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Production of Inorganic Membranes with SSZ-13 Zeolite for Gas Separation

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Zeolite for Gas Separation**

**(Produção de Membranas Inorgânicas com Zeólita SSZ-13
para Separação de Gases)**

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*- I dedicate this work to the memory of my beloved grandmother, Vera Lúcia.
Her love and wisdom remain everlasting sources of inspiration and longing.*

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List of Abbreviations and Acronyms

A

Al^{IV} – Tetrahedrally coordinated aluminum

$\text{Al}^{\text{IV}}_{\text{dist.}}$ – Distorted tetrahedrally coordinated aluminum

Al^{V} – Pentacoordinated aluminum

Al^{VI} – Hexacoordinated aluminum

ANP – National Petroleum, Natural Gas and Biofuels Agency (*Agência Nacional do Petróleo, Gás Natural e Biocombustíveis*)

ATR – Attenuated Total Reflectance

B

BET – Brunauer-Emmett-Teller model

C

CA – Citric Acid

CDTN – Nuclear Technology Development Center (*Centro de Desenvolvimento de Tecnologia Nuclear*)

CHA – Topology of the Chabazite Zeolite

C_R – Relative Crystallinity (%)

D

d_{6r} – Double six-ring

DFT – Density Function Theory

NLDFT – Non-local Density Functional Theory

d_p – Pore Diameter

XRD – X-ray Diffraction

E

EFKA – Dispersant EFKA FA 4663

8-MR – eight-membered ring

ETD – Everhart-Thornley Detector

F

FAU – Topology of the Faujasite Zeolite

4-MR – Four-membered ring

FTIR – Fourier Transform Infrared Spectroscopy

FWHM – Full Width at Half Maximum

G

NG – Natural gas

LNG – Liquefied Natural Gas

I

IAST – Ideal adsorbed solution theory

ICSD - Inorganic Crystal Structure Database

IUPAC – International Union of Pure and Applied Chemistry

IZA – International Zeolite Association

K

K_H – Henry's constant

L

LABMEC – Mechanical Testing Laboratory (Laboratório de Ensaaios Mecânicos)

LED – Low Energy Detector

LEGGA - Laboratory of Geodynamic, Geochronological, and Environmental Studies
(Laboratório de Estudo Geodinâmicos, Geocronológicos e Ambientais)

LFD - Large Field Detector

LMN - Nanostructured Materials Laboratory (Laboratório de Materiais Nanoestruturados)

LMCNano - Laboratory of Nanostructured Ceramic Materials (Laboratório de Materiais Cerâmicos Nanoestruturados)

LMEVCL - Laboratory of Scanning Electron Microscopy and Laser Confocal Microscopy (Laboratório de Microscopia Eletrônica de Varredura e Confocal Laser)

M

μ -CT – X-ray Computed Microtomography

N

NIH – National Institute of Health

P

P_A – Open porosity

PNM – XPoreNetworkModeling

P_T – Total porosity

PTFE – Polytetrafluoroethylene

PVA –Polyvinyl alcohol

Q

$q_{\max}$ - Adsorptive capacity

S

SAC – Steam-assisted crystallization

SEM – Scanning Electron Microscopy

SH – Henry’s selectivity

S_{IAST} – IAST selectivity

6-MR - Six-membered ring

S_{BET} – BET surface area

S_{EXT} – t-plot external surface area

Si(0Al) – Tetrahedrally coordinated silicon with zero aluminum neighbors

Si(1Al) – Tetrahedrally coordinated silicon with one aluminum neighbor

Si(2Al) – Tetrahedrally coordinated silicon with two aluminum neighbors

S_{MICRO} – t-plot microporous area

sod – Sodalite building unit

T

TBA – Tert-butyl alcohol

T_C – Crystallite size

TMAdaOH – N,N,N-Trimethyladamantan-1-aminium hydroxide

U

UFMG – Federal University of Minas Gerais (*Universidade Federal de Minas Gerais*)

