive thickness and cracking.

Strict control of these parameters is essential to produce high-quality membranes, ensuring a balance between permeability and selectivity. Dip-coating is a versatile and efficient method, but its success depends on fine-tuning these factors to meet the requirements of the intended application [80,83–87].

An alternative approach is the use of microwave technology for both seed preparation and membrane synthesis. Microwave irradiation can influence the membrane's microstructure—such as crystal size, morphology, orientation, and thickness—while enabling the production of defect-free membranes, further enhancing performance [78,88,89].

Wang [78] produced a DDR-type zeolite membrane and showed that, compared to conventional hydrothermal synthesis, microwave heating significantly accelerated DDR membrane crystallization kinetics, reducing synthesis time from 2–6 days to just 1 hour. The membrane thickness was also reduced from approximately 5 μm to less than 1.5 μm . The final

performance of the membranes for CO₂/CH₄ separation showed a CO₂ permeability of 4.7×10^{-7} mol/(m²·s·Pa) and a CO₂/CH₄ selectivity of 190 at a pressure drop of 0.14 MPa.

3.5.2 Fundamentals of the Gas Separation Process by Zeolite Membranes

Transport through the zeolite layer can be described by the sequential phenomena of adsorption, diffusion, and desorption (Figure 11). Generally, it is assumed that diffusion is the slowest step, while sorption and desorption occur infinitely fast and are in equilibrium. Surface or intracrystalline barriers are not considered in this model, as they would introduce additional resistance to transport, requiring more complex descriptive models. Thus, in summary, the main separation mechanisms that contribute to good selectivity in a high-quality membrane (i.e., defect-free) are:

(1) **Adsorption Selectivity:** This occurs when, in a gas mixture, one gas is adsorbed much more strongly than another (for example, CO₂ adsorbs more strongly on the zeolite surface due to its higher quadrupole moment compared to CH₄ molecules) [6,16,19]. Adsorption selectivity is generally the dominant separation mechanism at low temperatures.

(2) **Diffusion Selectivity:** This occurs when, in a gas mixture, the molecules of one gas are smaller and diffuse through the zeolite's micropores much faster than the larger gas molecules (for example, because the kinetic diameter of N₂ is smaller than CH₄, its diffusivity is faster) [5,6,11]. The contribution of diffusion to selectivity increases with temperature.

(3) **Size Exclusion (Molecular Sieving):** This happens when a component can or cannot permeate through the zeolite pores (for example, CH₄ has a larger kinetic diameter, often similar to the size of small zeolite micropores (8MR), so CH₄ molecules may not enter the zeolite pores, whereas smaller molecules like N₂ preferentially permeate) [3,5].

Among these types, adsorption and diffusion are the most studied and discussed mechanisms.

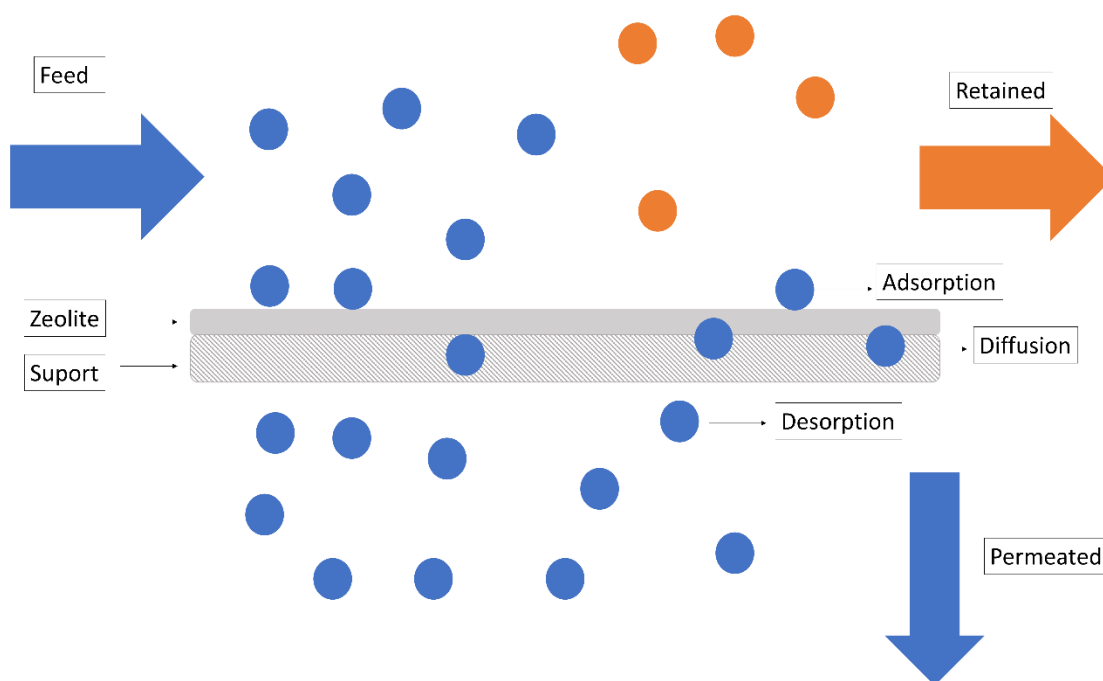


Figure 11. Schematic representation of the gas separation process. Adapted from [63].

3.5.2.1. Pemeation: Adsorption

Gas permeation in zeolitic membranes is governed primarily by adsorption and diffusion mechanisms. Among these, adsorption plays a crucial role, as it constitutes the initial stage in the separation of gas molecules through the zeolite framework. In general, the performance of a zeolitic membrane in gas separation depends strongly on the affinity between the gas molecules and the surface of the zeolite pores [5–7]. At low to moderate temperatures (up to approximately 100–200 °C, depending on the zeolite structure and polarity), zeolites typically exhibit high adsorption selectivity [6,11,12]. Under these conditions, the gas component with the most affinity for the zeolite surface tends to occupy the adsorption sites preferentially, therefore blocking or limiting the permeation of other components with lower adsorption selectivity.

Zeolites being crystalline aluminosilicates with well-defined microporous networks, provide an excellent platform for studying adsorption phenomena due to their tunable framework composition, uniform porosity, and high thermal stability. The electrostatic potential generated by the framework's negative charge, coupled with the confined pore

environment, creates adsorption sites capable of selectively interacting with gas molecules of different sizes, polarizabilities, and quadrupole moments [90–92].

The adsorption of gas molecules on a given zeolite depends on both the adsorbate characteristics, such as polarizability and dipole or quadrupole moments, and on the adsorbent's properties, which include polarity, topology, structural flexibility, pore size, and the nature of extra-framework cations used to balance the framework's negative charge [16,93]. Among these, polarity is one of the most influential parameters and depends on zeolite's chemical composition. Small modifications in the Si/Al ratio can significantly alter the adsorption behavior, favoring certain gases over others. Zeolites with high silica content tend to be thermally more stable, as breaking Si–O bonds require more energy than breaking Al–O bonds. Moreover, high-silica zeolites are more hydrophobic, reducing the need for pre-gas and improving the performance in separations such as CO₂/CH₄ mixtures [6,16].

Remy *et al.* investigated the effect of both the compensating cations and the Si/Al ratio in KFI-type zeolites on CO₂ separation. They concluded that the type of cation strongly affects CO₂ adsorption: metals with smaller ionic radii favor higher CO₂ uptake because they do not block access to the internal cavities of the zeolite. Zeolites with Si/Al ratios between 3 and 5 were reported to exhibit the best performance for CO₂/CH₄ separation under low-pressure conditions [11].

The Si/Al ratio and the distribution of extra-framework cations significantly influence adsorption selectivity within zeolitic structures [90,94]. A low Si/Al ratio increases the negative charge of the framework, leading to a higher number of compensating cations (Na⁺, K⁺, Ca²⁺). These cations generate localized electrostatic fields that interact strongly with polar or quadrupolar molecules [91,94–96]. Consequently, gases such as CO₂—characterized by a large quadrupole moment and moderate polarizability—exhibit stronger interactions with cationic sites than less polar molecules such as CH₄ or N₂ [90,95]. In contrast, CH₄ adsorption is mainly driven by dispersion forces and confinement within ultramicropores (as in KFI-type zeolites), whereas N₂, with a smaller quadrupole moment, typically displays weaker adsorption energies [90,96,97]. This molecular distinction explains the typical adsorption order observed for aluminosilicate zeolites: CO₂ > CH₄ > N₂.

Outside the framework of composition, surface chemistry—particularly the presence of silanol (Si–OH) groups—also plays a decisive role in adsorption behavior. Isolated silanol groups act as polar adsorption sites, enhancing interactions with CO₂ through dipole–

quadrupole coupling or weak hydrogen bonding. Typically, clustered silanol groups enhance the hydrophilicity of the surface, thereby competing with CO₂ adsorption under humid conditions. Recent studies have demonstrated that controlling silanol density, either through post-synthetic treatments or ion exchange, effectively tunes both CO₂ affinity and moisture resistance in zeolitic adsorbents. This highlights the dual importance of framework structure and surface functionality in determining overall adsorption performance.

The equilibrium between the gas phase and the adsorbed phase in zeolites represents the maximum affinity of the material for a given gas at constant temperature and is typically described by adsorption isotherms. These mathematical models or plots relate the amount of gas adsorbed per unit of mass of adsorbent (q) to the equilibrium pressure (P). Modeling adsorption isotherms is essential to determine the maximum adsorption capacity and to simulate material performance in separation systems, such as those based on the Ideal Adsorbed Solution Theory (IAST).

Among the most widely used models for solid–gas systems, the Langmuir model assumes monolayer adsorption on homogeneous sites, described as:

$$q = \frac{q_{\text{m}\acute{\text{a}}\text{x}} * bP}{1 + bP} \quad \text{Equation 1}$$

where $q_{\text{m}\acute{\text{a}}\text{x}}$ is the theoretical maximum adsorption capacity (mmol g^{−1}), representing monolayer saturation, and b is the Langmuir equilibrium constant (bar^{−1}), related to the adsorbate–adsorbent affinity [91,92,96,98].

However, due to surface heterogeneity in zeolites—arising from different cationic sites and pore types—more complex models are often required, such as the Dual-Site Langmuir (DSL) model. The DSL model assumes the existence of two distinct types of adsorption sites (sites 1 and 2), each with its own maximum capacity ($q_{\text{m}\acute{\text{a}}\text{x},1}$, $q_{\text{m}\acute{\text{a}}\text{x},2}$) and affinity constants (b_1 , b_2) [91,92,96,98]:

$$q = \frac{q_{\text{m}\acute{\text{a}}\text{x},1} * b_1 * P}{1 + b_1 * P} + \frac{q_{\text{m}\acute{\text{a}}\text{x},2} * b_2 * P}{1 + b_2 * P} \quad \text{Equation 2}$$

In this framework, high-affinity sites (often associated with cations) are modeled separately from lower-energy sites (typically silicate or aluminate portions of the framework). When adsorption sites exhibit a broad distribution of energies, models such as Tóth and Sips can better represent the isotherm of curvature. The choice of model should be guided by both the fitting quality and physical interpretability. Comparative studies recommend testing multiple models (Langmuir, DSL, Tóth, Sips, virial), as they may yield different IAST predictions for mixture behavior [94,97,99,100].

In industrial practice, gas separation involves multicomponent mixtures. Although pure-component adsorption data provide critical insights into capacity and affinity, they do not directly describe the competitive equilibrium that occurs when several gases are adsorbed simultaneously. Experimental determination of mixture adsorption equilibria is often complex and time-consuming; thus, the Ideal Adsorbed Solution Theory (IAST), proposed by Myers and Prausnitz (1965), is widely applied to predict mixture adsorption equilibria from pure-component isotherms [90–92,99].

IAST is based on a thermodynamic analogy between gas adsorption and vapor condensation, treating the adsorbed phase as an ideal solution. Its central assumptions are: (a) the total surface area or adsorption volume is constant for all components, and (b) the spreading pressure (π) of each pure component is equal to that of all components in the mixture at the same reduced spreading pressure or adsorption potential.

Once the pure-component isotherms are fitted to a reliable model (e.g., Langmuir, Tóth, or DSL), IAST can be applied to calculate the adsorption capacity of each component i in the mixture (q_i) for a given total pressure and gas-phase composition. The thermodynamic selectivity of component i over component j is expressed as [90–92,99]:

$$\alpha_{i/j} = \frac{x_i/y_i}{x_j/y_j} \text{ Equation 3}$$

where x_i , x_j are the mole fractions of components i and j in the adsorbed phase (calculated via IAST), and y_i , y_j are their respective mole fractions in the equilibrium gas phase. The IAST approach is crucial for evaluating the separation potential of zeolites for mixtures such as CO₂/CH₄, CO₂/N₂, and CH₄/N₂ under realistic operating conditions [99,100]. Although IAST represents an idealized approximation, it generally provides accurate predictions for zeolites,

particularly when adsorption is predominantly physical (physisorption) and intermolecular interactions in the adsorbed phase are minimal [90,96,97,101].

Once individual isotherms are properly described, the IAST framework enables reliable prediction of multicomponent adsorption equilibria and selectivity. This theoretical approach has proven highly effective for many zeolite–gas systems, offering a practical route to assess separation performance prior to conducting complex mixture experiments. Nevertheless, the accuracy of IAST predictions depends on the quality of the fitted isotherms and the absence of significant non-idealities or diffusion limitations [99,100].

In practical operation, real gas streams frequently contain impurities and moisture. Water molecules compete strongly for the same polar sites that attract CO₂, thereby reducing adsorption capacity under humid conditions. This challenge has motivated the design of zeolites with hydrophobic surfaces or optimized Si/Al ratios to balance CO₂ capacity and moisture tolerance [11,90]. Furthermore, in dynamic applications such as pressure swing adsorption (PSA) or membrane-based separations, the kinetics of adsorption and diffusion through micropores become decisive factors in determining process efficiency. Thus, by combining equilibrium data, kinetic measurements, and structural characterization offers a comprehensive understanding of how framework chemistry and morphology govern separation performance.

In summary, gas adsorption in zeolites is dictated by the synergy between framework electrostatics, surface functionality, and the molecular properties of the adsorbates. Insights derived from isothermal modeling and theoretical selectivity predictions form the basis for evaluating and optimizing the materials synthesized in this work. By correlating adsorption behavior with spectroscopic indicators such as Si/Al ratio, cation distribution, and silanol density, it becomes possible to rationalize the observed trends in CO₂, CH₄, and N₂ uptake, thereby guiding structural modifications aimed at enhancing performance in future gas separation applications [91,95].

3.5.2.2. Permeation: Diffusion

The second stage in the separation by zeolite membranes occurs through the surface diffusion of the gas. Diffusion is a central physicochemical phenomenon in membrane separation, defined as the spontaneous movement of gas molecules from a region of higher

concentration (or partial pressure) to one of lower concentrations. This movement continues until equilibrium is reached [6,15]. Diffusion is the central mechanism governing permeation and can occur in different ways, depending on the size of the gas molecules and the pore characteristics (Figure 12). Gas transport through a membrane, known as permeation, is governed by this concentration difference or, more precisely, by the partial pressure difference (ΔP) of the gas between the feed and permeate sides. Permeation is, therefore, a passive transport process that does not require external energy (ATP) to occur, depending solely on the partial pressure gradient as its driving force.

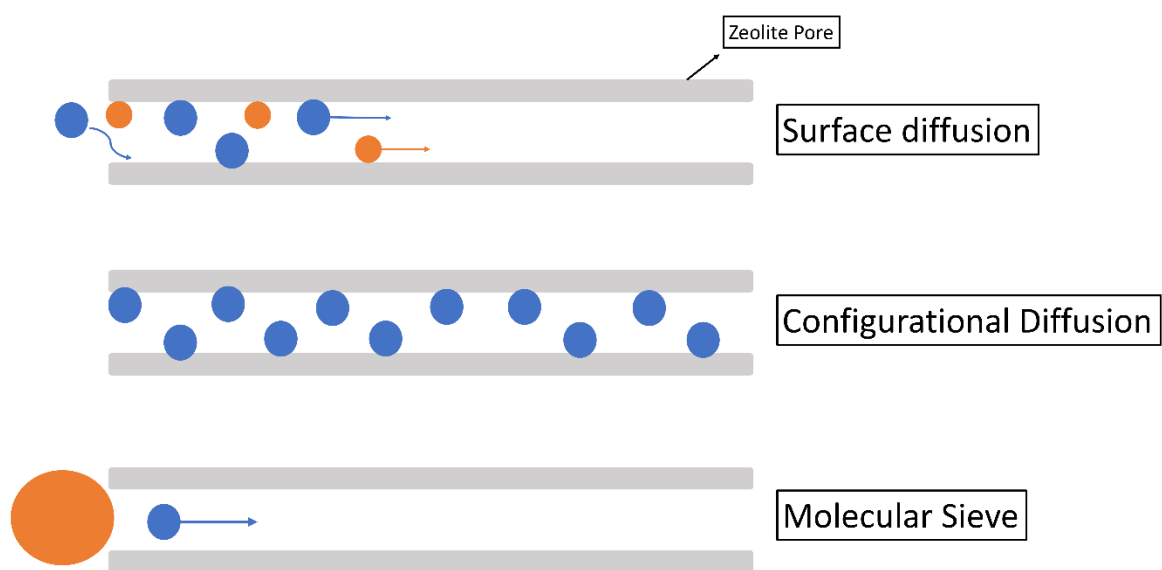


Figure 12. Transport mechanism through microporous zeolitic membranes. Adapted from [102].

The most common model for dense membranes is the solution–diffusion mechanism. This model establishes the basis for understanding transport in polymers and nonporous membranes, where permeation occurs in three stages:

1. **Absorption (Solution):** The gas dissolves on the feed surface of the membrane.
2. **Diffusion:** The gas migrates through the membrane thickness, driven by the concentration gradient.
3. **Desorption:** The gas is released on the permeated side surface.

The permeation rate is then described by the permeability (P), which is the product of the diffusion coefficient (D) (related to the mobility of the gas within the matrix) and the solubility coefficient (S) (related to the gas affinity with the membrane material):

$$P = D * S \text{ Equation 4}$$

In porous membranes, particularly in microporous ones such as zeolites, transport is dominated by mechanisms critically dependent on the relationship between the molecular size of the gas and the pore diameter. Transport is not merely a matter of solubility and diffusion within the matrix but also of detailed interactions between the molecules and the pore walls.

One of the most common mechanisms is Knudsen diffusion, a mass transport phenomenon that occurs on a molecular scale and is characterized by the movement of molecules through extremely small pores. It occurs when the pore diameter is smaller than the mean free path of the gas molecules. It is commonly observed in porous membranes with nanometric porosity, where the mean free path of the molecules is comparable to the pore size. The movement of molecules is dominated by pore characteristics such as size and shape, and molecular properties like size and molecular mass [5,6,63].

In this regime, molecules collide more frequently with the pore walls than with each other. Knudsen diffusivity is derived from geometric parameters related to the membrane and the kinetic velocity of the gas [102]. This explains why smaller molecules, such as hydrogen (H₂), diffuse faster than larger molecules like CO₂ or methane (CH₄). Knudsen diffusion is especially relevant in systems where pores are so small that the diffusion rate of molecules is significantly reduced, resulting in a phenomenon known as "Knudsen-controlled diffusion." Thus, defect size plays an important role, and the defect area fraction must be less than 10 ppm for a zeolite membrane to operate in the molecular sieving regime [5,6,102,103].

The second mechanism, surface diffusion, refers to a process in which molecules adsorb on the pore walls and migrate from one side of the membrane to the other. The amount of gas transported depends both on the extent of adsorption and the mobility of the diffusing components. The contribution of each of these processes to overall gas transport varies with operating conditions, including composition, pressure, and temperature. This type of diffusion occurs at low temperatures when gas molecules cannot escape the potential field of the surface because the interaction between the internal surface and gas molecules becomes stronger than their kinetic energy. Surface diffusion occurs when at least one of the feed components preferentially adsorbs on the membrane surface. This mechanism can be relevant and even dominant when the surface area is high, and the concentration of adsorbed molecules on the surface is significant [102,104,105].

Another important mechanism is molecular sieving, which occurs when the membrane pore size is comparable to the dimensions of the diffusing molecules. In this scenario, smaller molecules permeate the membrane, while larger molecules are rejected. Molecular size is described by the kinetic diameter, and although there is no specific model to calculate diffusivity, it is observed that in materials like zeolites, the network structure is not completely rigid. This allows molecules to pass through apparently smaller pores due to the redistribution of energy stored in the pressure gradient. Additionally, adsorption selectivity has little influence on this mechanism [6,102–104].

A particular case of this phenomenon is activated molecular sieving, which occurs when the zeolite pores are significantly smaller than the diffusing molecules. Under these conditions, repulsive forces dominate, and molecules require additional “activation energy” to pass through the pores. This mechanism becomes more relevant at high temperatures, where the available thermal energy facilitates the efficient separation of molecules with subtle size differences. It is important to highlight that substance transport in membranes may involve multiple mechanisms acting simultaneously. However, in microporous membranes, more advanced models have been developed to describe these processes [80,82,102,105].

Finally, the mechanism of configurational diffusion occurs when the size of the gas molecules is comparable to the pore diameter of the zeolite. In this case, diffusion is highly dependent on the shape and size of the molecules as well as on the pore structure. This mechanism is responsible for the high selectivity of zeolite membranes in separating molecules with very close sizes, such as propane (C_3H_8) and propylene (C_3H_6). Additionally, under high-pressure conditions or for gases with high affinity for zeolite, surface diffusion may dominate the process, where gas molecules move along the pore walls or form a dense phase inside the pores [102,104,105].

The gas separation performance in zeolite membranes is influenced by the adsorption and diffusion of gas components through their channels. To properly describe permeation in these membranes, it is essential to consider the interaction between adsorption and diffusion. Modeling this process is based on Fick’s law and the generalized Maxwell-Stefan (MS) theory [102,104,106].

Fick’s law assumes that mass transport is driven by concentration gradients without accounting for frictional forces between gas components, making it suitable only for single-component systems [106]. The Maxwell-Stefan theory was initially developed separately by

James Clerk Maxwell for dilute gases and Josef Stefan for fluids. The generalized MS approach considers both gas non-idealities and interactions between components during the diffusion process. This approach is currently widely accepted as the best way to model mass transport in zeolite membranes, especially for multicomponent mixtures [6,82,102,104–107].

To evaluate the performance of a good gas separation membrane, some parameters are commonly used: the rate at which molecules permeate the membrane is described as permeance or permeability (π , P), which is the flux normalized by the driving force, i.e., the pressure difference, and the ideal separation selectivity ($\alpha_{i/j}^0$), which is the ratio of permeances for two different components, i and j , measured independently with pure feed (or single gas permeation) [64]. The separation selectivity of the gas mixture is usually determined by the Wicke–Kallenbach method, called the real separation factor ($\alpha_{i/j}$). Permeability strongly depends on the effective membrane layer thickness. To fairly compare membranes of different materials, permeability is calculated by multiplying permeance by membrane thickness [7,15,64,76].

$$\pi_i = \frac{Q}{A_m \Delta P_i} \quad \text{Equation 5}$$

$$\alpha_{i/j}^0 = \frac{\pi_i^0}{\pi_j^0} \quad \text{Equation 6}$$

$$\alpha_{i/j} = \frac{y_i/y_j}{x_i/x_j} \quad \text{Equation 7}$$

$$P = \pi_i * \delta \quad \text{Equation 8}$$

Where Q is the moles of component i permeated through the membrane during time t (s); ΔP_i is the partial pressure difference (i.e., $\Delta P_i = P_{i,f} - P_{i,p}$, where $P_{i,f}$ e $P_{i,p}$ are the partial pressures of gas component i at the feed and permeate sides, respectively); π_i^0 and π_j^0 are the pure gas permeances of components i and j , respectively; x and y are the mole fractions of the feed and permeate gases, respectively; δ is the membrane thickness; and P_i is the membrane material permeability for component i [15,64,103].

Several factors influence selectivity and permeation in zeolite membranes, such as pore size—smaller pores increase selectivity but may reduce permeation rate, while larger pores allow higher flux but can compromise selectivity. Temperature also plays an important role, as increasing temperature generally increases diffusion rate but may reduce adsorption, depending

on the gas and zeolite. Lastly, pressure is another crucial factor, since the pressure difference across the membrane is the driving force for permeation. Higher pressures increase gas flux but can saturate zeolite pores, especially for gases with high affinity for the material [64,102,106].

The diffusion process plays a crucial role in the overall performance of zeolite membranes for gas separation, as it directly determines the transport rate of molecules through the microporous network. In these materials, diffusion occurs via complex interactions between the gas molecules and the internal surface of the crystalline framework. The diffusivity of gases within zeolites depends on several structural and physicochemical parameters, including pore size and shape, connectivity between channels, and the presence of intracrystalline defects or mesoporous domains that can act as transport shortcuts [15,104–106]. Additionally, the Si/Al ratio of the zeolite framework strongly affects the electrostatic field strength inside the pores, which modulates the strength of adsorption sites and consequently the mobility of adsorbed molecules [108]. A higher Si/Al ratio generally reduces the number of cationic adsorption sites, favoring faster diffusion due to weaker molecule–surface interactions [109].

Another key property influencing gas diffusion is the crystallite size of the zeolite membrane. Smaller crystallites shorten the diffusion path length and reduce intracrystalline resistance, enhancing overall permeation [107]. Similarly, high membrane crystallinity and strong intergrowth between zeolite crystals minimize non-selective defects, improving the uniformity of diffusion pathways [6,104,108]. The pore dimensionality also has a significant effect: one-dimensional channels, such as in MFI-type zeolites, impose stronger confinement and molecular sieving effects, whereas three-dimensional frameworks like FAU and KFI enable higher diffusivity due to more interconnected pathways [106,109]. Furthermore, post-synthetic modifications, such as ion exchange, surface functionalization, or framework dealumination, can be employed to tune diffusivity and selectivity by altering the polarity, hydrophilicity, and effective aperture of the pores [104].

Overall, gas separation through zeolite membranes results from the combined effects of adsorption and diffusion processes. Adsorption governs the initial capture and concentration of molecules within the pores, while diffusion controls their transport and eventual permeation through the membrane. An optimal balance between both mechanisms is therefore essential for achieving high separation efficiency. Materials that exhibit strong but reversible adsorption together with high diffusivity for the target gas typically yield superior performance. Consequently, the rational design of zeolite membranes must consider both thermodynamic

(adsorption) and kinetic (diffusion) parameters to maximize selectivity and permeability. Recent studies highlight that fine-tuning pore architecture, composition, and surface chemistry enables tailored control over these mechanisms, paving the way for next-generation membranes capable of high-efficiency separations in energy, environmental, and industrial applications [6,104,105,107].

3.5.2.3. Robeson's Plot

The development of zeolite membranes for N₂/CH₄ separation has proven to be a challenge, as both gases have very similar kinetic diameters (N₂ = 0.364 nm and CH₄ = 0.374 nm). Although some studies have reported N₂-selective membranes, CH₄ tends to be preferentially adsorbed due to its higher polarizability ($26 \times 10^{-25} \text{ cm}^3$) compared to N₂ ($17.4 \times 10^{-25} \text{ cm}^3$), which hinders efficient nitrogen separation [13,73,74,108]. Therefore, the N₂/CH₄ separation in zeolite membranes occurs predominantly via diffusion selectivity, as N₂, being a smaller molecule, diffuses more rapidly through the membrane than CH₄. As a result, N₂ occupies the zeolite pores and inhibits the passage of CH₄, increasing the overall process selectivity [5,6,108].

The Robeson's Plot is a fundamental tool in the field of gas separation by membranes, as it illustrates the relationship between permeability and selectivity of various membrane materials for specific gas pairs. Published by Robeson [109] the plot presents the performance of numerous membranes by correlating, on a log-log scale, the permeability (X-axis) and the selectivity (Y-axis), defined as the ratio between the permeabilities of two gases.

The main objective of Robeson's Plot is to highlight the trade-off between permeability and selectivity. In general, materials with high permeability tend to exhibit low selectivity, and vice versa. This is because more open structures facilitate the transport of multiple gas species, reducing the membrane's ability to differentiate between them [5,6,79,109,110].

In 1991, Robeson established an empirical upper limit, known as the *upper bound*, which defines the ideal relationship between these two parameters. This limit was revised in 2008 to include newer high-performance materials. A membrane is considered innovative when its experimental data surpasses this limit curve, demonstrating superior gas separation performance [109,110].

The Robeson's Plot is widely used in the development of new membranes, as it helps researchers design materials that overcome the limitations imposed by the trade-off. Additionally, it allows for objective comparisons between different materials in specific applications and highlights research trends in the field. Advanced materials, such as mixed-matrix membranes (MMMs) and metal-organic frameworks (MOFs), have been developed with the goal of exceeding the Robeson limit, offering new solutions for gas separation in both industrial and scientific contexts [6,64,109,110].

However, data on N₂/CH₄ separation using zeolite membranes is still limited compared to other binary gas mixtures. The challenge of this separation lies not only in the similar kinetic diameters of the molecules but also in the fact that both gases are weakly adsorbing, making membrane selectivity rely almost exclusively on preferential diffusion. In the Robeson's Plot (Figure 13), the selectivity for N₂/CH₄ is generally around 10, much lower than the selectivity values reported for CO₂/CH₄, which can reach up to 1000.

Compared to the 2008 upper bound for polymeric membranes, zeolite membranes have shown only modest improvements in selectivity. The highest reported selectivity value was 14.8, achieved with SSZ-13, while the highest N₂ permeance recorded was $8.67 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ [111]. Zeolites such as SAPO-34 and SSZ-13 exhibited good permeance values, whereas DD3R-type membranes showed lower performance. The SSZ-13 membrane furthest from the upper bound was produced via seeded gel synthesis and had a reduced thickness (1.2 μm), achieving a selectivity of 13.5 and an N₂ permeance of $8.5 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ [108].

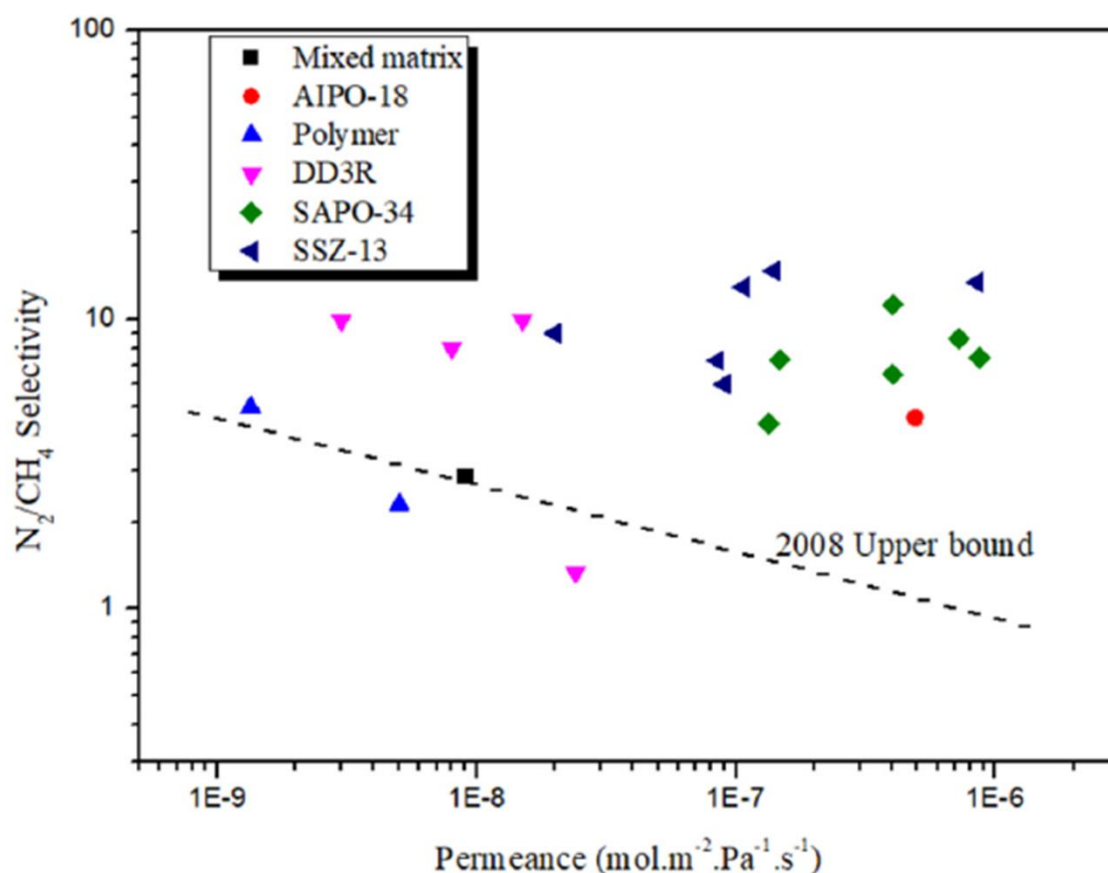


Figure 13. Robeson plot of recent major results on zeolite membranes for N₂/CH₄ separation. A standard membrane thickness of 1 μm was considered to draw the 2008 upper limit for membranes. Adapted from [5].

N₂-selective membranes are particularly advantageous in natural gas processing, as they allow CH₄ to be retained in the retentate stream, reducing recompression costs. However, due to the complexity of achieving efficient separation, there are still few studies in the literature focused on zeolite membranes specifically designed for this application.

3.5.3. Small-Pore Zeolites for Gas Separation

Small-pore zeolite membranes have emerged as highly promising materials for gas adsorption and separation due to their unique structural properties and superior performance compared to other types of membranes, particularly polymeric ones. These zeolites consist of crystalline frameworks of tetrahedra (TO₄, T = Si, Al, B, Ti, P, etc.) with uniform and well-defined pore sizes, enabling molecular sieving effects that selectively allow passage of molecules based on size and shape [64,112].

Small-pore zeolites (8MR) are a specific type of zeolite composed of eight tetrahedra connected through shared oxygen atoms. Different connection and stacking modes result in distinct framework structures [5,112]. The 8MR pores in these zeolites create cavities—essentially void spaces within the crystal structure—that restrict the passage of larger molecules. Therefore, these zeolites are particularly useful for the adsorption and separation of small molecules and ions, as their typical pore sizes are less than 4 Å [6,112]. Some examples of this zeolite class include DDR ($3,6 \times 4,4\text{\AA}$) [6], LTA ($4,1 \times 4,1\text{\AA}$) [112], CHA ($3,8 \times 3,8\text{\AA}$) [4], KFI ($3,9 \times 3,9\text{\AA}$) [12,13], (3,9 ERI ($3,6 \times 5,1\text{\AA}$) [113] and MER ($3,4 \times 5,1\text{\AA}$) [114,115]. These dimensions are comparable to the kinetic diameters of many industrially relevant molecules such as CO₂ (0.330 nm), CH₄ (0.374 nm), N₂ (0.364 nm), O₂ (0.346 nm), and H₂ (0.289 nm) [3–5,113] allowing for selective adsorption and diffusion based on molecular size and shape, which facilitates gas mixture separation.

In addition, the small pores of 8MR zeolites provide sufficient stability to withstand hydrothermal conditions ($>700\text{ }^{\circ}\text{C}$), making them suitable for use across a wide range of temperatures and in harsh chemical environments without losing their porous structure or adsorption/separation properties. Finally, they exhibit high surface area due to their highly crystalline porous structure, offering extensive adsorption interface and promoting effective interactions between gas molecules and the active sites of the zeolite, thus improving separation efficiency [61,73,112].

A key feature that makes 8MR zeolites particularly attractive for membrane or adsorption applications is their structural porosity, which allows molecular discrimination through either size exclusion or dynamic effects such as trapdoor mechanisms and framework flexibility. In these cases, adsorption selectivity and capacity can be further enhanced by cation relocation or framework adjustments induced by guest molecules, often resulting in exceptionally high selectivities [61,64,91,112].

Several important factors must be considered when selecting a small-pore zeolite for membrane fabrication, including the gas components involved, the availability of the synthesis method, membrane cost, and, when possible, modifications to enhance the zeolite properties—such as acid or base treatment, ion exchange with metal ions, and the use of agents to reduce crystal size and improve adsorption—aiming to overcome potential limitations in membrane efficiency [11,13,60]. Among the various modifications explored, most authors agree that the

best separation results are obtained with small-pore zeolite membranes having a low Si/Al ratio or, in some cases, aluminum-free zeolites. This is because aluminum tends to cause defect formation in the zeolite film, hindering the development of a continuous zeolitic layer on the membrane [6,11,61,64,112].

Regarding the crystal size, Yang *et al.* [13] reported an innovative route for nanoscale KFI synthesis, employing β -cyclodextrin as a crystal growth inhibitor. This method reduced the crystal size from approximately 3 μm to 50–100 nm, simplified the synthesis process, and eliminated the need for high-temperature calcination. The resulting nano-KFI displayed enhanced structural properties, including a surface area of $370\text{ m}^2\cdot\text{g}^{-1}$ and a pore volume of $0.22\text{ cm}^3\cdot\text{g}^{-1}$. Adsorption performance was also significantly improved, with a 64% increase in CH_4 uptake compared to conventional KFI, reaching $1.34\text{ mmol}\cdot\text{g}^{-1}$ at 298 K and 1 bar—the highest reported among commercial zeolites. CH_4/N_2 selectivity ranged from 4.2 to 4.4, while CO_2/N_2 and CO_2/CH_4 selectivities were approximately 350–400 and 120–140, respectively. Demonstrating that crystal size reduction is an effective strategy for enhancing gas separation performance.

Similarly, Kencana *et al.* [67] demonstrated the high efficiency of nanocrystalline Ag-ZK-5 (Ag-ZK-5(n)) for selective CH_4/N_2 separation. The material achieved a CH_4 uptake of $1.6\text{ mmol}\cdot\text{g}^{-1}$ and an IAST selectivity of 11.8, surpassing microcrystalline Ag-ZK-5(m). Its superior performance was attributed to nanocrystallinity ($\sim 100\text{ nm}$), which shortens diffusion paths, and the presence of highly electronegative Ag^+ cations, enhancing CH_4 interactions. Ag-ZK-5(n) exhibited rapid adsorption kinetics ($<1\text{ min}$ to equilibrium), excellent regenerability over 10 cycles, strong dynamic performance in breakthrough tests (selectivity 8.5), and a high isosteric heat of adsorption ($29.6\text{ kJ}\cdot\text{mol}^{-1}$), reflecting strong CH_4 – surface interactions and homogeneous Ag^+ distribution. These findings underscore the potential of Ag-ZK-5(n) as a high-performance adsorbent for methane–nitrogen separation.

Thompson [116] investigated the adsorption properties of Na-SSZ-13, a small-pore CHA zeolite, via breakthrough experiments for gases such as CO_2 , CH_4 , C_2H_6 , H_2S , and H_2O . The results highlighted a strong preference for more polarizable species ($\text{H}_2\text{O} > \text{H}_2\text{S} > \text{CO}_2 > \text{C}_2\text{H}_6 > \text{CH}_4$) and high adsorption capacities for CO_2 and CH_4 (3.57 and $3.52\text{ mol}\cdot\text{kg}^{-1}$, respectively), reflecting the heterogeneous adsorption surface influenced by Al and Na^+ cations. These observations indicate that Na-SSZ-13 is an efficient adsorbent for separating CO_2 , H_2S , and

other natural gas impurities, exhibiting high selectivity and robust performance in reactive gas mixtures.

In his study, Zhang [20] successfully fabricated SSZ-13 zeolite membranes with thicknesses between 0.4 and 0.7 μm by performing hydrothermal synthesis at lower temperatures to exploit the slower crystallization kinetics, which favors the formation of smaller zeolite crystals and, consequently, thinner zeolite membranes. High-silica SSZ-13 membranes demonstrated excellent CO_2 permeance, with values of $5.4 \times 10^{-6} \text{ mol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$, and for CO_2/CH_4 separation, they exhibited CO_2 permeance of $4.8 \times 10^{-6} \text{ mol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$ and CO_2/CH_4 selectivity of 153 at room temperature and a pressure of 0.14 MPa.

Zhang [77] also studied the deposition of β -cyclodextrin (CD) in the preparation of zeolite seeds for the fabrication of defect-free SAPO-34 (CHA structure) membranes. CD is commonly used in zeolite synthesis to reduce zeolite crystal size [13], and its use in membrane production led to an increase in CO_2/CH_4 separation selectivity. At a feed pressure of 4.6 MPa, the selectivity increased by 150% for a membrane that initially had low selectivity, while CO_2 permeance decreased by only 22%.

In his study, Li [108] developed high-performance SSZ-13 membranes for gas separation using nanosized seeds prepared via ball milling and hydrothermal synthesis. Optimization of the synthesis process significantly improved membrane performance in separating CO_2/CH_4 and N_2/CH_4 mixtures. The SSZ-13 membranes were characterized for the individual permeance of CO_2 , N_2 , and CH_4 , as well as their ideal selectivities. Moreover, the effects of temperature, pressure, feed flow rate, and humidity on separation performance were evaluated. After process modifications, three produced membranes showed an average CO_2 permeance of $1.16 \times 10^{-6} \text{ mol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$ (equivalent to 3554 GPU) and an average CO_2/CH_4 selectivity of 213 for a 50%/50% CO_2/CH_4 mixture. These results indicate good reproducibility of the synthesis method. Additionally, the membrane demonstrated N_2 permeance of $1.07 \times 10^{-7} \text{ mol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$ (320 GPU) and N_2/CH_4 selectivity of 13, also for a 50%/50% N_2/CH_4 mixture. The SSZ-13 membrane maintained stable performance even in the presence of humidity, showing good CO_2/CH_4 separation efficiency over more than 100 hours of testing at 348 K.

Collectively, these studies highlight the crucial role of pore size, crystal dimension, cation composition, and framework modifications in optimizing the adsorption and separation performance of small-pore zeolites. Such insights guide the design of high-performance zeolite

membranes and adsorbents for applications in natural gas purification, CO₂ capture, and other industrial gas separations.

EXPERIMENTAL SECTION

4. EXPERIMENTAL SECTION

4.1. List of Materials (alphabetical order)

- α -Al₂O₃, Almatis – CT 3000 LS SG, average particle size (d₅₀) of 0.5 μ m, 99.8%.
- Aluminum wire, 0.2 mm diameter, 10 m length, Sigma-Aldrich, 99.999%.
- Aluminum hydroxide, Al(OH)₃, AmBeed, 99.8%.
- Aluminum isopropoxide, Al[OCH(CH₃)₂]₃, Sigma-Aldrich, < 98%.
- Camphene, Sigma-Aldrich, 99.5%.
- Colloidal silica, SiO₂, Ludox® AM-30, Sigma-Aldrich, 30 wt.% suspension in H₂O.
- Colloidal silica, SiO₂, Ludox® AS-40, Sigma-Aldrich, 40 wt.% suspension in H₂O.
- EFKA FA 4663 – EFKA.
- Ethyl orthosilicate, Si(OC₂H₅)₄ or TEOS, Sigma-Aldrich, 98%.
- Potassium hydroxide, KOH, Sigma-Aldrich, 90%.
- Polyvinyl alcohol, PVA, Sigma-Aldrich, 87–90%.
- Strontium nitrate, Sr(NO₃)₂, Sigma-Aldrich, 99%.
- Ultrapure water, with a resistivity of 18 M Ω ·cm, supplied by an Arium® Mini Sartorius water purification system.

4.2. Production of Ceramic Samples

The production of α -alumina (α -Al₂O₃) substrates was carried out using the freeze-casting technique, following the methodology adopted by Silva *et al.* [29]. To optimize the processing parameters, monoliths were initially produced by mixing alumina, the solvent camphene, the dispersant EFKA FA 4663, and the binder polyvinyl alcohol. Mechanical stirring (Disperser, IKA T25 ULTRA TURRAX) was performed at 80 °C for 5 minutes at 8000 RPM to break up potential agglomerates formed in the suspension. Solid loading ratios of 15%, 20%, and 25% α -Al₂O₃ were tested, corresponding to 85%, 80%, and 75% of liquid phase, respectively, in a weight-to-weight (w/w) system. The dispersant and binder were used in concentrations of 2% and 1%, respectively, relative to the mass of solid content.

After dispersion, the alumina suspension was poured into a mold placed on a high thermal conductivity copper rod partially immersed in liquid nitrogen. The equipment used for

ceramic suspension solidification is shown in Fig. 14 and was developed at LMCNano. It included a high thermal conductivity copper cylinder immersed in a liquid nitrogen bath. A type T thermocouple and four heating resistors connected to an on-off controller were assembled around the copper cylinder to regulate the temperature of the copper surface. The investigated freezing temperature was $-170\text{ }^{\circ}\text{C}$.

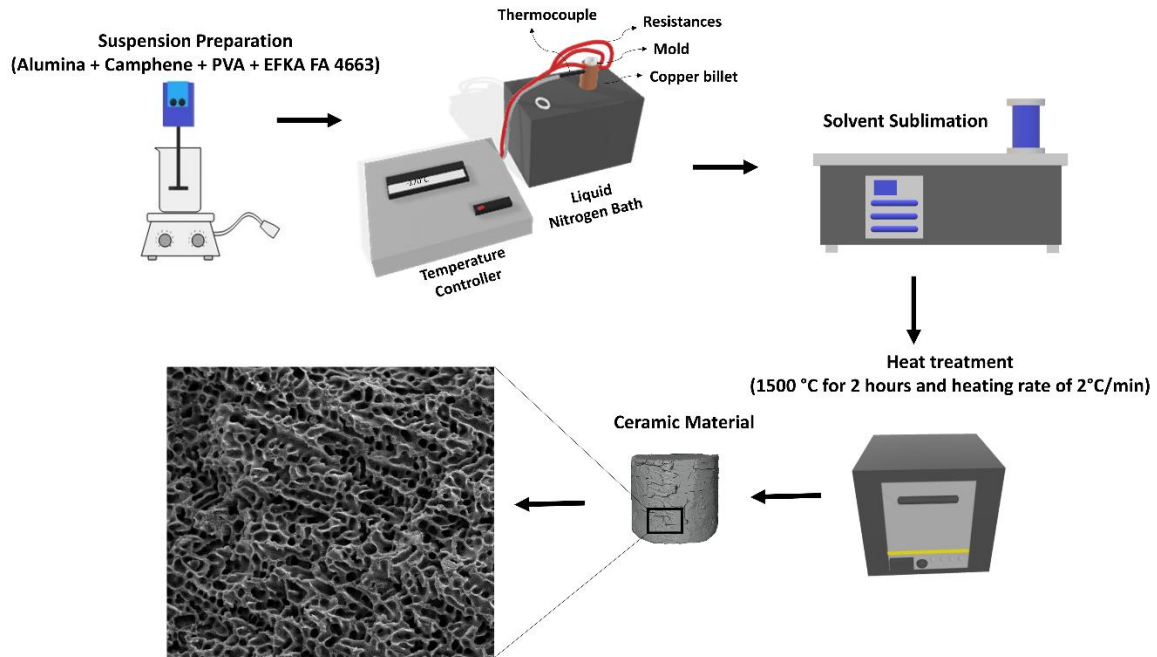


Figure 14. Schematic presentation of the freeze-casting process. Adapted from [32].

Figure 15 shows the molds and the prepared alumina monoliths. Molds made of Technyl® (Nylon 6 polyamide (PA)), copper, and a combination of Technyl/copper were tested (Fig. 15 (a)). The molds were 1.4 cm in height and 2.3 cm in diameter. The inner surfaces of the molds were lubricated with silicone, and the top part of the molds was left open under ambient temperature and pressure conditions. The average freezing time for the monoliths was 4 minutes for the Technyl mold, 2 minutes for the Technyl/copper mold, and 30 seconds for the copper mold.

This study aimed was to evaluate how different mold materials influenced pore formation in the monolith, considering the varying thermal conductivities of copper and Technyl. These differences consequently led to variations in the structure and mechanical properties, with the goal of identifying optimal conditions for adapting the system to tubular

geometries and fabricating a membrane with both good mechanical strength and appropriate porosity.

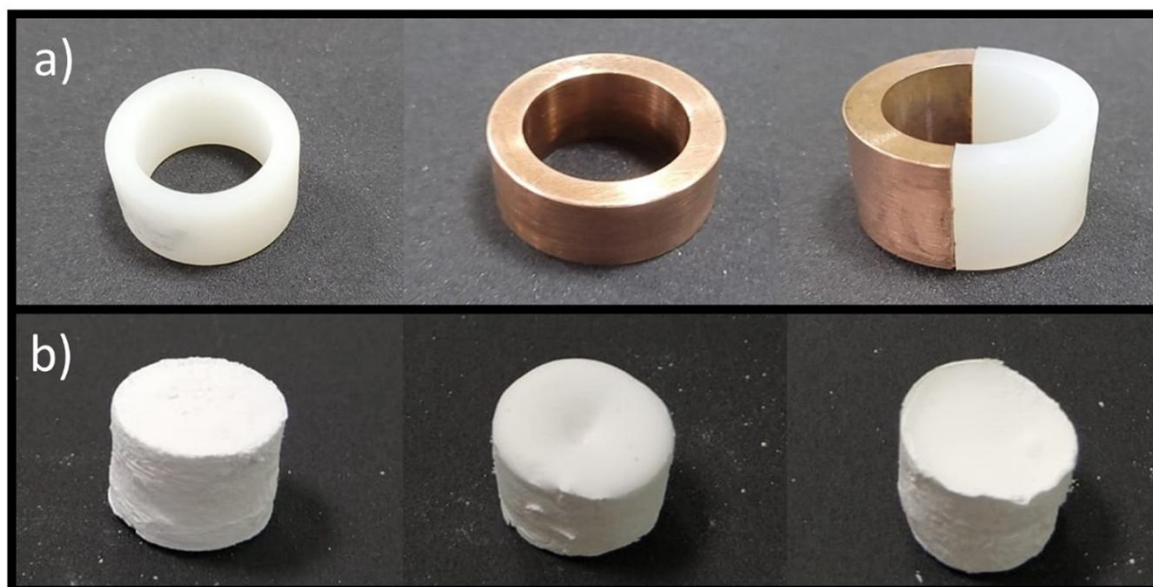


Figure 15. (a) molds used and (b) monoliths produced during the *freeze-casting* process.

After the suspensions were frozen, the samples were removed from the molds and placed on a tray cooled with liquid nitrogen. Solvent sublimation was carried out in a freeze-dryer (TERRONI LS3000, condenser temperature: $-110\text{ }^{\circ}\text{C}$, pressure: $75\text{ }\mu\text{mHg}$) for 24 hours to form the green body. The freeze-dried alumina monoliths were then sintered in a muffle furnace (Nabertherm) at a heating rate of $2\text{ }^{\circ}\text{C}/\text{min}$ and held at $1500\text{ }^{\circ}\text{C}$ for 2 hours. Figure 15b shows the image of the sintered alumina monoliths.

Following the monolith studies, the system illustrated in Figure 14 was adapted to produce ceramic tubes (Figure 16). The manufacturing process involves using a copper rod with a cavity into which the alumina suspension is poured. Then, a Technyl® (Nylon 6, polyamide – PA) fitting is added to ensure the complete formation of the tube. This approach enabled the estimation of the mechanical properties of the resulting tubes based on the previous monolith molding tests.

The suspension formulation employed a solid loading of 25% $\alpha\text{-Al}_2\text{O}_3$ and 75% camphene (solvent), with the addition of the dispersant EFKA FA 4663 and the binder polyvinyl alcohol at concentrations of 2% and 1%, respectively, relative to the mass of the solid

content. The subsequent steps following tube fabrication were identical to those used for the monoliths.

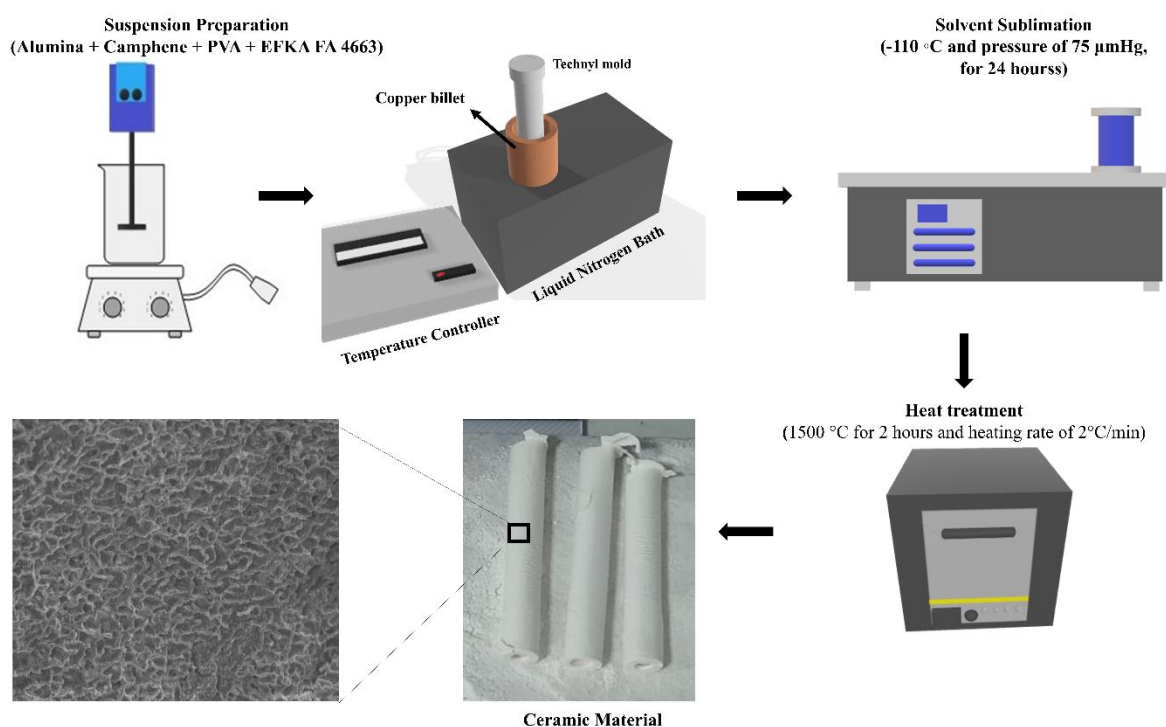


Figure 16. Preparation of Freeze-Casting Tubes.

4.3. Synthesis of KFI Zeolite

One of the main challenges in synthesizing KFI zeolite without the use of an organic structure-directing agent lies in its similarity to other zeolites, particularly in the synthetic pathway [69]. Various methodologies are described in the literature, differing in the choice of precursors (aluminum, silica, and mineralizing agent), molar ratios, and synthesis time. Verduijn [117] in his patent, mentions that the presence of strontium is crucial to produce KFI, as in its absence the gel would crystallize into zeolite L. However, years later, this hypothesis was challenged by Garces *et al.* [118] who reported the synthesis of zeolite L using strontium under hydrothermal conditions, employing a methodology very similar to that of KFI. Their gel composition was $2.3\text{K}_2\text{O}:\text{Al}_2\text{O}_3:0.1\text{SrO}:10\text{SiO}_2:160\text{H}_2\text{O}$, synthesized at $150\text{ }^{\circ}\text{C}$ for 230 hours.

Other studies in the literature also report the synthetic route similarities between KFI and zeolite L [69,117,118] Russell *et al.* [69] conducted a study varying the aluminum source

($\text{Al}(\text{OH})_3$ and aluminum wire) and the silicon source (Ludox® AM-30, HS-30, HS-40, LS-30, or silicic acid). In their procedure, the aluminate solution prepared using aluminum wire was left at approximately 20 °C for 2 days until the wire had completely dissolved. The synthesis was performed hydrothermally using a gel composition of $2.3\text{K}_2\text{O}:\text{Al}_2\text{O}_3:0.1\text{SrO}:10\text{SiO}_2:160\text{H}_2\text{O}$, with synthesis temperatures ranging from 100 to 150 °C. They concluded that the optimal conditions for obtaining KFI with nearly 95% purity involved the use of aluminum wire and Ludox® AM-30 at 150 °C for approximately 3 days of hydrothermal synthesis.

Based on these findings, the present study investigated varying the aluminum and silicon sources to determine the most effective synthetic route for producing pure KFI zeolite. The synthesis preparation scheme is shown in Figure 17.

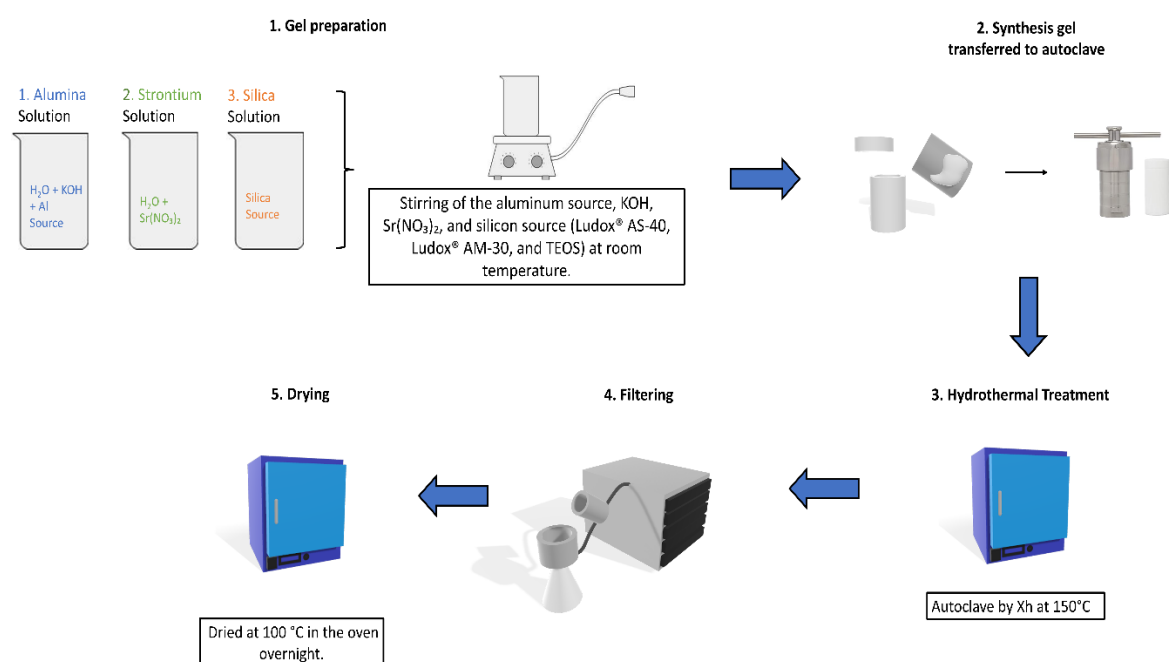


Figure 17. Schematic presentation of the synthesis of KFI zeolite.

4.3.1 Study of Different Silicon and Aluminum Sources

For all syntheses, the mass of KOH was kept constant. The synthesis followed two methodologies with slight modifications [69,75] essentially involving the preparation of three solutions. First, the aluminate solution was prepared by dissolving 3.052 g of KOH in 7.5 mL of water, followed by the addition of an aluminum source under stirring. The stirring time varied depending on the aluminum source: for $\text{Al}(\text{OH})_3$, the solution became translucent after 10

minutes of stirring with slight heating (a mass correction was applied to account for water loss due to heating); for aluminum wire, the solution was stirred without heating for 48 hours until it became translucent; and for aluminum isopropoxide, the solution was stirred for 1 hour to achieve the same result.

In a separate beaker, the silica solution was prepared by weighing the appropriate mass of the chosen silica source. Finally, the strontium solution was prepared by dissolving $\text{Sr}(\text{NO}_3)_2$ in water.

A precursor gel with a molar composition of $2.3\text{K}_2\text{O}:\text{Al}_2\text{O}_3:0.1\text{SrO}:10\text{SiO}_2:160\text{H}_2\text{O}$ was obtained, where the silica solution was added dropwise to the strontium solution. This step proved to be critical, as the resulting mixture exhibited high viscosity when Ludox® AS-40 was used, to prevent effective stirring. Subsequently, the aluminate solution was added to the mixture, and the resulting gel was stirred for 6 minutes at room temperature. The gel was then transferred to a Teflon-lined stainless-steel autoclave (Parr reactor model 4838) and statically heated at $150\text{ }^\circ\text{C}$ for 72 hours.

Finally, the synthesized product was washed with water using a vacuum filtration system and dried at $100\text{ }^\circ\text{C}$ in an oven overnight. After grinding in an agate mortar and pestle, the product was obtained as a white powder. A summary of the synthesis conditions for all prepared samples is presented in Table 1.

Table 1. Summary of the syntheses studied and nomenclature used.

Aluminum Source	Silica Source	Molar Ratio
Al(OH)₃	Ludox® AS-40	$\text{Al}_2\text{O}_3: 2.3 \text{ K}_2\text{O}: 10 \text{ SiO}_2: 0.1 \text{ Sr}(\text{NO}_3)_2: 160 \text{ H}_2\text{O}$
	Ludox® AM-30	$\text{Al}_2\text{O}_3: 2.3 \text{ K}_2\text{O}: 10 \text{ SiO}_2: 0.1 \text{ Sr}(\text{NO}_3)_2: 160 \text{ H}_2\text{O}$
	TEOS	$\text{Al}_2\text{O}_3: 2.3 \text{ K}_2\text{O}: 10 \text{ SiO}_2: 0.1 \text{ Sr}(\text{NO}_3)_2: 160 \text{ H}_2\text{O}$
Aluminum Wire	Ludox® AS-40	$\text{Al}_2\text{O}_3: 2.3 \text{ K}_2\text{O}: 10 \text{ SiO}_2: 0.1 \text{ Sr}(\text{NO}_3)_2: 160 \text{ H}_2\text{O}$
	Ludox® AM-30	$\text{Al}_2\text{O}_3: 2.3 \text{ K}_2\text{O}: 10 \text{ SiO}_2: 0.1 \text{ Sr}(\text{NO}_3)_2: 160 \text{ H}_2\text{O}$
	TEOS	$\text{Al}_2\text{O}_3: 2.3 \text{ K}_2\text{O}: 10 \text{ SiO}_2: 0.1 \text{ Sr}(\text{NO}_3)_2: 160 \text{ H}_2\text{O}$
Al(O-i-Pr)₃	Ludox® AS-40	$\text{Al}_2\text{O}_3: 2.3 \text{ K}_2\text{O}: 10 \text{ SiO}_2: 0.1 \text{ Sr}(\text{NO}_3)_2: 160 \text{ H}_2\text{O}$
	Ludox® AM-30	$\text{Al}_2\text{O}_3: 2.3 \text{ K}_2\text{O}: 10 \text{ SiO}_2: 0.1 \text{ Sr}(\text{NO}_3)_2: 160 \text{ H}_2\text{O}$
	TEOS	$\text{Al}_2\text{O}_3: 2.3 \text{ K}_2\text{O}: 10 \text{ SiO}_2: 0.1 \text{ Sr}(\text{NO}_3)_2: 160 \text{ H}_2\text{O}$

4.3.2. Study on Crystal Size Reduction

The production of small-sized zeolite crystals is essential for the fabrication of high-quality zeolite membranes, as it directly influences membrane uniformity, density, and selectivity [12,13,77,119]. Smaller crystals promote the formation of compact and continuous layers, minimizing structural defects that could impair membrane performance in separation processes [5,6,79,82,105].

Parameters such as the amount of water in the synthesis of gel, stirring time, and hydrothermal synthesis duration play a critical role in controlling crystal size. The water-to-precursor ratio affects both the nucleation rate and crystal growth, with higher water content favoring the formation of smaller nuclei [120]. The gel stirring time influences reagent homogenization, ensuring a more uniform distribution of nucleation sites. Meanwhile, the hydrothermal synthesis duration dictates crystal growth—shorter durations can limit excessive growth, resulting in smaller particles better suited for membrane formation [20,111,119]. Other studies have explored additional approaches, such as ultrasound-assisted stirring and the use of crystal growth inhibitors, to further reduce crystal size [12,13,77]. Based on these considerations, we conducted a study to investigate and adapt parameters previously reported in the literature to obtain smaller crystals and optimize zeolite membranes aimed at high-performance industrial applications.

Initially, the water ratio was varied using aluminum hydroxide and Ludox® AM-30 as the aluminum and silica sources, respectively, as these materials demonstrated the best crystallinity and purity in the study described in Section 4.3.1. Water molar ratios of 200, 240, 280, and 320 were investigated. A summary of the synthesis conditions for all prepared samples is provided in Table 2.

Table 2. Summary of the syntheses studied and nomenclature used.

Water ratio	Gel stirring time	Hydrothermal synthesis time	Molar ratio
160	6 min	72 h	Al ₂ O ₃ : 2.3 K ₂ O: 10 SiO ₂ : 0.1 Sr(NO ₃) ₂ : 160 H ₂ O
200	6 min	72 h	Al ₂ O ₃ : 2.3 K ₂ O: 10 SiO ₂ : 0.1 Sr(NO ₃) ₂ : 200 H ₂ O
240	6 min	72h	Al ₂ O ₃ : 2.3 K ₂ O: 10 SiO ₂ : 0.1 Sr(NO ₃) ₂ : 240 H ₂ O
280	6 min	72 h	Al ₂ O ₃ : 2.3 K ₂ O: 10 SiO ₂ : 0.1 Sr(NO ₃) ₂ : 280 H ₂ O
320	6 min	72 h	Al ₂ O ₃ : 2.3 K ₂ O: 10 SiO ₂ : 0.1 Sr(NO ₃) ₂ : 320 H ₂ O

4.4. Production of KFI Membranes

4.4.1 Study on Silica Layer Deposition

Aiming to develop a membrane suitable for gas separation applications, an initial step involved the formation of a protective silica layer capable of isolating the macroporous α -alumina support from the zeolite seeds subsequently deposited. This layer serves to prevent zeolite crystal penetration into the internal structure of the support during the crystal growth stage, thereby avoiding performance losses in the final material [19,121].

Silica deposition tests were first conducted on commercial ceramic tubes (Tecnicer Cerâmica, inner diameter: 8 mm, outer diameter: 12 mm). The tubes were cut to an average length of 4.50 cm and cleaned using an ultrasonic bath with isopropyl alcohol, acetone, and deionized water. Each cleaning step lasted 20 minutes per solvent. Following the cleaning process, the silica coating solution was prepared. The goal was to adopt a fast and simplified method for coating the α -alumina tubes using Ludox® AS-40 (Sigma-Aldrich, 40 wt%) as the silica source, as detailed below:

- I. Ludox® AS-40 (liquid reagent at room temperature) was diluted in ethanol under magnetic stirring to obtain a 3 wt% silica solution.

Silica layer deposition was carried out using a dip-coating technique (Figure 18), under the following parameters [19,83,84,86,87,122]

- I. The tubular substrates underwent two immersion cycles, each lasting 30 seconds, with an initial immersion and withdrawal speed of 60 mm/s. However, as reported in the literature, the immersion speed directly influences the thickness and uniformity of the deposited layer [86,87]. Therefore, additional speeds of 30, 90, and 100 mm/s were investigated using the optimized 3 wt% Ludox® AS-40 solution.
- II. After silica deposition, the tubes were dried at room temperature for 20 minutes, followed by drying in an oven at 70 °C for 2 hours between each coating cycle.
- III. Finally, after the drying stage, the tubes were thermally treated in a muffle furnace for 3 hours at 400 °C, with heating and cooling rates of 1 °C/min.

Silica deposition on the tubes produced via the *freeze-casting* technique was performed following the same methodology, with the addition of a single preliminary sanding step to ensure a smooth and defect-free surface. The schematic representation and summary of the experimental conditions are in Figure 18 and Table 3.

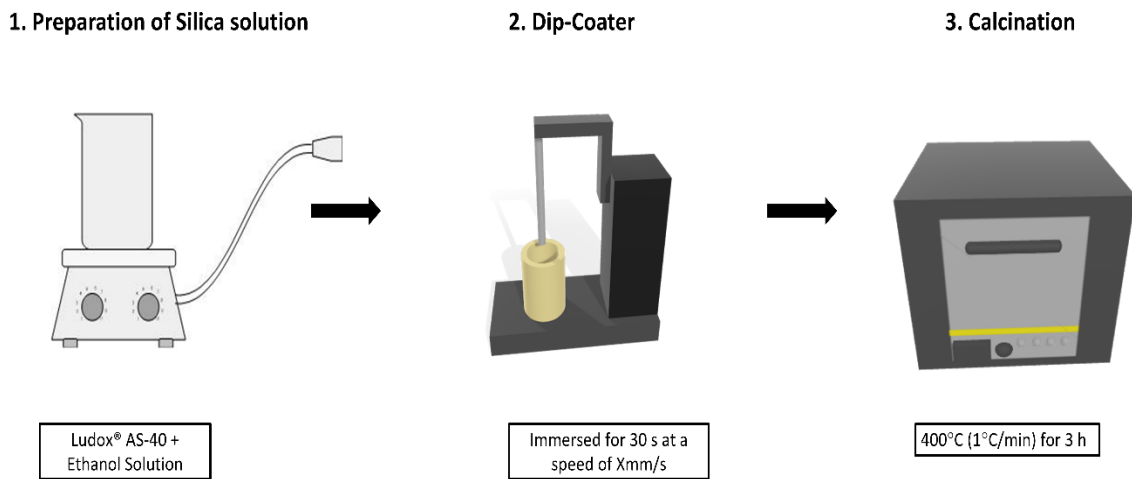


Figure 18. Schematic of silica layer deposition on α -alumina tubes.

Table 3. Summary of the depositions conditions and nomenclature used.

Samples	Tube Type	Silica Solution Concentration (w/w)	N° of depositions	Immersion/ Withdrawal speeds (mm/min)
Tube 1	Commercial	3	2	30
Tube 2	Commercial	3	2	60
Tube 3	Commercial	3	2	90
Tube 4	Commercial	3	2	100
Tube 5	<i>Freeze - Casting</i>	3	2	90

4.4.2 Study on Zeolite Seeds Deposition and Growth of the KFI Membrane

The deposition of KFI zeolite seeds was carried out following the methodology of [123] with some modifications. Initially, seed deposition was performed on commercial silica-coated tubes to determine the optimal conditions for zeolite seeding. The zeolite seed was synthesized using $\text{Al}(\text{OH})_3$ as the aluminum source and Ludox® AM-30 as the silica source, with a water ratio of 200, stirred for 6 minutes, followed by a 3-day hydrothermal synthesis.

To optimize the deposition conditions, the following parameters were investigated: seed suspension concentration (1%, 2%, and 3% in aqueous medium), immersion time (30 and 60 seconds), and number of coating cycles (2 and 3 layers). The immersion speed was fixed at 90 mm/s, with drying between depositions carried out for 20 minutes at room temperature followed by 2 hours at 70 °C. Zeolite membrane synthesis was performed hydrothermally (for 6 and 18 hours) on the outer surface of α -alumina supports, both commercial and those produced via the freeze-casting technique. The support characteristics included an average pore size of 0.1 μm , a diameter of 15 mm, a length of 45 mm, and an effective surface area of 950 mm².

The methodology aimed to develop a simpler and faster approach for zeolite seed layer deposition, as described below:

I. In a 50 mL beaker, the zeolite seed was diluted in water to concentrations of 1%, 2%, and 3% (w/w). This suspension was stirred magnetically for 15 minutes and then sonicated for 10 minutes before starting the deposition process.

II. Zeolite seed deposition was performed using the dip-coating technique (Figure 19), with the following parameters:

- a. The substrates were immersed twice for either 30 or 60 seconds, with immersion and withdrawal performed at a speed of 90 mm/min;
- b. After each deposition cycle, the tubes were dried at room temperature for 20 minutes, followed by oven drying at 70 °C for 2 hours.

III. After the drying stage, the tubes were subjected to thermal treatment in a muffle furnace at 150 °C for 3 hours, with heating and cooling rates of 1 °C/min.

Once the optimal conditions were determined, the optimized methodology was applied using a zeolite seed with a reduced crystal size, obtained from a synthesis gel stirred for 2 hours and hydrothermally treated for 24 hours. This approach was implemented on both commercial tubes and those produced by the freeze-casting method. Figure 19 presents a schematic summary of the membrane synthesis procedure, and on Table 4 presents a summary of the experimental conditions.

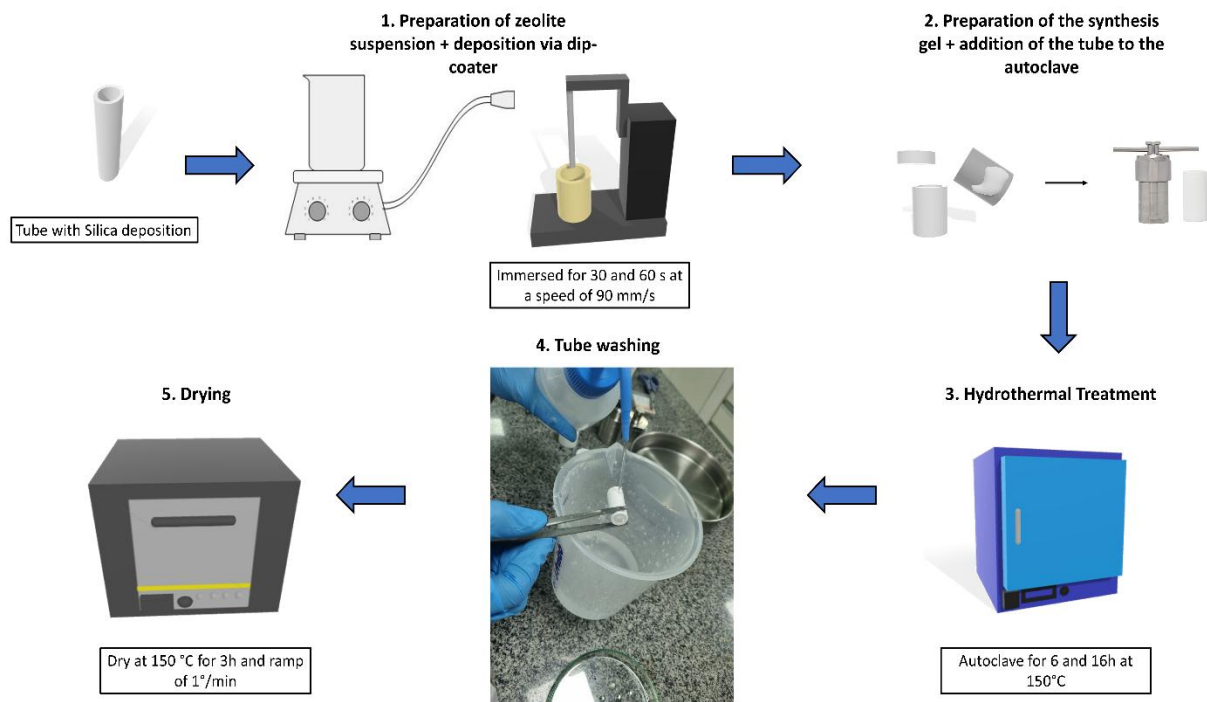


Figure 19. KFI membrane preparation methodology.

Table 4. Summary of the depositions conditions and nomenclature used.

Samples	Tube Type	N° of depositions and immersion time (s)	Seed Concentration (%)	Hydrothermal treatment
Tube 1	Commercial	2; 30 s	1	16
Tube 2	Commercial	3; 30 s	1	16
Tube 3	Commercial	2; 30 s	2	16
Tube 4	Commercial	3; 30 s	2	16
Tube 5	Commercial	2; 30 s	3	16
Tube 6	Commercial	3; 30 s	3	16
Tube 7	Commercial	2; 60 s	1	6
Tube 8	Commercial	3; 60 s	1	6
Tube 9	Commercial	2; 60 s	2	6
Tube 10	Commercial	3; 60 s	2	6
Tube 11	Commercial	2; 60 s	3	6
Tube 12	Commercial	3; 60 s	3	6
Tube 13	Commercial	2; 60 s	1	16
Tube 14	Commercial	3; 60 s	1	16
Tube 15	Commercial	2; 60 s	2	16
Tube 16	Commercial	3; 60 s	2	16
Tube 17	Commercial	2; 60 s	3	16
Tube 18	Commercial	3; 60 s	3	16
Tube 19	<i>Freeze - Casting</i>	3; 60 s	2	6
Tube 20	<i>Freeze - Casting</i>	3; 60 s	2	16

4.5. Characterization Techniques

In the absence of explicit mention of the equipment location or responsible personnel, characterization techniques were carried out at the Laboratory of Nanostructured Ceramic Materials (LMCNano) of the Faculty of Technology, University of Brasilia (FT/UnB), or at its annex located at SG9.

4.5.1. Characterization of Ceramic Supports

4.5.1.1. Scanning Electron Microscopy (SEM)

SEM images were obtained at the Laboratory of Geodynamic, Geochronological and Environmental Studies (LEGGA) of the Institute of Geosciences, University of Brasilia (UnB), using a FEI Quanta 450 microscope equipped with a low-vacuum secondary electron detector (LFD), operating at 10–20 kV. Additional images were acquired at the Laboratory of Microscopy and Microanalysis, Institute of Biological Sciences (UnB), using a JEOL JSM-7001F microscope with a secondary electron (SE) detector, operating at 10–20 kV. Further analysis was performed at the Microscopy Center of the Federal University of Minas Gerais (UFMG) using a Thermo Fisher/FEI Quanta 200 FEG microscope with an ETD secondary electron detector, operating at 5–20 kV.

Samples were mounted on carbon tape and sputter-coated with carbon. Magnifications ranging from 50x to 20,000x were employed. Particle size analysis was performed using ImageJ software (version 1.54d), developed by the National Institutes of Health (NIH), based on an average of 300 particles per sample.

4.5.1.2. X-ray Microcomputed Tomography (μ CT)

X-ray microtomography was employed to assess the three-dimensional morphology of the alumina monoliths using a μ CT – HeliScan MKI (FEI). Acquisitions were conducted using Qrumba software version 1.1.2.231 under operating conditions of 100 kV, 70 μ A current, 1 $\times$ 1 camera binning, and a maximum voxel size of 6.6 μ m.

Image data were processed and reconstructed in 3D using the Pymango software package. Total porosity and pore size distribution were analyzed using AMIRA-AVIZO 3D software.

4.5.1.3. Archimedes Method

The porosity of the ceramic samples was measured by the Archimedes method, according to ASTM B962-13. This method is based on Archimedes' principle, which states that an object submerged in a fluid experiences a buoyant force equal to the weight of the displaced fluid. This allows determination of the sample volume and, consequently, its porosity [124].

The dry mass (m_s) of the ceramic material was first measured in air. Then, the immersed mass (m_i) was recorded using the apparatus shown in Figure 20. After immersion, the sample was promptly removed from the liquid, gently wiped with damp cotton to remove surface water, and weighed again to determine the wet mass (m_u).

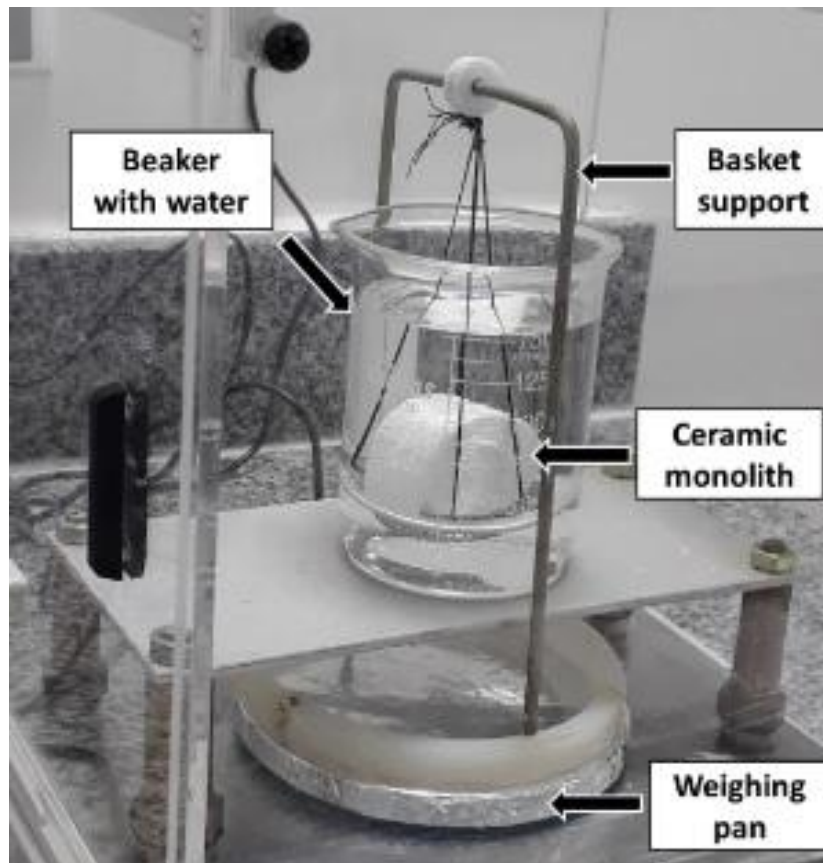


Figure 20. Measurement by the Archimedes method of mass of a ceramic monolith submerged in water.

The measured values were used to calculate the apparent volume (V_a), the open pore volume (V_{pa}), and the solid volume (V_s) of the samples using equations (9), (10), and (11), respectively.

$$V_a = \frac{m_u - m_i}{\rho_{H_2O}} \text{ Equation 9}$$

$$V_{pa} = \frac{m_u - m_s}{V_a} \text{ Equation 10}$$

$$V_s = \frac{m_u - m_i}{\rho_s} \text{ Equation 11}$$

Where, ρ_{H_2O} is the density of water (0,998 g/cm³) and ρ_s is the density of the solid (Al₂O₃ = 3,97 g/cm³). Subsequently, the total porosities were calculated according to equations (12) and (13):

$$\textbf{Total Porosity (\%)} = \frac{V_a - V_s}{V_a} \text{ Equation 12}$$

$$\textbf{Open Porosity (\%)} = \frac{V_{pa}}{V_a} \text{ Equation 13}$$

4.5.1.4. Mechanical Compression Tests

The compressive strength tests were performed uniaxially on cylindrical samples ($\Phi 1.45$ cm $\times$ 1.45 cm), with a minimum of 7 samples per system. The tests were carried out at the Nuclear Technology Development Center (CDTN) of the Federal University of Minas Gerais (UFMG), using a universal testing machine (model 5882, 5 kN load cell, Instron) at a strain rate of 0.5 mm/min.

4.5.2 Zeolite Characterization

4.5.2.1. Powder X-Ray Diffraction (XRD)

Diffraction patterns of the zeolite samples were obtained using a Shimadzu Lab XRD-6000 diffractometer with CuK α radiation ($\lambda = 0.15409$ nm) operating at 40 kV and 30 mA. Scans were performed at 0.2°/min step size and 0.02° increment over a 2θ range from 5° to 40°. Zeolite identification was carried out by comparing the five most intense peaks to the KFI zeolite standard.

The interplanar spacing d_{hkl} for the (100) structural plane was calculated using Bragg's law (Equation 14):

$$n \cdot \lambda = 2 \cdot d_{hkl} \cdot \sin \theta \quad \text{Equation 14}$$

For a cubic system, the unit cell parameter a_0 is given by:

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \quad \text{Equation 15}$$

Combining the above, we obtain:

$$a_0^2 = \frac{\lambda^2}{4 \left(\frac{\sin^2 \theta}{h^2 + k^2 + l^2} \right)} \quad \text{Equation 16}$$

In Equation 14, n is an integer (considered as 1), λ is the X-ray wavelength, and θ is the incidence angle. In Equation 15, h, k, l are the Miller indices, and a_0 is the cubic unit cell parameter. Calculations were performed using OriginPro 2018 (version 9.5.1.195).

The crystallite size (D) estimated by Equation 17 was also calculated,[125] while the crystallinity of the samples was calculated using the method already reported in the literature and is found in Equation 18 [69,126]. The standard for comparison of the peaks and phases used was synthesized by Lievens in 1992 and presents the ICSD standard 1629739 [127].

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \quad \text{Equation 17}$$

$$\% \text{ Crystallinity} = \frac{\text{Crystalline Area}}{\text{Amorphous Area}} \cdot 100 \quad \text{Equation 18}$$

In Equation 17, K is a constant related to the shape of the crystallites of the analyzed phase (0.94 for circular/spherical shape), and β is the full width at half maximum (FWHM) of the 200-reflection peak (obtained by fitting the signal with a *Voigt* peak). In Equation 18, the Crystalline Area was obtained by calculating the area under the diffraction peaks of the samples, while the Total Area was calculated as the total area of all diffraction peaks of the samples. The reaction yield (based on mass) was also calculated to assess the influence of different aluminum and silicon sources in the syntheses and the water ratio on the final yield [119]. The software

used for processing data and generating all graphs was OriginPro 2018 (version 9.5.1.195) from OriginLab Corporation.

4.5.2.2. Fourier Transform Infrared Spectroscopy in Attenuated Total Reflectance Mode (FTIR-ATR)

Infrared spectra were obtained using a Nicolet iS50 spectrometer (Thermo Fisher). Spectra were acquired in transmission mode, with 64 scans and a resolution of 4 cm^{-1} in the range $3500\text{--}400\text{ cm}^{-1}$. Data processing and graph generation were performed using OriginPro 2018 (version 9.5.1.195) from OriginLab Corporation.

4.5.2.3. Solid-State Nuclear Magnetic Resonance Spectroscopy (RMN-SS).

NMR-SS spectra of the zeolite samples were acquired on a Bruker Magneto Ascend 600 Console Avance III HD spectrometer at the analytical center of the Institute of Chemistry at UnB. The instrument operates in a magnetic field of approximately 14 T (corresponding to 600 MHz for ^1H) and is equipped with a 4 mm probe. Samples were packed into zirconia rotors with Torlon caps under the following conditions for each nucleus:

- For ^{29}Si (119,237 MHz), spinning at 10 kHz with heteronuclear decoupling, a pulse of $4.25\text{ }\mu\text{s}$ ($\pi/4$) and a 20 s pulse delay, totaling 2048 acquisitions per spectrum. Tetramethylsilane ($\delta = 0\text{ ppm}$), $\text{Si}(\text{CH}_3)_4$ was used as the external standard.
- For ^{27}Al (156,4 MHz) spinning at 10 kHz with heteronuclear decoupling, a pulse of $0.4\text{ }\mu\text{s}$ ($\pi/4$) and a 1 s pulse delay, totaling 512 acquisitions per spectrum. The standard was a 0.1 M solution of aluminum nitrate (III) in deuterated water ($\delta=0\text{ ppm}$).

All data were processed using SpecManager (version 10.8, ACD/Labs) and OPUS (version 3.1, Bruker). Deconvolution was performed using OMNIC software (version 8.0.342, Thermo Fisher Scientific) and modeled using the Voigt function. Quantification of each chemical environment was performed by deconvoluting the NMR signals in the peak regions, using the relative percentages of each signal area [58].

Where TTT can be Si or Al. The Si/Al ratio in the zeolite framework can be calculated from the intensity of the peaks corresponding to different chemical environments, according to the equation below [68].

$$\frac{Si}{Al} = \frac{\sum_{n=0}^4 I_{Si(nAl)}}{\sum_{n=0}^4 \left(\frac{n}{4}\right) I_{Si(nAl)}} \quad \text{Equation 19}$$

Where $I_{Si(nAl)}$ is the intensity of the NMR signal attributed to the Si(nAl). The software used to obtain all graphs was OriginPro 2018 (version 9.5.1.195) from OriginLab Corporation.

4.5.2.4. Scanning Electron Microscopy (SEM)

The microscopy images were obtained using a JEOL instrument, model JSM 7100F, equipped with a low-energy detector (LED) operating under high vacuum, and coupled with an EDS system from Thermo Scientific, model NSS Spectral Imaging, operating at an accelerating voltage of 5 kV and 18 mA. Samples were metallized, mounted on carbon tape, and coated with sputtered carbon. Imaging was performed under high vacuum conditions. Particle size measurements of the ceramic samples were conducted using the software ImageJ (version 1.54d) from the *National Institutes of Health* (NIH), with an average of 400 particles counted.

4.5.2.5. Textural Analysis

The textural properties of the synthesized materials were assessed through nitrogen adsorption isotherms obtained at 77 K (-196 °C) using a Quantachrome Instruments Autosorb model 7 IQ-XR-XR (2 stations). Before adsorption measurements, samples were degassed by heating under vacuum at a rate of 5 °C/min for 30 minutes at 80 °C and 10 hours at 150 °C.

The specific surface area (combining micropore and external surface areas) was calculated from the nitrogen adsorption isotherms using the Brunauer-Emmett-Teller (BET) method [128,129] in the relative pressure range P/P_0 from 0.007 to 0.30.

$$\frac{p/p_0}{n(1-p/p_0)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} (p/p_0) \quad \text{Equation 20}$$

$$a_s(BET) = n_m \cdot L \cdot \sigma_m / m \quad \text{Equation 21}$$

Where n is the specific amount adsorbed at relative pressure p/p° , n_m is the monolayer capacity, C is a parameter exponentially related to the adsorption energy of the monolayer, σ_m

is the molecular cross-sectional area, and a_s (BET) is the specific surface area of the adsorbent with mass m [128,129].

Using the nitrogen desorption isotherm and applying the t-plot method provided by the Quantachrome data reduction software (modeling by the de Boer method) in the relative pressure range P/P_0 from 0.15 to 0.50, the micropore area, external surface area, and micropore volume were calculated. Pore volume and pore size were obtained from the adsorption branches using the non-local density functional theory (NLDFT) model provided by the Quantachrome data reduction software (modeling of Ar at 87 K in a zeolite/silica with spherical/cylindrical pores).

4.5.3 Characterization of KFI Membranes

4.5.3.1. Scanning Electron Microscopy (SEM)

The microscopy images were acquired using a JEOL JSM 7100F instrument equipped with a low energy detector (LED) operating under high vacuum, coupled with an EDS system from Thermo Scientific, model NSS Spectral Imaging, operating at 5 kV and 18 mA. Samples were metallized, supported on carbon tape, and coated with sputtered carbon. Imaging was performed under high vacuum conditions.

4.5.3.2. X-ray Microcomputed Tomography (μ CT)

X-ray microcomputed tomography images were obtained to evaluate the three-dimensional morphology of alumina monoliths using a μ CT – HeliScan MKI, FEI. Acquisitions were performed using the software Qrumba 1.1.2.231 under the conditions of 100 kV voltage, 70 μ A current, 1×1 camera binning, and a maximum voxel size of 6.6 μ m. The Pymango software was used for data processing and 3D reconstruction of monolith images. To assess total porosity and pore size distribution, reconstructed images were processed using AMIRA-AVIZO 3D software.

4.5.3.3. Gas Adsorption and Separation prediction on Zeolitic Materials

The characterization of gas adsorption equilibrium on the KFI zeolite was performed to determine the adsorption capacity and selectivity of the sample under conditions relevant to gas separation processes. Single-component adsorption isotherms were measured using a Quantachrome Instruments Autosorb model 7 IQ-XR-XR (2 stations) over a pressure range of 0 to 1 bar at 298 K. Prior to measurements, the samples were degassed under vacuum by heating at a rate of 5 °C/min for 10 hours at 150 °C to remove impurities and pre-adsorbed water molecules.

The experimental single-component adsorption equilibrium data for each gas (adsorbed amount, q , as a function of pressure, P) were fitted using the Langmuir isotherm model (Equation 1). Despite its simplicity, this model is widely employed for microporous materials such as zeolites and assumes that adsorption occurs in a monolayer, where all adsorption sites are energetically equivalent and no interactions occur between adsorbed molecules at adjacent sites [12,74,96,98].

Selectivity was calculated based on the Ideal Adsorbed Solution Theory (IAST) who allows us the calculation of the thermodynamic selectivity of the zeolite for the separation of component i relative to component j ($\alpha_{i/j}$) under a given total pressure (P_{total}) and gas-phase composition (y_i, y_j) (Equation 3).

RESULTS

AND

DISCUSSION

5. RESULTS & DISCUSSION

5.1. Characterization of Monoliths Produced via *Freeze-Casting*

5.1.1. Structural Characterization Based on SEM and μ CT Images

Microscopy analyses were employed to investigate the pore morphology formed during the freezing stage of the freeze-casting process. Figure 21 presents SEM micrographs along the axial plane of samples synthesized using camphene as the solvent, with solid loadings of 15, 20, and 25 vol% alumina, produced in different molds. The pore structure exhibits a well-defined dendritic pattern [27,28,48]. For all three mold types, minimal formation of agglomerates was observed, indicating effective dispersion of the solute in the solvent medium [29,30,48].

The dispersant EFKA FA 4663 was instrumental in reducing the aggregate size of alumina particles suspended in camphene, thereby enhancing the development of dendritic structures during solidification and increasing the resulting pore size [29,48]. This improvement is attributed to the increase in the critical particle engulfment velocity (V_{cr}), as proposed by Stefanescu [48], described in Equation 21, where D represents the particle diameter. Below this critical velocity, particles are repelled rather than entrapped by the advancing solidification front. Consequently, camphene crystals could grow by pushing the solute particles over a broader velocity range, leading to the formation of fine dendritic structures with elongated pores and small branches.

$$V_{cr} \approx \frac{1}{D} \quad \text{Equation 21}$$

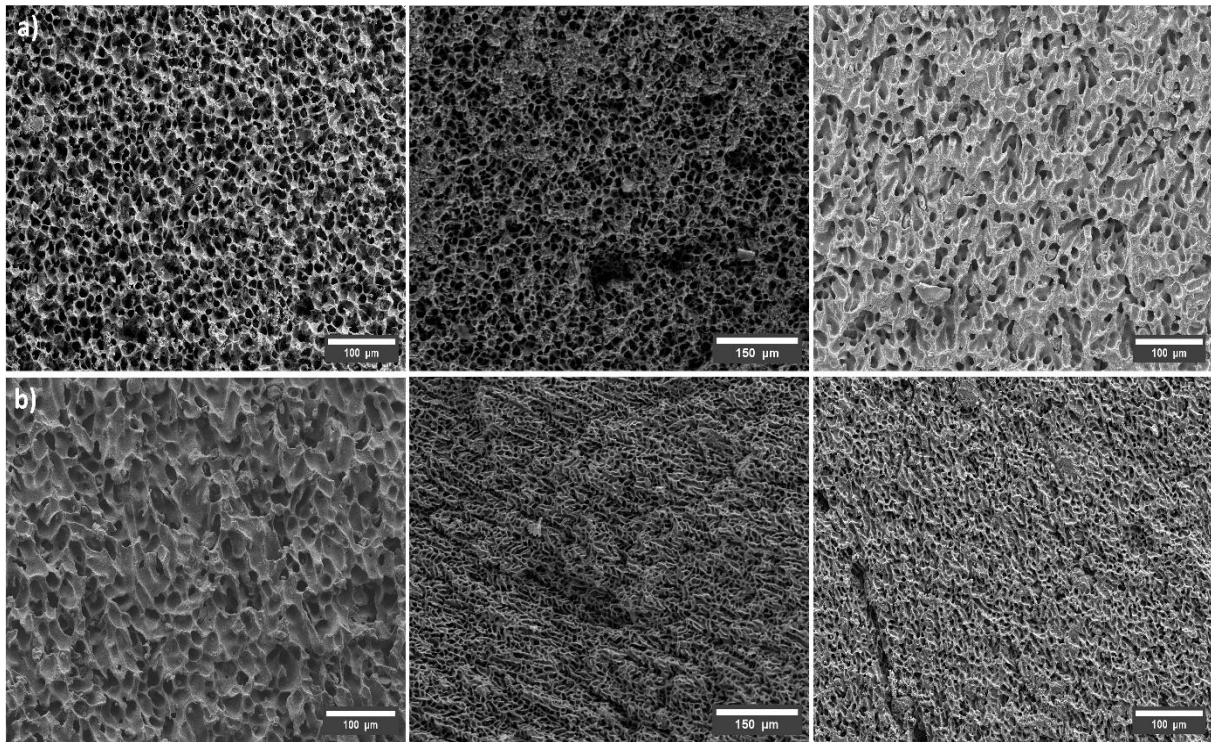


Figure 21. SEM images at 200× magnification of the longitudinal section of the α -Al₂O₃ monoliths, solids loading of 15, 20 and 25 vol%, solids loading (left to right): (a) technyl mold; (b) copper mold.

Wang *et al.* [43] highlighted in their study that the use of molds with low thermal conductivity, such as polyacetal (technyl), promotes the unidirectional growth of crystals—meaning that the pore structure develops from the bottom to the top of the samples. Additionally, the resulting pores exhibit a highly anisotropic morphology within the solidification plane. For the samples produced using this mold, micrographs (Fig. 22 (a)) revealed that in the lower region of the samples—closer to the bottom of the mold and in direct contact with the copper rod—rapid cooling led to accelerated camphene crystal formation due to the high solidification front rate, facilitated by the unidirectional growth promoted by the low thermal conductivity of technyl [48]. The nucleation and growth of numerous dendritic crystals colliding with one another resulted in an interconnected solid structure, which pushed the particles into the interdendritic spaces, yielding branched and densely packed pores [33,130].

By comparing the microstructural cross-section images of the samples produced using the copper mold (Fig. 21 (b)), notable differences in microstructure can be observed. The morphology of the dendritic connections in this case formed more aligned pore structures, with nearly continuous pore channels along the transverse section [29,130]. This is attributed to the

faster heat transfer from the copper base toward the top of the monolith [131]. The distinct physical properties of each mold material enabled the samples to freeze at different cooling rates, even when the suspensions were at similar initial temperatures [43]. As the suspension in contact with the copper rod began forming frozen solvent layers, the cooling rate decreased with increasing distance from the copper base. Meanwhile, the thermal gradient along the mold walls remained, increasing the radial cooling rate and thus promoting bidirectional crystal growth. As a result, the formed ceramic dendrites were broader, and the pore channels became larger and more elongated [22,131,132].

The main influence of solid loading variation is observed in the total porosity of the material, since suspensions with higher solid content contain less solvent, thereby producing samples with lower porosity [27]. However, the effect of solid content on the final structure can also be observed in the micrographs (Fig. 21). This occurs because an increase in solid content may hinder the rejection of particles at the solidification fronts, especially when particle agglomeration is present, leading to the formation of thicker pore walls in the final ceramic material as the solid content increases [22,28,31]. Moreover, the presence of additional solid particles provides more sites for heterogeneous nucleation during solvent freezing, resulting in a more homogeneous pore structure.

SEM images of the samples fabricated using the technyl/copper mold, along with a schematic representation of the mold and the proposed cooling front, are shown in Figure 22. It can be observed that in the region defined as the transition zone—where the solidification fronts from the technyl wall and the copper wall converge—a perpendicular alignment of the pores was formed. The portion of the ceramic material adjacent to the copper side of the mold exhibited more aligned structures, forming continuous channels that became less evident near the transition region. Eventually, the structure transitioned to the one observed on the technyl side, where the formed dendrites displayed lower pore alignment.

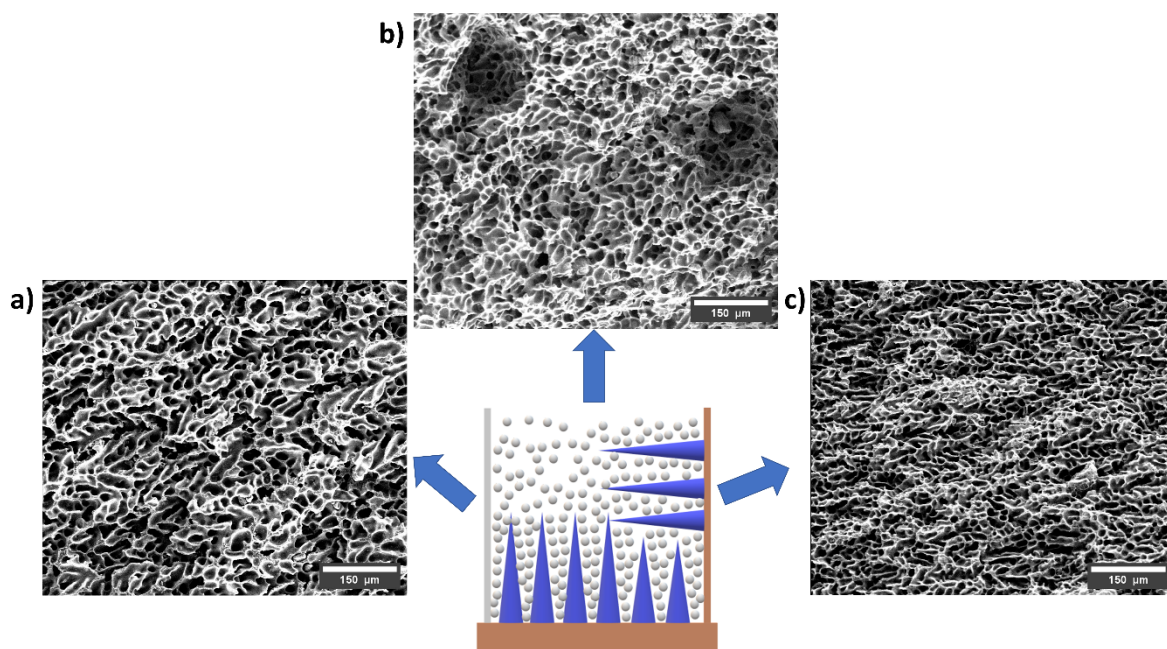


Figure 22. SEM images with different magnifications of the longitudinal section of α -Al₂O₃ monoliths, solid load of 20 vol%. for the technyl-copper mold with a magnitude of 200x: (a) technyl region; (b) transition region; (c) copper region.