USA – United States of America

V

V_{μ} - Micropore volume by the t-plot method

V_p – Pore volume

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Resumo

Neste estudo, foram desenvolvidas membranas inorgânicas do tipo SSZ-13/ α -Al₂O₃, com foco em aplicações futuras para a separação gasosa de componentes do gás natural. A produção envolveu a otimização do suporte cerâmico por *freeze-casting* e o desenvolvimento da fase ativa de zeólita SSZ-13 por diferentes métodos de síntese, com destaque para a rota assistida por micro-ondas. O estudo dos suportes cerâmicos evidenciou que o tipo de dispersante (ácido cítrico e EFKA FA 4663) utilizado no processo de *freeze-casting* impactou nas propriedades microestruturais e mecânicas. Monólitos cerâmicos preparados com o dispersante ácido cítrico e o solvente álcool *tert*-butílico apresentaram porosidade de até 60,4%, boa conectividade entre os poros e resistência à compressão de até 7,9 MPa, características adequadas para seu uso como substrato de membranas. Na síntese da zeólita SSZ-13, a escolha do contra-íon revelou que o potássio (K⁺) favoreceu a formação de cristais cúbicos altamente cristalinos (97,9%) e homogêneos. Além disso, a aplicação de radiação micro-ondas combinada com a adição de sementes de SSZ-13 permitiu reduzir drasticamente o tempo de síntese (de 4 dias para 60 minutos) e o tamanhos dos cristais (de $5.67 \pm 0.07 \mu\text{m}$ para $0,645 \pm 0,016 \mu\text{m}$). A zeólita SSZ-13, produzida via síntese assistida por micro-ondas em 60 minutos, apresentou ainda elevada cristalinidade (97%) e grande área superficial específica ($694,9 \text{ m}^2 \cdot \text{g}^{-1}$), evidenciando seu potencial como fase ativa em membranas. As membranas inorgânicas produzidas por *dip-coating*, utilizando as sementes produzidas via síntese assistida por micro-ondas e via síntese hidrotérmica, exibiram camadas zeolíticas finas e homogêneas, com espessuras entre 1,86 e 6,43 μm , e alto grau de recobrimento sobre os suportes de α -Al₂O₃. Estudos teóricos de adsorção (IAST) demonstraram elevada seletividade para CO₂ nas misturas CO₂/CH₄ e CO₂/N₂, reforçando o potencial da SSZ-13 como fase ativa em processos de separação gasosa. Dessa forma, os resultados obtidos confirmam o sucesso na produção de membranas SSZ-13/ α -Al₂O₃ com propriedades estruturais e adsorptivas otimizadas para sua fase ativa, estabelecendo parâmetros importantes para estudos futuros voltados à otimização do desempenho e aplicação de membranas zeolíticas em processos de separação de misturas de gases representativas do gás natural.

Palavras-chave: Zeólita SSZ-13, síntese assistida por micro-ondas, monólitos cerâmicos, *freeze-casting*, membranas inorgânicas.

Abstract

In this study, inorganic SSZ-13/ α -Al₂O₃ membranes were developed, focusing on future applications for gas separation of natural gas components. The production involved optimization of ceramic support by freeze-casting and the development of the active SSZ-13 zeolite phase through different synthesis methods, with emphasis on the microwave-assisted route. The study of the ceramic supports showed that the type of dispersant (citric acid and EFKA FA 4663) used in the freeze-casting process affected the microstructural and mechanical properties. Ceramic monoliths prepared with citric acid as dispersant and tert-butyl alcohol as solvent exhibited porosity of up to 60.4%, good pore connectivity and compressive strength of up to 7.9 MPa, characteristics suitable for their use as membrane substrates. In the synthesis of SSZ-13 zeolite, the choice of counter-ion revealed that potassium (K⁺) favored the formation of highly crystalline (97.9%) and homogeneous cubic crystals. In addition, the application of microwave radiation combined with the addition of SSZ-13 seeds allowed a drastic reduction in synthesis time (from 4 days to 60 minutes) and crystal size (from $5.67 \pm 0.07 \mu\text{m}$ to $0.645 \pm 0.016 \mu\text{m}$). The SSZ-13 zeolite produced via microwave-assisted synthesis in 60 minutes also exhibited high crystallinity (97%) and large specific surface area ($694.9 \text{ m}^2 \cdot \text{g}^{-1}$), demonstrating its potential as an active phase in membranes. The inorganic membranes produced by dip-coating, using seeds obtained via microwave-assisted synthesis and hydrothermal synthesis, exhibited thin and homogeneous zeolitic layers, with thicknesses between 1.86 and 6.43 μm , and a high degree of coverage over the α -Al₂O₃ supports. Theoretical adsorption studies (IAST) demonstrated high selectivity for CO₂ in CO₂/CH₄ and CO₂/N₂ mixtures, reinforcing the potential of SSZ-13 as an active phase in gas separation processes. Thus, the results obtained confirm the successful production of SSZ-13/ α -Al₂O₃ membranes with optimized structural and adsorptive properties for their active phase, establishing important parameters for future studies aimed at optimizing the performance and application of zeolitic membranes in gas mixture separation processes representative of natural gas.

Keywords: SSZ-13 zeolite, microwave-assisted synthesis, ceramic monoliths, freeze-casting, inorganic membranes.

1. Introduction and Objectives

1.1. Introduction

The increasing exploration and utilization of natural gas (NG) play a fundamental role in global energy needs [1]. According to projections from the *Annual Energy Outlook* and the *United States Department of Energy*, global demand for NG is expected to increase at an annual rate of 2.3% over the coming years [2, 3]. Although it is a non-renewable energy source, NG has relatively lower carbon emissions compared to fossil fuels such as coal [1, 4–6]. Therefore, it is considered a cleaner energy alternative, playing an essential role as a bridge in the global energy transition to renewable sources [1, 6]. In terms of energy efficiency, raw NG presents some limitations due to its composition. Composed mainly of hydrocarbons such as methane (CH_4) and ethane (C_2H_6), it also contains diluent gases such as carbon dioxide (CO_2) and nitrogen gas (N_2), which, when present in excess, reduce the internal energy of the fuel, impacting its calorific value and contributing to the formation of pollutant compounds in the atmosphere [3–5, 7, 8]. According to Brazilian specifications from the National Agency of Petroleum, Natural Gas and Biofuels (ANP), a maximum range of 6 to 18 mol% of inert diluent gases is allowed in the composition of produced and imported NG, in order to preserve the fuel's calorific capacity [9, 10].