The phenomenon observed in the so-called transition region is attributed to the low thermal conductivity of the technyl portion of the mold ($0.23 \text{ W} \cdot \text{m}^{-1} \text{ K}^{-1}$ at 293 K [133]) compared to the high thermal conductivity of the copper section ($400 \text{ W} \cdot \text{m}^{-1} \text{ K}^{-1}$ at 170 K [134]). This contrast in thermal conductivity caused the copper side to cool more rapidly than the technyl side, resulting in a temperature gradient not only in the vertical direction (associated with the unidirectional freezing front) but also in the horizontal direction, thereby promoting bidirectional solidification. Solvent crystals were initially nucleated on the copper side of the mold and subsequently grew in a long-range dendritic pattern oriented by the temperature gradient along both vertical and horizontal directions [135].

To further elucidate the phenomena involved in camphene freezing during the *freeze-casting* process, three-dimensional reconstructions were obtained via X-ray microcomputed tomography (μ CT), using the AMIRA-AVIZO 3D software. This analysis aimed to investigate the influence of different mold materials on the final structure of the produced monoliths. Figures 23 (a), 24 (a), and 25 (a) display the samples sectioned parallel to the freezing direction. For any analysis using this software, it was first necessary to isolate the relevant voxels, which typically involved selecting appropriate thresholding values and slicing parameters. In Figures 23, 24, and 25 (b), (c), and (d), the applied thresholding process is shown, which differentiates

voxels with positive intensity values (gray or white) from those with negative values (black), assigning a value of 1 to non-zero voxels to distinguish solid material from empty space (pores) within the software.

This step enabled the quantification of various parameters, including relative material volume, porosity, and pore surface area, as well as the overall macrostructure of the monolith. For the sample produced using the technyl mold (Fig. 23), the 3D reconstructions confirmed the unidirectional growth of the pore channels in the resulting materials. The sample exhibited a denser structure, in agreement with the observations from the SEM micrographs.

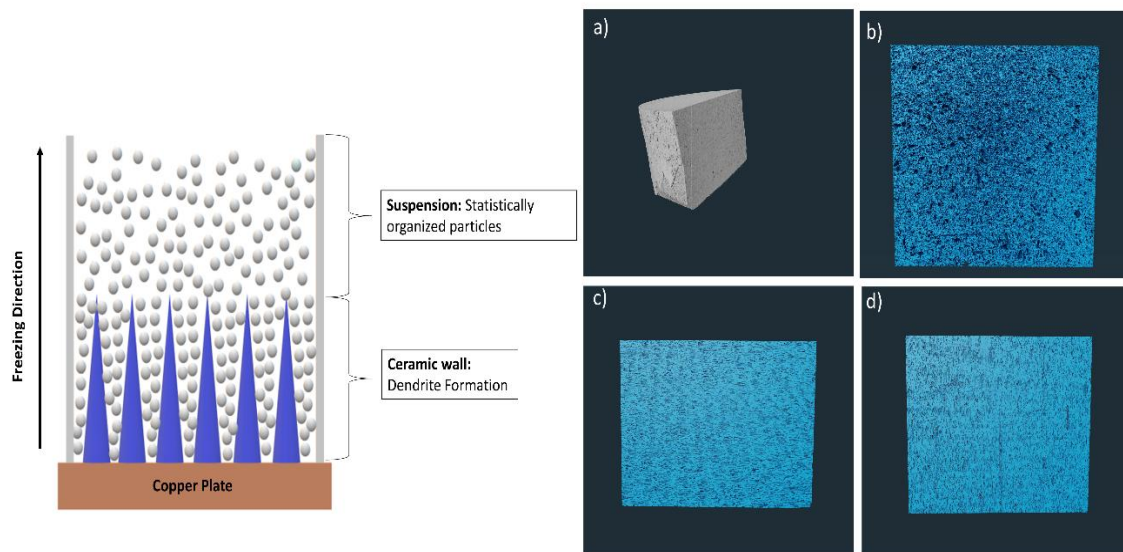


Figure 23. On the left side there is a representation of the freezing direction in the mold used and on the right side (a) 3D reconstruction of the α - Al_2O_3 monoliths with a solid load of 20% produced in the cutting of the technyl mold; (b) removal of a central subvolume representative of the porosity of the material with front, (c) side and (d) top views.

As shown in Figure 24, the ceramic material produced using copper mold exhibits a temperature gradient distribution along the length of the cylindrical mold, from bottom to top. As the freezing front advances, the temperature at any given position within the mold gradually decreases, maintaining a consistent temperature gradient. Camphene in the suspension freezes upon contact with two distinct cold sources: one in the axial direction, corresponding to the copper rod at the bottom of the system, and another in the radial direction, related to the mold walls [136].

Figure 24 (b) reveals the formation of a conical cavity with its apex at the center of the sample, resulting in a bulging effect at the top of the monolith. Although some studies in

literature have employed bidirectional freezing, to the best of our knowledge, none have reported the emergence of such a cavity in the resulting materials. It is believed that one of the primary factors contributing to this phenomenon in the present work is the use of temperatures very close to that of liquid nitrogen, combined with a temperature control system capable of maintaining an almost constant thermal gradient throughout the freezing process. In contrast, previous studies typically employed freezing temperatures ranging from 0 to $-50\text{ }^{\circ}\text{C}$, without precise temperature control [42,43,131,136–138].

Therefore, the extremely low freezing temperature of $-170\text{ }^{\circ}\text{C}$ significantly influenced the nucleation and growth behavior of camphene crystals. Under such conditions of deep supercooling, the nucleation rate of camphene surpassed the crystal growth rate, resulting in the formation of a large number of small crystals. Consequently, the final porous microstructure exhibited uniform and fine pores [22,49,50].

Another contributing factor to the formation of this cavity was the disparity in thermal conductivity between copper and technyl. The copper mold cooled more rapidly when in contact with the copper rod immersed in liquid nitrogen. This difference in thermal conductivity enabled the copper mold to initiate a secondary freezing front at the mold's edges, promoting initial nucleation in these regions—contrary to the behavior observed in the monolith produced using the technyl mold, where nucleation occurred unidirectionally from the base near the copper rod [139].

Hence, the formation of the central cavity in the sample likely resulted from the opposing forces of camphene crystal growth converging toward the center, where the three possible freezing fronts generated during the *freeze-casting* process intersected, causing a collapse in that region.

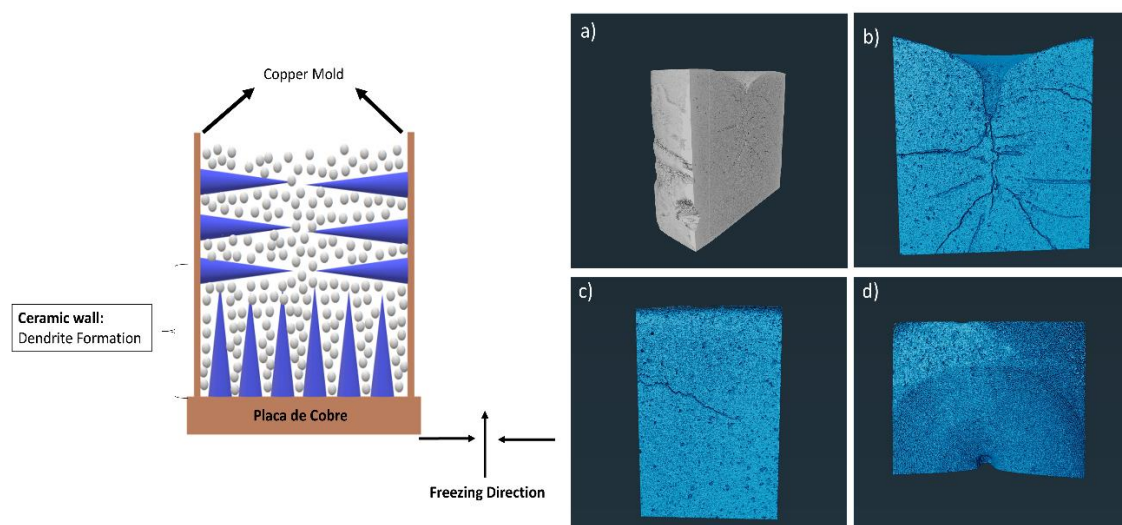


Figure 24. On the left side there is a representation of the freezing direction in the mold used and on the right side (a) 3D reconstruction of the α - Al_2O_3 monoliths with a solid load of 20% produced in the cutting of the copper mold; (b) removal of a central sub subvolume representative of the porosity of the material with front, (c) side and (d) top views.

Figure 25 presents images of the monoliths produced using the technyl/copper mold, where the formation of a cavity is once again observed. However, in this case, the cavity was displaced toward the technyl region of the mold, confirming the hypothesis that the copper section of the mold served as a potential source for the initiation of an additional freezing front. The formation of the cavity near the copper region was likely the result of the collapse of freezing fronts—propagating both axially and radially—within the technyl region, as a consequence of the significant difference in thermal conductivity between the two materials.

Another possible explanation for this phenomenon, contributing to cavity formation, is related to the polarity of the solvent used in the *freeze-casting* process. Tang *et al.* [136], in their study, reported the fabrication of alumina monoliths using water (a polar solvent) as the dispersing medium and copper molds, in which no cavity formation was observed in the final monoliths. Therefore, given that camphene (a non-polar solvent) was used as the dispersing medium in the present work, it is hypothesized that the solvent's polarity may influence the number of nucleation sites, thereby affecting the grain growth process and the development of porosity in the monolithic structures.

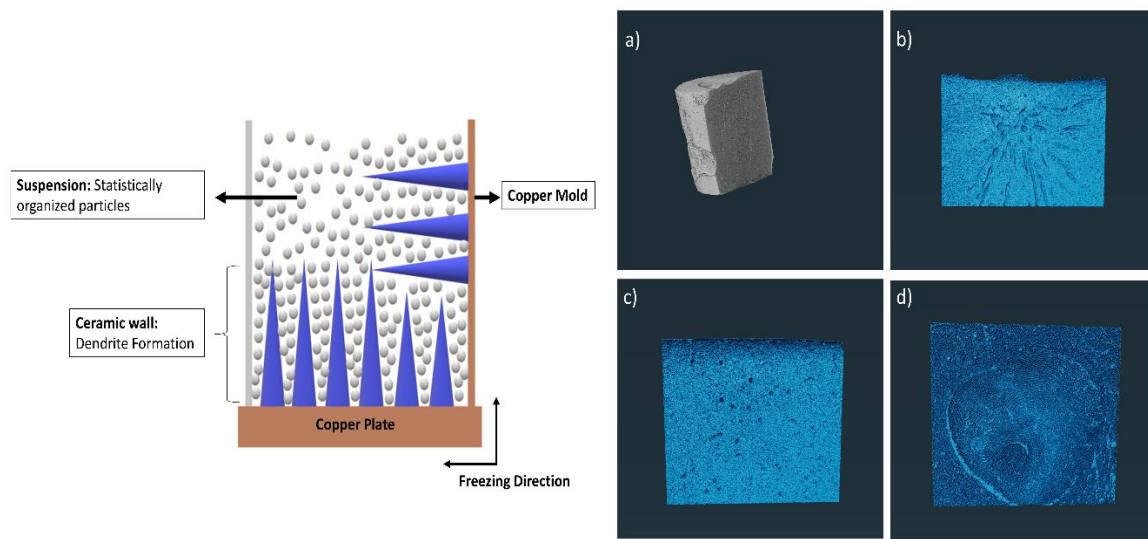


Figure 25. On the left side there is a representation of the freezing direction in the mold used and on the right side (a) 3D reconstruction of the α - Al_2O_3 monoliths with a solid load of 20% produced in the cutting of the technyl/copper mold; (b) removal of a central subvolume representative of the porosity of the material with front, (c) side and (d) top views.

Freezing conditions can significantly influence the homogeneity of the microstructure and the morphology of the pores, affecting both the solidification and dispersion processes, and preventing the entrapment of particles at the solidification fronts. In this context, an analysis of the grain size distribution of α - Al_2O_3 after the sintering stage was conducted, as illustrated in Figure 26, for samples produced with 20% solid loading.

The grain size distribution for the sample produced using the copper mold was more narrowly concentrated around $0.443 \pm 0.010 \mu\text{m}$, whereas the average grain size was $0.606 \pm 0.036 \mu\text{m}$ for the sample prepared with the technyl mold and $0.485 \pm 0.006 \mu\text{m}$ for the sample produced with the technyl/copper mold.

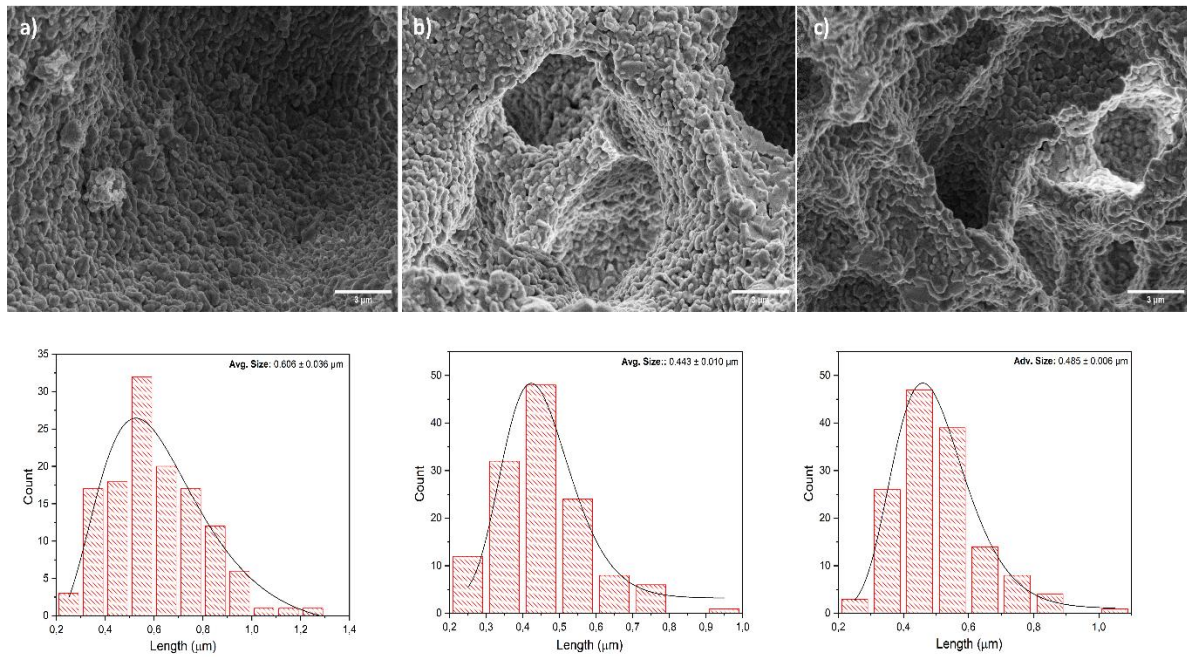


Figure 26. SEM images of the longitudinal section of α -Al₂O₃ monoliths, 20% solid loading by volume for the molds a) technyl; b) copper and c) technyl/copper, including the particle size histogram.

In the literature, it is noted that grain growth can occur when the density of the green body (i.e., the material after the freezing step and before sintering) is affected by a redistribution and increase in solid concentration during the solidification phase. The solidification of a more dilute suspension can lead to particle redistribution if the solid/liquid interface pushes the particles instead of engulfing them, resulting in an increased concentration of particles in the remaining liquid phase [49,140].

However, a slight reduction in the average grain size was observed for the sample produced using copper mold. This may be attributed to the deep supercooling conditions at $-170\text{ }^{\circ}\text{C}$, which promoted an extremely rapid solidification front (estimated at approximately $102\text{ }\mu\text{m/s}$ [50]), causing near-instantaneous freezing of the particles closest to the base of the monolith (i.e., the denser region), in direct contact with the surface of the copper rod located at the base of the *freeze-casting* system [131]. This effect releases heat into the system, leading to a deceleration of the solidification front and the formation of a temperature gradient along the length of the material. Consequently, a more gradual solidification occurs, resulting in the characteristic morphology and porosity of the structure [40,50,132].

It is well established that under high cooling rates, nucleation is kinetically more favorable than crystal growth; therefore, a porous structure with smaller pore diameters can be achieved [44]. Deville *et al.* [141] employed high-resolution X-ray tomography to study the solidification

process of particles with varying sizes and under different cooling rates and observed a correlation between the velocity of the solidification front and the final structure obtained. Thus, the use of molds with different thermal conductivities results in distinct cooling rates during solvent freezing, leading to morphological variations along the freezing direction. In the case of the monolith produced with the copper mold, the increased cooling rate likely enabled more efficient particle rearrangement and packing, thereby reducing the grain size along the solidification direction [47].

5.1.2. Physical and Mechanical Characterization Based on Porosity and Mechanical Compression Data.

Figure 27 presents the total and open porosity values obtained using the Archimedes method, as well as the total porosity calculated using the AMIRA-AVIZO 3D software from microcomputed tomography (μ CT) images for the alumina monoliths produced with different molds.

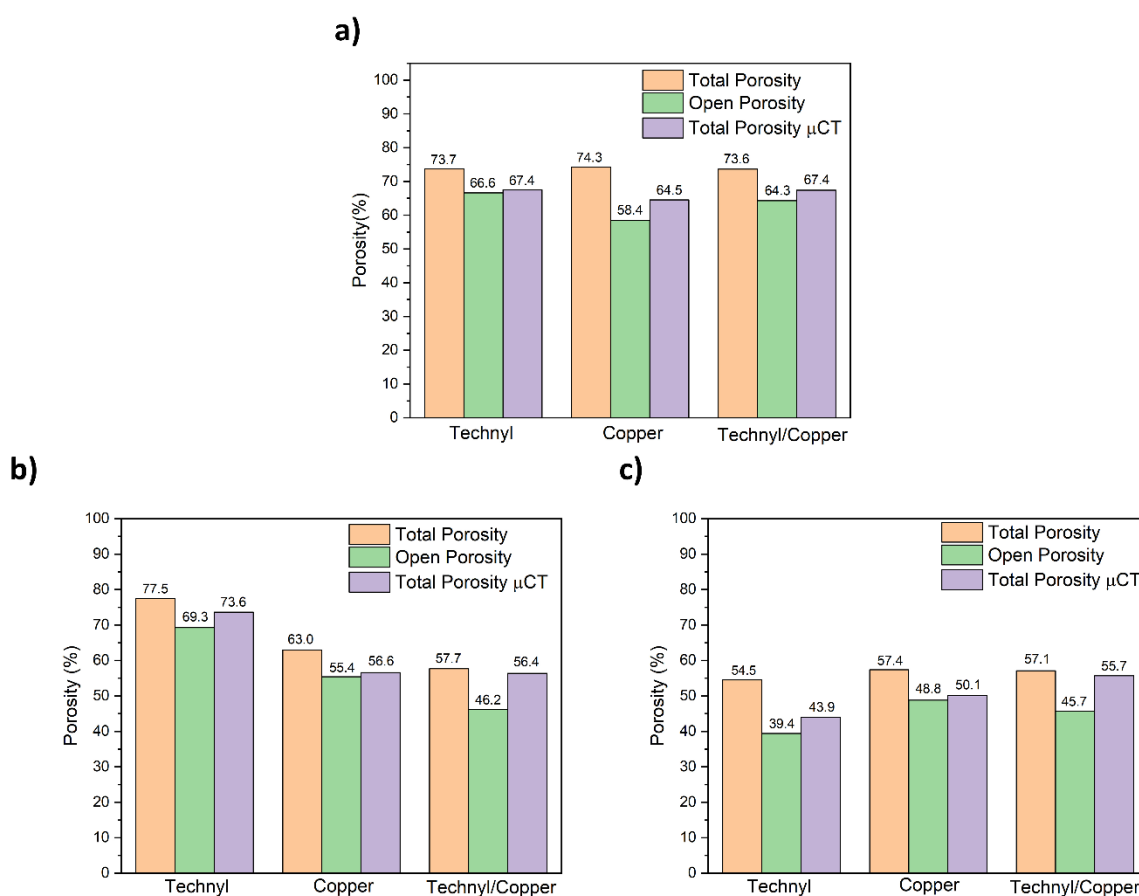


Figure 27. Total and open porosity and total porosity by μ CT of α -Al₂O₃ monoliths prepared with solids concentration of a) 15 vol%, b) 20 vol% and c) 25 vol% using technyl, copper and technyl/copper molds.

When considering only the variation in solid content within the suspension, it is known that the porosity of the sintered materials replicates the original structure of the solvent. In cases where solidification is unidirectional, porous channels are formed from the bottom to the top of the samples. Total porosity, defined as the sum of closed and open porosity (with open pores being highly permeable and interconnected, and closed pores being isolated or connected only to adjacent pores without permeability), can be adjusted by varying the amount of alumina and solvent in the original suspension. Another influential factor is the freezing kinetics [27,33,142].

Analyzing the variation in solid content, it was observed that total porosity (Fig. 27) ranged from approximately 70% to 50% for suspensions containing 15% and 25% solid volume, respectively. The suspensions with 15 vol% alumina exhibited the highest total porosity across all mold types when compared to the other systems. This result was expected [31], as lower solid loadings correspond to higher solvent content, and therefore lead to higher porosity. The process is fundamentally based on the interaction between solid particles and solidification front. During freezing, the solvent solidifies, and the higher solvent volume (inversely proportional to solid content) leads to a larger pore volume, and vice versa [30,131].

Through μ CT images and the AMIRA-AVIZO 3D software, it was also possible to generate a pore network simulating voids and channels—an extremely useful tool to determine the degree of pore interconnectivity, presence of defects (such as bubbles or cracks that may occur during suspension pouring, freezing, or sublimation steps), as well as to assess open and closed porosity. As this type of analysis requires high computational power, pore network modeling is not always cost-effective compared to the Archimedes method.

The results (Fig. 27) revealed only a small variation in porosity values measured by the Archimedes method—around 5%—indicating that the dispersion and freezing methodologies were effective, as non-uniform samples could result in discrepancies between porosity values obtained by different techniques. As seen in Figures 23–25, μ CT proved essential in detecting internal defects, including visible bubbles (e.g., Fig. 24 (b)). However, the monoliths did not show large agglomerates or voids (as seen in both SEM and μ CT images) which could significantly impact the final porosity.

When considering only the different molds used for ceramic formation, the samples produced with the technyl mold showed the highest total porosity. This is due to the strong relationship between solvent crystal thickness and the velocity of the solidification front. Faster

freezing rates results in greater supercooling at the base of the monolith, influencing the crystal tip thickness. This occurs because faster growth is directed along with the temperature gradient. In the case of the technyl mold, growth occurs predominantly from bottom to top, while lateral growth along the horizontal axis becomes increasingly limited due to the low thermal conductivity of technyl. As a result, the formation of a second freezing front from the mold walls is delayed, producing a finer final structure [33,50,133].

In contrast, with the copper mold, this phenomenon is more constrained due to competition between two solidification fronts: one ascending from the bottom and the other originating from the mold walls. This occurs due to the rapid cooling enabled by the high thermal conductivity of copper [134]. Such dynamics result in more defined pores with increased branching, which ultimately influences the material's final porosity. This supercooling behavior was previously discussed in the analysis of SEM images (Fig. 21), where samples produced with the copper mold exhibited transversal microstructures with distinct morphologies in dendrite and pore connections. Our study suggests that in the copper mold, as heat transfer decreases from the flat base toward the mold walls, the cooling rate along the suspension also decreases. Consequently, the dendrites become thicker, forming larger and more organized pore channels with better connectivity and more uniform porosity [131,132].

The samples produced with the technyl/copper mold formed a pore morphology in which the dendritic structure became more visible, potentially indicating lower interconnectivity compared to the copper mold system. However, it is assumed that the supercooling and cooling rate behavior in this hybrid mold is more similar to that observed in the technyl mold. This is supported by the fact that the samples produced with the technyl/copper mold exhibited porosity levels relatively close to those of the technyl system. This suggests that the vertical freezing front from the copper base dominates channel and pore formation, while neither the low thermal conductivity of the technyl section nor the high conductivity of the copper section significantly influences lateral dendrite growth. Thus, materials produced using technyl and technyl/copper molds displayed similar porosity profiles.

Finally, when examining open porosity (i.e., the volume of interconnected pores), the monoliths exhibited high levels of open porosity. This is an important characteristic, as high open porosity indicates a highly connected structure, which is advantageous for gas separation applications by enhancing gas flow [22]. Comparing open porosity across different molds, it is evident that the monoliths produced with the copper mold—and to a lesser extent the

technyl/copper mold—exhibited the lowest values. A possible explanation lies in the faster cooling kinetics associated with these molds, compared to those of the technyl mold. This supercooling promotes the rapid nucleation of the ceramic material, which in turn limits grain growth—an effect previously discussed in the grain size distribution analysis (Fig. 26). The rate at which the solvent crystallizes around suspended particles directly affects the formation of aligned structures and the degree of porosity [41,46]. Furthermore, this reduces the formation of closed pores, as during the final sintering stage of freeze-cast ceramics, closed porosity is eliminated by diffusion mechanisms through vacancies along grain boundaries—a process directly influenced by grain growth during freezing [27,37,46].

It is worth emphasizing that a deeper understanding of freezing kinetics is essential for achieving targeted porosity levels, which are a determining factor in the performance of these materials for a wide range of applications.

To obtain more precise data on how different molds affect total porosity and pore size distribution, samples with 20% solid loading were analyzed using AMIRA-AVIZO 3D software based on μ CT images. As shown in Figure 28 (a), the monoliths prepared with the copper mold (including the technyl/copper hybrid) exhibited a high concentration of small pores ($<10\text{ }\mu\text{m}$), due to the high freezing rate and bidirectional solidification. In contrast, the alumina monoliths produced with the technyl mold displayed more than 50% of pores in the 20–30 μm range, with a significant portion ($\sim 25\%$) in the 10–20 μm range. Thus, it was confirmed that pore size control is strongly dependent on the solidification rate, where faster freezing—promoted by the copper mold—results in smaller pores [41]. These results validate the high degree of structural control achievable with the *freeze-casting* technique and suggest that the material exhibits low resistance to mass transport.

Figure 28 (b) shows the pore network image of the monolith produced using the technyl mold, revealing not only a large number of pores but also high pore connectivity. This is a desirable property, as highly interconnected pores enable the transport of fluids and gases through the material, which is often advantageous in applications such as filtration membranes, tissue engineering scaffolds, among others [22,50,130].

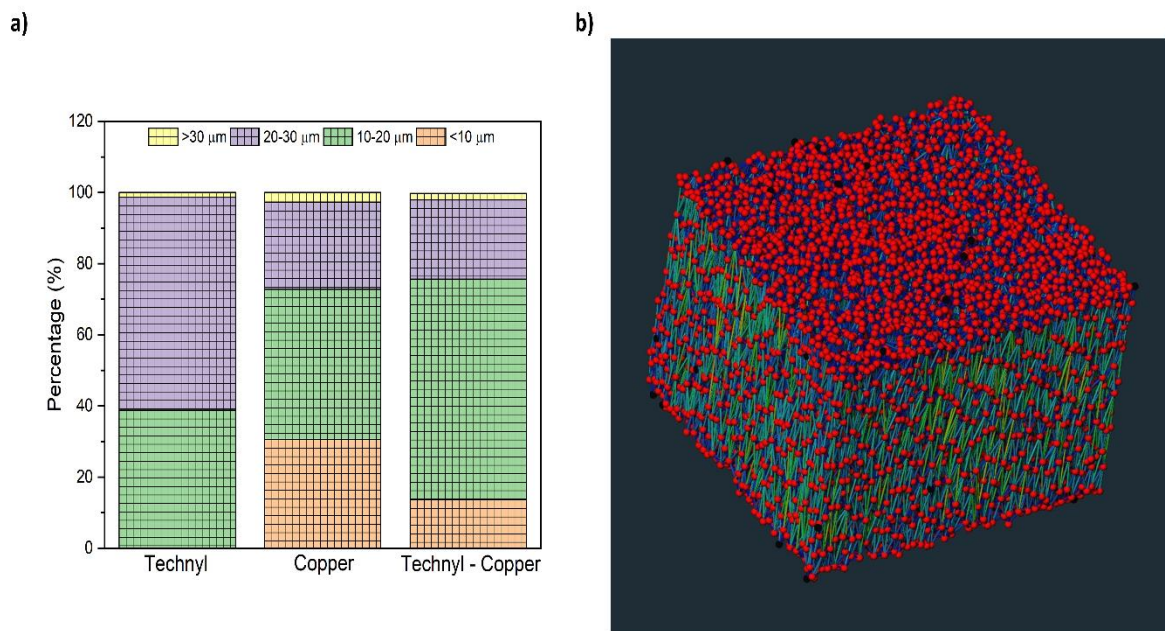


Figure 28. Identification of porosity for α -Al₂O₃ monoliths prepared with 20 vol% solids load a) pore size distribution of the monolith and b) pore network of the monolith produced in the Technyl mold where the spheres represent the pores and the lines the connections between the pores.

In general, the produced supports exhibited a highly satisfactory total porosity when compared with data reported in the literature [19,23,29,37]. However, beyond adequate porosity, mechanical strength is a crucial property for many applications. The literature indicates that mechanical properties tend to decrease significantly with increasing porosity. Therefore, a thorough investigation of the balance between porosity and mechanical properties of the produced monoliths is essential.

The results, summarized in Figure 29, demonstrate that the ceramic materials produced exhibit high mechanical strength. Even samples with considerable porosity showed good resistance, with the choice of mold—and consequently, the freezing method—playing a significant role in this property. Initially assessing the influence of solid loading, it was observed that lower solid contents resulted in the lowest compressive strengths. Samples with 15% solid loading yielded substrates with compressive strengths ranging from 10 to 20 MPa. As the solid loading increased, the substrates became stronger, reaching values between 25.4 and 34.1 MPa at 25% solid concentration.

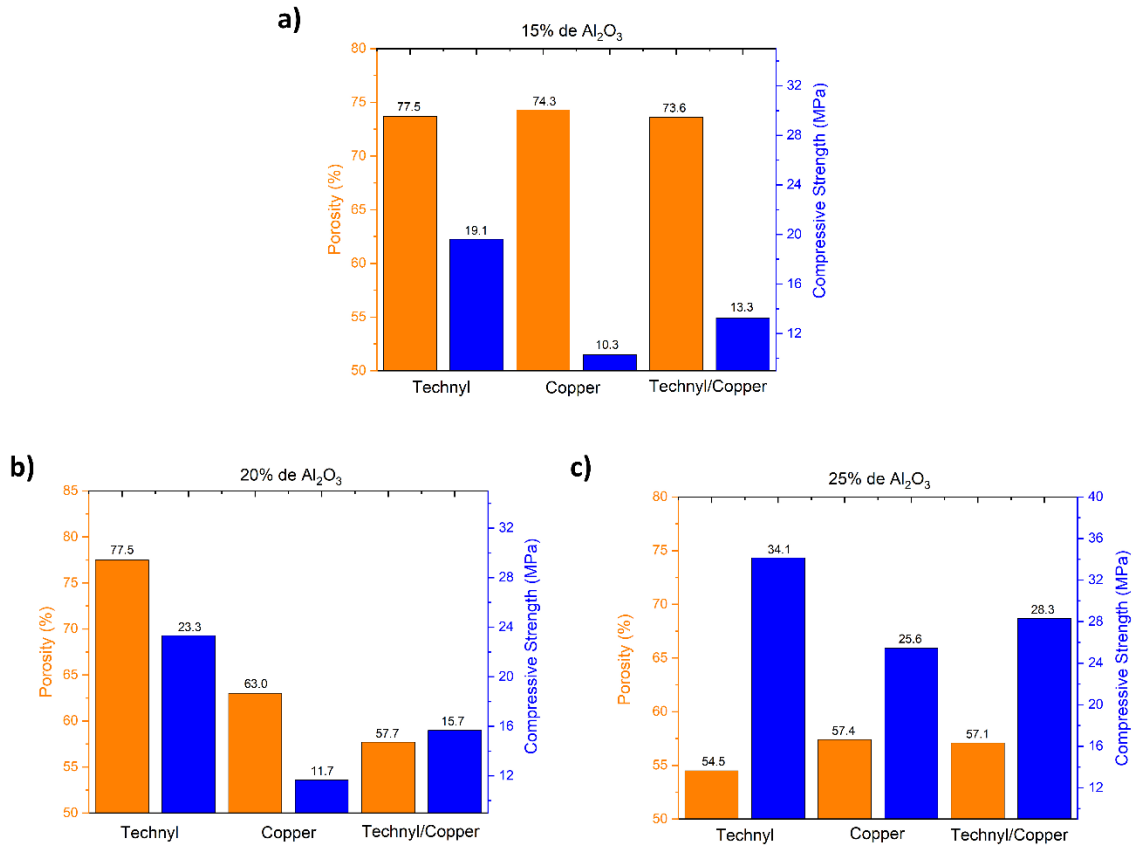


Figure 29. Comparison between porosity and compressive strength for α - Al_2O_3 monoliths prepared with solid loading of (a) 15%; (b) 20% and (c) 25%.

It is well established that the compressive strength of samples with anisotropic structures is oriented along the freezing direction and the formation of the ceramic structures relative to the applied stress [132]. As shown by the SEM images (Fig. 22) of the technyl/copper mold, the ceramic structures exhibited perpendicular growth (relative to adjacent regions) in the so-called transition zone. In other regions, crystal growth resulted in structures regularly separated by pore channels with abundant connections between dendrites. When force is applied along the direction of the transition region, the material can sustain a higher load, which explains why the samples produced with the technyl/copper mold exhibited the second highest compressive strength.

Finally, the samples frozen bidirectionally with the copper mold exhibited significantly lower compressive strength compared to those produced with the other molds. Cross-sectional microstructures produced using the copper mold (μ CT and SEM images) show microstructural differences and a reduction in dendritic connectivity. This transverse connectivity to the freezing direction arises because, at the initial freezing stage, ice crystal growth is restricted by

the development of freezing fronts-oriented perpendicular to each other. This induces preferential growth of camphene crystals along the radial plane of the monolith (as shown in Figure 5 for the copper mold) [136]. During freezing, the solidification front aligns parallel to both perpendicular temperature gradients, causing the camphene crystals to grow converging toward the monolith's center, resulting in a porous ceramic with a structure resembling radial freezing (commonly used in tube production) after solvent sublimation and sintering [19,24,136].

Thus, materials with a structure where the applied compressive force is not parallel to the freezing direction are expected to collapse more easily due to the random distribution of pore channels along the radial direction. This, combined with small defects observed in the μ CT images, acts as a failure point, resulting in inferior mechanical properties for materials produced with the copper mold [132,136].

5.1.3. Characterization of *freeze-casting* tubes.

In this work, the initial study involved producing monoliths using bidirectional growth, which allowed us to investigate the effect of different solid/volume concentrations on the final structure. Varying these conditions enabled us to identify the optimal concentration, resulting in a balanced combination of high mechanical strength and efficient pore connectivity. Based on this result, we proposed reproducing this ideal condition in a tubular system, aiming to maintain the favorable structural properties observed in the monoliths while leveraging the tubular geometry to optimize fluid or gas flow. This approach ensures that the final material preserves both mechanical integrity and transport efficiency, which are essential for separation, adsorption, and membrane applications.

Based on the favorable combination of high porosity and adequate mechanical strength, the system containing 20 vol% of solid loading was selected for the fabrication of *freeze-casting* tubes intended for the preparation of KFI zeolite membranes. Figure 30 displays SEM images of the fabricated tube (Fig. 30 (a–c)), as well as a schematic illustration of the radial freezing of the ceramic suspension (Fig. 30 (d)).

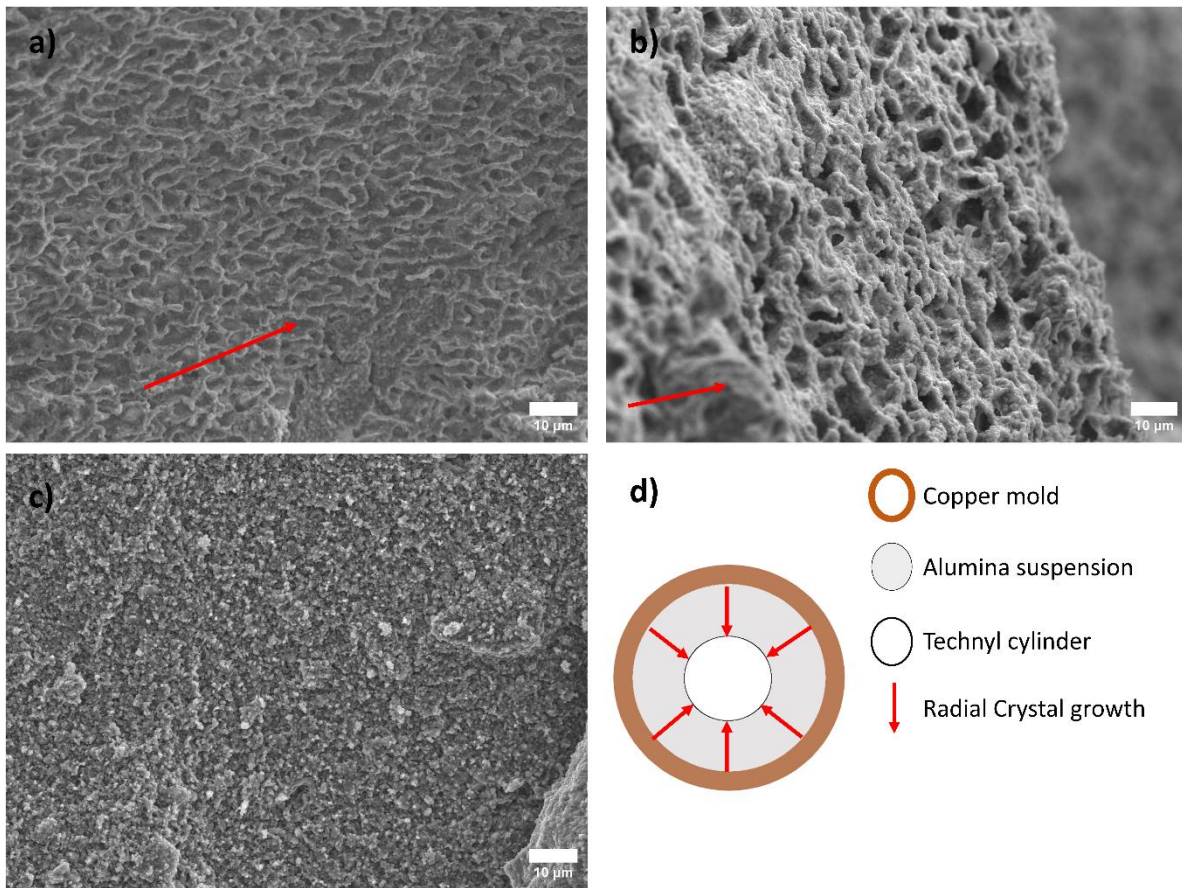


Figure 30. SEM images of the α - Al_2O_3 tube with 20% solid loading where (a) external part; (b) lateral part; (c) internal part of the tube and (d) schematic representation of the radial freezing of the ceramic suspension, adapted from [31].

The SEM images confirm that the tube fabrication process preserved the alignment of the pores, with well-oriented channels perpendicular to the substrate surface observed consistently throughout the entire tube. This finding demonstrates that the *freeze-casting* technique, under the specific experimental conditions and using the apparatus developed in our laboratory, is effective for producing tubular geometries, in agreement with previous studies [19,31,143–145]. The observed perpendicular pore alignment across all tube regions demonstrates that the camphene-based *freeze-casting* process successfully yielded a suitable substrate for zeolite membrane formation.

The fabrication of tubular supports with aligned porosity provides significant advantages for gas separation applications. Radially aligned pores, achieved by controlling the direction of solidification, generate channels with low tortuosity and high interconnectivity, which enhance gas permeability and reduce flow resistance across the membrane. Such anisotropic architectures facilitate efficient mass transport, as the aligned channels act as direct diffusion

pathways, minimizing pressure drops and improving overall performance. Moreover, the directional freezing process allows precise tuning of pore morphology, including size, shape, and orientation, by adjusting solid loading, freezing temperature, and mold material. This level of structural control is essential not only for achieving high open porosity but also for providing mechanically robust support that can sustain thin, selective layers such as zeolites, MOFs, or other ceramic membranes. Previous studies have demonstrated that aligned pore networks promote uniform flow distribution and enhance coupling between the support and active layer, thereby improving both selectivity and flux in gas separation processes [22,43,135,138,143–145]. Therefore, the strategic alignment of porosity in freeze-cast tubular substrates directly contributes to the development of high-performance membrane systems.

Table 5 presents the total and open porosity values determined via the Archimedes method. Similar to the monolith fabrication, the use of a copper mold, due to its high thermal conductivity ($400 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ [134]), strongly influenced the solidification kinetics and, consequently, the porosity of the freeze-cast tubes. Monoliths produced in copper molds exhibited the lowest open porosity values, likely because the tubular geometry imposes geometrical constraints on directional solidification, resulting in a less open pore structure. In contrast, monolithic samples allow for more uniform and controlled solidification, promoting the formation of interconnected, open pores.

Table 5. Summary of porosity on the *freeze-casting* tubes.

Tube	Total Porosity (%)	Open Porosity (%)	Close Porosity (%)
1	61.1	55.9	5.2
2	52.8	44.9	7.8
3	59.5	52.1	7.5
Average	57.8 ± 4.4	51.0 ± 5.6	6.9 ± 1.4
Monoliths	63.0 ± 2.4	55.4 ± 3.8	7.6 ± 0.9

The observed reduction in total porosity (from 63% to 57%) when transitioning from a monolithic shape to a tubular one, even while maintaining similar basic *freeze-casting* parameters, is often attributed to changes in the thermal boundary conditions that affect the porosity gradient during freezing. In the monolith sample, the temperature gradient along the

freezing axis can result in one highly porous region (where ice grew freely) and another region (near the heat source or the center of the block) where freezing was slower, allowing particles to pack slightly more before ice removal, resulting in a slightly lower, but still high, porosity (e.g., 63%) [32,134,136].

When switching to a tubular geometry, mainly if radial freezing (through the tube wall) is employed, the surface-area-to-volume ratio and the distance the freezing front travels are different. This can lead to more efficient packing of the tube walls (reducing porosity to 57%) or a greater tendency to form finer ice channels, resulting in a denser overall porous architecture. This alteration in the radial gradient can lead to a more uniform distribution of smaller pores, but consequently, a lower average total porosity compared to the more "open" structure of the monolith [19,43,136,145].

Transitioning from a flat to a cylindrical mold increased the contact area between the ceramic suspension and the mold, reducing the thickness of the ceramic layer in contact with the copper [32,134,136]. This likely amplified the effects of solidification parameters—such as freezing rate and temperature—leading to the formation of smaller camphene crystals at higher densities and, consequently, slightly lower overall porosity. Additionally, rapid thermal conduction through the copper walls may have affected the suspension viscosity and the mobility of solid particles, resulting in faster freezing and less open porosity. These observations are consistent with literature reports showing that freeze-cast tubes often exhibit radially aligned pores with reduced interconnectivity compared to monoliths, which can limit permeability and efficiency in applications such as tubular membrane supports [145].

In this study, the average grain size in the tubes ($0.327 \pm 0.001 \mu\text{m}$) was slightly smaller than that of the monoliths ($0.443 \pm 0.010 \mu\text{m}$), consistent with the expected effect of radial alignment and increased densification. Although mechanical compression tests were not performed on the tubes, it is reasonable to assume that the dendritic morphology and radial pore alignment observed in the SEM images contribute to improved mechanical resistance. Radial pore orientation promotes uniform stress distribution along the tube wall, reducing localized stress concentrations that could lead to failure [24,31,35,136,145]. Furthermore, dendritic branches of the cell walls act as internal supports, increasing structural rigidity, and preventing collapse under axial loads. This combination of anisotropic alignment and internal reinforcement enables the *freeze-casting* tubular geometry to maintain integrity under

compression, making it competitive for applications requiring both lightweight and mechanically robust structures [1,35,122,145].

When evaluating materials for zeolite membrane fabrication, it is essential to carefully consider the properties of both monoliths and tubes supports, as they directly impact the final membrane performance. Key parameters include total and open porosity, pore alignment, mechanical stability, compressive strength, permeability, and structural uniformity, all of which influence gas separation efficiency, membrane durability, and ability to withstand harsh operational conditions. Industrial practice further supports this choice: tubular geometries are widely used due to their ease of handling, optimized flow distribution, integration into commercial membrane modules, and mechanical robustness provided by radially aligned pores. Considering these factors, the tubular geometry was selected to produce the KFI zeolite membrane, offering a combination of efficient gas separation performance and practical feasibility for industrial application.

5.2. Characterization of KFI Zeolites

Before proceeding with the presentation and discussion of results, it is essential to highlight the relevance of a more in-depth investigation into the synthesis of KFI zeolites. According to Russel and Verduijn [69,117], the successful synthesis of pure KFI zeolites (containing Sr and K, with cubic morphology and purity $\geq 95\%$) is achieved when the molar variations of Al_2O_3 , SiO_2 , and K_2O do not exceed 10 mol%. This observation underscores the critical importance of preparing the aluminate solution and selecting suitable reagents to ensure the success of the synthesis. Russel [69] *et al*, further emphasize the challenge of obtaining phase-pure KFI in the Sr–K system, as L and W-type zeolites frequently emerge as secondary phases. In this context, the Sr^{2+} and K^+ ions act as structure-directing agents, influencing the formation of the final framework topology, including the cage and ring structures characteristic of KFI-type zeolites.

Based on preliminary synthesis attempts, it was concluded that the preparation of the aluminate solution and the selection of the silicon source are key factors for obtaining the desired KFI framework. This is because the composition of the aluminate solution directly dictates the relative proportions of Al_2O_3 , SiO_2 and K_2O available in the reaction medium.

Therefore, a systematic study was conducted to evaluate the relationship between these three components by varying both the aluminum and silicon sources used in the synthesis.

5.2.1. Study of Different Silicon and Aluminum Sources

5.2.1.1. $\text{Al}(\text{OH})_3$ as the Aluminum Source

X-ray diffraction (XRD) patterns were acquired to confirm whether the synthesized zeolite corresponded to the KFI structure and to evaluate parameters such as crystallinity, interplanar spacing, and crystallite size. These diffraction patterns were then compared to the standard K-KFI zeolite reference pattern [127], as shown in Figure 31.

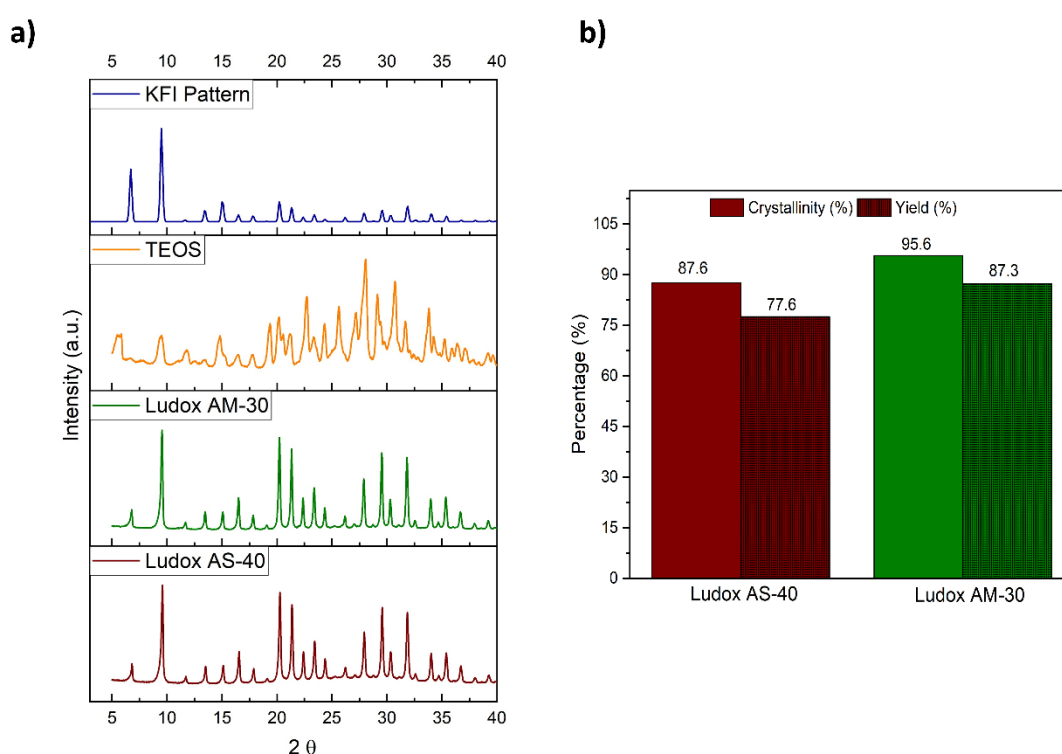


Figure 31. (a) Crystallographic patterns and (b) crystallinity and yield values for the syntheses using $\text{Al}(\text{OH})_3$ as the aluminum source and with different silicon sources.

An initial analysis of the XRD patterns (Figure 31 (a)) reveals that the samples synthesized with Ludox® AS-40 and Ludox® AM-30 as silicon sources exhibit distinct diffraction peaks characteristic of KFI-type zeolites. For the sample synthesized with Ludox® AS-40, peaks were observed at $2\theta = 6.8^\circ, 9.62^\circ, 20.28^\circ, 21.34^\circ$, and 29.52° , while the sample synthesized with Ludox® AM-30 displayed peaks at $2\theta = 6.8^\circ, 9.56^\circ, 20.22^\circ, 21.34^\circ$, and 29.52° . These

reflections correspond to the (110), (200), (330), (420), and (611) planes, respectively [127], confirming that both silicon sources are suitable for the synthesis of phase-pure KFI zeolites.

In contrast, the sample synthesized with TEOS exhibited diffraction peaks at $2\theta = 5.46^\circ$, 9.56° , 11.80° , and 14.82° , which, although slightly shifted, are associated with the (100), (110), (001), and (210) planes of L-type zeolites [118]. The overall diffraction profile suggests the presence of a phase mixture, with certain peaks resembling those of the KFI structure. Therefore, additional characterization is necessary to confirm the crystalline phase of the sample. A plausible explanation for the presence of impurities lies in the nature of TEOS as an organosilicon compound containing four ethoxy groups bonded to Si. During gelation, these groups are hydrolyzed and released (via the reaction $\text{Si}(\text{OC}_2\text{H}_5)_4 + 2 \text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4 \text{C}_2\text{H}_5\text{OH}$). Upon subsequent hydrothermal treatment in the autoclave, ethanol release may increase internal pressure at elevated temperatures, potentially disrupting the equilibrium conditions required for KFI crystallization.

As previously discussed in this work and reported in the literature, the molar ratio of Al_2O_3 , SiO_2 , and K_2O is a determining factor in the formation of secondary building units (SBUs) and the overall crystallization of the zeolite framework. The mixed-phase diffraction pattern observed for the TEOS-derived sample strongly suggests that this optimal compositional ratio was not achieved during synthesis.

Finally, a comparative analysis of the unit cell parameters for the synthesized samples was conducted further to evaluate their structural alignment with the reference KFI framework. These parameters are presented in Figure 31 (b) and summarized in Table 6. KFI zeolite, also known as ZK-5, crystallizes in a body-centered cubic structure with a lattice parameter of $a_0 = 18.685 \text{ \AA}$ and belongs to the $\text{Im}\bar{3}\text{m}$ space group. Depending on the nature of the charge-compensating cation used during synthesis, the unit cell may sometimes be described as a primitive cubic pseudocell, with $a' = a / (2)^{1/2}$.

Table 6. Structural parameters of the samples.

Samples	$d_{200} (\text{\AA})^a$	$a_0 (\text{\AA})^b$	% error	$D (\text{nm})^c$	Phase Identified (XRD)
Ludox® AS-40	9.23	18.60	0.30	44.40	KFI
Ludox® AM-30	9.27	18.62	0.18	42.12	KFI
TEOS	-	-	-	15.11	KFI + L + T + W
Reference (KFI)	9.329	18.658			KFI

^aInterplanar spacing of the structural plane 200, estimated by Equation 12. ^bUnit cell parameter of KFI, estimated by Equation 13. ^cCrystallite size calculation from Equation 15.

It can thus be observed that, when applying Equation 15 to predict the d_{200} value of the synthesized zeolites (based on the position of their (200) reflection around 9.47°), the results closely match the reference values. This not only confirms the validity of the applied equation but also indicates that the synthesized materials exhibit structural characteristics consistent with those of the KFI-type zeolite. Among the samples, the one synthesized using Ludox® AM-30 displayed superior crystallinity (95.6%) and good yield, indicating a favorable interaction between the aluminum and silicon sources. A possible explanation for this enhanced performance lies in the differences in surface area between the two silica precursors. Ludox® AS-40 [146] possesses a specific surface area in the range of 129–155 m²/g with particle sizes between 20–24 nm, while Ludox® AM-30 [147] exhibits a higher surface area, ranging from 198–258 m²/g. Although the technical specifications of Ludox® AM-30 do not specify particle size, it is reasonable to assume smaller particle dimensions compared to Ludox® AS-40, as materials with higher surface areas generally consist of finer particles. This difference in surface area likely contributed to better dispersion of the aluminate solution and more efficient formation of the TO₄ tetrahedra within the KFI zeolite framework.

The ATR-FTIR spectra of the synthesized zeolite samples are presented in Figure 32. It can be observed that the stretching vibrations of the O–H bonds appear at higher frequencies for samples synthesized using Al(OH)₃, indicating stronger interactions between the zeolite framework and adsorbed water within the KFI zeolite. The corresponding band positions are summarized in the adjacent table.

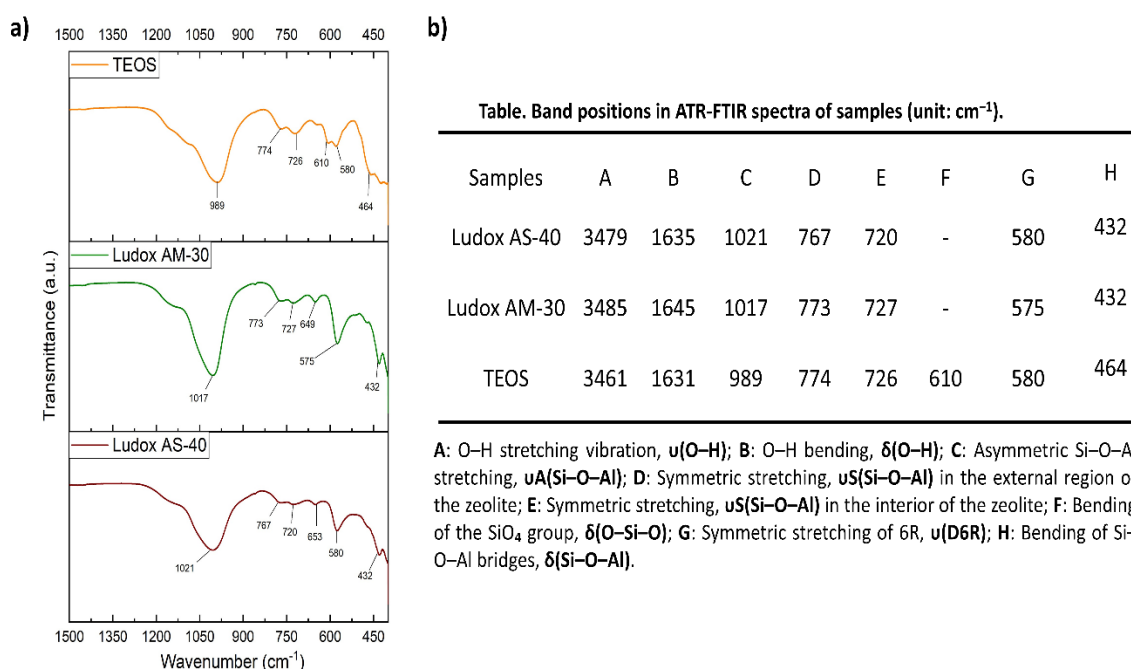


Figure 32. (a) ATR-FTIR spectra for the synthesis using $\text{Al}(\text{OH})_3$ as the aluminum source and with different silicon sources; (b) Table with the band positions in the ATR-FTIR spectra of samples (unit: cm^{-1}).

The first class of vibrational modes common to all zeolites and attributed to the internal vibrations of the TO_4 tetrahedron includes the two most intense bands in the FTIR spectrum: the strongest appearing in the range of $950\text{--}1250\text{ cm}^{-1}$ and a moderately intense band between $420\text{--}500\text{ cm}^{-1}$ [148]. It was observed that the samples previously identified by XRD as KFI exhibited a slight shift to higher wavenumbers, following the trend Ludox® AS-40 > Ludox® AM-30 for the C vibrations, while the H vibrations showed approximately the same values.

The external linkage frequencies, which are sensitive to the topology and structural building units of the zeolite frameworks, are primarily observed in two spectral regions: $500\text{--}600\text{ cm}^{-1}$ and $300\text{--}420\text{ cm}^{-1}$. A moderately intense band in the first region is associated with the presence of a double ring (D-ring) polyhedra, found in zeolites with D-4 and D-6 rings, such as KFI. The position of this band can also reflect the structural type and class of the zeolite. For KFI, symmetric stretching of the D-ring appears consistently around 540 and 585 cm^{-1} , regardless of the Si/Al ratio. In contrast, zeolites T and L, commonly observed as impurities in KFI synthesis, exhibit this D-6 ring vibration at higher frequencies, approximately 623 and 606 cm^{-1} , respectively, and may also present minor shoulders at lower or higher wavenumbers [148].

In all synthesized samples, bands corresponding to six-membered ring stretching were clearly observed.

The morphology of the samples was evaluated using Scanning Electron Microscopy (SEM), as shown in Figure 33. This characterization technique is essential for assessing the presence of impurities in the samples, since KFI-type zeolites are reported in the literature to exhibit a cubic crystal morphology. In contrast, zeolite L forms cylindrical particles, zeolite T forms hexagonal bars, and zeolite W forms tetragonal rods [69,113,114,118]. SEM imaging also provides insights into particle size and growth shape, critical parameters for the uniform fabrication of thin membranes.

The significance of the silicon source used in KFI synthesis is immediately evident. The samples synthesized with Ludox® AS-40 and Ludox® AM-30 (Figure 33 (a) and (b)) displayed a distinctive cubic morphology characteristic of KFI-type zeolites, with no visible amorphous aggregates or particles indicative of other zeolite phases. This suggests a high degree of phase purity in both samples. On the other hand, using TEOS as the silicon precursor resulted in samples containing a significant level of impurities. This was evident from the presence of cylindrical particles, indicative of zeolite L, as well as rod- and bar-shaped particles characteristic of zeolites L and T, respectively, within the TEOS-derived sample [113,118].

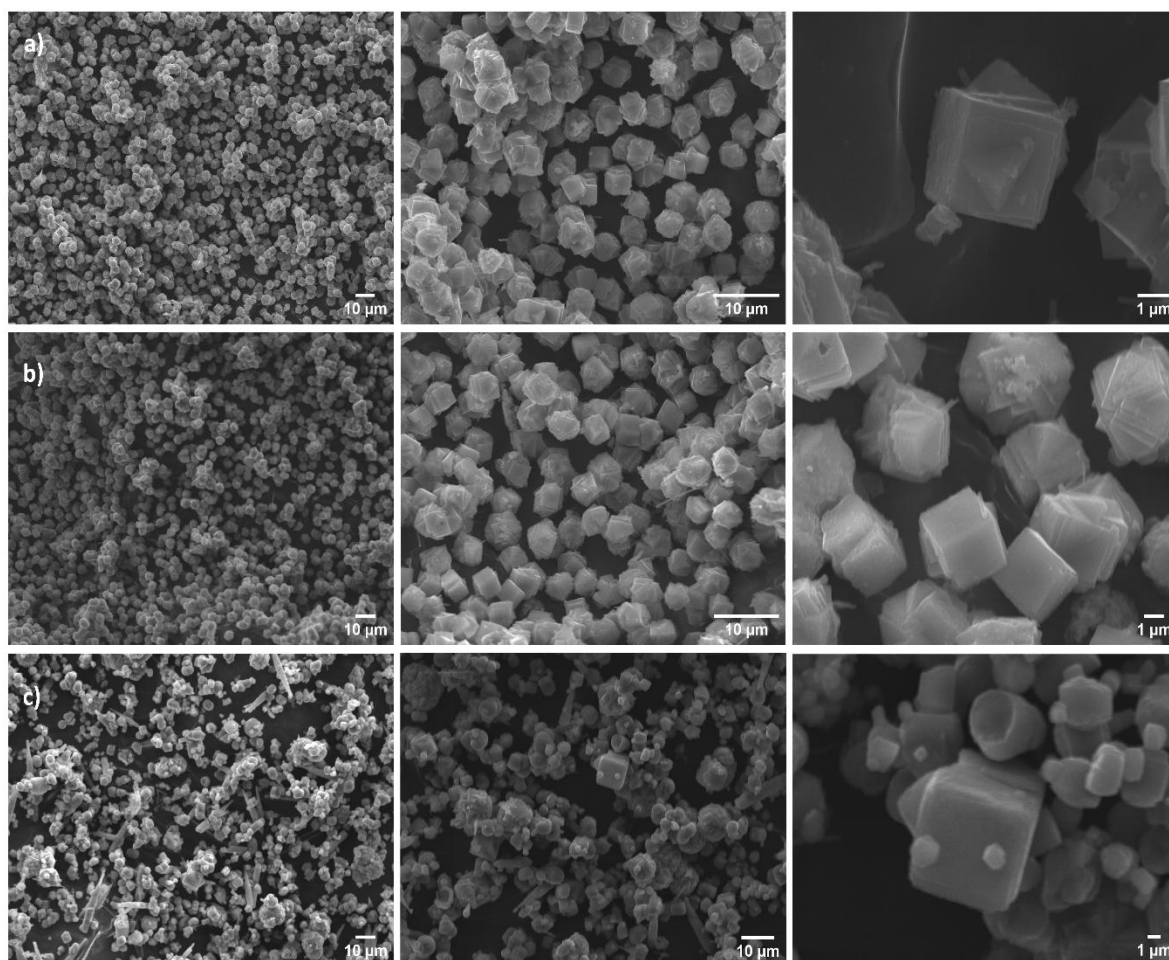


Figure 33. SEM images for the KFI syntheses using $\text{Al}(\text{OH})_3$ as an aluminum source where (a) Ludox® AS-40; (b) Ludox® AM-30 and (c) TEOS as a silica source.

Appendix 1 and Table 7 present the Si/Al molar ratios obtained by EDS, as well as the particle size distributions derived from the SEM images, aiming to provide a more in-depth analysis of the influence of different precursors on the properties of the final material. The sample synthesized with Ludox® AS-40 exhibited the smallest average crystal size of 2.64 μm , while the sample prepared with Ludox® AM-30 presented a slightly larger average crystal size of 3.12 μm . This difference is most likely related to the higher specific surface area of the silicon source, which may have influenced the nucleation and growth dynamics of the zeolite crystals.

Table 7. The Si/Al ratio and the mean crystal size distribution.

Samples	Si/Al ^a	Molar Ratio of (Al ₂ O ₃ + SiO ₂ + K ₂ O) (%)	Mean Crystal Size (μm) ^b
Ludox® AS-40	3.5	10.61	2.64 ± 0.02
Ludox® AM-30	3.8	12.30	3.12 ± 0.03
TEOS	2.0	8.19	-

^amolar ratio calculated from EDS; ^baverage particle size distribution obtained by SEM.

Structural and dynamic information about molecular species can be investigated using the solid-state nuclear magnetic resonance technique with magic angle spinning (MAS-NMR). The chemical shift, which is highly sensitive to the local electronic environment, is widely employed to distinguish and identify different coexisting species in zeolites, providing detailed structural insights into the observed nuclei. The connectivity and spatial proximity between distinct structural units in zeolites can be explored through ²⁹Si–²⁹Si and ²⁹Si–²⁷Al correlation spectra, since the order and arrangement of these nuclei directly influence the physicochemical properties of the material. For instance, the distribution of aluminum significantly affects both the location and strength of acidic sites [149,150].

Figure 34 presents the ²⁷Al NMR spectra of the analyzed samples, revealing the distribution of different aluminum species. Both samples exhibit an intense signal around 60 ppm, corresponding to tetrahedrally coordinated aluminum incorporated into the zeolite framework (Al (Td)), in addition to a weaker peak near 0 ppm, attributed to octahedrally coordinated extra-framework aluminum (Al (Oh)). Moreover, a low-intensity signal appears around 30 ppm, characteristic of either five-coordinated aluminum or distorted extra-framework tetrahedral aluminum species [56,66,68,150]. According to the literature, this latter signal is often associated with dealumination processes—namely, the partial removal of aluminum from the framework—resulting in the formation of penta-coordinated aluminum species (Al (I)) [10,151,152]. However, as the samples were not subjected to aluminum extraction treatments, the presence of this peak suggests that only a limited fraction of the aluminum was effectively incorporated into the final crystalline structure.

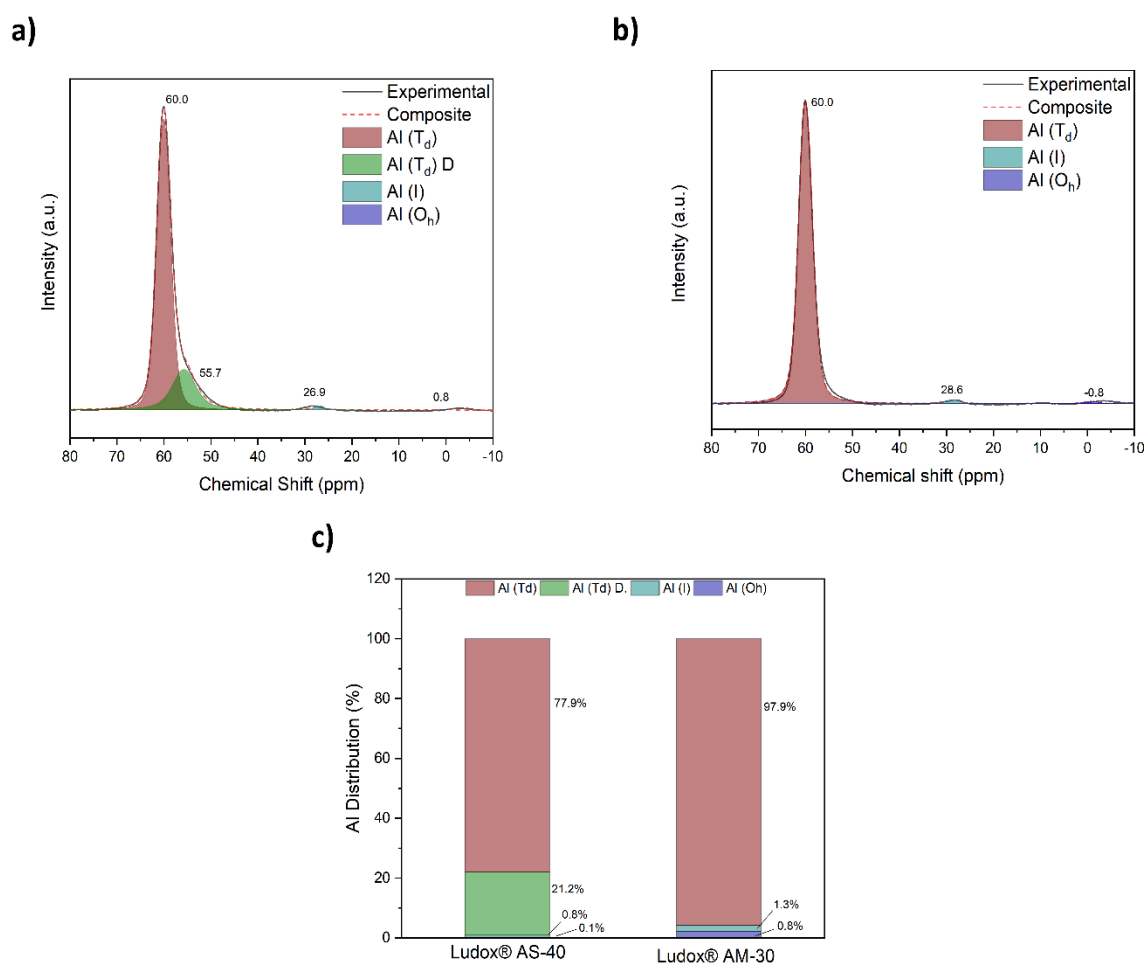


Figure 34. ^{27}Al RAM-NMR spectra for samples with $\text{Al}(\text{OH})_3$ as aluminum source where (a) refers to the sample with Ludox® AS-40 and (b) to samples with Ludox® AM-30 as silicon source and (c) the relative percentage of chemical environments

In Figure 34 (c), it is observed that the proportion of penta-coordinated aluminum is low in both samples, accounting for 1.8% in the sample synthesized with Ludox® AS-40 and 2.0% in that synthesized with Ludox® AM-30, indicating a limited degree of structural disruption of aluminum. Notably, the sample prepared with Ludox® AS-40 displays a high-intensity peak at 56 ppm (Figure 34 (a)), corresponding to 36.1% of the total aluminum content (Figure 34 (c)). This signal is attributed to distorted tetrahedral aluminum located outside the crystalline framework (Al (Td) D) [151] and its presence indicates a considerable degree of partial degradation of the zeolite structure. This interpretation is further supported by lattice parameter analyses, which revealed a 0.3% deviation from the crystallographic standard of the KFI phase, while the sample synthesized with Ludox® AM-30 exhibited a smaller deviation of 0.18% and no such peak in the NMR spectrum.

The observed distortion can again be explained by differences in surface area between Ludox® AS-40 [146] (129-155 m²/g) and Ludox® AM-30 [147] (198-258 m²/g). These textural differences between the two colloidal silica precursors may have directly influenced the homogeneity and dispersion of the aluminate solution during synthesis, promoting more effective formation of the TO₄ (T = Si or Al) structural units of the KFI zeolite. Thus, the higher surface area of Ludox® AM-30 likely provided a more favorable environment for nucleation and orderly crystal growth, whereas Ludox® AS-40 may have contributed to the slight distortion of tetrahedral aluminum located outside the zeolite framework.

The ²⁹Si NMR spectra, along with the distribution of the different silicon species present in the samples, are shown in Figure 35. The silicon environments typically reported for KFI zeolites are classified according to the number of neighboring aluminum atoms substituting silicon in the tetrahedral framework (denoted as Si (nAl), where *n* ranges from 0 to 4), each characterized by distinct chemical shifts.

The Si (0Al) environment, corresponding to silicon atoms bonded exclusively to four other silicon atoms (Si (4Si)), is typically observed as two peaks at approximately –115 and –110 ppm. The Si (1Al) environment, attributed to species such as Si (3Si,1Al) and/or Si (3Si,1OH), exhibits a peak centered around –105 ppm. The Si (2Al) species, associated with structural units like Si (2Si, 2Al), Si (2Si, 1Al, 1OH), and/or Si (2Si, 2OH), appears near –98 ppm. The Si (3Al) environment, involving species such as Si (1Si, 3Al), Si (1Si, 2Al, 1OH), Si (1Si, 1Al ,2OH), and/or Si (1Si, 3OH), is detected in the region around –95 ppm. Finally, the Si (4Al) environment, associated with Si (4Al), Si (3Al, 1OH), Si (2Al, 2OH), Si (1Al, 3OH), and/or Si (4OH) species, produces a signal around –85 ppm [66,149,150,152].

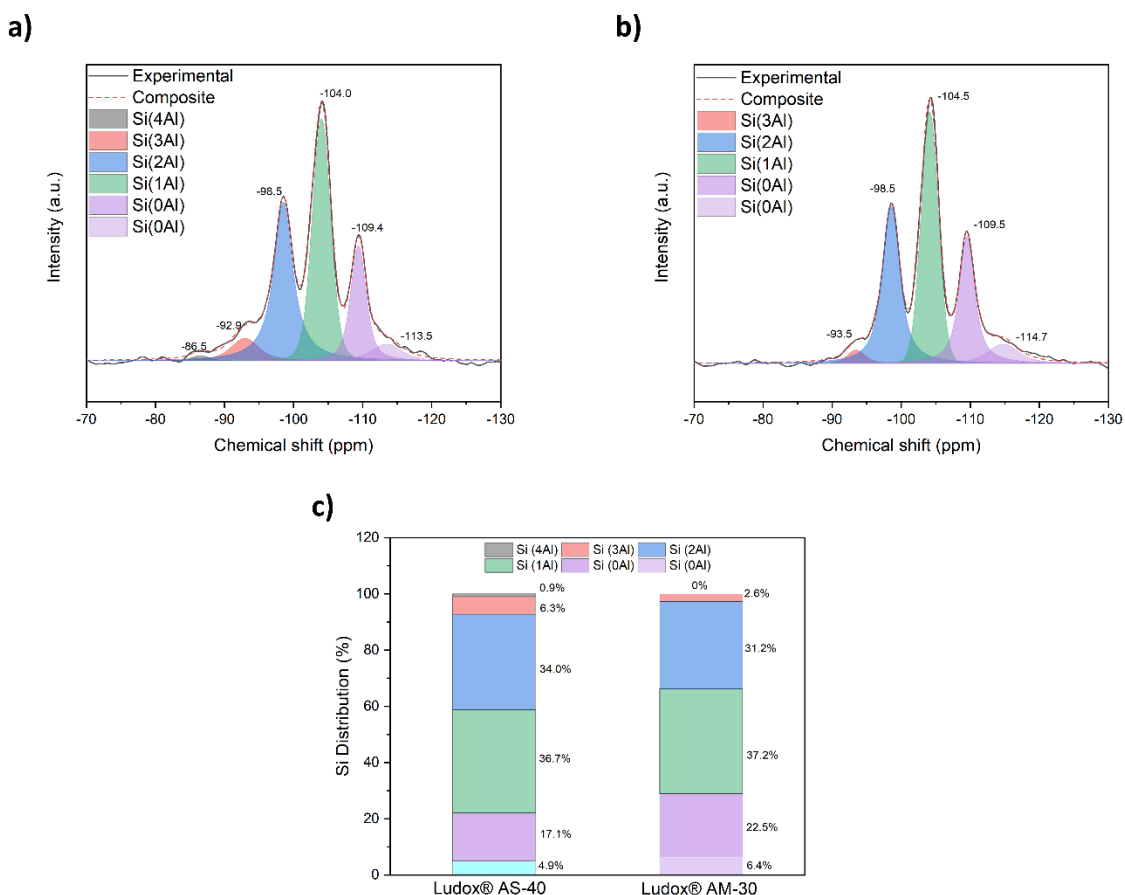


Figure 35. ^{29}Si RAM-NMR spectra for samples with $\text{Al}(\text{OH})_3$ as aluminum source where (a) refers to the sample with Ludox® AS-40 and (b) to samples with Ludox® AM-30 as silica source and (c) the relative percentage of chemical environments.

For the sample synthesized using Ludox® AS-40, the ^{29}Si NMR spectra revealed signals at -113.5 , -109.4 , -104.0 , -98.5 , -92.9 , and -86.5 ppm, corresponding to the structural species Si(0Al), Si(0Al), Si(1Al), Si(2Al), Si(3Al), and Si(4Al), respectively. In contrast, the sample prepared with Ludox® AM-30 exhibited signals at -114.7 , -109.5 , -104.5 , -98.5 , and -93.5 ppm, attributed to the species Si(0Al), Si(0Al), Si(1Al), Si(2Al), and Si(3Al), respectively. The presence of three high-intensity peaks in the regions around -100 , -110 , and -115 ppm in both samples indicates of the formation of the KFI-type zeolite structure.

Notably, the sample synthesized with Ludox® AM-30 showed relatively higher intensities for the Si(1Al), Si(2Al), and Si(3Al) signals compared to the Ludox® AS-40-based sample. This behavior suggests a higher relative silicon content within the framework, as NMR signal intensity is directly proportional to the number of silicon atoms present in each chemical environment [56,68,150]. The absence of the characteristic Si(4Al) peak in the Ludox® AM-30 sample further supports this interpretation, indicating a less distorted framework with lower

aluminum incorporation in substitutional positions. This interpretation is consistent with both the X-ray diffraction and ^{27}Al NMR data, which also points to a more ordered network.

Based on the relative area of the signals assigned to the various silicon environments ($n\text{Si}$), the molar Si/Al ratio was estimated using Equation 19, resulting in values of 3.0 and 3.7 for the samples synthesized with Ludox® AS-40 and Ludox® AM-30, respectively. Although the Si/Al ratio determined by NMR tends to underestimate the actual value, since terminal hydroxyl groups are counted as aluminum-containing species [66]. The estimated values are close to those obtained by energy-dispersive X-ray spectroscopy (EDS), which were 3.4 and 3.7, respectively.

These findings demonstrate that the synthesis of KFI-type zeolites using $\text{Al}(\text{OH})_3$ and without the addition of organic structure-directing agents was successful, yielding materials with high Si/Al ratios and high phase purity—particularly for the sample synthesized with Ludox® AM-30. This feature is especially advantageous for membrane applications, as higher aluminum contents increase the hydrophilicity of the surface, which can negatively affect separation performance in systems containing water vapor due to the strong affinity of the hydrophilic zeolite structure for H_2O molecules [15].

The evaluation of textural parameters was conducted via nitrogen physisorption at $-196\text{ }^\circ\text{C}$. Essentially, this method relies on the interaction between gas-phase molecules (adsorbate) and the surface of a solid phase (adsorbent). Due to van der Waals forces, a monolayer of gas molecules is adsorbed onto the surface of the solid as the relative pressure is gradually increased. The volume of N_2 introduced into the sample chamber is known, and by measuring the system pressure, the amount of nitrogen adsorbed by the sample can be calculated [128]. The resulting adsorption isotherms for the synthesized samples are shown in Figure 36 and Appendix 2 and 3.

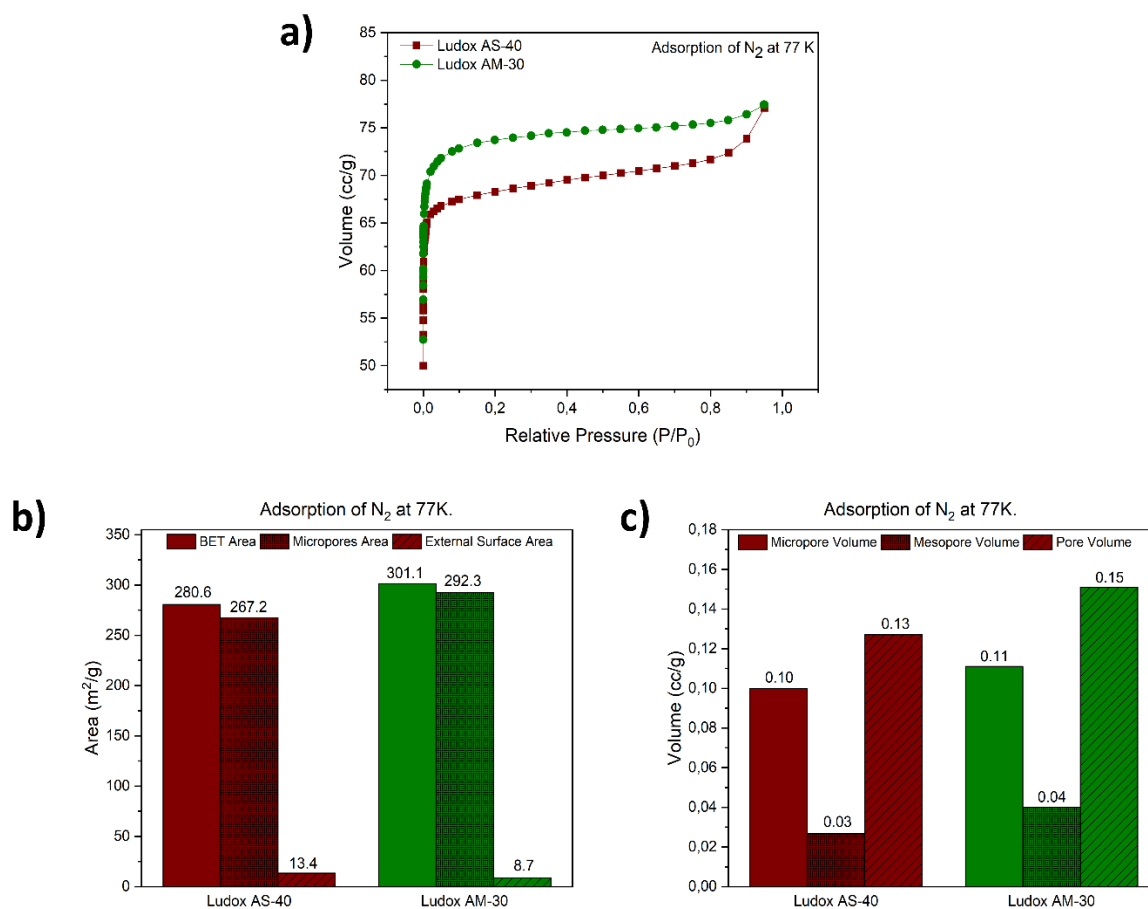


Figure 36.(a) N₂ adsorption/desorption isotherm; (b) BET area, micropore area calculated by the t-Plot method in the region 0.15 to 0.5 and (c) pore volume calculated by the t-Plot method in the region 0.15 to 0.5 for samples using Al(OH)₃ as the aluminum source and with different silicon sources.

The adsorption/desorption isotherms of the synthesized zeolites indicate the presence of micropores, evidenced by the significant N₂ adsorption at low relative pressures (P/P_0). The experimental curves shown in Figure 36 (a) reveal that the samples prepared with Ludox® AS-40 and Ludox® AM-30 exhibit a combination of type I (b) and IV (a) isotherms. These isotherms are characteristic of microporous and mesoporous solids with relatively small external surface areas. Type I isotherms are concave with respect to the P/P_0 axis, and the adsorbed quantity approaches a limiting value governed by the accessible micropore volume rather than the internal surface area. This pore filling occurs without capillary condensation and without a distinct monolayer formation process. Type I (b) isotherms are typically found in materials with a broader pore size distribution, including wider micropores and possibly narrow mesopores ($< \sim 2.5$ nm) [12,128].

Type IV isotherms are typical of mesoporous materials, in which adsorption initially occurs via monolayer–multilayer formation, followed by pore condensation. Pore condensation refers to the phenomenon where gas condenses into a liquid-like phase within pores at a pressure p lower than the saturation pressure p_0 of the bulk liquid. In Type IV (a) isotherms, capillary condensation is accompanied by hysteresis. This phenomenon occurs when pore widths exceed a certain critical limit, that is system- and temperature-specific. For example, during nitrogen and argon adsorption at 77 K and 87 K, respectively, hysteresis begins to appear in pores larger than approximately 4 nm. Consequently, the samples exhibited isotherms suitable for micropores and mesopores, resulting in an H4-type hysteresis loop characterized by two nearly horizontal and parallel branches in the relative pressure (P/P_0) range of approximately 0.9 to 1.0. H4-type hysteresis is commonly associated with aggregated zeolite crystals, some mesoporous zeolites, and micro-mesoporous carbons. The hysteresis observed at high relative pressures suggests the presence of additional mesopores or macropores generated by the aggregation of small crystals [13,128].

Initially, it is observed that all samples exhibit surface areas consistent with those reported in the literature. Both samples showed a high microporous surface area characteristic of zeolites, indicating high purity. These values are promising for membrane applications, as zeolites with elevated microporous areas demonstrate good performance in gas adsorption [11–13,67,70,74], which is a critical initial step in gas separation using zeolitic membranes.

This adsorption likely occurs because micropore filling by physisorption generally occurs at low pressures; the pressure range depends on the shape and size of the micropores, the size of the probe molecule, and its interactions with both the adsorbent and neighboring molecules. Adsorption in very narrow micropores (i.e., “ultramicropores” such as KFI, which has a pore diameter of 0.39 nm and a maximum included sphere diameter within the cage of 1.07 nm) involves overlapping adsorption forces and occurs at very low relative pressures. The pore sizes calculated by the DFT method were 0.94 and 0.68 nm for the Ludox® AS-40 and Ludox® AM-30 samples, respectively (Table B.1).

This discrepancy may potentially be attributed to the use of nitrogen as the adsorbate, which may not be ideal for accurately assessing micropore size distribution. The quadrupolar nature of nitrogen molecules leads to specific interactions with surface functional groups and exposed ions, affecting both the orientation of adsorbed nitrogen molecules and the micropore filling pressure [128]. In contrast, argon lacks such specific interactions, making argon

adsorption at 87 K a preferred method to directly correlate pore filling pressure with confinement effects, especially in zeolitic materials. As a continuation of this work, the pore size distribution of the KFI zeolite will be re-evaluated using argon as the adsorbate.

5.2.1.2. Aluminum Wire (AW) as Aluminum Source

X-ray diffraction (XRD) patterns were obtained to confirm whether the synthesized zeolite corresponded to the KFI structure and to determine parameters such as crystallinity, interplanar spacing, and crystallite size. The resulting diffraction patterns were then compared with the standard pattern of K-KFI zeolites [127], as illustrated in Figure 37.

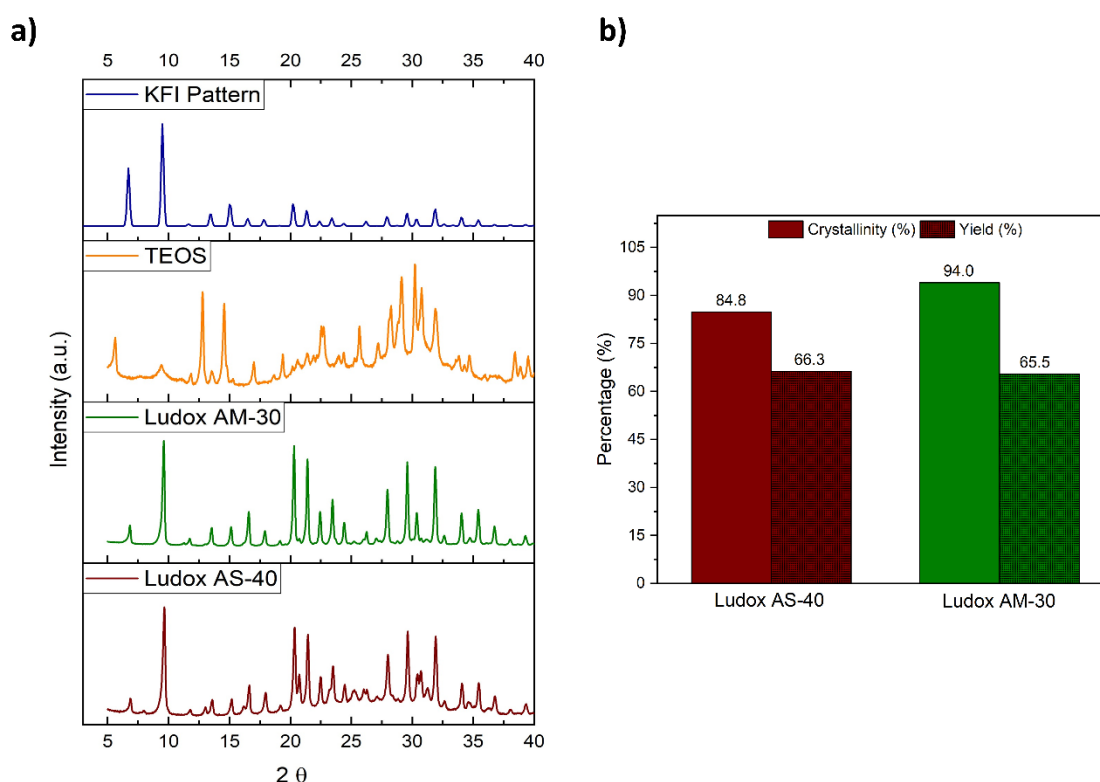


Figure 37.(a) Crystallographic patterns and (b) crystallinity and yield values for the syntheses using AW as the aluminum source and with different silicon sources.

Initially, the XRD patterns confirmed the formation of the KFI zeolite in samples synthesized with Ludox® AS-40, which exhibited characteristic peaks at 2θ values of 6.90, 9.66, 20.23, 21.44, and 27.98°. Similarly, samples synthesized with Ludox® AM-30 showed peaks at 2θ values of 6.84, 9.62, 20.28, 21.38, and 27.98°, corresponding to the (110), (200), (330), (420), and (611) planes, respectively.

However, in the sample prepared with Ludox® AS-40, additional peaks were detected at 2θ values of 13.02, 16.16, 25.26, 26.24, 30.72, and 31.26°, which are not present in the standard KFI diffraction pattern. These additional reflections suggest the presence of other zeolitic phases—possibly zeolite L, W, or T—indicating the formation of a multiphasic material. In contrast, the sample prepared with Ludox® AM-30 showed a purer KFI phase, as these extra peaks were absent.

One possible explanation for this difference lies in the variation in surface area between the two silica sources. The disparity in particle size likely influences the formation process of $\text{SiO}_4/\text{AlO}_4$ clusters (also known as secondary building units or SBUs), which are fundamental to zeolite framework formation. The smaller particle size and higher surface area of Ludox® AM-30 may have enhanced the interaction between the silicon and aluminum precursors, leading to a more homogeneous and cohesive precursor gel.

As observed in previous experiments and reported by Russel [69], the synthesis of KFI zeolite, due to the absence of an organic structure-directing agent, requires precise control over several critical parameters to ensure the formation of the correct building blocks and ultimately the KFI crystal structure. Among these parameters, the ratio of Al_2O_3 , SiO_2 , and K_2O is pivotal in determining the phase purity of the resulting material. Interestingly, this discrepancy did not significantly affect the purity of the KFI zeolite when $\text{Al}(\text{OH})_3$ was used as the aluminum source. This is likely due to the higher purity and better solubility of the aluminum hydroxide in the potassium aluminate solution.

For the sample synthesized using TEOS as the silicon source, the resulting material also exhibited a diffraction pattern indicative of a mixture of zeolitic phases. This behavior is likely due to increased pressure generated by the presence of ethoxy groups, which may have disrupted the optimal conditions required for SBU formation.

In contrast, during the synthesis using aluminum wire as the Al source, the preparation of the aluminate solution took approximately 48 hours. Even after this extended period, the solution remained slightly opaque, indicating incomplete solubilization. This may have negatively affected the final $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio in the gel, compromising the formation of a pure KFI phase. This observation aligns with the findings of Verduijn [117], who investigated the influence of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in zeolite synthesis and noted that, in the absence of strontium, zeolite L is typically favored, potentially forming a mixture with zeolite W at higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios.

Finally, the XRD patterns were used to calculate the unit cell parameters of the different synthesized samples, which were then compared with the standard KFI structure. These parameters are summarized in Table 8. The KFI zeolite, also known as ZK-5, crystallizes in a body-centered cubic structure with a unit cell parameter of $a_0 = 18.685 \text{ \AA}$ and belongs to the Im3m space group. Depending on the compensating cation used during synthesis, the samples may exhibit a primitive cubic pseudocell with $a' = a / (2)^{1/2}$.

Table 8. Structural parameters of the samples.

Samples	$d_{200} (\text{\AA})^a$	$a_0 (\text{\AA})^b$	% error	D (nm) ^c	Phase Identified (XRD)
Ludox® AS-40	9.12	19.11	2.41	35.22	KFI
Ludox® AM-30	9.21	18.59	0.36	40.57	KFI
TEOS	-	-	-	-	KFI + L + T + W
Reference (KFI)	9.329	18.658	-	-	KFI

^aInterplanar spacing of the structural plane 200, estimated by Equation 12. ^bUnit cell parameter of KFI, estimated by Equation 13. ^cCrystallite size calculation from Equation 15.

Once again, based on Equation 15, it is possible to estimate the expected value of d_{200} for the synthesized zeolites (from the position of the (200) reflection at $\sim 9.47^\circ$), which closely matches the reference pattern, confirming that the samples exhibit structural features consistent with the KFI zeolite.

When comparing the different silica sources (Ludox® AS-40 and Ludox® AM-30) it is observed that both samples display slight distortions or contractions in the crystal lattice. However, the sample synthesized with Ludox® AS-40 exhibited a higher deviation (2.41%), indicating greater structural distortion, which is consistent with the presence of additional peaks associated with zeolite L.

In contrast, samples synthesized using $\text{Al}(\text{OH})_3$ and aluminum wire (AW) with Ludox® AM-30 presented lower distortions, with relative errors of 0.18% and 0.36%, respectively, in the unit cell parameter. These lattice contractions or distortions may be attributed to differences in the particle sizes of silicon species in each precursor, which could slightly influence the interaction between aluminum and silicon during the formation of the crystal's building units ($\text{SiO}_4/\text{AlO}_4$ tetrahedra).

According to the literature, altering this ratio (particularly reducing the aluminum content in the final structure) can lead to voids in the centers of the 8-membered rings (8MRs) or even

to the compression of these rings [72,153]. Despite these variations, the results indicate that both samples are highly promising as seed crystals for the fabrication of zeolite membranes.

The ATR-FTIR spectra of the synthesized zeolite samples are shown in Figure 38, and the corresponding band positions are summarized in the adjacent table.

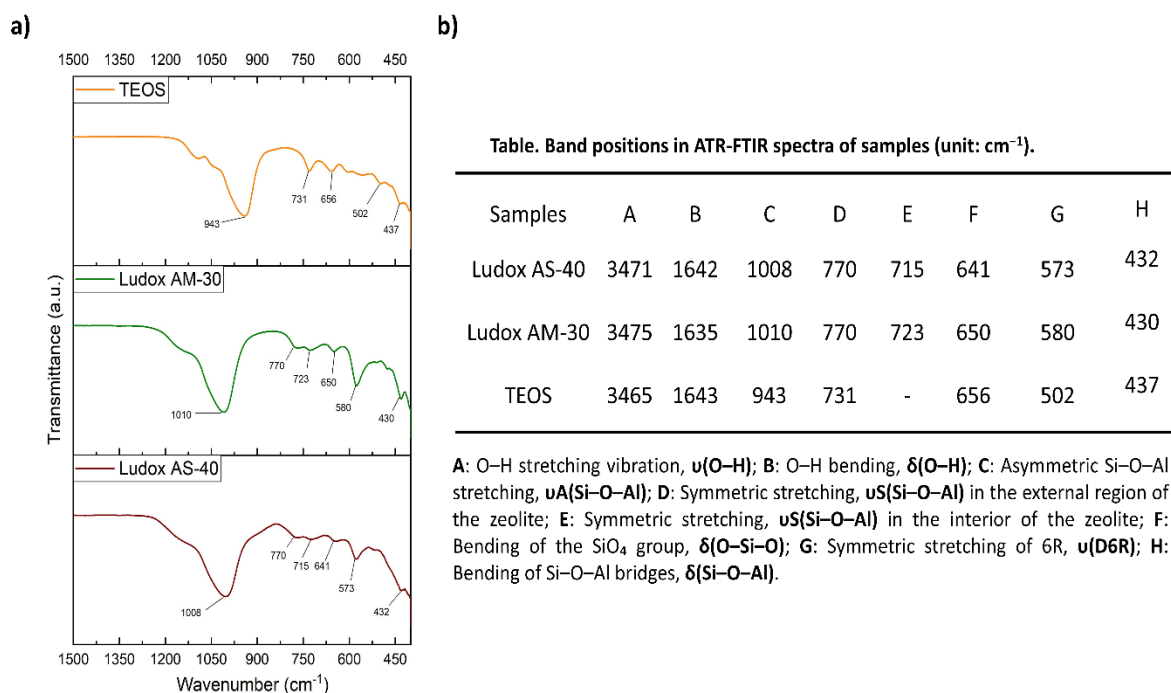


Figure 38. (a) ATR-FTIR spectra for the synthesis using AW as the aluminum source and with different silicon sources; (b) Table with the band positions in the ATR-FTIR spectra of samples (unit: cm⁻¹).

The vibrations common to all zeolites, attributed to the internal vibrations of the tetrahedral units, include the two most intense bands of the spectrum: the strongest, located in the 950–1250 cm⁻¹ region, and another of medium intensity in the 420–500 cm⁻¹ range [148]. It was observed that the samples identified as KFI by XRD showed slight frequency shifts in these bands. For vibration mode C, higher frequencies followed the order Ludox® AM-30 > Ludox® AS-40, whereas for vibration mode H, the trend was reversed (Ludox® AS-40 > Ludox® AM-30). This variation may be due to improved interaction between the aluminum wire and the Ludox® AM-30 silica source.

According to the literature, the stretching modes associated with vibration C are more sensitive to the Si/Al ratio in the zeolite framework and typically shift to lower frequencies as the aluminum content increases. Therefore, when comparing the synthesized samples with AW and $\text{Al}(\text{OH})_3$ as aluminum sources, the latter likely resulted in greater aluminum incorporation into the framework, thereby increasing the material's acidity [72,148].

In both synthesized samples, bands corresponding to six-membered ring stretching were observed. In the TEOS-based sample, XRD and SEM analyses indicated the formation of a zeolite mixture (KFI with possible contributions from L, T, or W phases). This sample exhibited the highest stretching frequencies and a shoulder at a lower frequency, providing further evidence for the presence of multiple zeolitic phases.

Other bands related to the framework topology are those attributed to external linkage modes, particularly the shoulder in the asymmetric stretching region ($\nu_{\text{A}}(\text{Si-O-Al})$), around $1050\text{--}1150\text{ cm}^{-1}$, which generally appears at higher frequencies than the main asymmetric band, and the symmetric stretching region ($\nu_{\text{S}}(\text{Si-O-Al})$) between $750\text{--}820\text{ cm}^{-1}$ [148]. Variations in the characteristics of the asymmetric shoulder—such as intensity, shape, and multiplicity—appear to correlate with topological features of the framework. These shoulders were observed in all samples, and the symmetric stretching bands $\nu_{\text{S}}(\text{Si-O-Al})$ showed slightly higher frequencies in the samples synthesized with aluminum wire compared to those synthesized with $\text{Al}(\text{OH})_3$.

The literature suggests that such variations are related to the extra-framework cation (in this study, K^+ and Sr^{2+}), with higher frequency values indicating that cation insertion may have caused structural distortion in the eight-membered rings [10,152]. This interpretation is supported by the unit cell parameter results, in which samples showed larger a_0 values and, consequently, greater deviation from the standard KFI cell.

A likely explanation again lies in the preparation of the aluminate solution. In samples synthesized with aluminum wire, incomplete dissolution of aluminum was observed even after 48 hours of stirring, with residual alumina particles remaining. This likely compromised the formation of the zeolite's structural building units.

Figure 39 presents SEM images of zeolites synthesized using aluminum wire as the aluminum source, combined with different silicon precursors. Once again, the influence of the silicon source on KFI zeolite formation is evident. Samples prepared using Ludox® AS-40 and Ludox® AM-30 (Figures 39 (a) and 39 (b)) displayed the characteristic cubic morphology of KFI zeolite. In the Ludox® AS-40 sample (Figure 39 (a)), aggregates of amorphous particles were observed, whereas in the Ludox® AM-30 sample (Figure 39 (b)), such aggregates were absent, indicating a higher degree of phase purity in the final material. This outcome is consistent with the XRD analysis, suggesting that the smaller particle size of the Ludox® AM-

30 precursor may have facilitated a more efficient interaction between silicon and aluminum atoms, promoting better crystallization of the KFI zeolite.

When TEOS was used as the silicon precursor (Figure 39 (c)), the resulting sample contained a significant amount of amorphous particle aggregates. Nonetheless, some areas of the sample exhibited both cubic and cylindrical crystal morphologies, suggesting the coexistence of KFI and zeolite L phases [69].

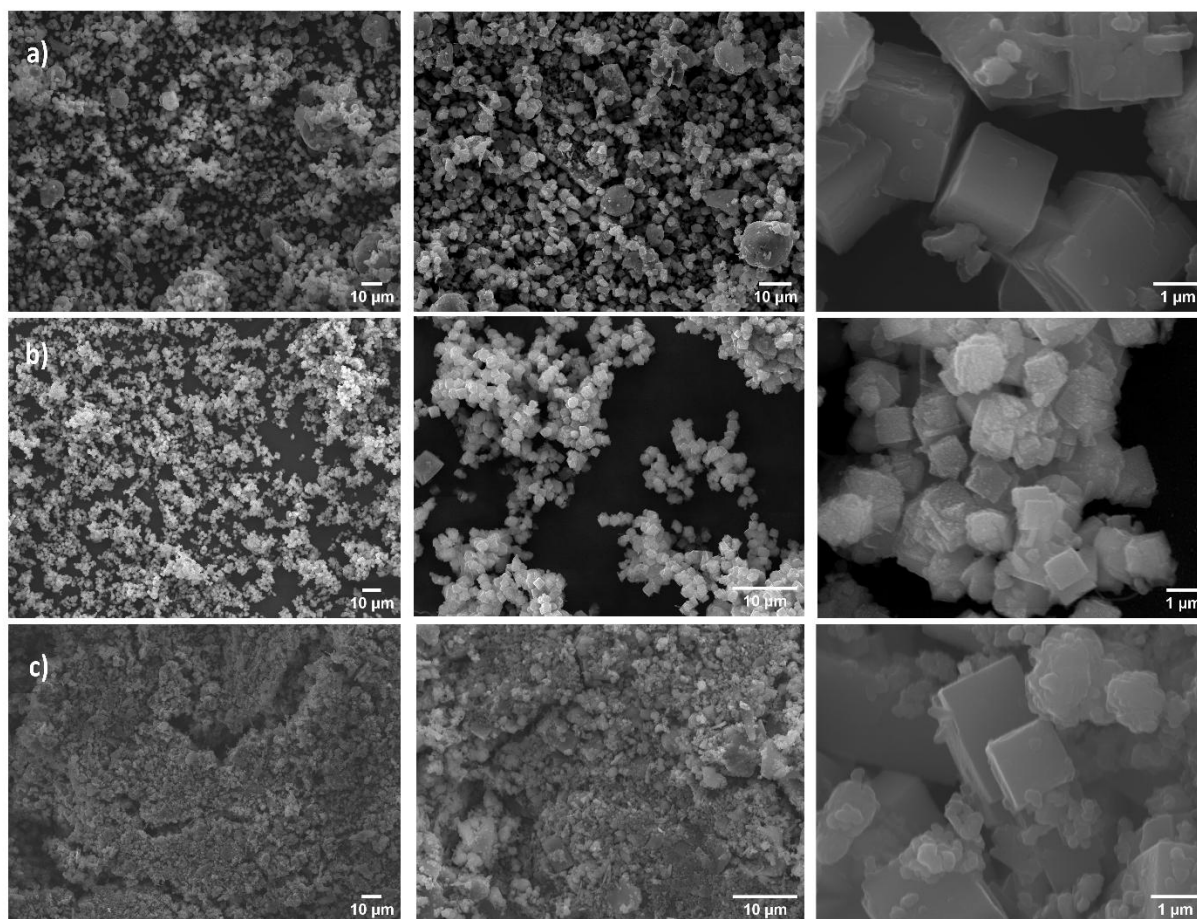


Figure 39. SEM images for the KFI syntheses using aluminum wire as the aluminum source where (a) Ludox® AS-40; (b) Ludox® AM-30 and (c) TEOS as the silica source.

The Si/Al molar ratios obtained by EDS analysis and the particle size distribution derived from SEM images are presented in Appendix 4 and Table 9, aiming to provide a more in-depth analysis of the influence of different precursors on the final material properties.

Table 9. The Si/Al ratio and the mean crystal size distribution.

Samples	Si/Al ^a	Molar Ratio (Al ₂ O ₃ + SiO ₂ + K ₂ O) (%)	Mean Crystal Size (μm) ^b
Ludox® AS-40	3.7	10.78	1.67 ± 0.01
Ludox® AM-30	3.3	14.13	1.16 ± 0.01
TEOS	1.9	8.63	-

^amolar ratio calculated from EDS; ^baverage particle size distribution obtained by SEM.

It was observed that syntheses employing aluminum wire resulted in smaller particle sizes compared to those using aluminum hydroxide. This difference may be attributed to the availability or chemical form of aluminum present in the final synthesis of gel. The sample prepared with Ludox® AS-40 exhibited a mean particle size of 1.67 μm, whereas the Ludox® AM-30 sample presented a smaller average size of 1.16 μm. These results indicate that the availability or chemical speciation of aluminum in the synthesis gel plays a more decisive role in determining particle size than the differences in surface area between the silicon sources (Ludox® AS-40 and Ludox® AM-30).

The organization and connection of secondary building units (SBUs) during synthesis directly influence the final morphology and crystallinity of the zeolite. In the case of KFI zeolite synthesis, which occurs without an organic structure-directing agent, the formation of SBUs is particularly complex. Several studies in the literature emphasize the critical importance of the availability of Al, Si, K, and Sr atoms for successful KFI zeolite construction [11,69,74,117,127].

SEM images of the samples clearly show that the choice of precursor significantly influences the average crystal size. The results indicate that the most pronounced reduction in crystal size is linked to the type of aluminum precursor used, with aluminum wire yielding the smallest observed crystal sizes.

A possible explanation for this difference lies in the chemical composition of the aluminum sources. According to the literature, the hydroxide concentration can affect crystallization kinetics, the final Si/Al ratio, crystal size, and the resulting zeolite phase [54,120]. When aluminum hydroxide is used in combination with potassium hydroxide, the hydroxide ion concentration (OH⁻) increases. Since both silica (SiO₂) and alumina (Al₂O₃) have low solubility in water, pH adjustment is required to solubilize the mixture and allow for the formation of Si–O–Si and Si–O–Al bonds through condensation reactions:



Silica dissolves extensively at pH values above 10.5, meaning that the OH^- concentration plays a key role in transporting reactive species from the solution phase to the growing crystals. An increase in hydroxide concentration can accelerate crystal growth and shorten the nucleation induction time. This effect can be attributed in part to the higher number of reactive species dissolved in the alkaline medium, which promotes more frequent encounters or collisions between precursor species in solution [54,120].

The increased growth rate following nucleation can be similarly explained: a higher concentration of dissolved precursors facilitates faster transport to the crystal surface, resulting in greater surface saturation and, consequently, faster reaction kinetics. Thus, the use of $\text{Al}(\text{OH})_3$ favored crystal growth, providing more suitable conditions for efficient nucleation and crystal development during synthesis.

The particle sizes obtained using aluminum wire were found to be smaller than typical values reported in the literature for KFI zeolites, which are generally around $\sim 3 \mu\text{m}$ [12,57,66,68,74]. This result is particularly promising, as various size-reduction strategies such as the use of crystal growth inhibitors or ultrasonic treatment are often required to achieve particles at the nanoscale [12,13,67]. Therefore, aluminum wire appears to be a promising precursor for studies aimed at reducing particle size. However, since samples synthesized with $\text{Al}(\text{OH})_3$ exhibit faster particle growth kinetics, smaller crystal sizes could potentially be obtained by decreasing the synthesis time, an investigation to be explored in future work.

Zeolites with smaller particle sizes play a crucial role in gas separation and are highly valued in membrane applications. This is because they generally offer a higher surface area per unit volume, providing more active sites for gas adsorption and diffusion, which enhances separation efficiency. Additionally, smaller zeolite particles provide shorter diffusion pathways for gas molecules through the membrane, improving transport rates and contributing to faster and more selective separations. Finally, smaller zeolite particles tend to exhibit higher structural stability, which improves membrane resistance under high pressure and temperature conditions, resulting in a more durable final membrane [3,13,15,76].

The ^{27}Al MAS NMR spectra and the distribution of aluminum species in the samples are shown in Figure 40.

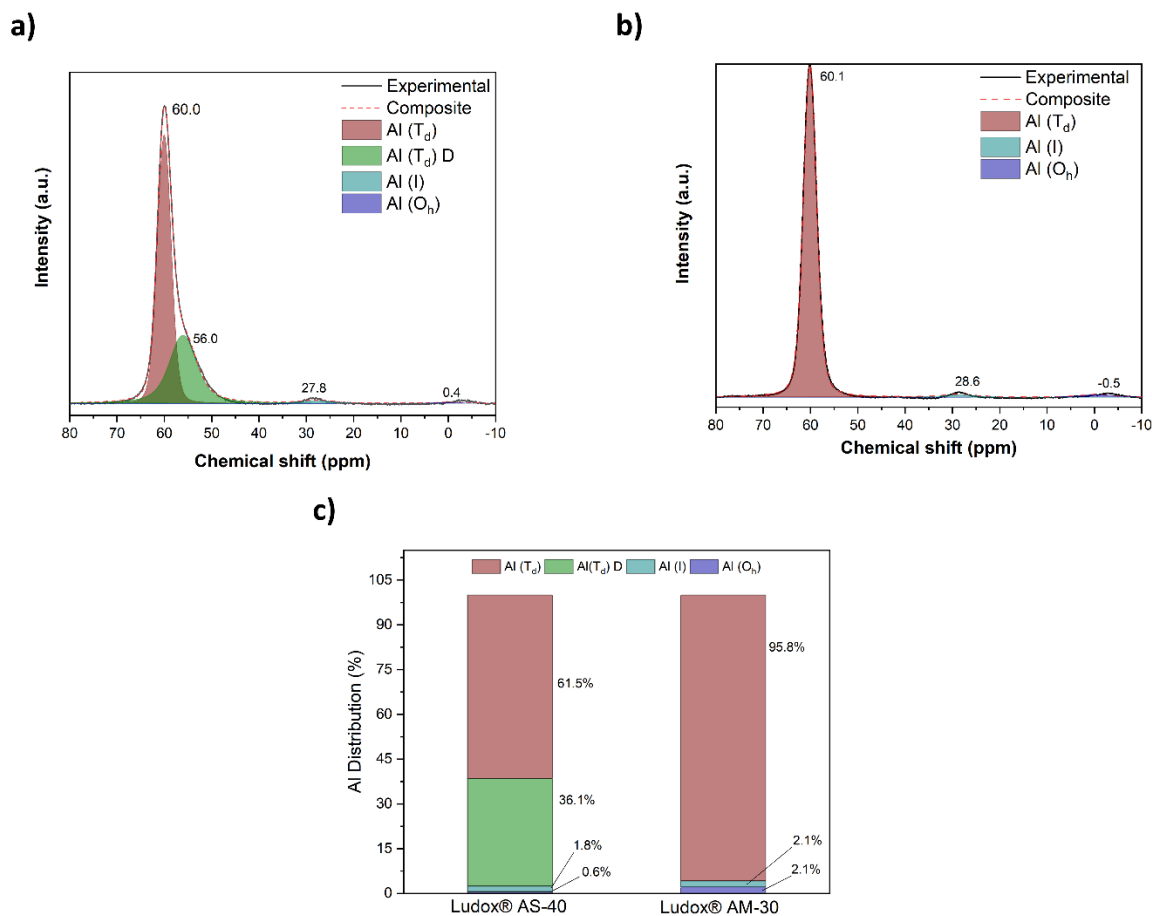


Figure 40. ^{27}Al RAM-NMR spectra for samples prepared using aluminum wire as aluminum source where (a) refers to the sample with Ludox® AS-40 and (b) to samples with Ludox® AM-30 as silicon source and (c) the relative percentage of chemical environments.

A strong resonance was observed around 60 ppm, attributed to tetrahedrally coordinated aluminum within the framework ($\text{Al}(\text{T}_d)$), along with a lower-intensity signal near 0 ppm, corresponding to octahedrally coordinated extra-framework aluminum ($\text{Al}(\text{O}_h)$) in both samples. Additionally, a low-intensity peak around 30 ppm was identified, characteristic of penta-coordinated aluminum or tetrahedrally coordinated aluminum in a distorted, extra-framework environment [56,66,68,137]. Once again, the peak observed at approximately 56 ppm is associated with the formation of penta-coordinated aluminum species ($\text{Al}(\text{I})$) [10,151,152].

In Figure 40 (c), it can be seen that the proportion of this penta-coordinated aluminum is relatively low in both samples, with values of 1.8% and 2.0% for the samples synthesized with

Ludox® AS-40 and Ludox® AM-30, respectively. These results indicate minimal disruption of the aluminum framework.

However, in the Ludox® AS-40 sample, a high-intensity peak was observed at 56 ppm (Figure 40 (a)), corresponding to a final proportion of 36% in the material (Figure 40 (c)). This signal is attributed to distorted extra-framework tetrahedral aluminum (Al (Td) D) [151]. The presence of this signal suggests considerable partial degradation of the zeolitic framework, consistent with unit-cell parameter calculations that showed a 2.4% deviation from the standard KFI structure. These values are notably higher than those obtained from samples synthesized with $\text{Al}(\text{OH})_3$ as the aluminum source, suggesting that using aluminum wire may yield a more defective, structurally distorted material.

A possible explanation for this structural distortion is the presence of non-characteristic KFI peaks in the XRD pattern of this sample, indicating a lower degree of phase purity when compared to the sample synthesized with Ludox® AM-30. Furthermore, SEM images revealed the formation of large aggregates of amorphous silica and the presence of elongated bar-shaped structures, typical of zeolites T and W. These observations suggest the formation of secondary zeolitic phases in addition to the desired KFI, indicating greater sample impurity. These impurities likely contributed to the development of the distorted aluminum environments within the material.

The ^{29}Si MAS NMR spectra, along with the distribution of the various silicon environments present in the samples, are shown in Figure 41. The structural environments of silicon commonly reported for KFI zeolites are classified according to the number of aluminum atoms substituting silicon in the tetrahedral framework (denoted as Si ($n\text{Al}$), where n ranges from 0 to 4), each associated with a specific chemical shift [66,149,150,152].

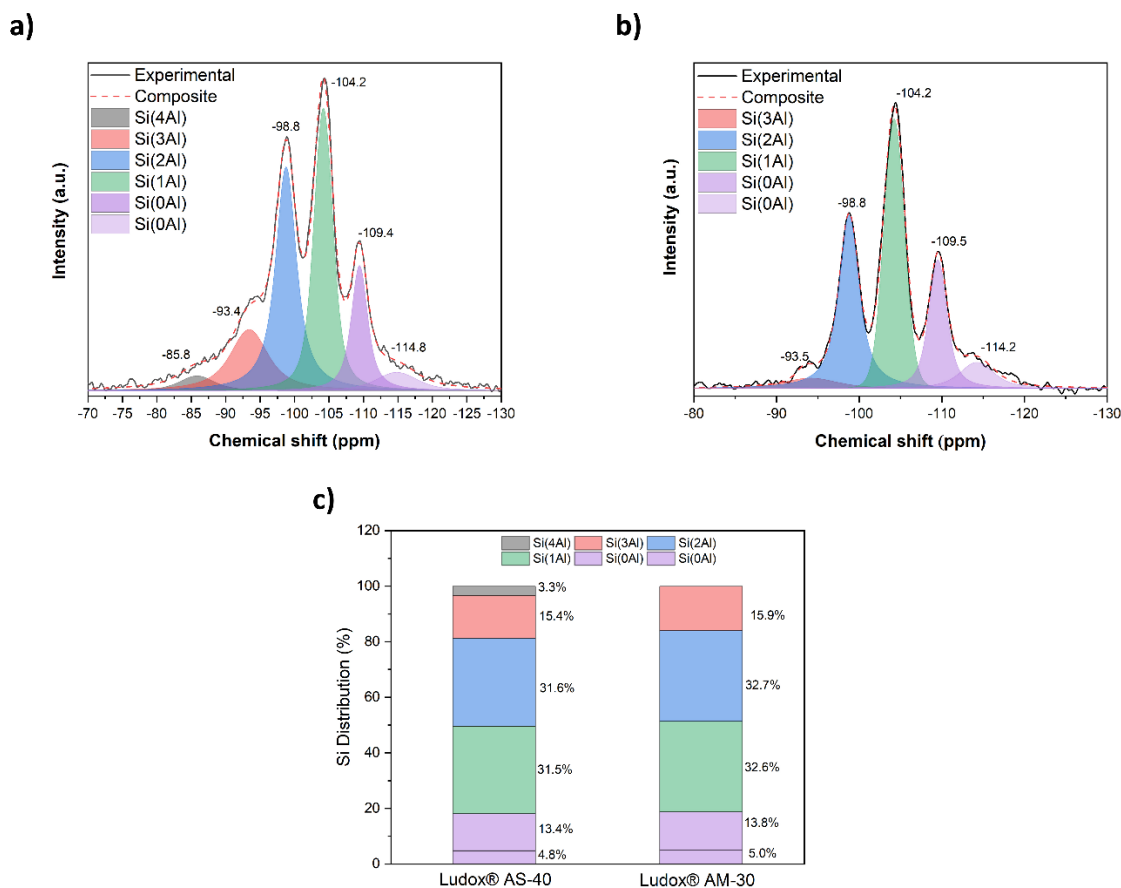


Figure 41. ^{29}Si RAM-NMR spectra for samples prepared using aluminum wire as the aluminum source where (a) refers to the sample with Ludox® AS-40 and (b) to samples with Ludox® AM-30 as the silica source and (c) the relative percentage of chemical environments.

For the sample synthesized with Ludox® AS-40, signals were observed at -114.8 , -109.4 , -104.2 , -98.8 , -93.4 , and -85.8 ppm, corresponding to the Si (0Al), Si (0Al), Si (1Al), Si (2Al), Si (3Al), and Si (4Al) species, respectively. For the sample synthesized with Ludox® AM-30, the signals appeared at -114.2 , -109.5 , -104.2 , -98.8 , and -93.5 ppm, which correspond to the Si (0Al), Si (0Al), Si (1Al), Si (2Al), and Si (3Al) environments, respectively. Notably, both samples exhibited three high-intensity signals in the regions of -100 , -110 , and -115 ppm, which are characteristic of the KFI-type structure.

Once again, the Ludox® AM-30 sample exhibited higher intensity signals corresponding to the Si (1Al), Si (2Al), and Si (3Al) environments compared to the Ludox® AS-40 sample. This suggests that the sample synthesized with Ludox® AM-30 is richer in silicon, as the intensity of each resonance is proportional to the number of silicon atoms present in that chemical environment [56,68,150]. The absence of the signal corresponding to the Si (4Al)

species in the Ludox® AM-30 sample, which is typically observed in more highly distorted KFI frameworks, supports previous observations from XRD and ^{27}Al NMR data indicating a more ordered structure.

From the relative areas of the Si (nAl) environments, the Si/Al ratios were estimated using Equation 19, yielding values of 3.0 and 3.7 for the Ludox® AS-40 and Ludox® AM-30 samples, respectively. In general, the Si/Al ratio determined by solid-state NMR tends to be lower than the actual value, as all terminal OH species in the zeolite are considered as associated with aluminum during the calculation process [66]. Nonetheless, these results are consistent with those obtained via EDS analysis, which yielded values of 3.7 and 3.3 for the respective samples.

These findings confirm the successful incorporation of aluminum into the KFI zeolite framework, resulting in materials with high silica content. This characteristic offers a notable advantage for membrane applications, as increasing the aluminum content typically enhances the membrane surface's hydrophilicity. Consequently, separation efficiency is reduced for gas mixtures containing water, due to the stronger affinity of water molecules for the more hydrophilic zeolite framework [15].

Finally, the evaluation of the textural properties was conducted via nitrogen physisorption at $-196\text{ }^{\circ}\text{C}$, and the resulting isotherms for the synthesized samples are presented in Appendix 2, Figure 42 and Appendix 5.

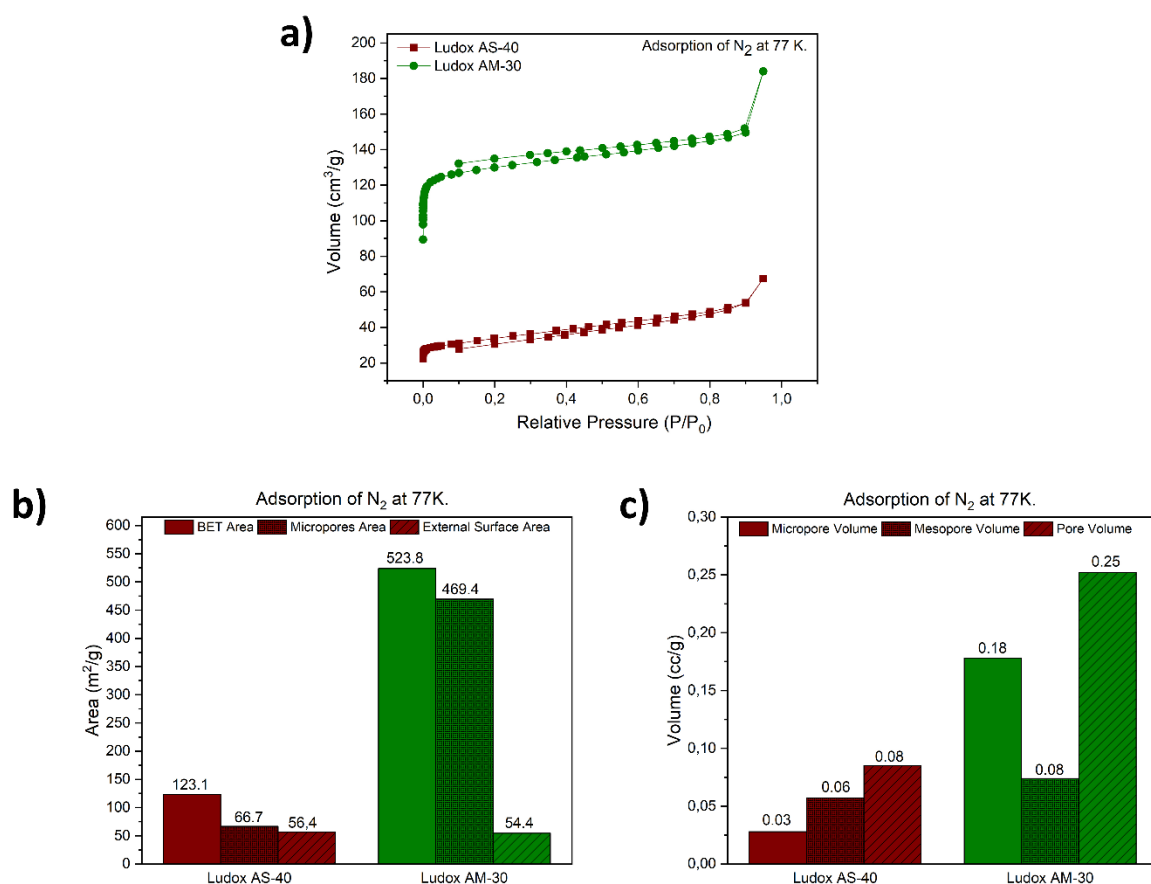


Figure 42. (a) N₂ adsorption/desorption isotherm; (b) BET area, micropore area calculated by the t-Plot method in the region 0.15 to 0.5 and (c) pore volume calculated by the t-Plot method in the region 0.15 to 0.5 for samples using AW as the aluminum source and with different silicon sources.

The experimental adsorption isotherms indicate that the samples synthesized with Ludox® AS-40 and Ludox® AM-30 (Figure 42 (a)) exhibit a combination of Type I(b) and Type IV(a) isotherms. The presence of hysteresis in the curves suggests the existence of mesopores in both samples, with hysteresis loops classified as Type H4 [128]. The sample synthesized with Ludox® AS-40 also displays features resembling Type II isotherms, which are characteristic of non-porous or macroporous solids, where unrestricted adsorption occurs, progressing from monolayer to multilayer adsorption at high relative pressures (p/p_0). This behavior is likely due to the increased amorphous material in the sample, which may have contributed to pore blockage and, consequently, to the macroporous characteristics. As evidenced by the sample's XRD patterns, showing diffraction peaks associated with other zeolite phases this phase mixture may have promoted amorphous content and pore obstruction through the accumulation of crystals with varying sizes and morphologies.

Analysis of Figure 42 (b) reveals that all samples exhibit surface areas within the reported literature range. The system synthesized with aluminum wire showed the highest specific surface area and micropore volume, compared with the system using $\text{Al}(\text{OH})_3$, consistent with the smaller crystal sizes observed in SEM images and the particle size distribution. The increase in micropore volume may be attributed to the fact that smaller crystals allow for the detection of a greater number of micropores, a phenomenon also reported in previous studies [12,13].

Interestingly, the trends in specific surface area and pore volume closely follow those of crystal size (Figure 39 (b) and Table 9). For instance, in the samples synthesized with Ludox® AM-30, the BET surface area increased from $301.1 \text{ m}^2 \text{ g}^{-1}$ and total pore volume of $0.15 \text{ cm}^3 \text{ g}^{-1}$ in the sample synthesized with $\text{Al}(\text{OH})_3$ (crystal size: $3.12 \text{ }\mu\text{m}$) to $523.8 \text{ m}^2 \text{ g}^{-1}$ and $0.25 \text{ cm}^3 \text{ g}^{-1}$ in the sample synthesized with aluminum wire (crystal size: $1.16 \text{ }\mu\text{m}$). This intriguing feature can be attributed to several factors:

- (1) the reduced crystal size exposes a greater external surface area ($8.72 \text{ m}^2 \text{ g}^{-1}$);
- (2) the smaller crystal size may have accelerated the crystallization process, leading to a more developed pore structure despite identical synthesis conditions and reaction times for both samples;
- (3) the presence of mesoporous structures generated by phase mixing or lower crystallinity [12,13,67].

It was also observed that the BET surface area ($523.8 \text{ m}^2 \text{ g}^{-1}$), the micropore surface area ($469.4 \text{ m}^2 \text{ g}^{-1}$), and the micropore volume ($0.18 \text{ cm}^3 \text{ g}^{-1}$) of the Ludox® AM-30 sample were the highest among all. This indicates a more complete pore network and higher crystallinity for this sample, in line with previous XRD analysis, reinforcing its potential for gas separation membrane applications.

Future studies will include analyses of CH_4 and CO_2 adsorption to predict the separation mechanism in KFI zeolite membranes. Furthermore, the pore sizes observed in the synthesized zeolite samples were notably larger than those reported in the IZA online database.

5.2.1.3. $\text{Al}(\text{O-i-Pr})_3$ as Aluminum Source

X-ray diffraction patterns were obtained to verify whether the synthesized material corresponded to KFI zeolite and to obtain information such as crystallinity, interplanar spacing, and crystallite size. These diffraction patterns were then compared to the standard pattern of KFI zeolites [127], as illustrated in Figure 43.

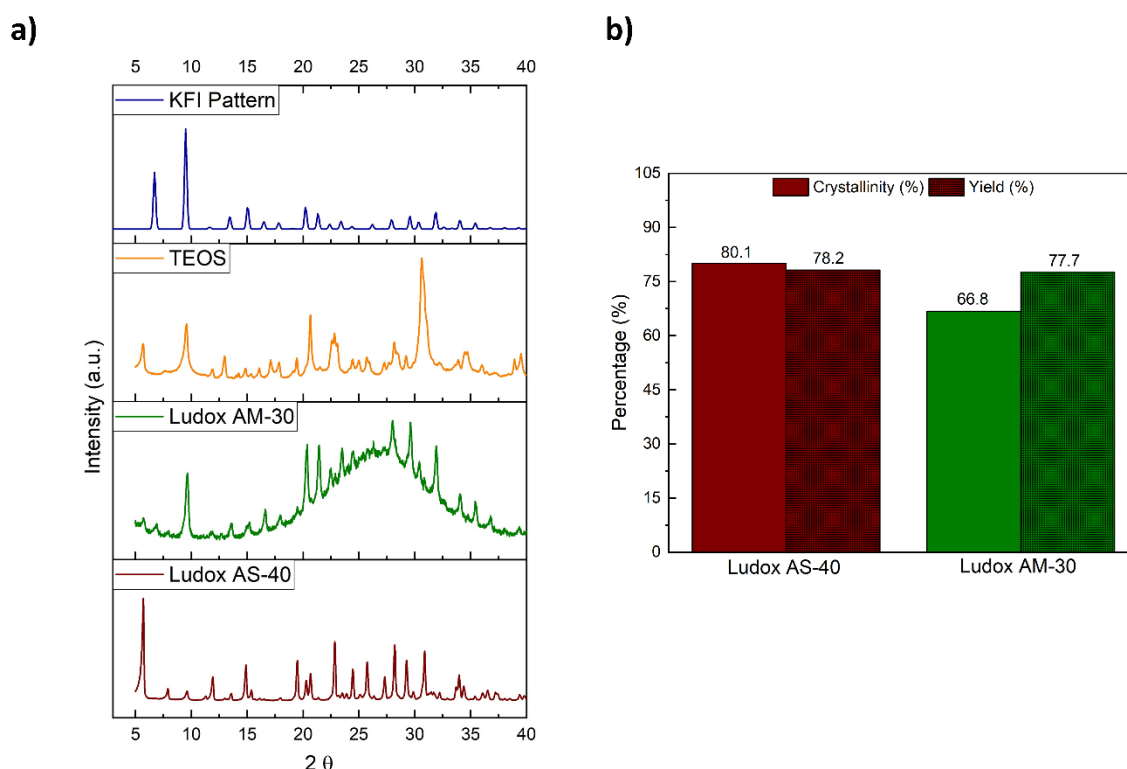


Figure 43. (a) Crystallographic patterns and (b) crystallinity and yield values for the syntheses using $\text{Al}(\text{O-i-Pr})_3$ as the aluminum source with different silicon sources.

It can be observed that the diffraction patterns confirmed that the synthesis using Ludox® AS-40 exhibited peaks corresponding to the LTL zeolite [105], with peaks at 2θ values of 5.7° , 11.92° , 22.8° , and 28.2° , assigned to the (100), (001), (221), and (411) planes of this zeolite, respectively. In contrast, the synthesis using Ludox® AM-30 yielded predominantly amorphous material. The few peaks observed in the diffractogram at 2θ values of 9.62° , 13.58° , 15.16° , 20.36° , 21.44° , and 29.56° , corresponding to the (200), (220), (301), (411), (420), and (611) planes, respectively, indicate the formation of KFI. However, this suggests that the crystallization time may have been insufficient to achieve fully crystalline KFI material.

A possible explanation again lies in the difference in surface area between the two silica sources employed. The silica with a higher surface area is likely to promote a more efficient interaction between the alumina and silica precursors, resulting in a final gel with $\text{SiO}_4/\text{AlO}_4$ units capable of forming the fundamental building blocks of the KFI crystal structure. To the best of our knowledge, no reports in the literature describe the synthesis of KFI zeolite using aluminum isopropoxide as the aluminum source; therefore, the data obtained in this study are promising.

In contrast, the synthesis using TEOS as the silicon source appeared crystalline, albeit with broadened peaks. Specifically, a peak at $2\theta = 9.44^\circ$, corresponding to the (200) crystallographic plane of KFI, was observed. Additionally, peaks at 2θ values of 5.64° , 11.74° , 19.42° , 20.66° , and 30.7° , corresponding to the (100), (001), (220), (301), and (222) planes of the L zeolite, respectively, indicate that the material exhibits a small degree of amorphous character (as suggested by peak broadening) and a preference for the L zeolite phase.

Finally, using the diffraction patterns, the lattice parameters of the synthesized samples were calculated and compared with those of the KFI structure. These parameters are presented in Table 10. The KFI zeolite, also known as ZK-5, possesses a body-centered cubic structure with a lattice parameter $a_0 = 18.685 \text{ \AA}$ and space group $\text{Im}\bar{3}\text{m}$. Depending on the compensating cation used during synthesis, these samples may exhibit a primitive cubic pseudocell with $a' = a/(2)^{1/2}$.

Table 10. Structural parameters of the samples.

Samples	$d_{200} (\text{\AA})^a$	$a_0 (\text{\AA})^b$	% error	$D (\text{nm})^c$	Phase Identified (XRD)
Ludox® AS-40	11.21	-	-	41.88	L
Ludox® AM-30	12.85	18.53	0.65	27.00	KFI (amorphous)
TEOS	-	-	-	21.07	KFI + L + T + W
Reference (KFI)	9.329	18.658	-	-	KFI

^aInterplanar spacing of the structural plane 200, estimated by Equation 12. ^bUnit cell parameter of KFI, estimated by Equation 13. ^cCrystallite size calculation from Equation 15.

It can be observed that by using Equation 15 to predict the $d_{(200)}$ value for the synthesized zeolites (based on the position of their 200 reflections at approximately 9.47°), the values obtained are close to the standard. This first validates the equations used and also confirms that the synthesized zeolites exhibit characteristics consistent with KFI. Even for the sample synthesized with Ludox® AM-30, which achieved only 20% crystallinity, it was possible to

observe that, in addition to the characteristic KFI peaks, the sample exhibited formation of the unit cell with a lattice parameter a_0 very close to the standard, with an error of only 0.65%. This suggests that further studies on this system are justified, especially since there are no reports in the literature using aluminum isopropoxide as the aluminum source and small changes such as synthesis time might promote complete formation of the structure.

The ATR-FTIR spectra of the synthesized zeolite samples are presented in Figure 44, and the band positions are summarized in the adjacent table.

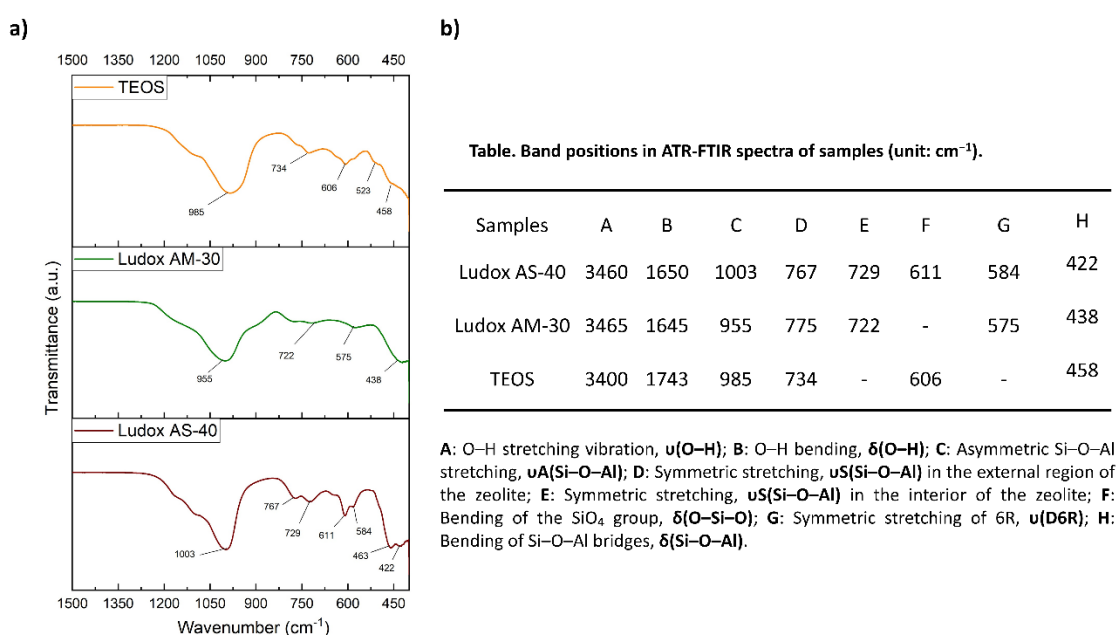


Figure 44.(a) ATR-FTIR spectra for the synthesis using $\text{Al}(\text{O-i-Pr})_3$ as the aluminum source and with different silicon sources; (b) Table with the band positions in the ATR-FTIR spectra of samples (unit: cm^{-1}).

The internal tetrahedral vibrations include the two most intense bands in the spectrum: the strongest between $950\text{--}1250\text{ cm}^{-1}$ and another of medium intensity between $420\text{--}500\text{ cm}^{-1}$ [148]. Despite the low crystallinity, the sample synthesized with Ludox® AM-30 exhibited values close to, yet slightly lower than those of the C vibrations, while showing higher values for the H vibrations. The stretching modes corresponding to the C vibrations are more sensitive to the Si/Al ratio in the zeolitic material's structure and typically shift to lower frequencies as the aluminum content increases. Therefore, it can be inferred that, albeit slightly, the samples showed good incorporation of aluminum despite their crystallinity, and a kinetic study with

extended hydrothermal synthesis time could yield a more crystalline and purer KFI zeolite [72,148].

Again, the sample synthesized with TEOS, due to impurities observed in the diffractograms and SEM images (L, T, or W zeolites), exhibited higher-frequency peaks, along with a lower-frequency shoulder, further supporting the formation of a mixture of these zeolites.

Other bands exhibiting characteristics related to the topology of the structure, attributed to external bonding modes, include the shoulders observed near 1050–1150 cm^{-1} in the asymmetric stretching region ($\nu\text{A}(\text{Si-O-Al})$), which generally present higher frequency values than the main stretching band, and the symmetric stretching region of the tetrahedron ($\nu\text{S}(\text{Si-O-Al})$) around 750–820 cm^{-1} [148]. The absence of this shoulder in the sample synthesized with Ludox® AM-30 is likely due to its low crystallinity. Nonetheless, the sample presented bands in characteristic regions of KFI, suggesting that with an in-depth crystallization study, this system could be optimized, enabling the synthesis of KFI zeolite via a methodology not yet reported in the literature.

Figure 45 displays SEM images of this set of samples. The use of aluminum isopropoxide as a precursor represents a novel approach according to our literature survey. Initially, when using Ludox® AS-40 (Fig. 45 (a)) as the silica source, the formation of L zeolite was observed, as evidenced by the diffractogram. The SEM images revealed many particles with cylindrical morphology and a considerable number of impurities, including elongated bar-shaped particles characteristic of T zeolite. For the sample synthesized with Ludox® AM-30 (Fig. 45 (b)) as the silicon source, amorphous aggregates were observed alongside a small fraction of cubic particles characteristic of the KFI zeolite, indicating limited formation of this phase, consistent with the diffractogram results. A kinetic study on this sample might promote the formation of KFI zeolite with a high degree of crystallinity and purity. The sample synthesized with TEOS (Fig. 45 (c)) showed several intense peaks in the diffractograms indicating the presence of

zeolitic phases; however, SEM images revealed spherical particles, indicating that the produced material does not correspond to KFI, L, W, or T zeolites.

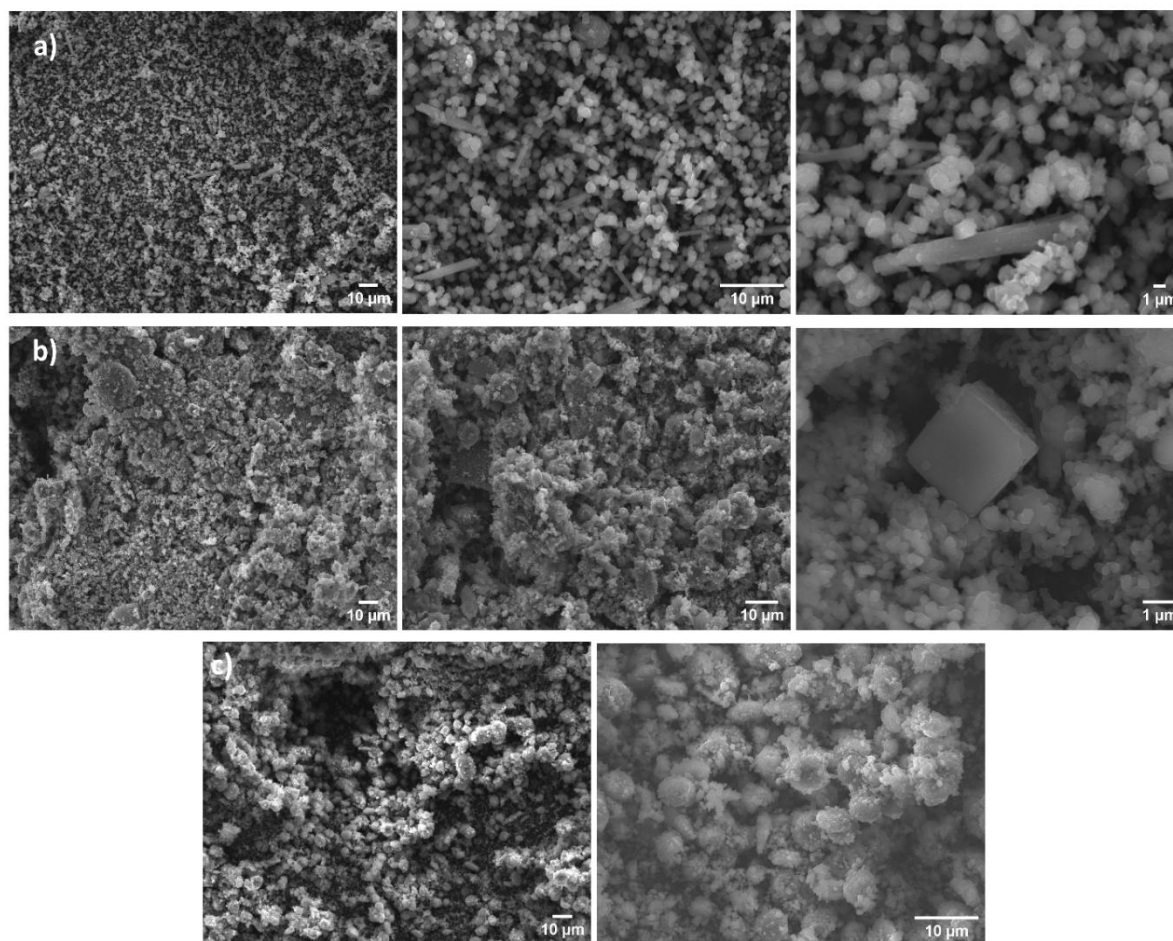


Figure 45. SEM images for the KFI syntheses using $\text{Al}(\text{O}-i\text{-Pr})_3$ as the aluminum source where (a) Ludox® AS-40; (b) Ludox® AM-30 and (c) TEOS as the silica source

Appendix 6 and Table 11 present the Si/Al ratios obtained by EDS alongside the particle size distributions derived from microscopy images. Initially, it was observed that the samples synthesized using TEOS, as previously discussed and corroborated by both diffractograms and SEM images, consisted of a mixture of different zeolites and exhibited reduced Si/Al ratios. This finding can be attributed to the limited availability of aluminum and silicon atoms, as discussed earlier. The scarcity of these fundamental atoms hindered the formation of Secondary Building Units (SBUs), thereby impeding the proper organization and three-dimensional growth of the zeolite framework.

Table 11. The Si/Al ratio and the mean crystal size distribution.

Samples	Si/Al ^a	Molar Ratio (Al ₂ O ₃ + SiO ₂ + K ₂ O) (%)	Mean Crystal Size (μm) ^b
Ludox® AS-40	3.1	10.43	1.01 ± 0.01
Ludox® AM-30	4.1	10.43	3.04 ± 0.01
TEOS	1.7	7.61	-

^amolar ratio calculated from EDS; ^baverage particle size distribution obtained by SEM.

Finally, the textural parameters were evaluated by nitrogen physisorption at -196 °C. The adsorption isotherms of the synthesized samples are presented in Figure 46 and Appendix 7.

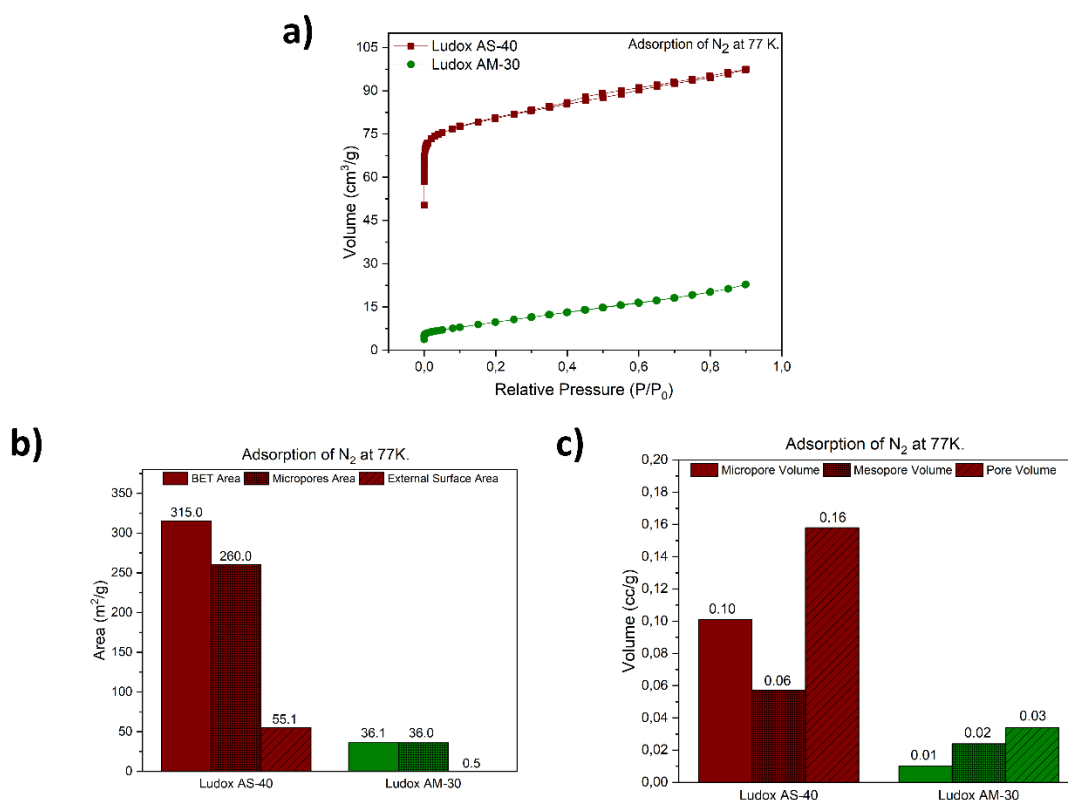


Figure 46. (a) N₂ adsorption/desorption isotherm; (b) BET area, micropore area calculated by the t-Plot method in the region 0.15 to 0.5 and (c) pore volume calculated by the t-Plot method in the region 0.15 to 0.5 for samples using Al(O-i-Pr)₃ as the aluminum source and with different silicon sources.

Both samples in Figure 46 (a) exhibit a combination of isotherm types, where the sample synthesized with Ludox® AS-40 shows a combination of Type I (b) and IV (a) isotherms, whereas the sample with Ludox® AM-30 displays a Type III isotherm. Type III isotherms do not exhibit the formation of a distinct monolayer, indicating relatively weak adsorbent-

adsorbate interactions, with adsorbed molecules clustering around more favorable sites on the surface of a non-porous or macroporous solid [128]. A plausible explanation is that the sample demonstrates low crystallinity, with a crystallinity percentage below 70%. Consequently, the significant presence of amorphous material contributed to high macroporosity in the sample.

Figures 46 (b) and 46 (c) present the main analyses derived from the adsorption isotherms, including the specific surface area determined by the BET equation, micropore area, external surface area, and micropore volume calculated via the t-plot method. These results indicate a low BET surface area and micropore volume.

5.2.2. Crystal Size Reduction Study

To conclude, a study was conducted to analyze the influence of water content in the synthesis with $\text{Al}(\text{OH})_3$ as the aluminum source. The motivation for this investigation stemmed from the need for a thin zeolitic layer on the membrane, which reduces resistance to gas transport and thereby increases permeate flux. Since gas separation occurs via adsorption and selective diffusion, a thinner layer allows target gases to pass through the membrane with shorter residence times, resulting in higher permeation rates without compromising selectivity. Moreover, a thinner zeolitic layer minimizes zeolite material consumption and facilitates uniform deposition on the support, reducing structural defects that could compromise membrane selectivity. This also contributes to reducing the fabrication and operational costs of such membranes [77,81,82,102,105,108,110,111,119] .

Empirical observations showed that using Ludox® AM-30, a colloidal silica with lower water content (70% by volume), not only improved the system's viscosity but also yielded materials with fewer impurities and better-defined crystals. The literature reports that increased water content may promote the breaking of Si–O–Si and Si–O–Al bonds, which can subsequently reorganize and recombine. This leads to enhanced chemical reactivity and reduced viscosity of the synthesis gel. Such viscosity reduction increases the mobility of species within the system [120]. Additionally, the presence of water can accelerate hydrolysis and condensation reactions. As a nucleophilic reagent, water enhances hydrolysis reactions, facilitating the formation of active species in solution for zeolite formation. Furthermore, water can enhance the synthesis kinetics by promoting the generation and transport of H^+ and OH^- hydrates [89]. Given that Ludox® AM-30 exhibited the best results in terms of material purity,

the effect of increasing the water content was investigated in order to improve gel agitation and assess its impact on the properties of the resulting material.

Figure 47 presents the XRD patterns of the samples from the water content study, synthesized over 72 h. First, analyzing the diffractograms, it is noteworthy that all samples exhibit peaks corresponding to the KFI zeolite. The samples with water-to-solid ratios of 200 and 240 showed high crystallinity, with peaks located at $2\theta = 6.68, 9.41, 20.12, 21.32$, and 29.22 for the 200 ratio, at $2\theta = 6.70, 9.38, 20.14, 21.24$, and 29.42 for the 240 ratio, at $2\theta = 6.63, 9.40, 20.12, 21.21$ and 29.42 for the 280 ratio and at $2\theta = 6.58, 9.39, 20.11, 21.21$ and 29.41 for the 320 ratio corresponding to the (110), (200), (330), (420), and (611) planes, respectively [127].

These results indicate that increasing the water content did not affect the formation of the KFI crystalline structure in the samples with ratios of 200, 240 and 280. However, the sample with a ratio of 320 showed a significant loss in crystallinity, suggesting possible system saturation. Furthermore, in all samples with higher water content, peak broadening was observed, particularly around $2\theta \approx 9.5$, corresponding to the (200) plane, with higher intensity than in the sample with a water ratio of 160 and the reference pattern.

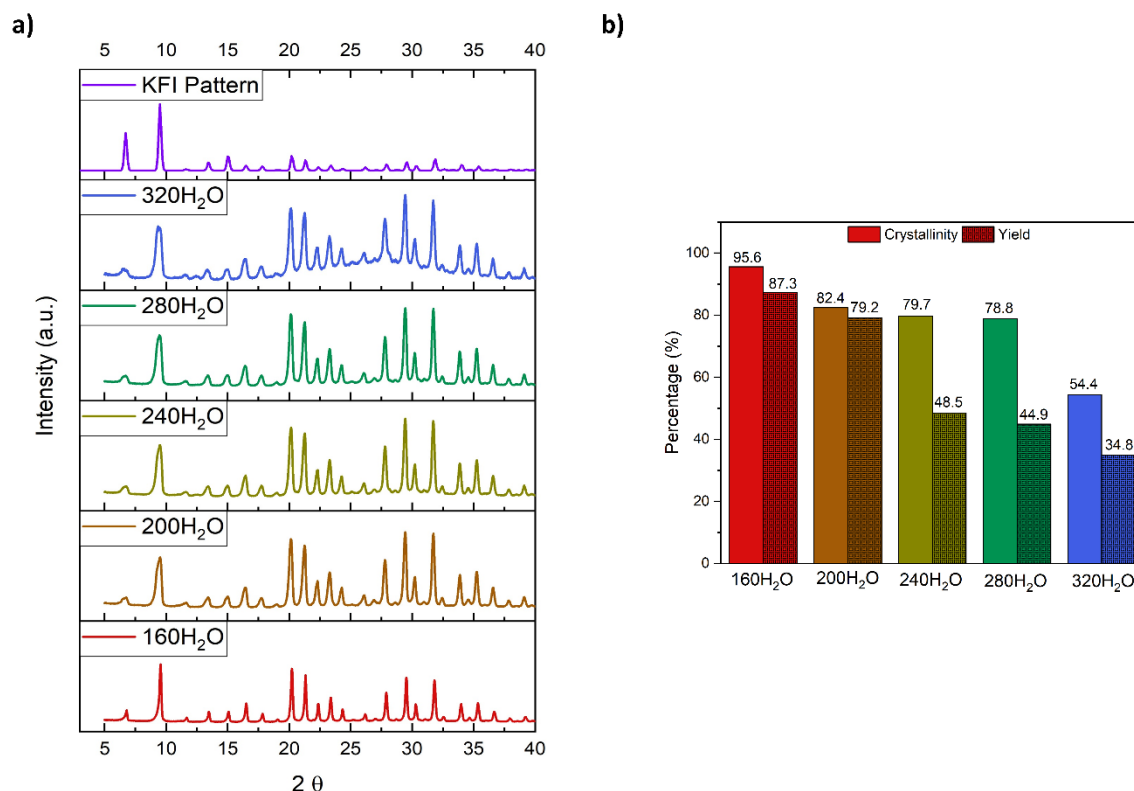


Figure 47.(a) Crystallographic patterns and (b) crystallinity and yield values for the syntheses using $\text{Al}(\text{OH})_3$ as the aluminum source, Ludox® AM-30 as silicon source and different water proportions.

An explanation for this observed phenomenon lies in the fact that a crystal is characterized by the ordered repetition of its unit cell. Differences in the arrangement of atoms within the unit cell can result in a preferred orientation of the crystalline grains, leading to significant variations in the relative intensities of the observed diffraction peaks [154]. These differences may have arisen from the increased water content in the channels and cavities, which enhances the material's thermodynamic stability through interactions among water molecules, cation, and the zeolite's structural elements. The organization of water and aqueous solutions plays a fundamental role in the construction of the final material structure [120]. While preferred orientation can be identified and compensated for during qualitative analysis, such as phase identification, it presents a greater challenge when attempting to perform quantitative analysis or determine precise unit cell parameters (Table 12). This is because the most intense peak may shift, thereby affecting the calculations.

Table 12. Structural parameters of water study samples.

Samples	d_{200} (Å) ^a	a_0 (Å) ^b	% error	D (nm) ^c	Phase Identified (XRD)
160H ₂ O	9.27	18.6	0.18	42.1	KFI
200H ₂ O	9.41	18.7	0.27	16.9	KFI
240H ₂ O	9.38	18.7	0.23	16.8	KFI
280H ₂ O	9.40	18.7	0.23	16.4	KFI
320H ₂ O	9.39	18.7	0.30	15.1	KFI
Padrão	9.3	18.6	-	-	KFI

^aInterplanar spacing of the structural plane 200, estimated by Equation 12. ^bUnit cell parameter of KFI, estimated by Equation 13. ^cCrystallite size calculation from Equation 15.

By using Equation 15 to estimate the $d_{(200)}$ value for the synthesized zeolites (based on the position of the (200) reflection around 9.3°), an increase in d -spacing was observed in accordance with the rise in water content. However, these values remained very close to that of the reference pattern. A possible explanation for this increase in interplanar spacing may lie in the presence of structural defects, such as atoms occupying distinct regions within the unit cell,

which may promote the growth of alternative planes. Additionally, differences in the synthesis gel (liquid-solid transition), leading to different atom arrangements and increase in the interplanar distance.

When evaluating the a_0 values of the samples, they were found to be very close to the reference standard, with errors around 0.2%, and a maximum error of 0.3% for the sample with a water ratio of 320, likely due to loss of crystallinity. This suggests that even with increased interplanar spacing and reduced crystalline phase, the final unit cell did not undergo significant distortions or lattice contractions.

Regarding the crystallite size, it decreased as the water content increased, although it remained relatively consistent. This reduction can be attributed to several factors, primarily related to the synthesis gel preparation and post-synthesis processes. Since the latter remained unchanged, it is suggested that the gel composition influenced the final crystallite size. Likely, the higher water proportion created a reaction medium with lower concentration and reduced pH, affecting both nucleation and crystal growth mechanisms. Nucleation, being the initial stage of zeolite crystal formation, is highly sensitive to changes in reaction conditions. A decrease in nucleation rate due to increased water content may have led to the formation of larger crystallites during this early stage. In the subsequent crystal growth stage, the higher water content promoted the aggregation of smaller nuclei into larger crystals. This could be due to a slower growth rate, allowing crystals to grow larger before merging or agglomerating with other crystals [89,155,156].

The ATR-FTIR spectra of the synthesized zeolite samples are shown in Figure 48, while the band positions are summarized in the adjacent table. The presence of bands assigned to molecularly adsorbed water is evident in all samples around 1600 and 3400 cm^{-1} . The infrared spectra of zeolites in the 1300–400 cm^{-1} region provides a distinct fingerprint of the framework, revealing structural characteristics of the zeolites. Framework-sensitive intertetrahedral bands, including Si–O–Al stretching, double rings, and pore openings, appear at similar positions in the spectra of samples with increasing water ratios. Notably, the increase in water content did not result in any shift in the characteristic band positions of the KFI zeolite [148,157].

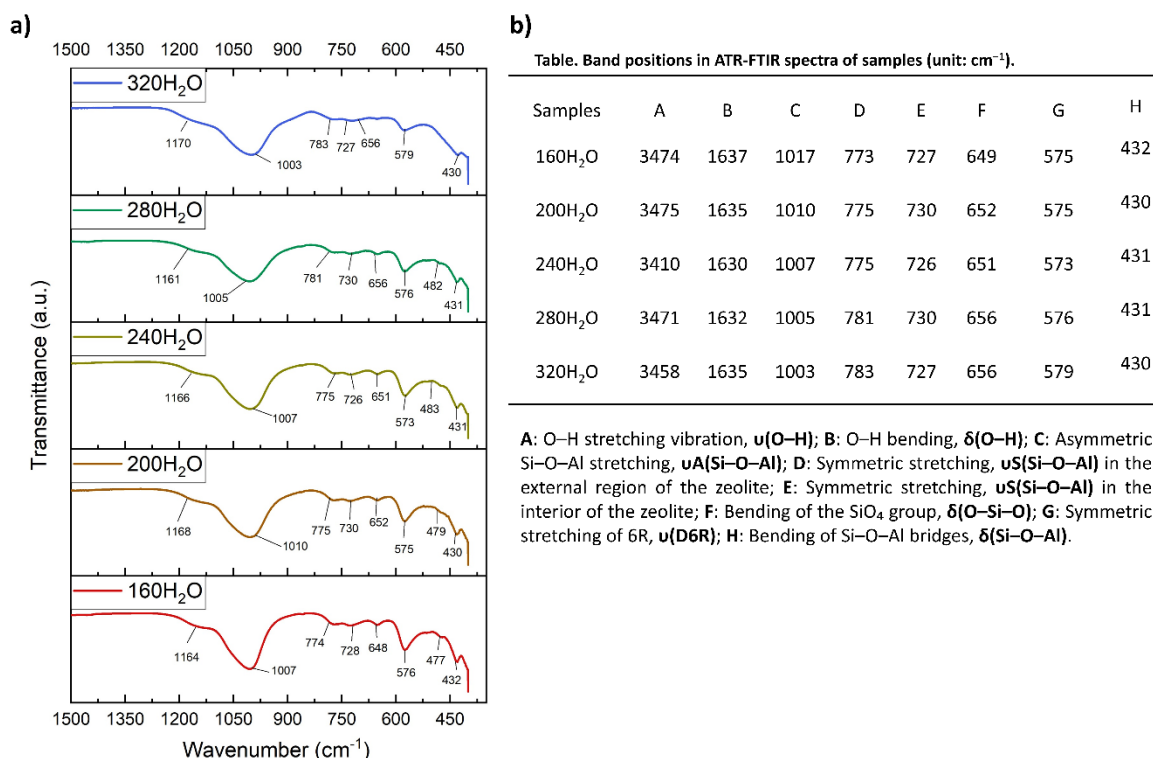


Figure 48. (a) ATR-FTIR spectra for the synthesis using $\text{Al}(\text{OH})_3$ as the aluminum source, Ludox® AM-30 as silicon source and with different water proportions; (b) Table with the band positions in the ATR-FTIR spectra of samples (unit: cm^{-1}).

It was also observed that, with an increase in water content to a ratio of 320, the material exhibited the presence of an amorphous phase, as evidenced by the XRD patterns and SEM images (Figure 49). The morphology of the zeolitic samples, along with the particle size distribution and the Si/Al ratio calculation, was also assessed using SEM images. The application of this characterization technique enabled determination of the degree of purity or impurity in the samples and identification of the amorphous fraction of the final material.

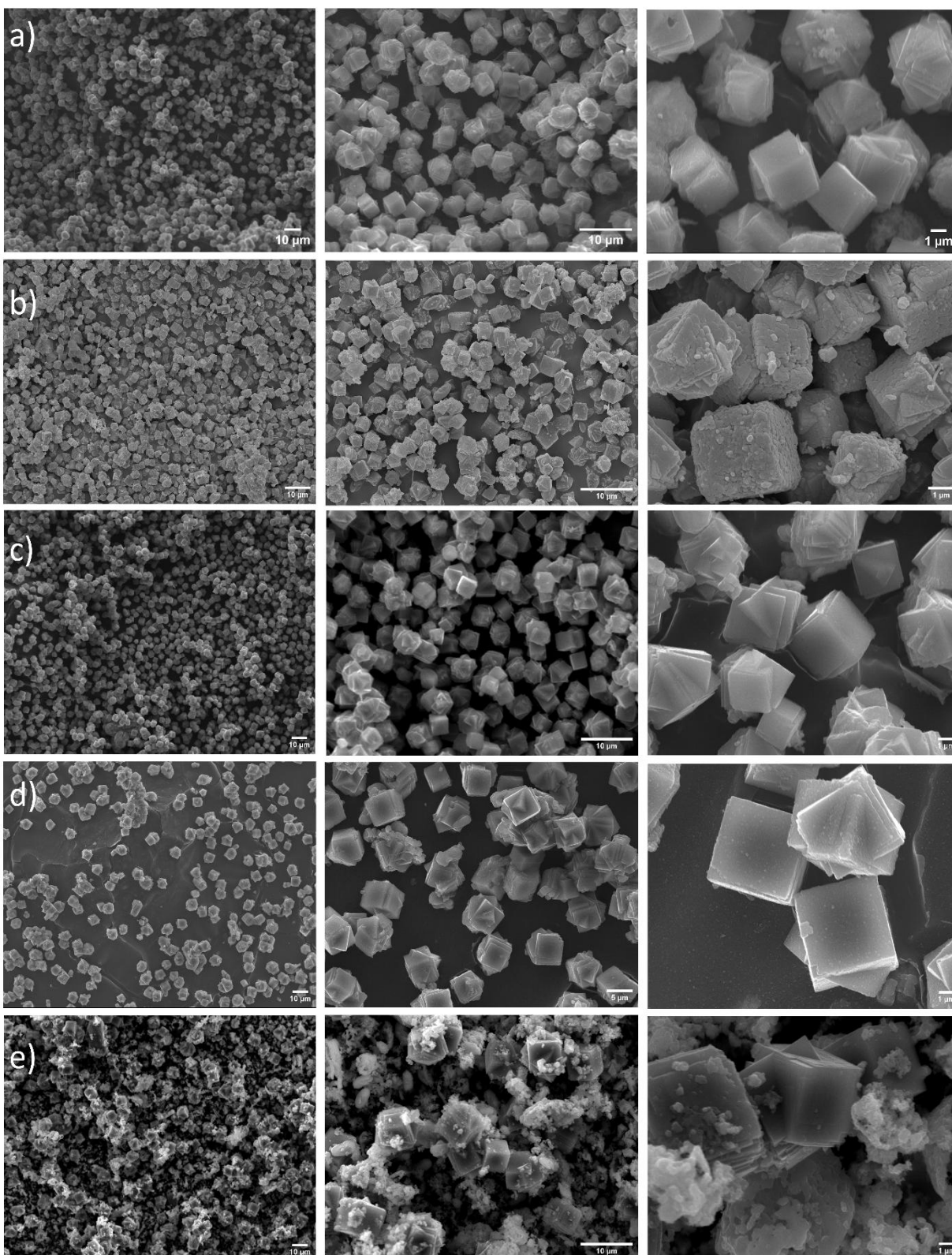


Figure 49. SEM images for the syntheses of zeolites using $\text{Al}(\text{OH})_3$ as an aluminum source, Ludox® AM-30 as silicon source and with different water proportions, where (a) $160\text{H}_2\text{O}$; (b) $200\text{H}_2\text{O}$; (c) $240\text{H}_2\text{O}$; (d) $280\text{H}_2\text{O}$ and (e) $320\text{H}_2\text{O}$

At first glance, it is evident that all the synthesized samples exhibited cubic-shaped particles characteristic of KFI zeolite, without the presence of particles with morphologies associated with other zeolite types. This indicates the exclusive formation of KFI zeolite in the final material, with no contamination from other zeolitic phases. Furthermore, as observed in the XRD patterns of the samples, the increase in water content also resulted in an increase in the amorphous fraction of the final material. This phenomenon likely occurred because the higher water content led to a more diluted synthesis gel, potentially decreasing the concentration of precursors (K^+ and Sr^{2+} ions) required for crystalline structure development. Such a reduction contributed to lower crystallinity and higher amorphous content in the final product. Additionally, it is important to emphasize that variations in water content can influence crystallization conditions, impacting, as previously discussed, both the nucleation and crystal growth rates, which may result in the formation of a less ordered structure and consequently a greater presence of amorphous material [54,89,156].

Based on the data presented in Table 13 (Appendix 8), particle size increased with higher water content. Particle size, in contrast to crystallite size, refers to the physical dimensions of individual particles, regardless of their internal structure. Although there is a relationship between particle size and crystallite size, this relationship is not necessarily linear. In the context of zeolites, particle size generally reflects the aggregation of multiple individual crystallites, each contributing to the overall structure of the particle. Therefore, the increase in particle size was influenced by the growth and distribution of constituent crystallites. Furthermore, other factors may have contributed to this increase, such as particle morphology, where the presence of an amorphous phase could have impacted the growth of particle size [12,89,156].

However, the sample with a water ratio of 200 (KFI-200H₂O) exhibited the smallest crystal size at $2.53 \pm 0.04 \mu m$, indicating that this composition offered optimal parameters and an effective reduction in crystal size. It is worth noting that studies are scarce in the literature employing this specific water proportion [10,11,13,57,66,70,126,127], highlighting the novelty of this finding. It is crucial to emphasize that increasing the water content is not the only factor influencing zeolite crystal size during synthesis. Other parameters, such as temperature, pH, reaction time, and precursor concentrations, play significant roles and may interact in complex ways with the water ratio. Therefore, individual studies for each synthesis system are necessary to understand how different variables affect the formation and size of the resulting crystals [54].

Table 13. Si/Al ratio and mean crystal size distribution for water proportion study.

Samples	Si/Al ^a	Mean Crystal Size (μm) ^b
160H ₂ O	3.8	3.12 ± 0.03
200H ₂ O	3.5	2.53 ± 0.04
240H ₂ O	3.4	3.10 ± 0.03
280H ₂ O	3.5	4.89 ± 0.04
320H ₂ O	3.8	4.91 ± 0.03

^amolar ratio calculated from EDS; ^b average particle size distribution obtained in SEM

Considering the significant reduction in crystal size observed for the sample synthesized with a water/gel ratio of 200 (KFI-200H₂O), magic angle spinning nuclear magnetic resonance (MAS NMR) analysis was performed to investigate the connectivity and proximity between different structural units within the zeolite framework. This analysis aims to assess whether the increase in water content during synthesis affected the organization and spatial arrangement of nuclei in the structure—factors that directly influence the physicochemical properties of the resulting material.

Figure 50 presents the NMR spectra of the ²⁷Al and ²⁹Si nuclei, along with the percentage distribution of chemical environments for the mentioned sample, allowing the identification and distribution of the distinct aluminum species within the zeolitic framework.

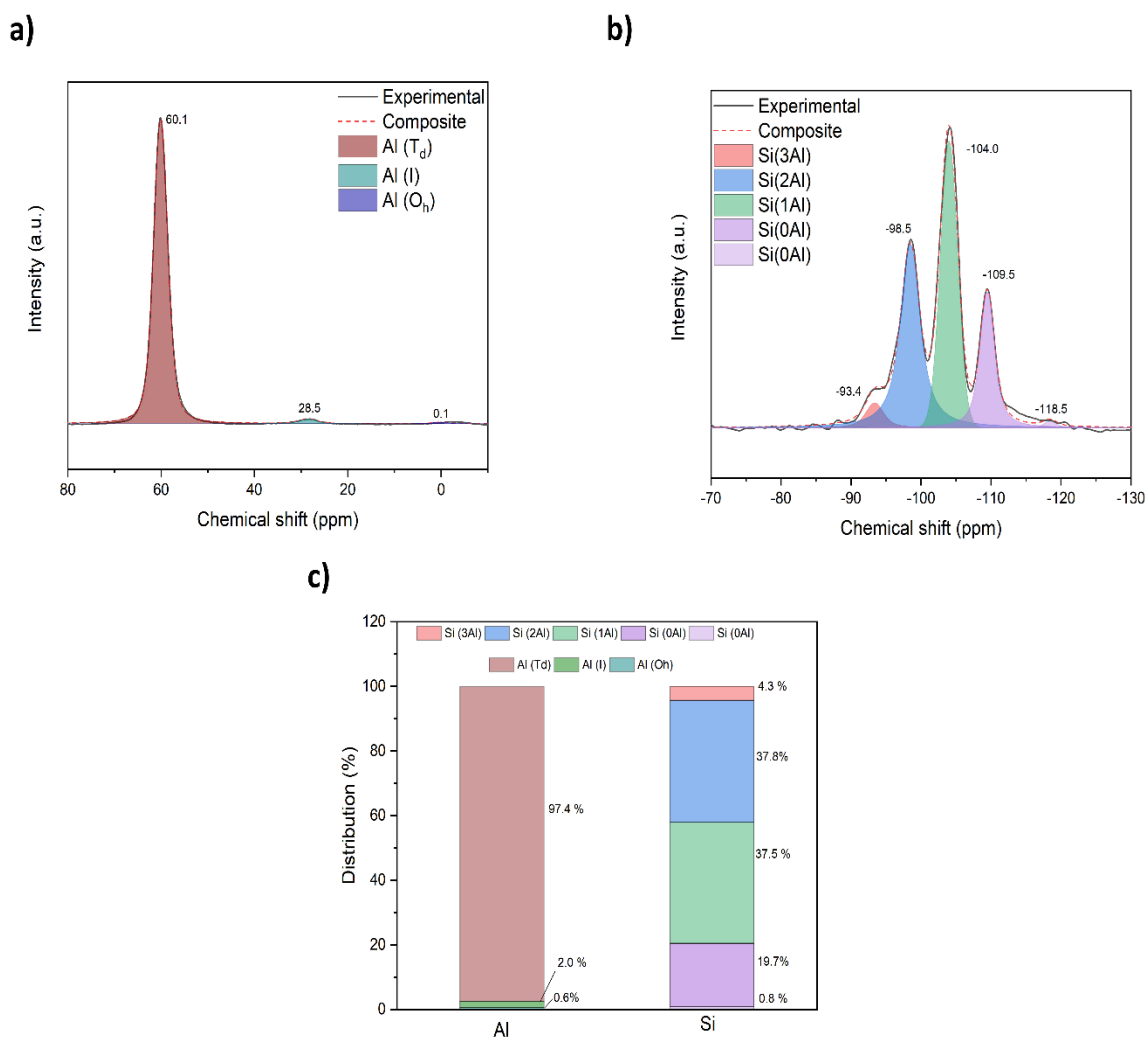


Figure 50. (a) ^{27}Al RAM-NMR spectra, (b) ^{29}Si RAM-NMR spectra and (c) the relative percentage of chemical environments for the syntheses using $\text{Al}(\text{OH})_3$ as an aluminum source, Ludox® AM-30 as silicon source for the KFI-200H₂O sample.

In the ^{27}Al NMR spectrum (Figure 50 (a)), a signal at 60 ppm was observed, corresponding to tetrahedrally coordinated aluminum incorporated into the framework ($\text{Al}(\text{T}_d)$). A weaker signal near 0 ppm was attributed to octahedrally coordinated aluminum located outside the crystalline framework ($\text{Al}(\text{O}_h)$), and a low-intensity signal around 30 ppm was associated with either penta-coordinated aluminum ($\text{Al}(\text{V})$) or extra-framework and distorted tetrahedral aluminum, with a distribution of 0.6%, indicating a low level of structural disturbance of Al [10,151,152].

The ^{29}Si NMR spectrum (Figure 50 (b)) revealed signals at approximately -118.5 , -109.5 , -104.0 , -98.5 , and -93.4 ppm, attributed to the structural species $\text{Si}(\text{0Al})$, $\text{Si}(\text{0Al})$, $\text{Si}(\text{1Al})$,

Si (2Al), and Si (3Al), respectively. The presence of three high-intensity peaks around -100 , -110 , and -115 ppm in both samples indicates the formation of a KFI-type zeolite structure.

The sample synthesized KFI-200H₂O exhibited relative signal intensities for the Si (1Al), Si (2Al), and Si (3Al) species comparable to those of the sample obtained with a ratio of 160 (Figure 35 (b)). This result suggests not only a relatively higher silicon content in the framework—since in NMR spectroscopy, signal intensity is proportional to the number of silicon atoms in each specific chemical environment [56,68,150] — but also indicates that the increased water content during synthesis did not significantly alter the incorporation pattern of silicon within the zeolite crystal lattice.

The absence of the characteristic Si (4Al) peak in the sample further supports this observation, indicating a less distorted structure with lower aluminum incorporation in substituent positions. This interpretation aligns with the results obtained from X-ray diffraction and ^{27}Al NMR, which also indicate a more ordered framework.

The Si/Al molar ratio was again calculated using Equation 19, yielding a value of 3.5, which is consistent with the value obtained by energy-dispersive X-ray spectroscopy (EDS). These results demonstrate that increasing the water proportion was effective, resulting in a material with a high Si/Al ratio, low lattice distortion, good crystallinity, and reduced particle size—characteristics that make this sample suitable as a seed for zeolitic membrane production.

The evaluation of the textural parameters for the water variation study samples was conducted by nitrogen physisorption at -196 °C. The main results are compiled in Figure 51 and Appendix 9.

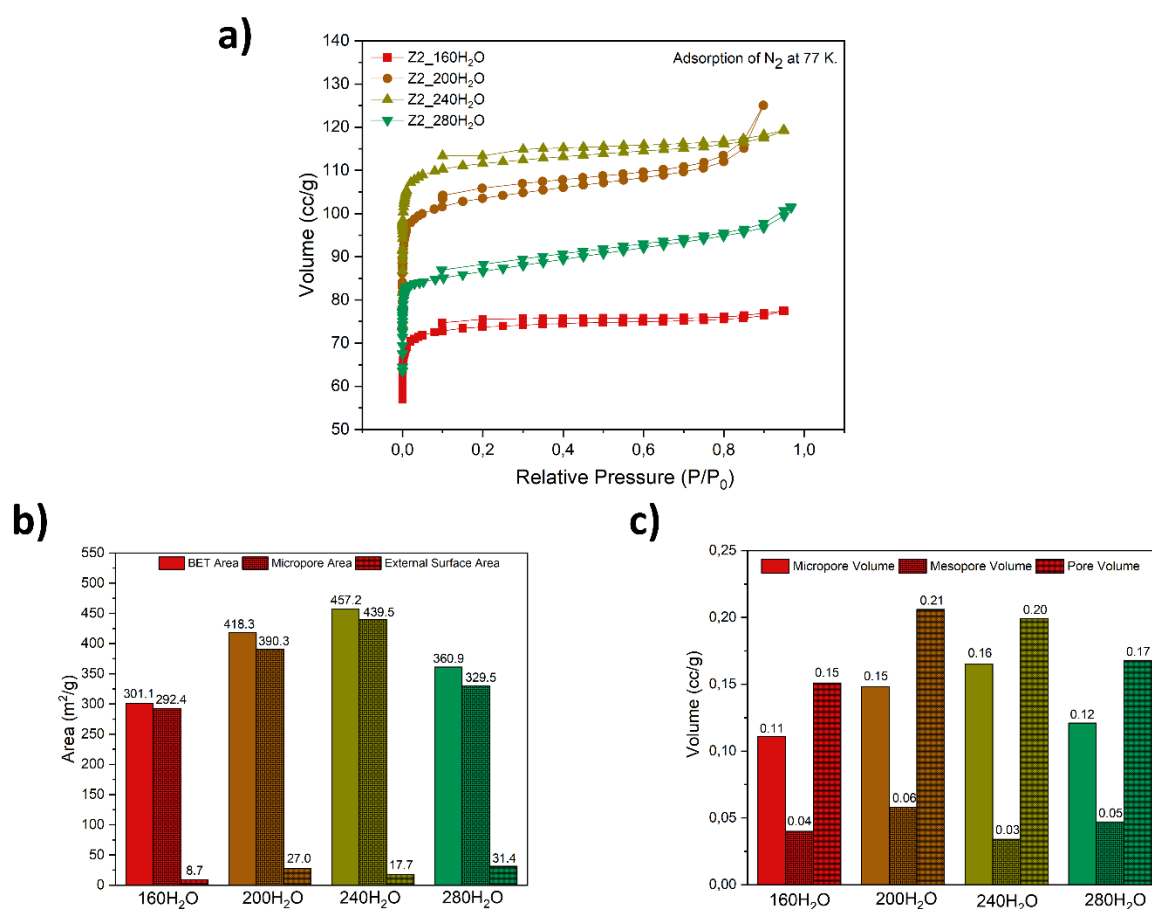


Figure 51. (a) N₂ adsorption/desorption isotherm; (b) BET area, micropore area calculated by the t-Plot method in the region 0.15 to 0.5 and (c) pore volume calculated by the t-Plot method in the region 0.15 to 0.5 for samples using Al(OH)₃ as an aluminum source, Ludox® AM-30 as silicon source and with different water proportions.

Initially, a considerable increase in BET surface area was observed (Figure 51 (b)), proportional to the increase in the water content. This increase most likely occurred due to the smaller crystallite sizes found in the samples with higher water proportions. Generally, the smaller the crystallites, the greater the specific surface area of the zeolite. This is because smaller crystallites offer a larger surface area relative to their total volume, which can enhance the adsorption capacity of the zeolite. The increase in surface area may also improve gas diffusion throughout the crystalline structure, as smaller crystallites facilitate faster molecular diffusion through the zeolite pores. This is particularly important in gas adsorption and separation applications, where efficient molecular diffusion through the pores is critical to membrane performance [54,89,156].

The pore size of zeolites plays a crucial role in determining the selectivity for specific gases that can be adsorbed within the structure. Smaller crystallites tend to exhibit more uniform and

narrower pore sizes, which can enhance zeolite selectivity for target molecules. However, it was observed that increasing the water content resulted in a rise in the pore sizes of the samples (0.68, 2.5 2.4, 2.4 nm, respectively ((Appendix 10)), with values higher than those typically expected for KFI zeolite (pore diameter of 0.39 nm and a maximum cage-inclusion diameter of 1.07 nm). This discrepancy may be attributed to the use of nitrogen as the adsorbate, which might not be ideal for accurately assessing micropore size distribution [128]. For a more reliable evaluation of whether the increased water proportion leads to an enlargement of cages and pore diameters, analysis using argon or carbon dioxide would be necessary, as these gases provide a more precise determination of pore size. Nevertheless, the sample with a water ratio of 200 (KFI-200H₂O), proved promising for gas separation applications due to its high surface area and lower amorphous content, which could otherwise limit separation efficiency.

The adsorption/desorption isotherms for the water variation study samples are shown in Figure 51 (a). The presence of micropores is evident in the samples, as indicated by the high adsorption at low relative pressure (P/P_0) values. The experimental curves show that both samples with increased water content exhibit a combination of Type I(b) and IV(a) isotherms. These isotherms are characteristic of microporous and mesoporous solids with relatively small external surface areas. The samples display a broad pore size distribution, encompassing wide micropores and possibly narrow mesopores ($< \sim 2.5$ nm), typical of Type I isotherms. Additionally, H4-type hysteresis loops were observed in the high-pressure region, indicating the formation of additional mesopores or macropores due to the aggregation of small crystals [12,13,128].

The sample, synthesized with a water/gel ratio of 200 (KFI-200H₂O), was characterized through gas adsorption analyses using CO₂ (273 K), Ar (88 K), and N₂ (77 K) to determine the pore size distribution. The results indicated that the zeolite exhibits average pore diameters of 0.349 nm, 0.552 nm, and 2.504 nm for CO₂, Ar, and N₂, respectively (Figure 52).

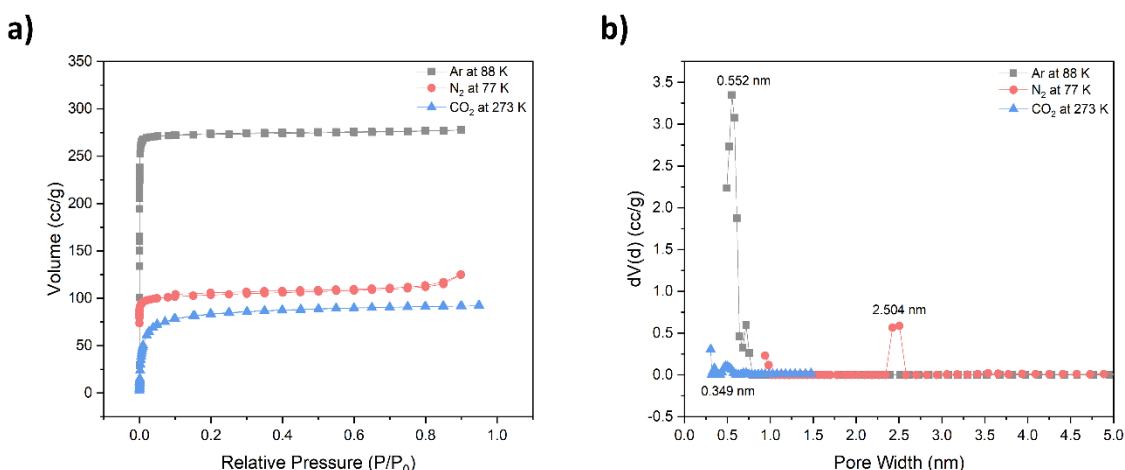


Figure 52. (a) adsorption/desorption isotherm and (b) pore size distribution calculated by the DFT method in the region 0.15 to 0.5 for the KFI-200H₂O sample

CO₂ at 273 K was selected for pore size determination due to its subcritical nature and its ability to access ultramicropores that are inaccessible to other adsorbents at cryogenic temperatures. With a kinetic diameter of 0.33 nm and a high saturation vapor pressure at 273 K (~ 3.5 MPa), CO₂ enables micropore analysis within a moderate pressure range (~ 0.1 to 100 kPa) and allows faster diffusion than under cryogenic conditions, making it possible to probe pores as small as 0.4 nm. This provides critical insights into the presence of ultrafine micropores and the material's adsorption capacity for small molecules [90,91,128,158].

Ar at 87 K was employed to characterize the surface and mesoporous structures, providing high resolution in the determination of the specific surface area. The KFI-200H₂O sample exhibited a BET surface area of $1020 \text{ m}^2 \cdot \text{g}^{-1}$, with 99.05% of the material being microporous. Although these results initially appear highly promising, caution is required, as the combination of type I and IV isotherms suggests possible multilayer adsorption not accounted for by the BET model, potentially leading to an overestimation of the apparent surface area. In contrast, CO₂ adsorption at 273 K, indicated a surface area of $414.2 \text{ m}^2 \cdot \text{g}^{-1}$, with 85.1% of this area being microporous. N₂ at 77 K allowed for a comprehensive analysis of both microporosity and mesoporosity over a wider pore size range, resulting in a BET surface area of $418.3 \text{ m}^2 \cdot \text{g}^{-1}$ and 93.3% microporosity.

In summary, although N₂ and Ar are conventional gases for textural characterization (including surface area), CO₂ is considered more effective for accessing and characterizing ultramicroporous regions due to its superior diffusion kinetics at 273 K. Therefore, the combination of these three gases provides a complementary approach, enabling precise

determination of pore size distribution, surface area, and micropore fraction, supplying essential information for understanding the material's suitability for gas separation applications.

5.3. Characterization of KFI Membranes

5.3.1. Silica Layer Deposition

Prior to the fabrication of the zeolite membrane, a preliminary step was performed to incorporate an intermediate silica layer between the zeolite coating and the substrate. This step aims to mitigate zeolite seeds intrusion, decreasing the membrane thickness and consequently enhancing the gas separation performance. Silica was chosen due to its chemical inertness toward various gases, which minimizes undesired reactions that could compromise the long-term stability of the membrane. Furthermore, silica exhibits high chemical compatibility with commonly used substrate materials such as alumina and stainless steel [19,84,159,160].

Figure 53 presents SEM images from tests conducted with different immersion and withdrawal rates of the substrate in the silica solution (3% w/w). This study was conducted because the immersion rate of the substrate in the precursor solution affects the interaction between the liquid and the material surface. A very high immersion rate may result in bubble formation or improper adhesion of the solution to the substrate. Conversely, a very low rate may lead to irregular liquid distribution, impacting the uniformity of the coating [83,86,87].

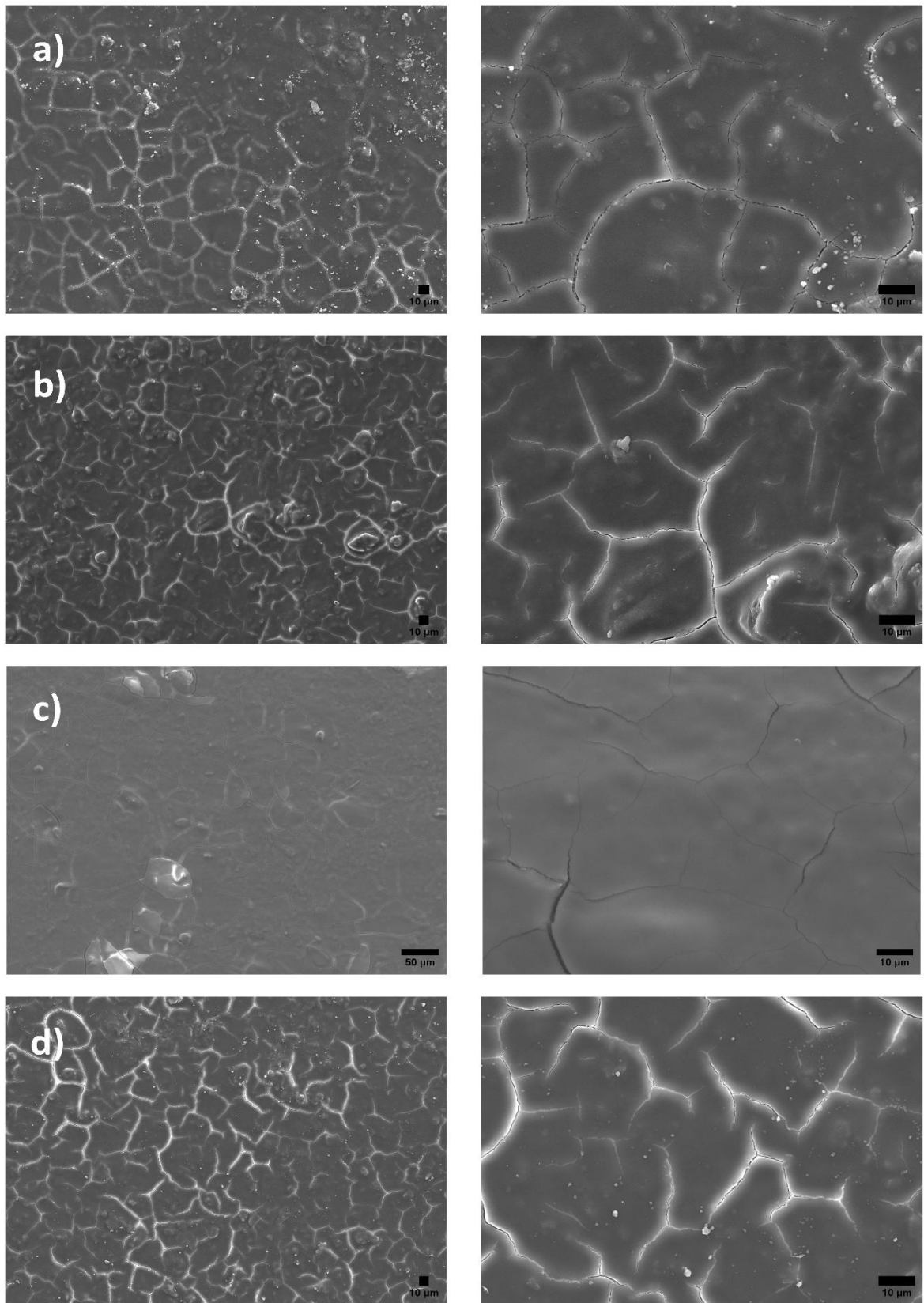


Figure 53. Silica coating (3% w/w) on commercial tubes using dip-coating at immersion/withdrawal speeds of (a) 30 mm/min; (b) 60 mm/min; (c) 90 mm/min; and (d) 100 mm/min.

Cracking of the deposited silica layer was observed at all tested withdrawal speeds (30, 60, and 100 mm/min). This cracking likely occurred during the drying step, as after removing the tube from the solution, the solvent (ethanol) begins to evaporate, causing volumetric shrinkage of the silica. If the evaporation rate is too rapid, internal stress within the film may exceed the mechanical strength of the material, resulting in the formation of small cracks. Additionally, during membrane calcination, the removal of residual solvent and densification of silica can further intensify mechanical stress [19,83,87,159].

The tube produced at a withdrawal speed of 90 mm/min (Figure 53 (c)) exhibited a smooth and uniform surface, likely because this speed promoted the formation of a thinner silica layer on the tube surface, reducing stresses generated during drying and calcination. It might have been expected that the tube withdrawn at 100 mm/min (Figure 53 (d)) would also present fewer cracks, since the slower removal of the tube from the suspension could promote better silica adhesion and formation of a uniform layer. However, this speed represents the limit of the dip-coater equipment used for silica deposition. Therefore, at 90 mm/min speed was selected for the deposition tests on *freeze-casting* tubes and for zeolitic seed deposition during KFI membrane production.

Figure 54 shows SEM images of the silica layer deposited on tubes produced via *freeze-casting*, where deposition was performed under optimal conditions for commercial tubes: immersion and withdrawal speed of 90 mm/min and an immersion time of 30 s. It can be observed that after two silica depositions, the membrane is homogeneous and free of visible cracks. This indicates the membrane's potential suitability for separation applications. As discussed, the presence of larger and directionally oriented (dendritic) pores generated by the *freeze-casting* technique contributed to a more uniform silica layer deposition via dip-coating. The porous channel structure facilitated infiltration of the colloidal suspension, resulting in a more homogeneous and stable coating on the support surface. Furthermore, the elongated pore geometry enhanced the mechanical adhesion of the deposited layer, reducing the occurrence of defects such as cracks or delamination, which are commonly observed in supports with lower porosity. Therefore, the combination of *freeze-casting* with camphene and dip-coating enables the development of ceramic structures with improved adhesion, coating homogeneity, and superior performance in separation applications [19,83,87]. This is an exceptional result, given that depositing a film with pore sizes significantly different from those of the commercial tube could have caused cracking [19].

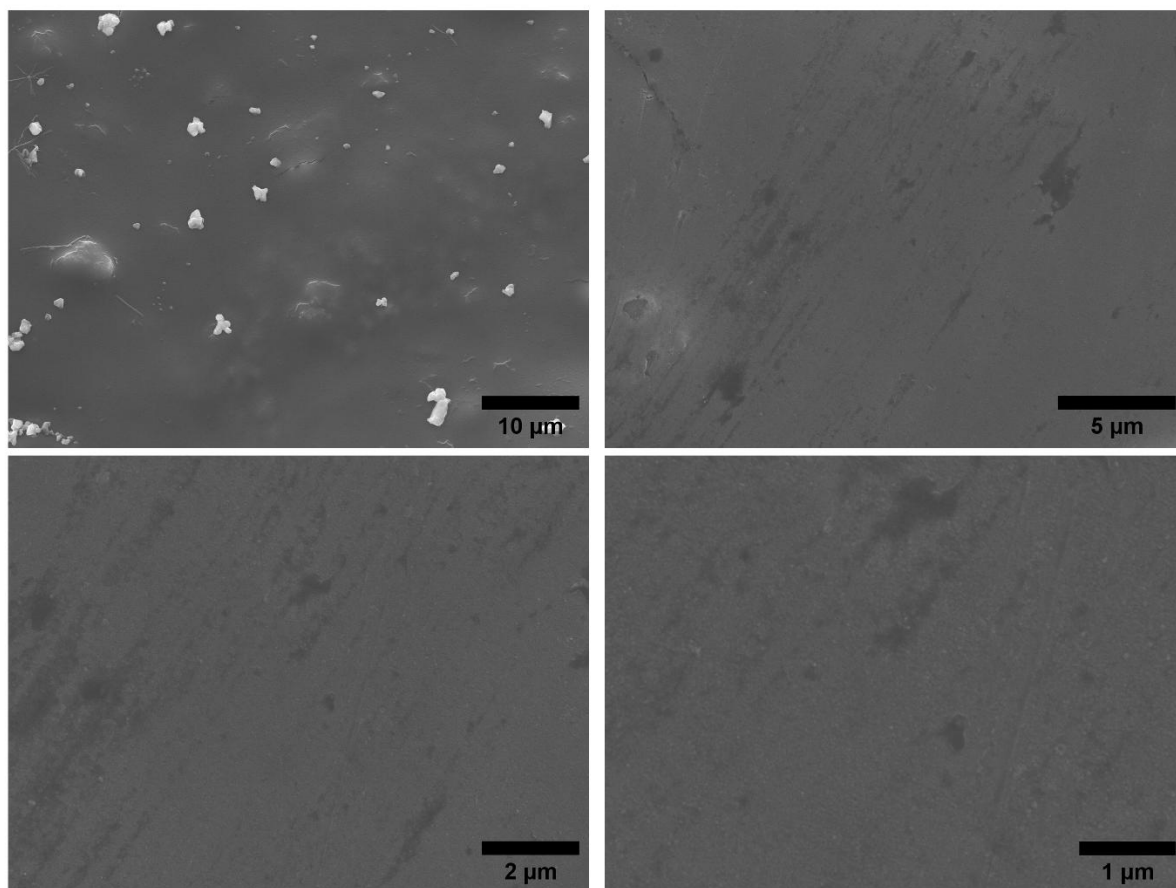


Figure 54. Silica coating (3% w/w) on *Freeze-Casting* tubes using dip-coating at immersion/withdrawal speeds of 90 mm/min immersion time of 30s with different magnifications.

A cross-section of the tubes was examined to determine the silica layer thickness and assess its uniformity. SEM images, presented in Figure 55, revealed that the added layer was approximately $5.11 \pm 0.03 \mu\text{m}$ and $3.00 \pm 0.05 \mu\text{m}$ thick for the commercial and freeze-cast tubes, respectively. This indicates that the 90 mm/min dip-coating speed provided optimal coverage with fewer defects, while producing a thin and uniform layer along the tube. The improved adhesion observed in the *freeze-casting* tube is likely related to its porous structure, which allows for a more efficient deposition of the colloidal suspension and reduces excessive material accumulation on the surface. Consequently, the resulting silica layer is thinner, more uniform, and mechanically stable, minimizing residual stresses during drying and thermal processing and enhancing the overall structural integrity of the coating.

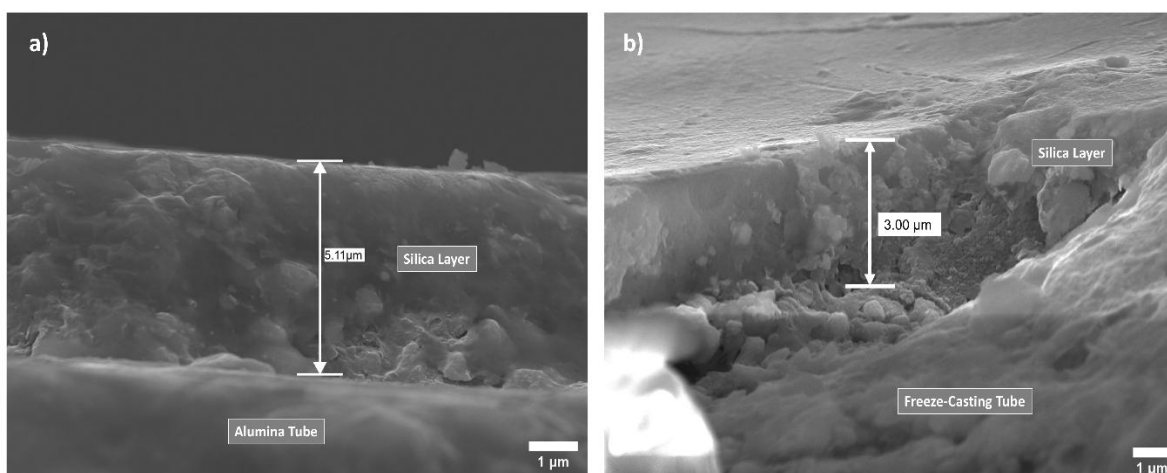


Figure 55. Silica layer thickness measured from a cross-section of (a) commercial tube and (b) freeze-casting tube.

Therefore, it can be concluded that the presence of this silica layer provided a smooth, continuous, thin, and uniform surface for both types of tubes (commercial and *freeze-casting*). Additionally, the silica can be functionalized to facilitate the deposition of zeolitic seeds during membrane growth. This intermediate layer acts as an effective barrier against the formation of zeolite agglomerates within the support, and minimizes the leaching of aluminum from the substrate during the secondary growth of the zeolite.

Besides serving as a physical and chemical barrier, this intermediate layer enhances zeolite adhesion to the substrate, promoting the formation of stable chemical bonds between the two components and mitigating structural defects that could negatively affect membrane selectivity. In particular, silica fills micropores and cracks present in the substrate, such as those formed in *freeze-casting* tubes, resulting in a more homogeneous surface and reducing the likelihood of defect formation during zeolite deposition. This structural improvement prevents gas permeation through non-selective pathways, significantly enhancing the separation process efficiency.

5.3.2. KFI Membrane

The concentration of the zeolite seed solution plays a crucial role in the secondary growth of a zeolitic membrane, mainly when the dip-coater technique is employed [83–87]. Concentration directly affects the amount of material deposited on the membrane layers during immersion. A very low concentration may result in insufficient deposition of zeolite particles, compromising the formation of a solid and uniform layer. Conversely, excessive concentration

can lead to over-deposition of particles, hindering the formation of a controlled porous layer and compromising membrane quality [3,6,80,87,110].

Furthermore, solution concentration also influences the structural properties of the membrane, such as the thickness of the deposited layers and the density of the zeolite network. At optimal concentrations, zeolite particles distribute uniformly over the substrate, favoring controlled growth and the formation of a porous structure suitable for specific applications, such as gas separation or catalysis [6,19,83,84,87,122]. Therefore, optimizing the concentration of the zeolite seed solution is essential for producing high-quality and efficient membranes, allowing more precise control over the physical and chemical properties of the final membrane.

Accordingly, an initial study was carried out to determine the ideal zeolite seed solution concentration for obtaining a uniform layer on the substrate, where immersion time (30 s) and hydrothermal treatment time (16 h) were kept constant. SEM images are presented in Figures 56, 57, 58.

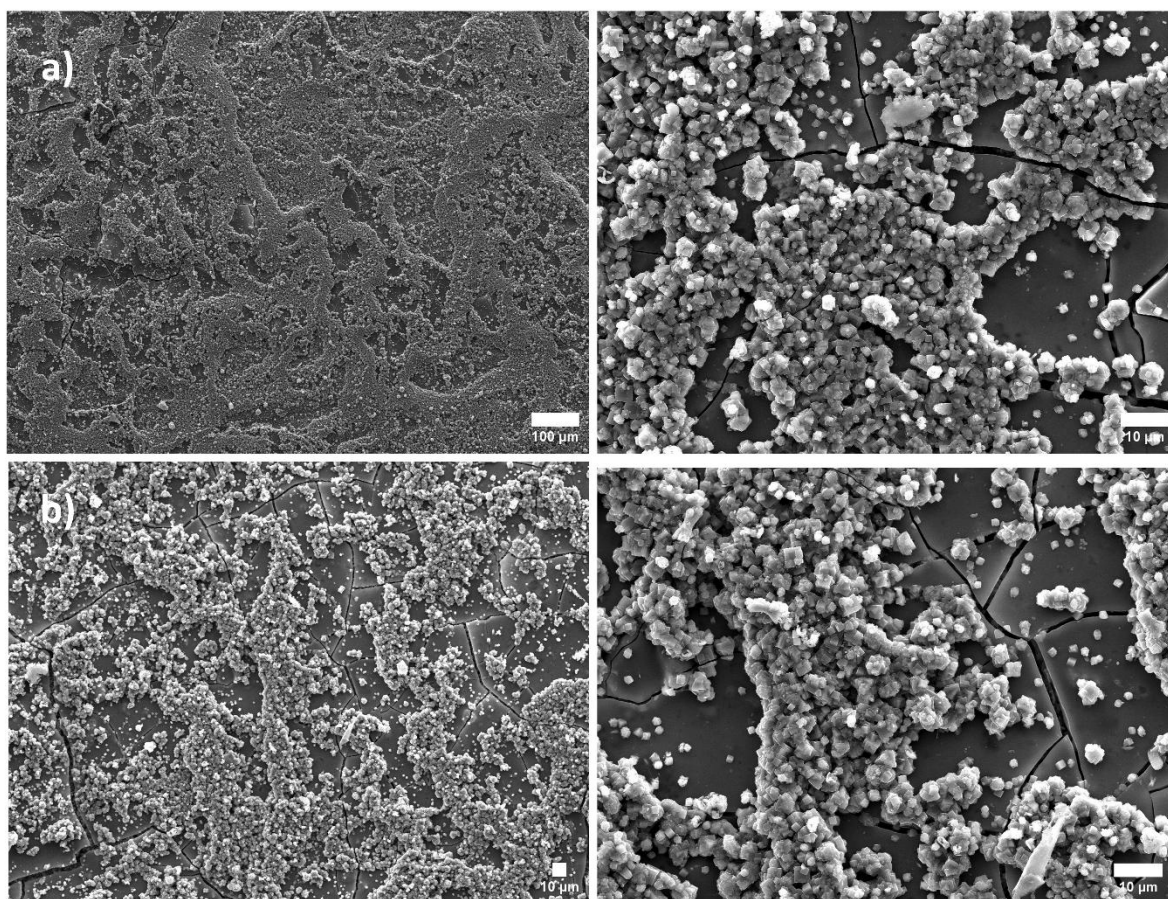


Figure 56. SEM images of the membranes with a 1% concentration showing (a) 2 depositions and (b) 3 depositions (30 s immersion) followed by 16 h of hydrothermal synthesis.

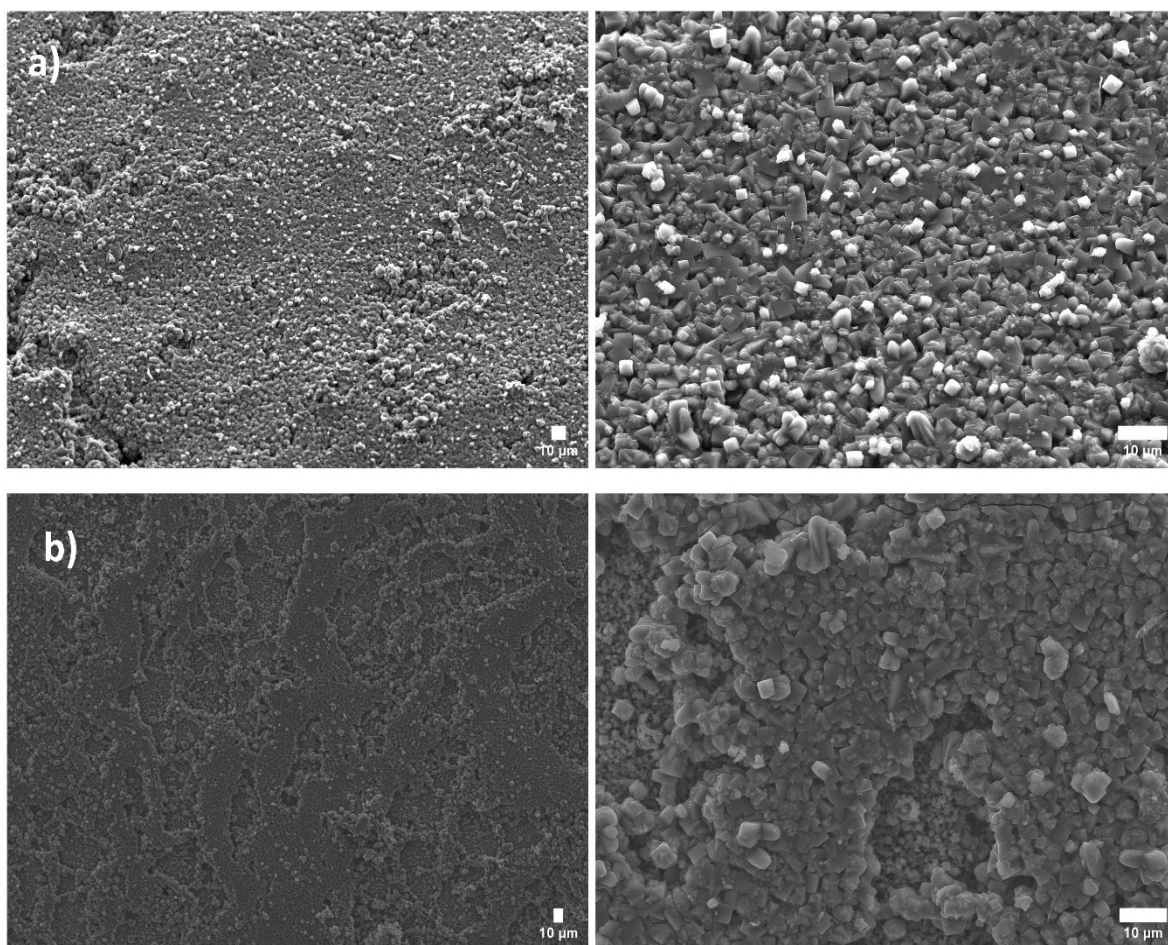


Figure 57. SEM images of the membranes with a 2% concentration showing (a) 2 depositions and (b) 3 depositions (30 s immersion) followed by 16 h of hydrothermal synthesis.

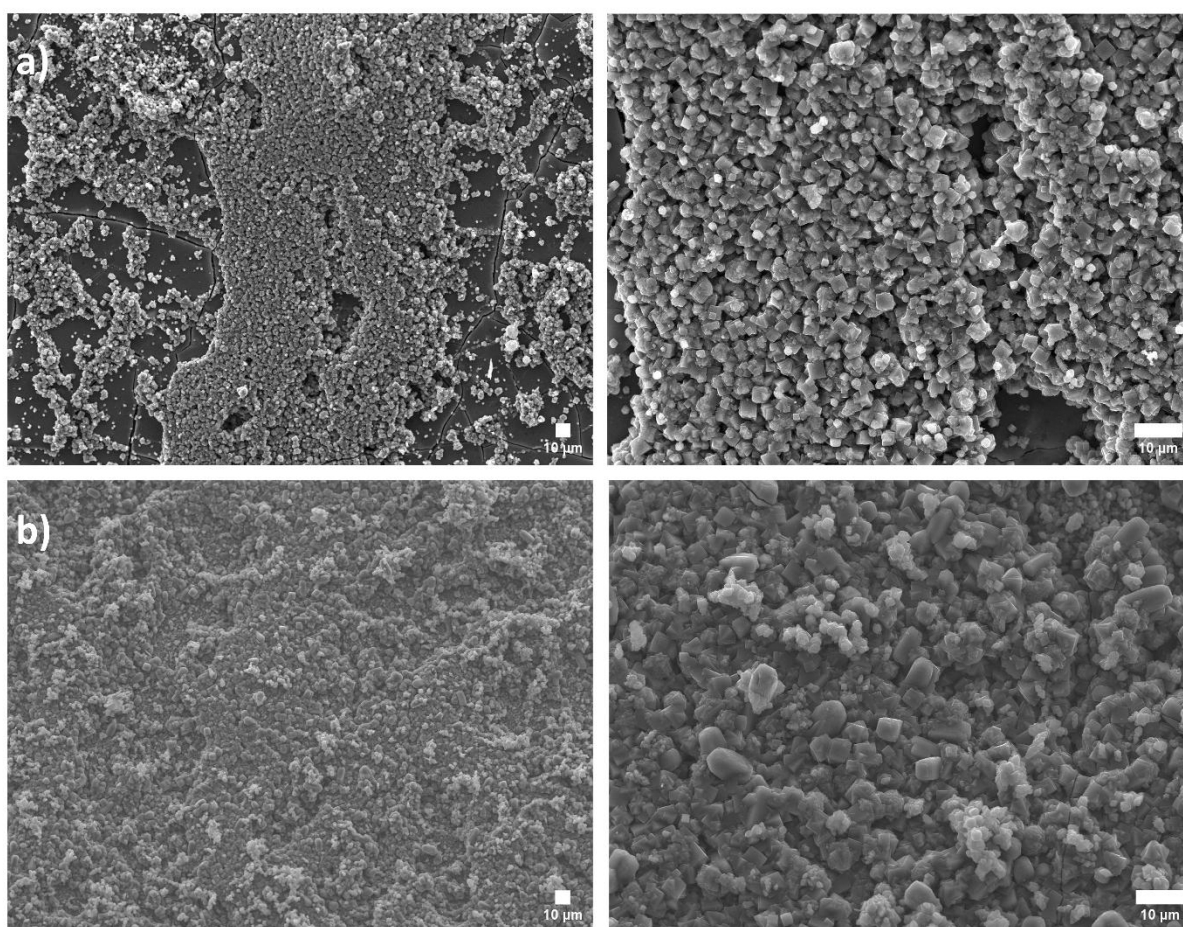


Figure 58. SEM images of the membranes with a 3% concentration showing (a) 2 depositions and (b) 3 depositions (30 s immersion) followed by 16 h of hydrothermal synthesis.

Figures 56 and 58, corresponding to seed solutions with 1% and 3% concentration, respectively, exhibit areas with deposition defects, thereby compromising the adequate growth of the KFI zeolite layer. In membranes prepared with 1% concentration, the zeolite amount was insufficient to promote the formation of a continuous zeolitic layer, while membranes with 3% concentration showed regions with overlapping zeolite layers as well as areas with low KFI zeolite presence and the presence of structures characteristic of W zeolite. These results indicate that possible system saturation occurred in some membrane regions due to excessive KFI zeolite concentration, affecting the uniformity, distribution of the layers and the possibility of promoting the growth of other zeolitic structures.

Such defects would substantially impair the separation efficiency of a gas mixture, as structural imperfections cause the formation of regions with irregular porosity or even voids, interfering with proper gas diffusion control [104–106,160]. Consequently, this would result in non-uniform permeability, allowing some molecules to pass through without the desired

separation. Moreover, structural defects could negatively affect membrane selectivity by facilitating the passage of undesired components or reducing adsorption capacity [79,83,85,87,102,105]. Thus, the presence of these flaws compromises membrane efficiency, directly impacting its performance in gas separation and purification processes.

In contrast, membranes produced using the 2% concentration solution (Figure 57) showed more uniform growth. Even with only two depositions (Figure 57 (a)), a multilayer formed, which could negatively affect membrane efficacy, especially in gas separation processes. Inadequate overlap of zeolite layers can lead to reduced porosity and structural uniformity, impairing the membrane's ability to selectively absorb molecules. Excessive zeolite accumulation in certain areas may create denser regions, hindering molecular flow through pores and reducing separation efficiency. Additionally, uneven layers can create defects and failures, forming alternative pathways for gas passage that compromise membrane integrity and selectivity [83,84,87,102,104,105,119]. Therefore, ensuring controlled and uniform zeolite layer deposition is crucial to optimizing membrane performance in separation applications.

To optimize the production of a zeolite membrane with a uniform and thin film, a study was conducted focusing on modulating the immersion time, which was increased to 60 seconds. This adjustment aimed to achieve more homogeneous coverage of the zeolitic layer, ensuring uniform distribution of zeolite crystals over the substrate. Additionally, the hydrothermal treatment time was reduced to 6 hours to inhibit excessive zeolite layer growth. Reducing the layer thickness is critical for membrane efficiency, as thinner layers provide higher diffusion rates and lower gas flow resistance without compromising selectivity. This procedure also seeks to balance zeolite crystallization control to obtain a stable and effective separation structure while minimizing structural defects that could impair membrane performance. The SEM images are presented in Figures 59, 60 and 61.

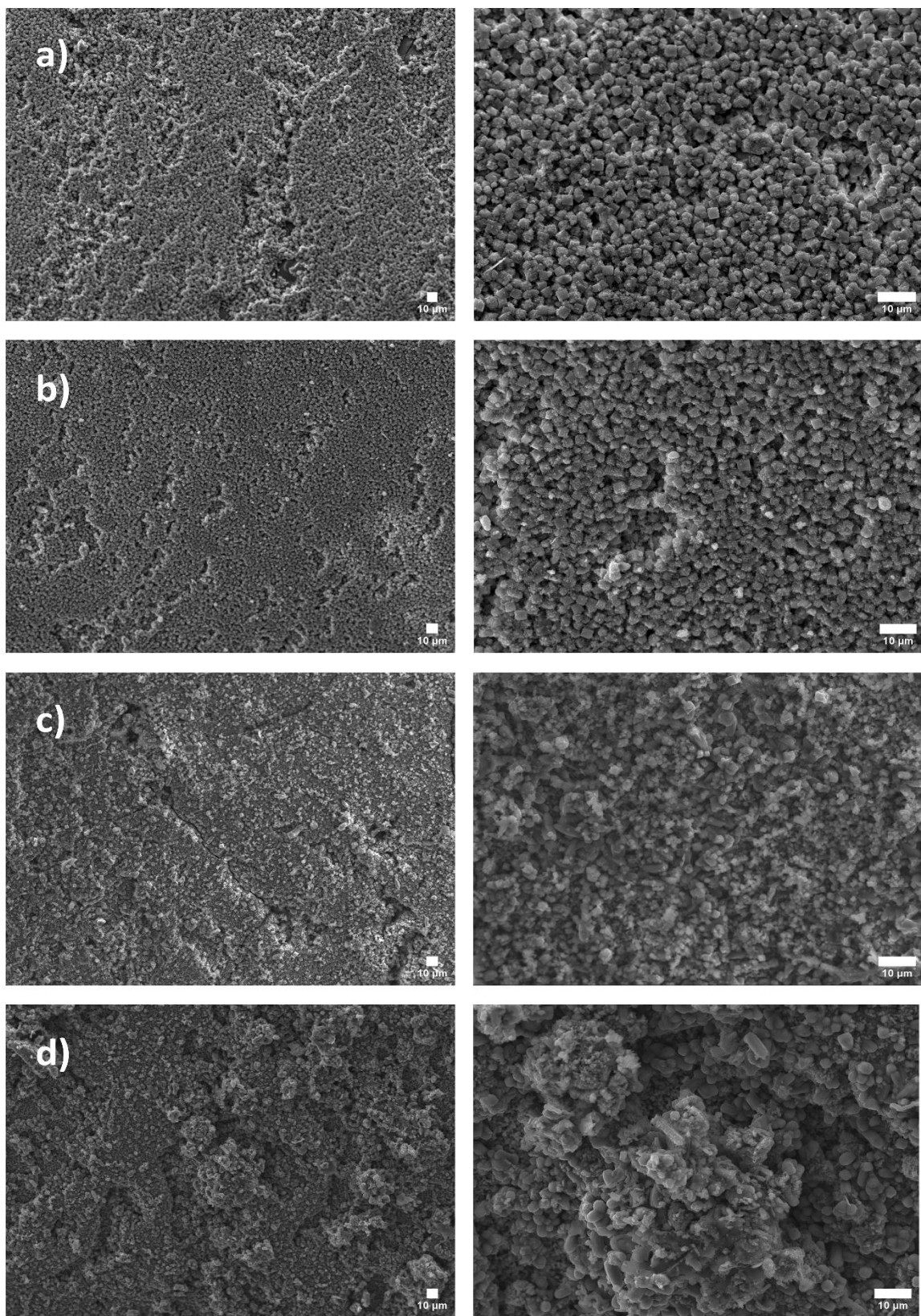


Figure 59. SEM images of 1% membranes: (a, b) 2 and 3 depositions after 6 h of hydrothermal synthesis, and (c, d) 2 and 3 depositions after 16 h of hydrothermal synthesis.

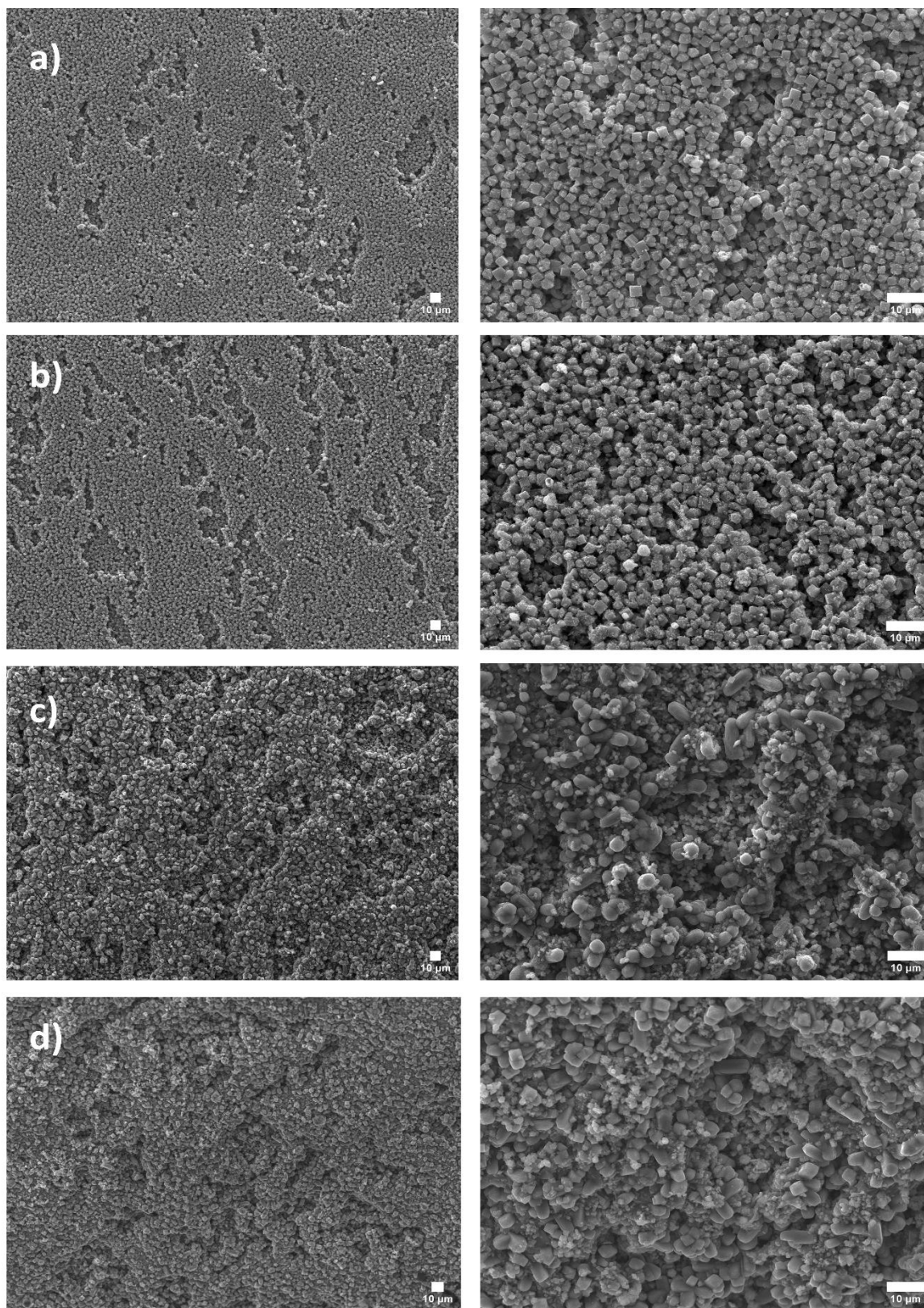


Figure 60. SEM images of 2% membranes: (a, b) 2 and 3 depositions after 6 h of hydrothermal synthesis, and (c, d) 2 and 3 depositions after 16 h of hydrothermal synthesis.

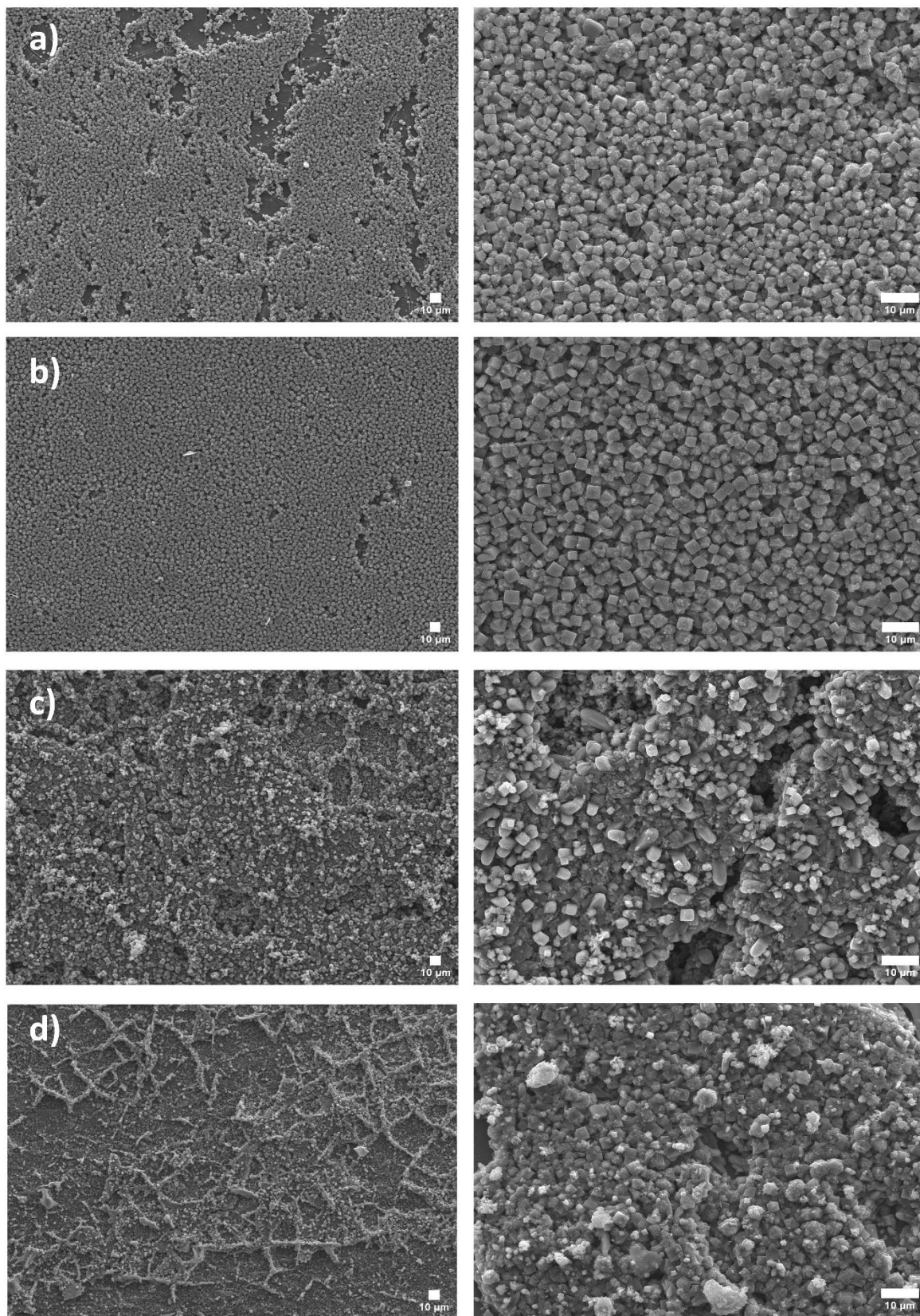


Figure 61. SEM images of 3% membranes: (a, b) 2 and 3 depositions after 6 h of hydrothermal synthesis, and (c, d) 2 and 3 depositions after 16 h of hydrothermal synthesis.

Initially, it was observed that all precursor solution concentrations yielded good surface coverage. However, the duration of the hydrothermal growth significantly impacted the morphology: samples grown for 6 hours showed more uniform coverage, whereas those grown for 16 hours exhibited regions with zeolite agglomerates. Based on these results, the three parameters identified as most influential in achieving both a homogeneous layer and the formation of multilayers were the immersion time, the number of depositions, and the hydrothermal synthesis time.

Optimizing the immersion time proved crucial. For instance, increasing the immersion time (e.g., from 30 to 60 seconds for the 1% system) significantly enhanced the uniform adhesion of zeolite crystals to the substrate surface (as shown in Figures 59) [83–87,161,162]. Reducing the hydrothermal treatment time to 6 hours further improved membrane uniformity, irrespective of the number of seed depositions (Figures 59, 60, and 61 (a) and (b)). In sharp contrast, membranes treated for 16 hours (Figures 59, 60, and 61 (c) and (d)) developed thicker multilayers and large zeolite agglomerates. This outcome is likely due to the prolonged crystal growth during extended hydrothermal treatment, which also favored the appearance or partial intergrowth of zeolite W due to the related crystalline structures [114,163,164]. Although zeolite W is reported to show good gas separation performance, the experiment continued despite minor crystalline impurities to evaluate the material's functional potential[114,115,123]. Crucially, decreasing the treatment time effectively interrupts crystal formation before excessive growth, leading to smaller crystals and a thinner, more uniform layer.

Layer thickness reduction is critical for improving membrane permeability, as thinner layers offer lower resistance to gas flow [78,83,84,119,162]. Moreover, the highly uniform layer and smaller crystal size—both achieved by early interruption of crystal growth—promote consistent pore distribution and the formation of defined transport channels, thereby enhancing membrane selectivity. The presence of smaller crystals also contributes to a higher surface area, optimizing the membrane's adsorption capacity and overall efficiency in gas separations [6,13,77,119,162]. Therefore, combining a reduced hydrothermal treatment time with a slight increase in immersion time is an effective strategy for producing a zeolitic membrane with controlled thickness, smaller crystals, and a highly homogeneous structure. These are essential factors for maximizing gas separation efficiency by effectively balancing selectivity and permeability. Consequently, cross-sectional cuts were performed on the 2% and 3% systems,

and analyzed via Scanning Electron Microscopy (Figures 62 and 63), to accurately determine the final zeolite layer thickness.

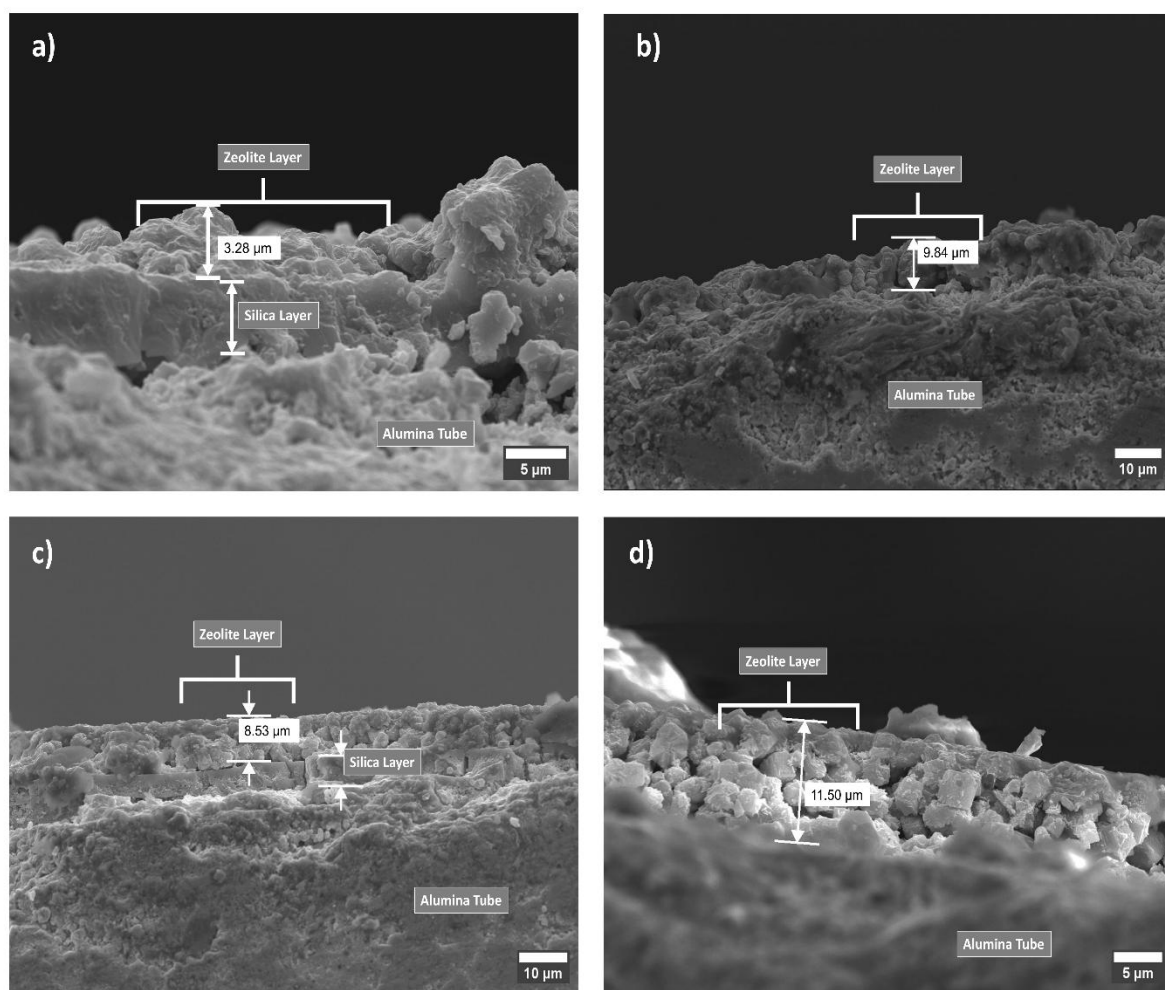


Figure 62. SEM images of the cross-section of 2% membranes: (a, b) 2 and 3 depositions after 6 h of hydrothermal synthesis, and (c, d) 2 and 3 depositions after 16 h of hydrothermal synthesis.

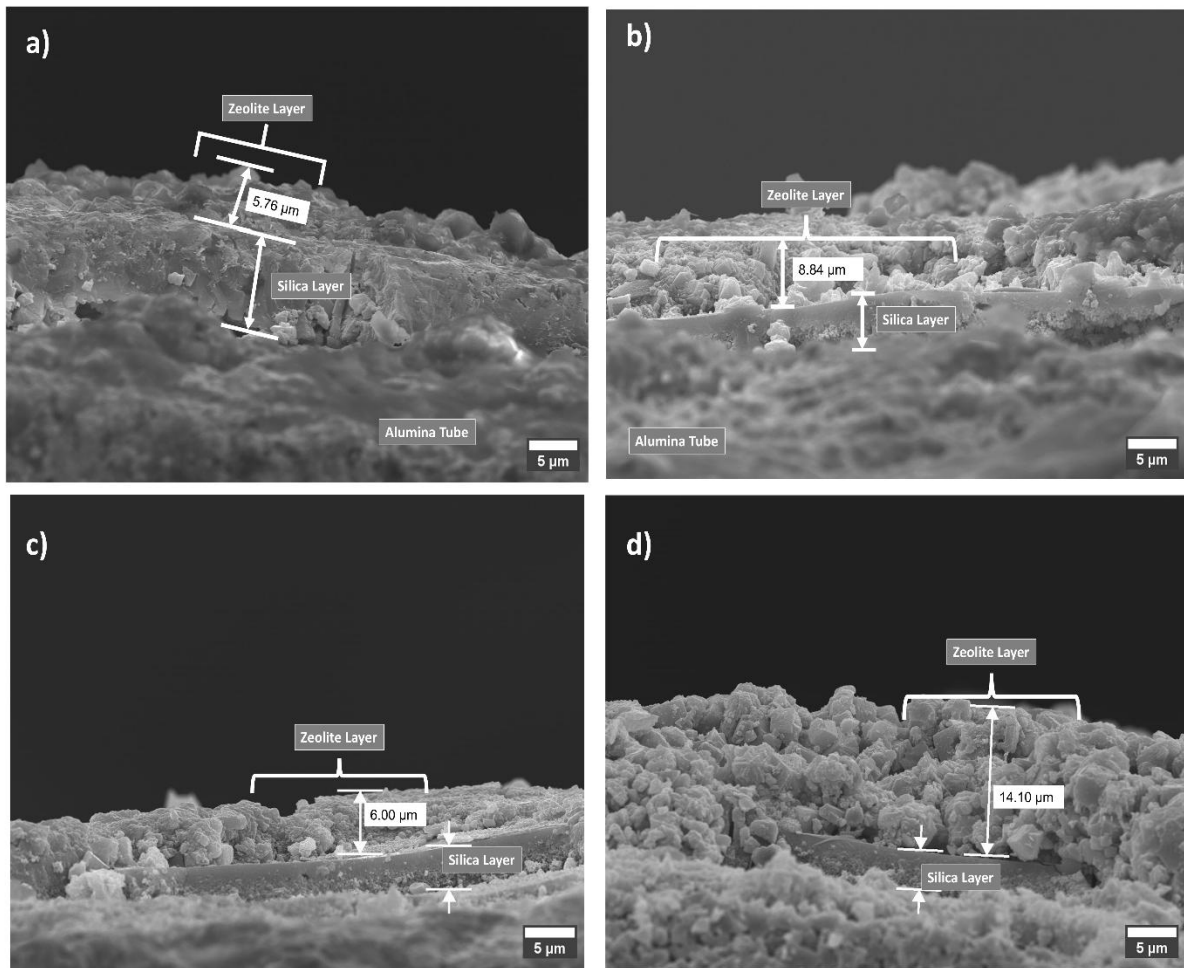


Figure 63. SEM images of the cross-section of 3% membranes: (a, b) 2 and 3 depositions after 6 h of hydrothermal synthesis, and (c, d) 2 and 3 depositions after 16 h of hydrothermal synthesis.

In Figure 62, the thicknesses corresponding to the 2% concentration system are shown. It is initially observed that both the number of depositions (2 and 3) and the increase in synthesis time (6 and 16 hours) promote a slight increase in membrane thickness, with thicknesses increasing in the order (a) < (b) < (c) < (d). Similarly, for the 3% concentration system (Figure 63), an increasing trend in thickness is observed with an increase in the number of depositions and synthesis time: (a) < (b) $\approx$ (c) < (d). A summary of the measured thicknesses is presented in the table below.

Table 14. Summary of Measured KFI Layer Thicknesses on Commercial Tubes

Samples	Membrane thicknesses (μm) ^a
2% seed concentration, 2 depositions, 6 h hydrothermal growth	3.28 ± 0.03
2% seed concentration, 3 depositions, 6 h hydrothermal growth	9.84 ± 0.04
2% seed concentration, 2 depositions, 16 h hydrothermal growth	8.53 ± 0.03
2% seed concentration, 3 depositions, 16 h hydrothermal growth	11.50 ± 0.04
3% seed concentration, 2 depositions, 6 h hydrothermal growth	5.76 ± 0.04
3% seed concentration, 3 depositions, 6 h hydrothermal growth	8.84 ± 0.02
3% seed concentration, 2 depositions, 16 h hydrothermal growth	6.00 ± 0.03
3% seed concentration, 3 depositions, 16 h hydrothermal growth	14.10 ± 0.03

^aaverage particle size distribution obtained in SEM

To improve separation performance, it is essential to minimize the negative effects of pressure drop in the support and concentration polarization. This can be achieved by reducing the thickness of the upper support layer (e.g., from 30 to 5–10 μm) and increasing feed flow rates [162]. Since the thickness variation in both membranes was not significant, the 2% and 3 depositions system appear promising for permeation tests on commercial and *freeze-casting* tubes, as it presented lower thickness, uniform coverage, and less zeolite agglomeration. SEM analysis was performed to investigate the morphology of these membranes and to assess the quality of the zeolite layer formed on the tailored supports. The images (Figure 64 and 65) below show the surface and cross-sectional views of the membranes, allowing the evaluation of crystal coverage, layer uniformity, and the interface between the zeolite film and the porous substrate.

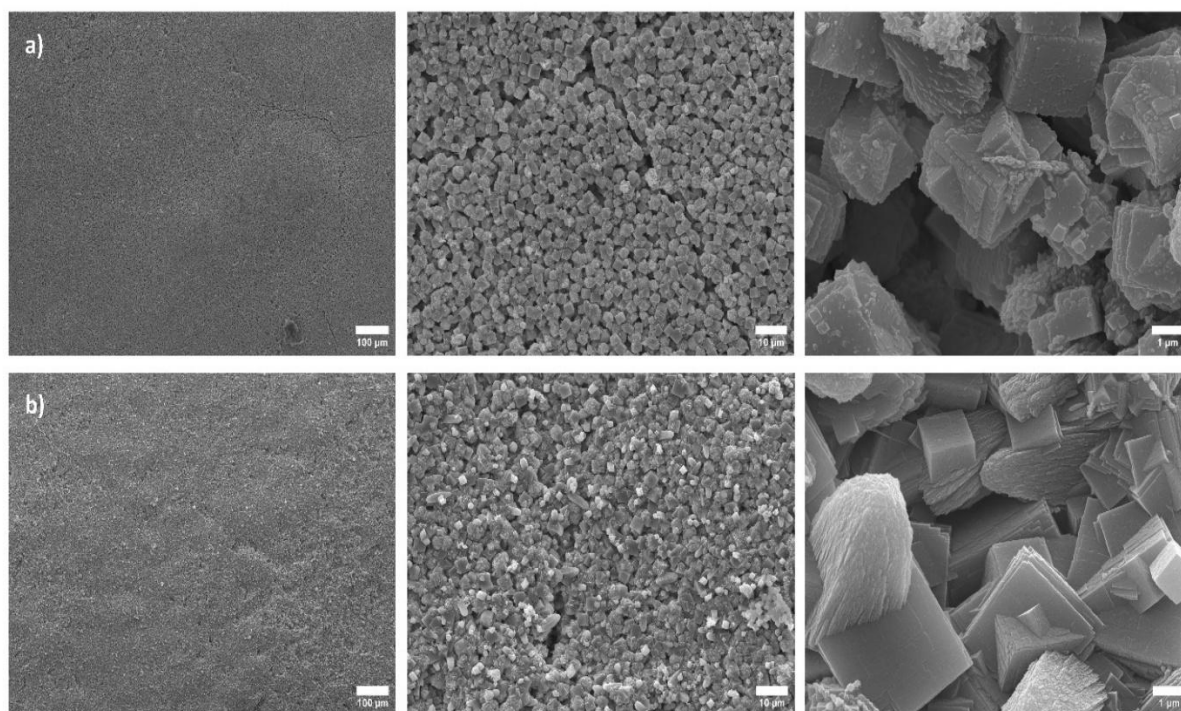


Figure 64. SEM images of 2% membranes on the *Freeze-Casting Tube*, 3 depositions after (a) 6 h and (b) 16h of hydrothermal synthesis.

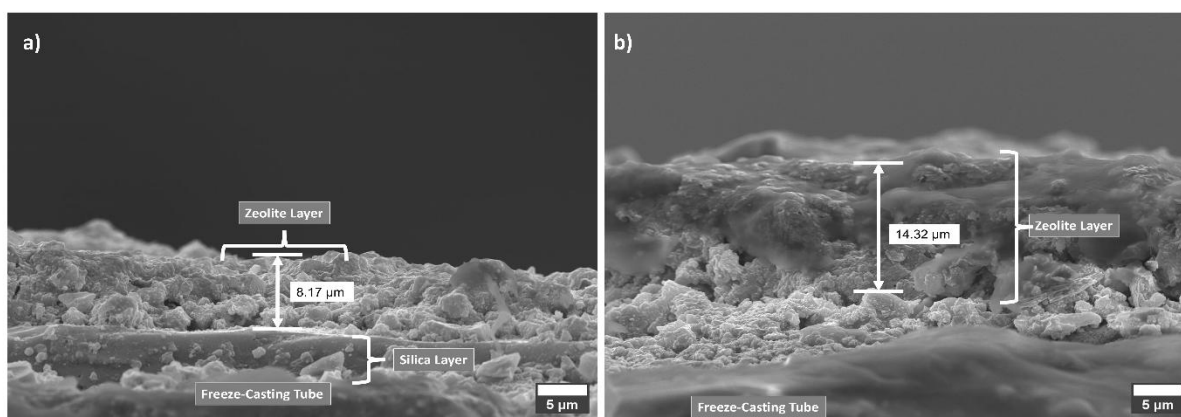


Figure 65. SEM images of the cross-section of 2% membranes on the *Freeze-Casting Tube*, 3 depositions after (a) 6 h and (b) 16h of hydrothermal synthesis.

Preparation of the KFI zeolite membrane on the freeze-cast tubular supports yielded a well-defined zeolite coating, despite the inherent challenges posed by the substrate. The freeze-cast tubes exhibit not only higher porosity than commercial ceramic supports but also a relatively rough surface, factors that could potentially hinder uniform zeolite deposition and promote local variations in layer thickness. Nevertheless, both samples successfully developed continuous zeolite layers, with regions displaying multiple stacked layers, indicating that the seeding and

hydrothermal growth procedures were effective in promoting nucleation and crystal growth across the porous and rough surface. The resulting zeolite layer thicknesses on the freeze-cast tubes were $8.17 \pm 0.09 \mu\text{m}$ and $14.32 \pm 0.27 \mu\text{m}$ (for 6h and 16h of hydrothermal synthesis, respectively), values comparable to those observed on commercial tubes ($9.84 \mu\text{m}$ and $11.5 \mu\text{m}$), demonstrating that, despite the higher porosity and surface roughness, a well-adhered and uniform coating was achieved with no evidence of zeolite intrusion or defects.

The use of *freeze-casting* tubes offers several advantages over conventional commercial supports. The highly porous and interconnected structure of the freeze-cast support allows for a reduction in mass transfer resistance, which can improve permeation rates during gas separation. Additionally, the tunable pore structure of *freeze-casting* ceramics enables optimization of mechanical strength while maintaining sufficient surface roughness to enhance zeolite attachment [19,23,24,38,143]. These features indicate that *freeze-casting* tubes are particularly attractive for the fabrication of high-performance zeolite membranes, as they provide a balance between adhesion, structural integrity, and transport properties.

5.3.3. Study of Gas Adsorption and Separation on Zeolitic Materials

The optimization of the synthesis parameters for the KFI zeolite revealed that the best experimental condition was achieved using aluminum hydroxide as the aluminum source, Ludox AM-30 as the silicon source, and a molar ratio of $\text{H}_2\text{O}/\text{SiO}_2$ of 200:10 (hereafter referred to as KFI-200H₂O). This condition resulted in a material with superior textural and structural characteristics, exhibiting high crystallinity (82.4%), a large proportion of tetrahedrally coordinated aluminum (97.4%, as confirmed by solid-state NMR analysis), and an improved BET surface area of $418.3 \text{ m}^2 \cdot \text{g}^{-1}$. Owing to its outstanding structural performance, this sample was selected for the evaluation of its practical potential in gas separation applications, a field of critical importance for CO₂ capture and emission mitigation, as well as for natural gas purification.

The adsorption performance of KFI-200H₂O was assessed by determining the pure gas adsorption isotherms (CO₂, CH₄ and N₂) under static conditions at 25 °C, as shown in Figure 66 and Table 15. These experimental data are essential for mapping the material's affinity and mass capacity under varying partial pressures. To quantify surface heterogeneity and adsorption kinetics, the experimental data were fitted to the Langmuir model. This model provides an

accurate representation of the adsorption behavior by assuming a single class of adsorption sites, where each site can adsorb only one molecule and no lateral interactions occur between adsorbed species. From this model, the parameters of maximum adsorption capacity ($q_{\text{máx}}$) and adsorption affinity (b) were obtained, providing valuable insight into the adsorbate–adsorbent interactions.

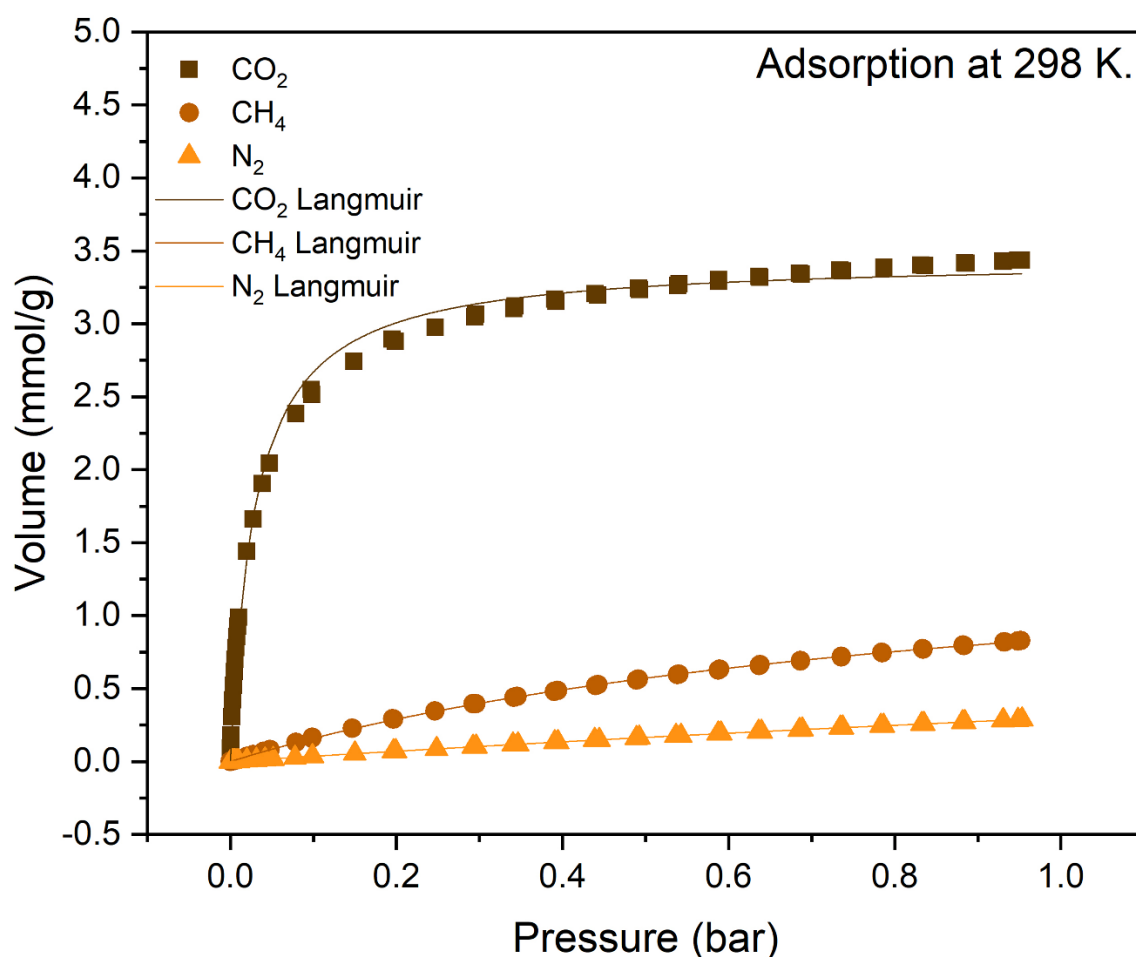


Figure 66. Adsorption isotherms of CO₂, CH₄ and N₂ on KFI-200H₂O at 298 K. The solid lines represent the Langmuir model fit.

Table 15. Fitted parameters of the Langmuir isotherm model and correlation coefficients for the adsorption of CO₂, CH₄ and N₂ on the zeolite KFI-200H₂O at 298 K.

Gas	q _{max} (mmol/g)	b	R ²
CO ₂	3.44 ± 0.02	0.5268 ± 0.018	0.997
CH ₄	1.61 ± 0.01	0.0302 ± 0.001	0.998
N ₂	1.56 ± 0.01	0.0300 ± 0.004	0.999

Analysis of the adsorption isotherms for the KFI zeolite revealed a clear distinction in equilibrium performance among the studied gases. Throughout the entire pressure range evaluated, the adsorption capacity followed the order: CO₂ > CH₄ > N₂. In particular, the maximum adsorption capacity for CO₂ was significantly higher, reaching 3.44 mmol·g⁻¹, surpassing both CH₄ and N₂, under identical conditions. This adsorption sequence is consistent with the decreasing order of the Langmuir constants (b) obtained, which reflects the intrinsic affinity of each adsorbate toward the microporous surface.

The dominant separation mechanism is based on selective adsorption, in which the KFI zeolite is particularly favored due to its narrow eight-membered-ring (8 MR) windows (~3.9 Å), whose size closely matches the kinetic diameter of CO₂ [11,70,74]. The exceptional affinity of KFI toward CO₂ is mainly attributed to an enhanced chemi- or physisorption mechanism, driven by both the structural features of the zeolite and the physicochemical properties of the CO₂ molecule. CO₂ is a linear molecule with a high quadrupole moment ($\mu_q = 4.3 \times 10^{-26}$ esu·cm²) [91], making it highly susceptible to interactions with localized electric fields within the zeolitic pores [11,70,92].

According to the literature, in KFI-type zeolites these fields are primarily generated by the charge-compensating cations (Na⁺, Li⁺, K⁺) located at ion-exchange sites, which act as preferential adsorption centers [11,127]. The resulting ion–quadrupole interaction is considerably stronger than the van der Waals forces that dominate the adsorption of less polar gases. Pham *et. al.* [165] reported that adsorption capacities are strongly correlated with the nature, location, and mobility of the extra-framework cations. Similarly, Remy *et. al.* [11] highlighted the correlation between the principal cation sites in KFI-type zeolites and CO₂ adsorption capacity, emphasizing that in K–KFI zeolites (i.e., containing K⁺ as the counterion),

CO₂ adsorption can be hindered. This occurs because K⁺ ions preferentially occupy the center of the flat eight-membered ring (α -cage), where they may partially block pore access due to their size and the measurement temperature.

Furthermore, the Si/Al ratio of the sample may have also contributed to the enhanced adsorption performance. The relatively low ratio (3.55) likely increased the number of charge-balancing cations available to interact with the gas molecules, thereby improving the overall adsorption capacity [12,13,92].

The adsorption of CH₄ and N₂ is typically governed by physisorptive dispersion forces (van der Waals interactions) and the pore-filling effect. Methane (CH₄) is a nonpolar tetrahedral molecule whose adsorption is primarily dictated by its polarizability and kinetic volume. Nitrogen (N₂), although possessing a quadrupole moment much smaller than that of CO₂, interacts more weakly with the adsorbent surface. The lower adsorption capacity of N₂ can be attributed to its lower polarizability compared to CO₂ and its weaker interaction energy with the adsorption sites.

However, despite the strong affinity of the synthesized zeolite toward CO₂, a notable improvement in the adsorption capacity of N₂ (1.56 mmol/g) was observed. The solid-state NMR characterization revealed a low degree of tetrahedral aluminum distortion, resulting in a sample with a significant increase in micropore area (390.3 m²/g) and ultramicropore size (0.35 nm). For N₂, whose kinetic diameter is smaller than that of CO₂, such defect minimization and the consequent formation of pores with critical dimensions enhance wall-to-wall interactions within the microporous framework. These structural modifications also intensify the internal electric field and favor interactions with the quadrupole moment of N₂, resulting in a higher affinity for this molecule [11,73,98,101].

From an applied standpoint, this improvement is relevant to air separation processes (O₂/N₂) and to the purification of N₂-containing gas streams, indicating that the modified KFI zeolite exhibits potential for use in Pressure Swing Adsorption (PSA) systems for oxygen generation or natural gas treatment.

Table 16 presents a comparison of the adsorption performance of the KFI-200H₂O sample with respect to other KFI zeolites reported in the literature. A remarkable N₂ adsorption capacity is observed for the sample, which can be attributed to a combination of structural and compositional factors: a favorable Si/Al ratio, the presence of the K⁺ cation that induces a

preferential path for the adsorption of N₂, and the high crystallinity combined with the high structural purity of the tetrahedral conformation of aluminum (T_d) of this sample.

Table 16. Comparative adsorption capacities of KFI zeolite for CO₂, CH₄ and N₂ at 298 K and at 1 bar (Langmuir model).

Zeolite (Reference)	Si/Al	Adsorption capacity (mmol g ⁻¹ STP)		
		CO ₂	CH ₄	N ₂
n-KFI [13]	2.29	-	1.34	0.55
US-KFI [12]	2.73	4.18	1.15	0.44
Ls,K-KFI [11]	1.67	1.80	0.03	-
Ag-KFI [67]	-	-	0.5	0.3
Na-KFI [70]	5.25	4.3	-	-
K-KFI [73]	4.59	3.00	0.79	0.42
K,Cs-KFI [101]	4.58	5.35	1.36	0.55
This Work	3.55	3.44	1.61	1.56

Accordingly, the excellent adsorption performance of the KFI-200H₂O zeolite confirms the successful optimization of the synthesis procedure and the high structural quality of the material obtained. The sample demonstrated superior CO₂ adsorption capacity, while the concurrent increase in N₂ uptake identifies this material is a promising seed candidate for the preparation of zeolitic membranes for gas separation applications.

The application of KFI zeolite in industrial gas separation processes requires evaluating its performance under multicomponent conditions, as gas–gas and gas–adsorbent interactions in binary or ternary systems differ substantially from those observed in pure-component adsorption studies. To this end, the Ideal Adsorbed Solution Theory (IAST) proposed by Myers and Prausnitz was employed, using the parameters obtained from the experimental adsorption isotherms of CO₂, CH₄ and N₂ [12,13,99,100,136,166].

The IAST model uses the fitted pure-gas adsorption isotherms (obtained through the Dual-Site Langmuir model) to predict the equilibrium behavior of binary gas mixtures. The main focus of this analysis is to determine the selectivity ($\alpha_{x/y}$) at relevant pressures and compositions

(typical of flue gas or raw natural gas), establishing the true potential of KFI-200H₂O as a high-performance material for CO₂, CH₄ and N₂. This theory is widely employed to predict the adsorption behavior of gas mixtures in microporous adsorbents such as zeolites [99,100]. IAST allows estimation of the adsorbed-phase composition from the pure-component isotherms, assuming that the adsorbed molecules behave as an ideal solution. This approach is particularly useful in systems where competitive interactions between molecules significantly influence the selectivity of the adsorbent [99,166].

The multicomponent adsorption equilibrium simulations were carried out for the binary mixtures CH₄/N₂, CO₂/CH₄ e CO₂/N₂, using KFI-200H₂O as the adsorbent, at room temperature (298 K) and total pressures up to 1 bar. The separation potential of the zeolite was evaluated as a function of gas mixture composition, varying the molar fraction of the lighter component from 0.1 to 0.9. This range covers a broad spectrum of compositions typically found in natural gas and flue gas streams. Such an approach enables the estimation of mixture adsorption behavior from pure-component data, providing valuable insight into the competitive adsorption mechanisms occurring within the zeolite framework. The results are presented in Figure 67 and Table 17 and Table B.1.

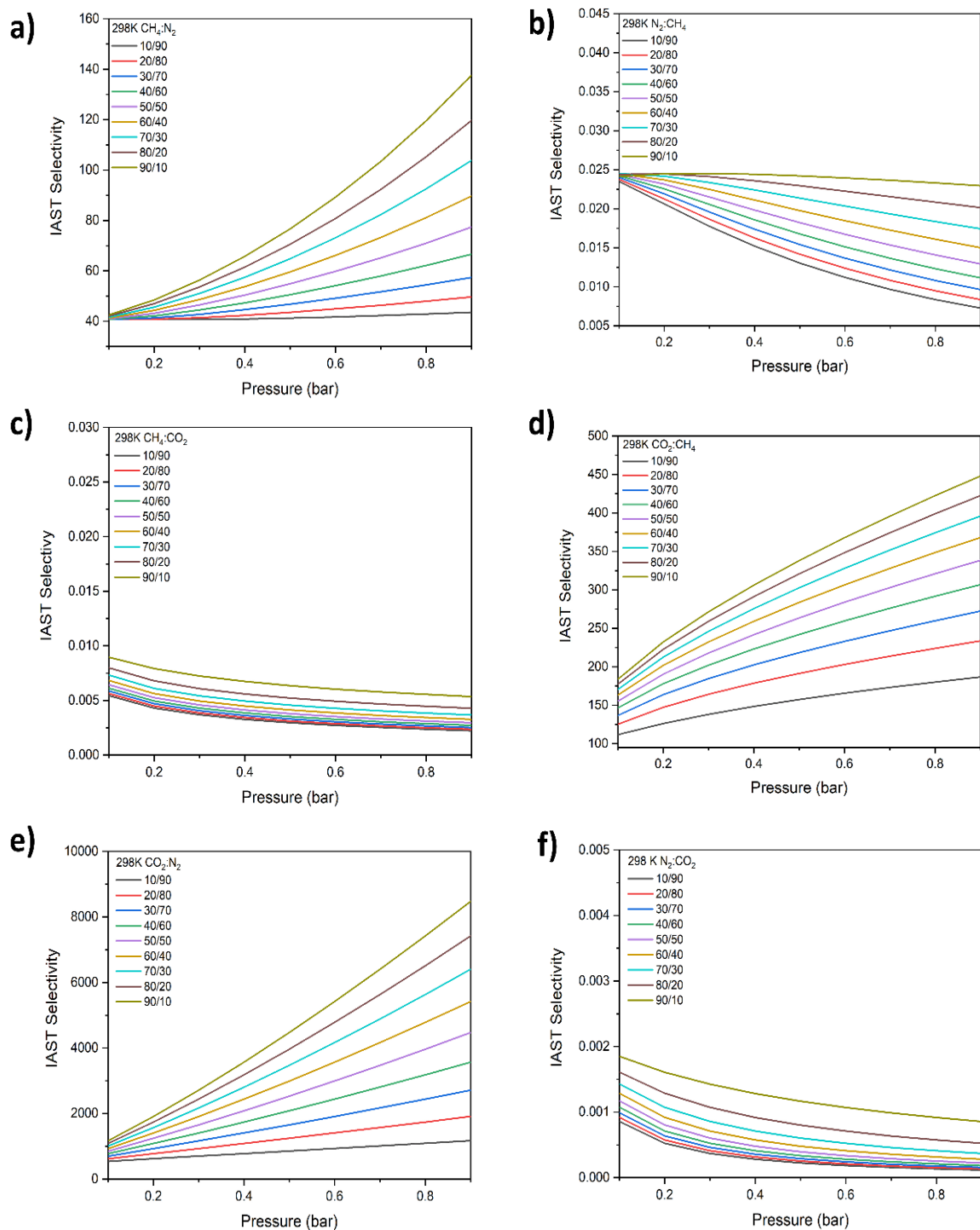


Figure 67. IAST selectivity of the KFI zeolite sample synthesized KFI-200H₂O for different binary gas mixtures: (a) CH₄/N₂, (b) N₂/CH₄, (c) CH₄/CO₂, (d) CO₂/CH₄, (e) CO₂/N₂ and (f) N₂/CO₂. The calculations were performed at 298 K and different pressure range for different mixture compositions.

Table 17. IAST selectivity values of the KFI zeolite sample (KFI-200H₂O) for different binary gas mixtures at 298 K and 1 bar.

Gas Composition (X ₁ /X ₂)	α -CH ₄ /N ₂	α -N ₂ /CH ₄	α -CH ₄ /CO ₂	α -CO ₂ /CH ₄	α -CO ₂ /N ₂	α -N ₂ /CO ₂
10/90	43.5	0.007	0.0022	186.7	1170.6	0.00012
20/80	49.6	0.008	0.0023	233.6	1911.9	0.00013
30/70	57.4	0.009	0.0025	272.4	2713.9	0.00015
40/60	66.6	0.011	0.0027	306.8	3569.4	0.00018
50/50	77.4	0.012	0.0029	338.5	4472.3	0.00022
60/40	89.7	0.015	0.0033	368.1	5417.6	0.00028
70/30	103.8	0.017	0.0037	396.0	6401.1	0.00037
80/20	119.7	0.020	0.0043	422.6	7419.8	0.00052
90/10	137.6	0.022	0.0053	448.1	8470.9	0.00085

The results revealed a clear trend in the selectivity order, following the sequence: CO₂/N₂ > CO₂/CH₄ > CH₄/N₂ > N₂/CH₄ > CH₄/CO₂ > N₂/CO₂. This hierarchy directly reflects the relative affinities of the gases toward the zeolite surface, as previously evidenced by the single-component adsorption capacities (CO₂ > CH₄ ≈ N₂). These trends are consistent with the microporous framework of KFI, which combines an optimal pore aperture and polar adsorption sites favorable for molecules with higher quadrupole moments, such as CO₂, while still exhibiting relatively strong interactions with CH₄ compared to N₂ [11–13,70,74].

For mixtures involving CO₂, the KFI zeolite showed a pronounced preference for this component. The selectivities for CO₂/CH₄ and CO₂/N₂ were notably high, representing the highest among all studied systems. This behavior is consistent with pure-component adsorption capacities, in which CO₂, due to its higher quadrupole moment and greater polarizability compared to CH₄ and N₂, interacts more strongly with the cationic and charge-compensating sites within the zeolitic structure. This stronger interaction results in significantly higher CO₂ adsorption capacity than for the other two gases (e.g., CO₂ > CH₄ > N₂). Therefore, the high

IAST-predicted selectivity for CO₂-containing mixtures (CO₂/CH₄ and CO₂/N₂) consistently reflects the intrinsic affinity order of the KFI zeolite: CO₂ > CH₄ > N₂ [12,13,72–74].

The exceptionally high selectivity observed in this work, particularly for CH₄/N₂ mixtures, highlights the remarkable potential of the synthesized KFI material for natural gas upgrading and purification applications. Interestingly, despite CH₄ and N₂ exhibiting similar adsorption capacities (1.61 and 1.56 mmol/g, respectively), the selectivity was found to be strongly dependent on the direction of the mixture. When CH₄ was considered the more strongly adsorbed component (CH₄/N₂ mixture), the selectivity reached up to 137.6, whereas for the reverse mixture (N₂/CH₄) the values were extremely low (~0.022) under identical conditions.

Physically, this indicates that CH₄, although similar in capacity to N₂, interacts more effectively with the microporous sites of the zeolite due to its higher polarizability and slightly larger kinetic diameter, which enhance dispersion interactions (gas–wall) and prolong its residence time within the pores. In contrast, N₂, with its higher quadrupole moment (while CH₄ lacks one due to its symmetry), tends to form weaker and more directional interactions with low-energy sites, resulting in less competitive adsorption in the presence of CH₄. Moreover, in KFI zeolites with 8-membered ring windows, the presence and mobility of extra-framework cations can selectively favor or block the passage/adsorption of certain gases. Possible cation rearrangements during adsorption may also create directional preferences for CH₄ over N₂ leading to apparent high α -CH₄/N₂ values under certain conditions [11,73,99,100,103,128].

It was also observed that in binary mixtures (X/Y), whenever component X exhibited a higher affinity, the selectivity increased progressively as the proportion of X in the gas mixture rose (from 10/90 to 90/10). This behavior is characteristic of systems in which the more strongly adsorbed component (X) preferentially occupies the higher-energy adsorption sites of the adsorbent. As the gas-phase concentration of X increases, surface coverage rises accordingly, and the preferential occupation of adsorption sites by X leads to a pronounced competitive exclusion of component Y. This cooperative or displacement effect becomes more significant at higher concentrations of the stronger component, amplifying the selectivity α (X/Y). Such behavior demonstrates the robustness of the KFI zeolite under high loading conditions of the target gas.

To validate the separation potential of the synthesized KFI-200H₂O zeolite and contextualize its performance, the IAST-derived selectivity values obtained for CO₂/N₂,

CO₂/CH₄ and CH₄/N₂ mixtures were compared with data from the literature for the same KFI structure (Table 18).

Table 18. Comparative IAST selectivities for gas mixtures on KFI zeolite at 298 K.

Zeolite (Reference)	Binary Mixture	Experimental Condition (p, X/Y)	$\alpha_{X/Y}$ (Selectivity)
n-KFI [13]	CH ₄ /N ₂	20/80 a 1 bar	4.2
Ag-KFI [67]	CH ₄ /N ₂	20/80 a 1 bar	29.6
This Work	CH₄/N₂	20/80 a 1 bar	49.6
US-KFI [12]	CH ₄ /N ₂	50/50 a 1 bar	4.6
DDR [97]	CH ₄ /N ₂	50/50 a 1 bar	3.3
This Work	CH₄/N₂	50/50 a 1 bar	77.4
n-KFI [13]	CO ₂ /N ₂	20/80 a 1 bar	379
This Work	CO₂/N₂	20/80 a 1 bar	1911.9
n-KFI [13]	CO ₂ /CH ₄	50/50 a 1 bar	130
DDR [97]	CO ₂ /CH ₄	50/50 a 1 bar	6.3
US-KFI [12]	CO ₂ /CH ₄	50/50 a 1 bar	739
This Work	CO₂/CH₄	50/50 a 1 bar	338.5
FAU [96]	CO ₂ /CH ₄	10/90 1 bar	61
This Work	CO₂/CH₄	10/90 a 1 bar	186.7

As expected, the KFI-200H₂O zeolite exhibited high selectivity for CO₂ over N₂ and CH₄, with considerably elevated values, in agreement with the literature reporting that low Si/Al ratio zeolites, particularly those containing exchangeable cations such as Na⁺ and K⁺, are excellent CO₂ adsorbents. This behavior can be attributed to the strong electrostatic interactions between the CO₂ quadrupole and the cations within the zeolitic framework, favoring the selective adsorption of carbon dioxide [11,73,74,101].

Notably, the $\alpha\text{-CH}_4/\text{N}_2$ values obtained in this study were 49.6 and 77.4, representing remarkably high results, especially when compared to adsorbents traditionally employed for CO_2 separations. Zeolites extensively studied for natural gas purification, such as DDR and CHA [20,77,78,119], are typically optimized for CO_2/CH_4 separation, and reports of such high selectivities for CH_4/N_2 mixtures are rare.

The exceptionally high $\alpha\text{-CH}_4/\text{N}_2$ observed for KFI-200 H_2O indicates that this material possesses a remarkable affinity for CH_4 relative to N_2 (despite their similar adsorption capacities), making it particularly suitable for the selective removal of N_2 (denitrogenation) from CH_4 streams. This characteristic is highly relevant for the upgrading of low-calorific-value natural gas, where efficient nitrogen removal is critical to meet product quality and safety specifications.

Overall, the selectivity values obtained in this work are significantly higher than those reported in references [12], [13], [67], [96] (faujasite zeolites) and [97] (DDR zeolite) indicating that the material exhibits unique or superior behavior for this particular separation. These results suggest that KFI is a highly promising candidate for selective CH_4 or CO_2 separation under mild conditions. Such information is essential for the design of natural gas purification processes, enabling optimization of both the adsorbent material and operating conditions, and providing a robust basis for evaluating its real performance in industrial gas separation applications [11,73,99,100,103,128].

The application of the IAST selectivity results in the performance of a zeolite membrane allows extrapolating the behavior of only the equilibrium adsorption stage to a dynamic transport regime, but with great caution since the permeability of a gas in a membrane depends on other factors. In microporous systems, the permeated flux is simultaneously governed by the thermodynamic affinity between the gas molecules and the pore surface (adsorption mechanism) and by their mobility within the pore network (kinetic mechanism) [95,97,167,168]. Thus, the effective membrane selectivity can be expressed as the product of adsorption and diffusion selectivities. For the KFI zeolite, the remarkably high IAST selectivity value obtained for the CO_2/N_2 pair (8470.9 at 298 K and 1 bar) indicates strong preferential adsorption of CO_2 , attributed to its higher polarizability and strong interactions with the framework cationic sites. This behavior suggests that, in a membrane composed of KFI, CO_2 transport would predominantly occur via surface diffusion, with the preferentially adsorbed

CO₂ migrating along the pore walls and displaces N₂, resulting in high CO₂ permeation selectivity [167].

As for the N₂/CH₄ system, the similar adsorption capacities suggest that the separation process is mainly controlled by molecular sieving kinetic effects, since N₂ has a smaller kinetic diameter and greater mobility in the zeolite channels. Although this system (CH₄/N₂) presents a high IAST selectivity of 137.6 under the same conditions [3,102]. In this case, permeation would be strongly dependent on pressure and temperature, since variations in these parameters alter the relative molecular mobility within the micropores and the availability of adsorption sites. Given that N₂ has a smaller kinetic diameter than CH₄, the KFI zeolite may favor the selective diffusion of N₂ if the effective pore size (~ 3.9 Å) restricts CH₄ access. Moreover, the high N₂ adsorption capacity observed experimentally may exert a dual influence on membrane performance: at elevated pressures, extensive pore filling by N₂ tends to reduce the adsorption differential between gases (the *pore-filling effect*), thereby decreasing operational selectivity; however, under conditions where N₂ is the minor component, this property could enhance the overall flux, increasing the total permeance [94,97,165,167,168]. Overall, the IAST results confirm the strong potential of the KFI zeolite for CO₂/N₂ separation, while highlighting the importance of kinetic factors and operating conditions in optimizing CH₄/N₂ separation performance.

Overall, the adsorption capacity and IAST selectivity results obtained for the KFI zeolite demonstrate outstanding performance when compared to values reported in literature. The material exhibited a remarkable affinity toward CO₂, combined with high adsorption capacity and exceptionally high IAST selectivity for CO₂/N₂, which clearly surpasses those typically observed for conventional zeolitic structures. These findings indicate that the KFI framework provides an optimal balance between adsorption strength and accessible microporosity, enabling efficient gas uptake and discrimination between molecules of similar size. In light of these results, the KFI zeolite can be considered a highly promising candidate for gas separation applications, particularly for CO₂ capture and purification processes, where both selectivity and adsorption capacity are critical parameters for technological advancement.

CONCLUSIONS And PERSPECTIVES

6. CONCLUSIONS and PERSPECTIVES

The present work focused on the development of KFI zeolite membranes, encompassing substrate preparation, zeolite synthesis optimization, membrane fabrication, and theoretical adsorption studies. The main findings and perspectives are summarized below.

6.1 CONCLUSIONS

The preparation of the ceramic supports involved the use of molds with distinct thermal conductivities, which induced specific freezing modes (unidirectional and bidirectional) and, consequently, led to specific pore orientations in the alumina-based materials. The camphene-based *freeze-casting* method enabled the fabrication of supports with a significant total porosity of around 60%.

The monoliths support prepared using the technyl mold exhibited a relatively disordered and inconsistent pore structure but displayed the highest compressive strength values (19.6, 23.3, and 34.2 MPa for 15%, 20%, and 25% solid loading, respectively). Conversely, the ceramic supports produced in the copper mold showed a more ordered pore alignment, lower total porosity (74.3%, 63.0%, and 57.4%), and reduced compressive strength (8.8, 11.9, and 25.5 MPa). The technyl/copper mold configuration successfully combined the main features of the two previous designs, exhibiting intermediate mechanical resistance (12.0, 15.7, and 28.3 MPa) and moderate porosity (73.6%, 57.7%, and 57.1%). These results unequivocally demonstrated that the freezing direction and the thermal conductivity of the mold have a substantial impact on the final structure, mechanical properties, and pore connectivity of the alumina supports. The technyl molds yielded supports with remarkable mechanical strength and high pore interconnectivity, which are essential characteristics for gas separation applications.

The subsequent development of tubular supports through camphene-based *freeze-casting* confirmed the versatility of this approach for obtaining highly aligned, radially oriented pore structures with adequate total and open porosity for use as substrates. Although the tubular geometry slightly reduced open porosity compared to monolithic structures, it significantly improved mechanical integrity due to its dendritic morphology and radial pore alignment, making the *freeze-casting* tubes suitable candidates for supporting thin zeolitic layers.

The preparation of the zeolitic material involved a systematic investigation of different aluminum and silicon sources, as well as the influence of the water ratio, to establish the

parameters governing the formation of the KFI zeolite framework. These studies revealed that only a narrow range of Si/Al ratios in the synthesis gel led to the formation of high-purity KFI zeolite. Syntheses performed using $\text{Al}(\text{OH})_3$ as the aluminum source indicated that the choice of the silicon precursor is crucial; samples prepared with Ludox® AS-40 and Ludox® AM-30 colloidal silica displayed the highest purity levels, unlike those employing TEOS. When aluminum wire was used as the Al source, the sample prepared with Ludox® AM-30 exhibited the fewest impurities and the best textural properties, with a BET surface area of 523.8 and a micropore area of 469.4 m^2/g , indicating that nearly 90% of its surface area arises from micropores. The use of aluminum isopropoxide ($\text{Al}(\text{O}-i\text{-Pr})_3$) as an aluminum source represents an innovative approach, and Ludox® AM-30 again proved to be the most suitable silicon source, yielding well-defined cubic crystals with KFI peaks and a unit cell parameter (a_0) closely matching the reference value (error of only 0.65%).

The systematic study on water content demonstrated its crucial role, revealing that increasing the water ratio did not significantly affect KFI phase formation but promoted simultaneous growth of crystalline and amorphous fractions, suggesting it modulates crystallization kinetics. Among the tested compositions, the sample synthesized with a water-to-solid ratio of 200 (KFI-200H₂O) showed the most promising characteristics, combining a high BET surface area (approximately 420 m^2/g), excellent crystallinity (82.4%), and minimal lattice distortion. These findings highlight the effectiveness of the synthesis approach without organic structure-directing agents, producing KFI zeolites with strong potential for gas separation.

Finally, the KFI-200H₂O zeolite demonstrated excellent adsorption capacity and high selectivity, as predicted by the IAST model. Single-component isotherms revealed a clear preference for CO₂ over CH₄ and N₂ ($\text{CO}_2 > \text{CH}_4 \approx \text{N}_2$), and the CH₄/N₂ mixture exhibited a remarkable selectivity ($\alpha\text{-CH}_4/\text{N}_2 \approx 137$), highlighting the material's ability to effectively separate components crucial for natural gas purification and CO₂ capture.

Membrane preparation involved a two-step approach: first, the deposition of a thin SiO₂ layer by *dip-coating* to improve adhesion, optimized at a withdrawal speed of 90 mm/min to minimize cracking. The thickness of this interlayer was controlled (up to 5.11 $\mu\text{m} \pm 0.03 \mu\text{m}$) for commercial and 3.00 $\mu\text{m} \pm 0.05 \mu\text{m}$ for freeze-cast tubes). The second step focused on the growth of the zeolite layer. A deposition time of 60 seconds and the use of 2% seed solution provided the optimal combination, yielding thinner layers with uniform crystal distribution and

excellent surface coverage, while minimizing agglomeration. SEM analysis confirmed layer thicknesses between 8.17 and 14.32 μm for freeze-cast tubes (depending on hydrothermal time) and a well-defined interface. This is the first study to report the preparation of KFI zeolite membranes with such controlled deposition and uniform coverage.

6.2 PERSPECTIVES

Future research should focus on advancing both the support structure and the functional evaluation of the KFI membranes.

1. **Structural Validation of Supports:** Further work should focus on the mechanical characterization of the fabricated tubes, particularly through compressive strength testing, to quantitatively assess their structural performance and validate the reinforcement expected from the aligned dendritic network. Such investigations, together with permeability and thermal stability assessments, will be essential to optimize the balance between porosity and mechanical strength, guiding the future development of advanced tubular supports.
2. **Fundamental KFI Study:** Future research should focus on a comprehensive structural and adsorption study of all synthesized zeolites to better elucidate the relationship between crystal size, framework organization, and adsorption behavior. A detailed investigation combining advanced characterization techniques—such as *in situ* XRD, MAS NMR, and gas adsorption isotherms with various probe molecules could provide valuable insights into the synthesis–structure–property relationships governing KFI zeolites.
3. **Dynamic Membrane Performance:** The crucial next step is to fabricate a gas separation module compatible with the tubular supports. This will enable the experimental application of the KFI membranes under dynamic permeation conditions to obtain direct and reliable permeability and selectivity results for relevant gas mixtures (CO_2/CH_4 , CH_4/N_2). This practical evaluation is essential for validating the material's potential and guiding the final optimization of substrate geometry, seed deposition, and crystallization kinetics for advanced gas separation technologies.

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7. REFERENCES

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APPENDIX

APPENDIX A: FIGURES

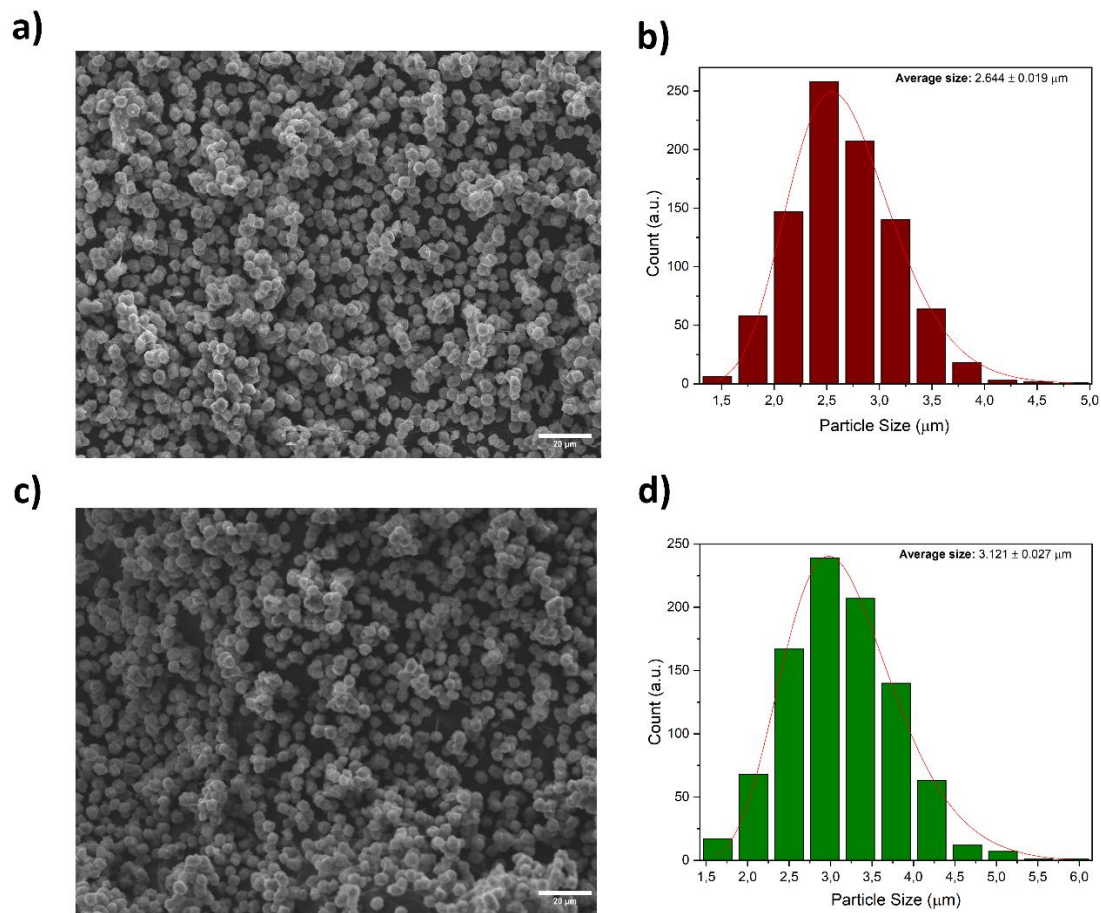


Figure A. 1. SEM image of samples with Al(OH)₃ as aluminum source and mean particle size distribution where (a, b) with Ludox® AS-40 and (c, d) Ludox® AM-30 as silica source.

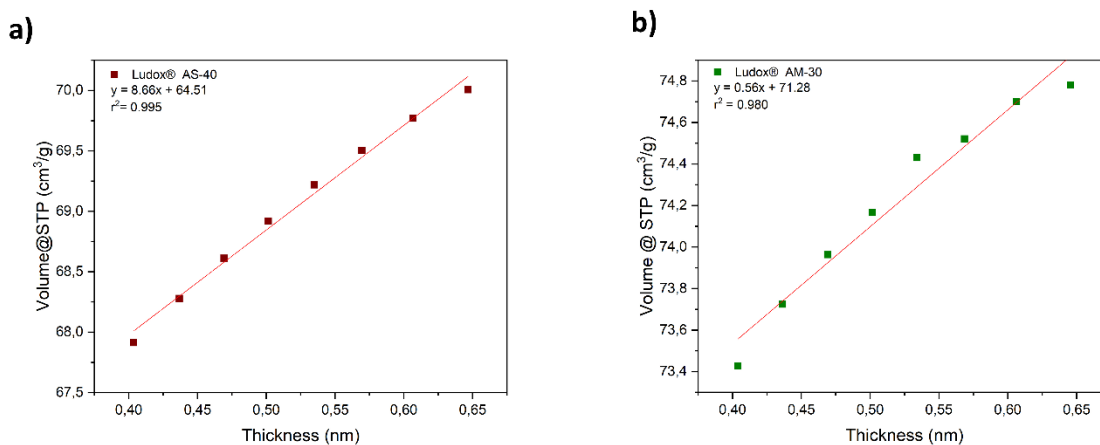


Figure A. 2. T-plot curve for samples with Al(OH)₃ as aluminum source and (a) Ludox® AS-40 and (b) Ludox® AM-30 as silica source.

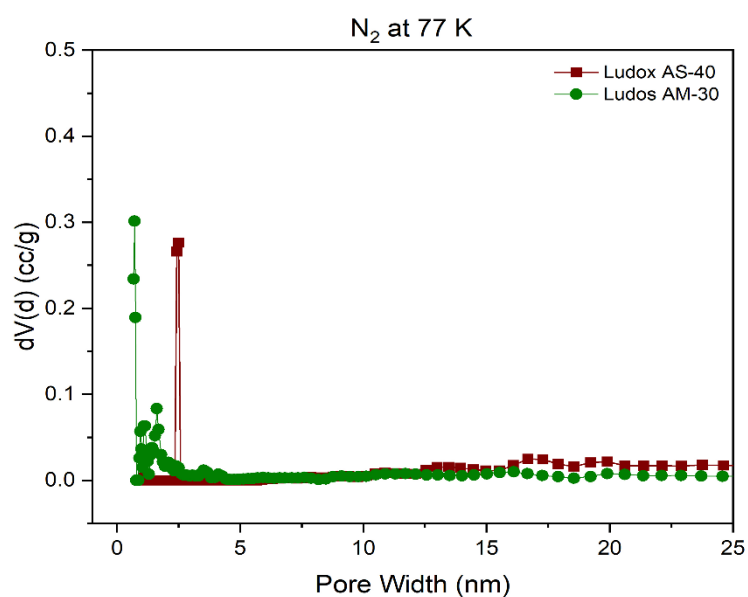


Figure A. 3. Pore size distribution calculated by the DFT method in the region 0.15 to 0.5 for samples with $Al(OH)_3$ as aluminum source and (a) Ludox® AS-40 and (b) Ludox® AM-30 as silica source.

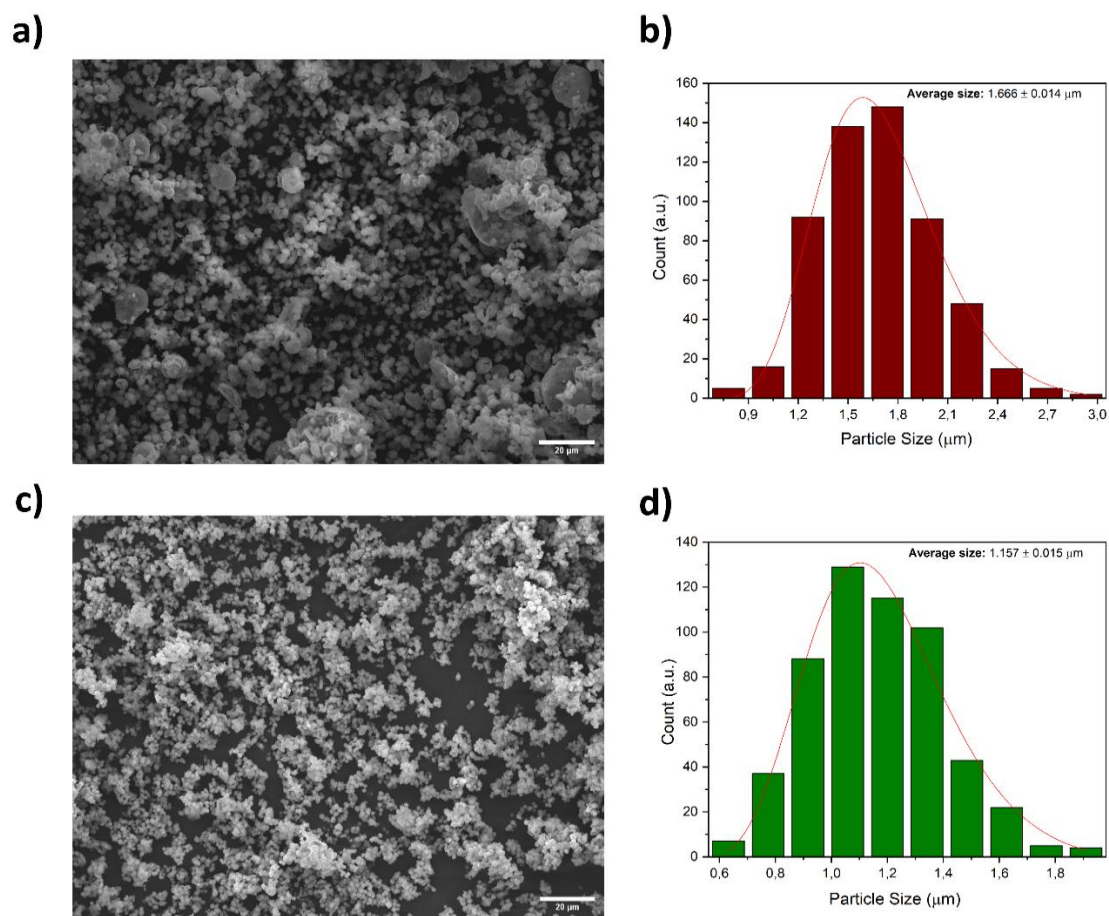


Figure A. 4. SEM image of samples with Aluminum Wire as aluminum source and average particle size distribution where (a, b) with Ludox® AS-40 and (c, d) Ludox® AM-30 as silica source.

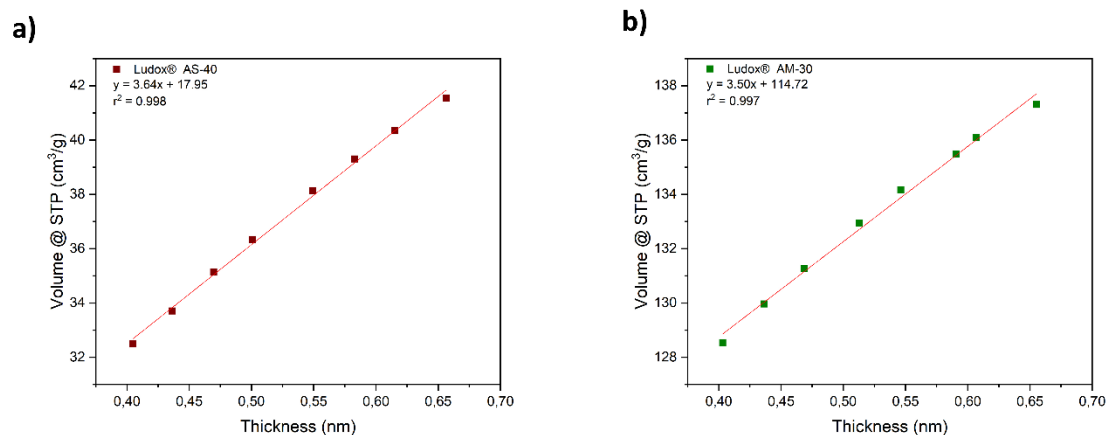


Figure A. 5. T-plot curve for samples with Aluminum Wire as aluminum source and average particle size distribution where (a) with Ludox® AS-40 and (b) Ludox® AM-30 as silica source.

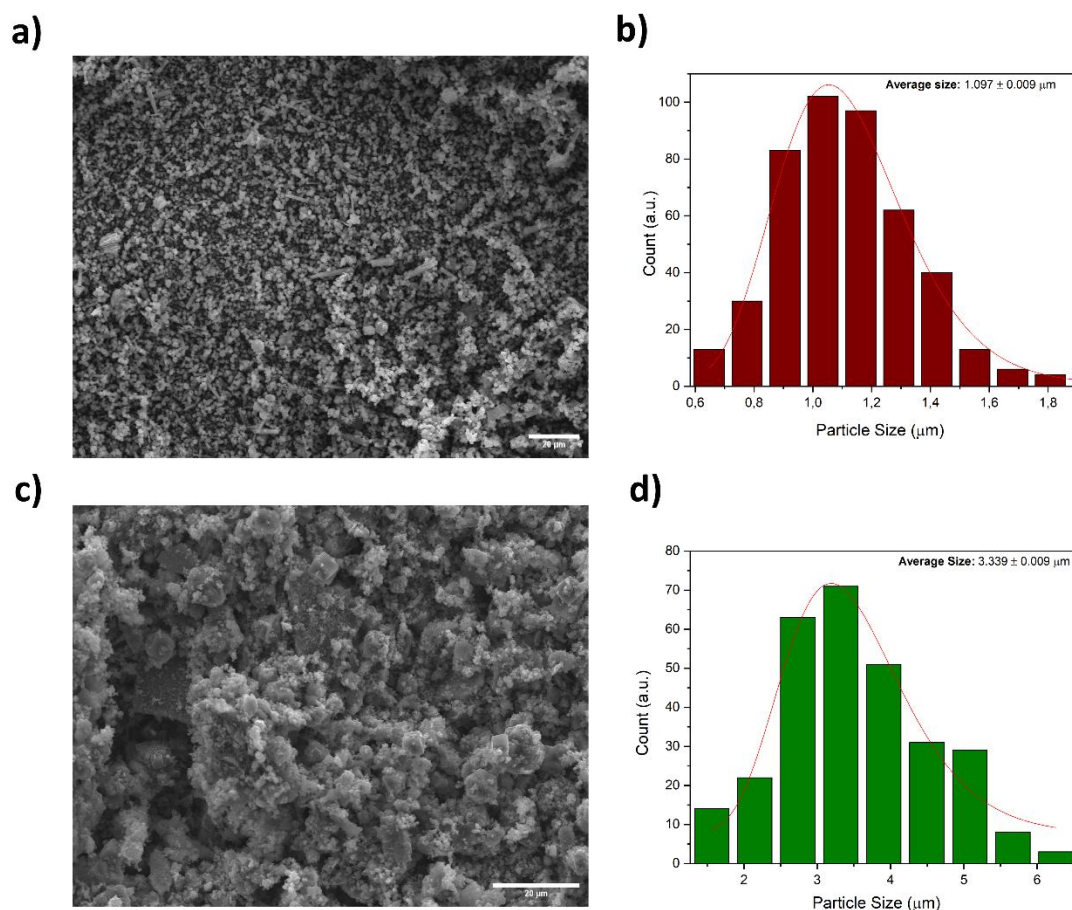


Figure A. 6. SEM image of samples with Al(O-*i*-Pr)₃ as aluminum source and mean particle size distribution where (a, b) with Ludox® AS-40 and (c, d) Ludox® AM-30 as silica source.

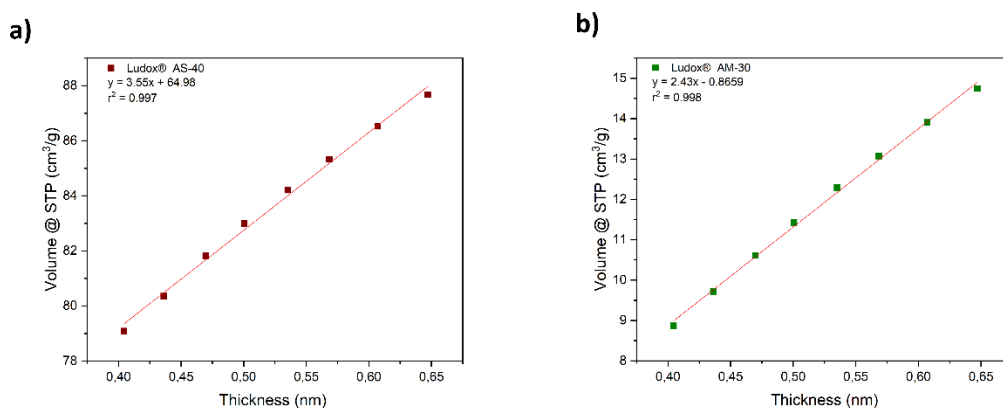


Figure A. 7. T-plot curve for samples with $\text{Al}(\text{O-i-Pr})_3$ as aluminum source and mean particle size distribution where (a) with Ludox® AS-40 and (b) Ludox® AM-30 as silica source.

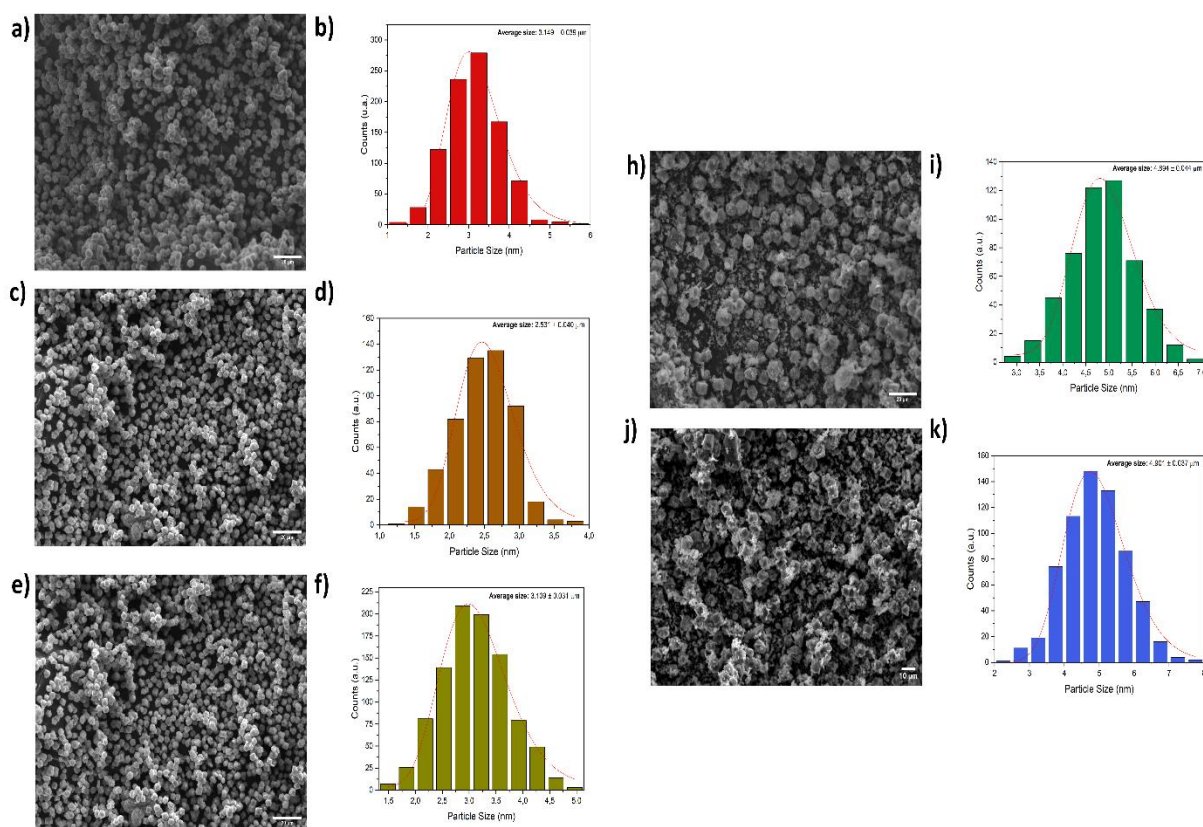


Figure A. 8. SEM image of samples with $\text{Al}(\text{OH})_3$ as aluminum source and average particle size distribution for the study of water with the proportions of (a, b) $160\text{H}_2\text{O}$; (c, d) $200\text{H}_2\text{O}$; (e, f) $240\text{H}_2\text{O}$; (h, i) $280\text{H}_2\text{O}$ and (j, k) $320\text{H}_2\text{O}$.

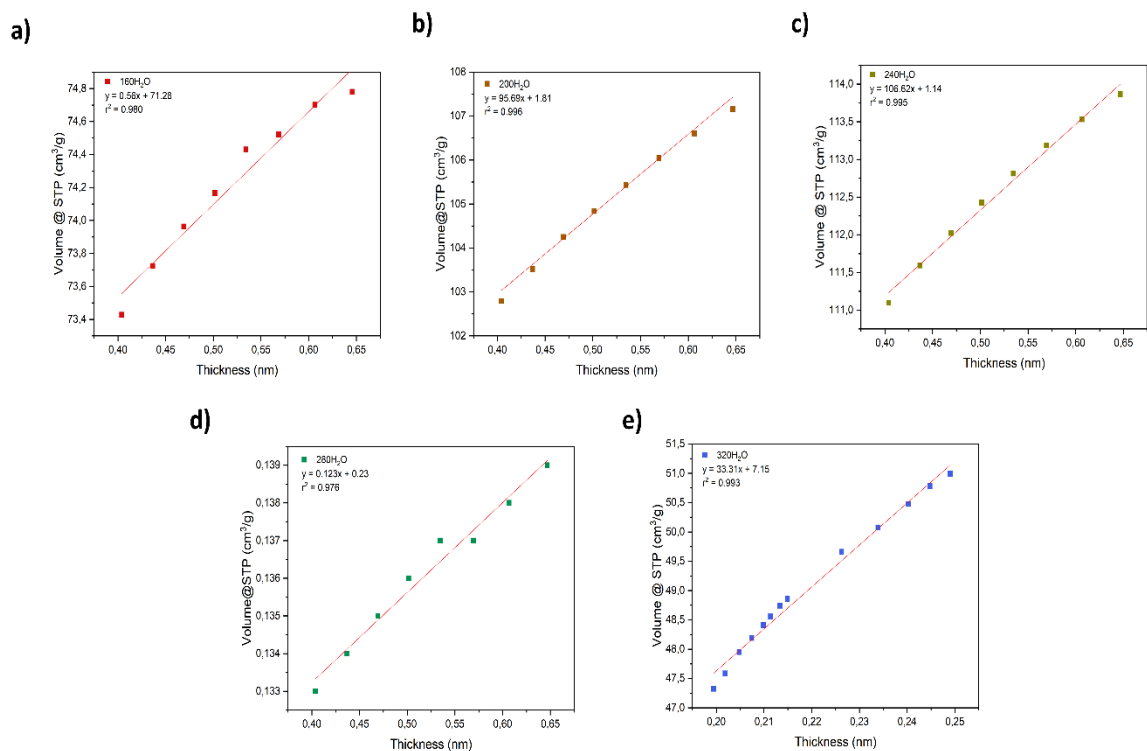


Figure A. 9. T-plot curve of samples with Al(OH)₃ as aluminum source for the study of water with the proportions of (a) 160H₂O; (b) 200H₂O; (c) 240H₂O; (d) 280H₂O and (e) 320H₂O.

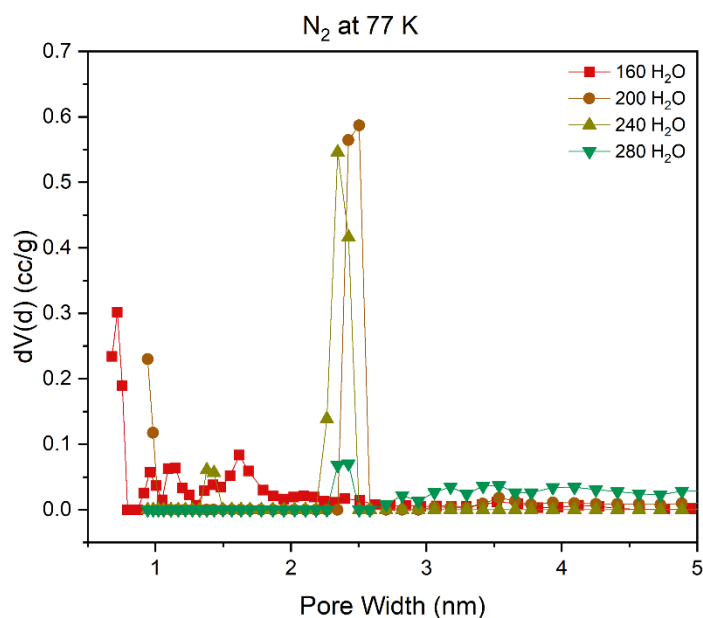


Figure A. 10. Pore size distribution calculated by the DFT method in the region 0.15 to 0.5 for samples with Al(OH)₃ as aluminum source and Ludox® AM-30 as silica source.

APPENDIX B: TABLES

Table B. 1. DSL parameters for the KFI-200H₂O sample

Gas	$q_{\text{máx},1}$	b_1	$q_{\text{máx},1}$	b_2
CO ₂	1.448166	6.833915	2.20350	73.136099
CH ₄	0.889906	0.097802	1.395958	1.256092
N ₂	-	0.191137	0.869898	0.276749

Table B. 2 Pore width calculated by the DFT method in the region 0.15 to 0.5 for samples with Al(OH)₃ as aluminum source and Ludox® AM-30 as silica source.

Sample	Pore Width (nm)
160 H ₂ O	0.68
200 H ₂ O	2.50
240 H ₂ O	2.42
280 H ₂ O	2.42

ATTACH MENTS

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Control of pore morphology and mechanical strength of alumina ceramics produced by freeze-casting

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ABSTRACT

In this work, unidirectional and bidirectional freeze-casting techniques were employed to fabricate alumina monoliths using camphene as solvent. Monolith samples with aligned porosity were produced in unprecedented molds designed using materials with different thermal conductivities (technyl and copper) and varying the alumina monoliths concentrations (15, 20 and 25 % of solid load). The total porosity of the produced monoliths ranged within 50–70 % and it was observed that the different molds did not influence the total porosity of the material. The SEM images showed that the samples produced in the technyl/copper mold presented a change on the perpendicular alignment of the pores in the transition region from copper to technyl. The copper side exhibited more aligned structures forming continuous channels, that become less noticeable when closer to the transition region, reaching the technyl region where the dendrites were not well aligned. The monoliths prepared in the technyl mold showed a better mechanical resistance with values of 19.6; 23.34 and 34.2 MPa for 15, 20 and 25 % of the solid load, respectively.

1. Introduction

Materials with ordered pore structure present diverse properties such as their high adsorption capacity, low thermal conductivity, excellent permeability and improved mechanical properties [1,2]. These characteristics boosted the use of these versatile materials in several applications, such as the preparation of inorganic membranes for microfiltration [1,3], gas separation [2,4], degradation of Fe-based materials [5], tissue engineering bone [6], continuous flow catalysts [7]. However, porous materials have a common limitation: the inherent lack of strength associated with porosity. Therefore, its application tends to be limited, demanding further studies on the design of a material that is at the same time porous and exhibits adequate mechanical properties for high pressure and temperature applications [8].

Among the methods for producing organized pore structure, the

freeze-casting is an attractive technique that has gained prominence in recent years, as it allows the preparation of materials with tailored pore microstructures. In addition, it is an ecologically friendly, economical and scalable method for industry [5,8,9]. Its potential arises from the possibility of tuning the pore morphology by precise control of the manufacturing parameters, especially those related to the freezing and solidification of the used solvent [10]. The technique consists on using stable colloidal solutions in which the solvent solidifies during the controlled cooling step. This is a fast process and freezing is almost instantaneous, resulting in the formation of solvent crystals that trap the colloidal particles [5,6]. The porosity, size and orientation of the generated pores after removing the frozen solvent depend on the morphology of the solvent crystals, which can be adjusted by the freezing conditions, such as temperature, cooling rate, solution concentration, precursor viscosity and additives [6,9,11]. Obviously, the

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Programa: Programa de pós graduação em Química

Nome completo: Anna Carolina Britto de Faria

Título do Trabalho: Production of inorganic zeolite membranes with KFI zeolite for gas separation.

Nível: () Mestrado (x) Doutorado

Orientador/a: Alysson Martins Almeida Silva