In this context, the use of membranes for gas mixture separation has been gaining prominence in the energy sector, as the separation of diluent gases from the NG mixture improves the fuel's calorific value, optimizing its use and minimizing costs related to storage and transportation [5–7, 11]. These membranes, when they are composed of ceramic/inorganic materials, present advantages such as low production cost, the ability to separate chemical species without phase change through simple processes, long service life and low environmental impact when compared to classical NG processing methods, such as amine-based absorption and cryogenic distillation [4, 5, 12–14].

To improve gas separation processes, the use of inorganic membranes is proposed, which, in a simplified manner, involves the deposition of porous species, such as zeolites, into a ceramic support (alumina, α -Al₂O₃) [5, 15–17]. Due to their intrinsic characteristics, zeolites confer membranes properties such as high surface area, competitive adsorption capacity and molecular sieving ability, providing differences in the diffusivity of components within their structures [5, 18, 19]. These characteristics enable the separation of gas mixtures where the kinetic diameter of the components is close to the pore size of the material composing the membrane, being especially interesting for gas purification applications present in NG, such as CO₂ (3.3 Å), N₂ (3.6 Å) and CH₄ (3.8 Å). The microporous SSZ-13 zeolite, with its pore size in the range of 3.8 Å, stands out as a promising choice for these applications [19–23].

The use of inorganic membranes has become increasingly relevant in recent years due to the limitations of polymeric membranes previously employed in this context. The investigation of inorganic materials for this application has the potential to promote changes in NG purification processes, reducing costs and allowing for lower emissions of pollutant gases [4, 5, 11, 14]. Thus, the present work aims to contribute to the study of the production and characterization of inorganic membranes of the SSZ-13/ α -Al₂O₃ type for future application in the separation of the main gases that compose the NG mixture. The choice of this material is based on its promising results observed in similar applications [19–23], which suggests its potential to improve the NG purification process. In this context, the production of ceramic supports via the freeze-casting process, together with the incorporation of SSZ-13 zeolite (synthesized through different synthetic routes) as the active phase of the membranes, is proposed as an innovative strategy in this field, expanding the range of processing routes explored for SSZ-13-based inorganic membranes.

1.2. Objectives

The general objective of this work is to synthesize and characterize inorganic SSZ-13/ α -Al₂O₃ membranes for assessment of membrane properties, such as zeolite layer thickness and deposition homogeneity, obtained with shorter synthesis time. In addition, these properties will be evaluated considering the potential of these membranes for gas separation applications.

The specific objectives of this work are:

- To produce and characterize the ceramic supports (monoliths and tubes) through the freeze-casting process, exploring variations in parameters such as the type of dispersant used and the freezing temperature of the materials.
- To synthesize and characterize SSZ-13 zeolite crystals through the hydrothermal process, controlling aspects such as the molar ratio of reagents, the type of structure-directing counter-ion used and synthesis time.
- To synthesize and characterize SSZ-13 zeolite crystals through the microwave-assisted synthesis process, controlling aspects related to the material's crystallization kinetics, such as synthesis time and particle size.
- To produce and characterize inorganic membranes of SSZ-13/ α -Al₂O₃, primarily controlling the thickness of the zeolite active layer, while varying parameters such as synthesis time and the type of SSZ-13 seed used.
- To correlate the adsorption parameters with the structure of SSZ-13 and compare them with inorganic SSZ-13/ α -Al₂O₃ membranes reported in the literature, in order to discuss the potential of the obtained membranes for membrane-based gas separation.

2. Theoretical Framework

This chapter presents, in a concise manner, the theoretical framework that supports the development of this thesis, addressing the importance of membrane-based processes in the treatment and purification of natural gas (NG). Initially, general aspects of NG are discussed, including demand, composition and classical treatment methods. Subsequently, fundamental concepts related to membranes are presented, including separation mechanisms and their application in NG processing. The freeze-casting technique for ceramic support production is then introduced as part of the approach explored in this thesis, followed by a discussion on the synthesis, structure and applicability of the SSZ-13 zeolite as the active phase. Finally, aspects related to the adsorption capacity of the SSZ-13 zeolite and the applicability of SSZ-13/ α -Al₂O₃ membranes in gas separation processes reported in the literature are described.

2.1. Natural gas

2.1.1. Global Demand and Production

Energy security is one of the most debated issues today, as it involves ensuring the continuous supply of energy to everyone. Alongside this concern, there is the pursuit of renewable energy sources or those with lower environmental impacts on the planet [1, 6]. In this context, natural gas (NG) is a non-renewable energy source that has shown a significant increase in its global production since it began to be exploited in the 1970s, being considered a versatile and efficient fuel [5]. In the last decade, NG registered a growth of 19.7% between 2014 and 2024. This expansion resulted in total production of 4.12 trillion cubic meters and a global total energy demand of 149 EJ (Exajoules) in the year 2024 [24], as shown in Figure 1.

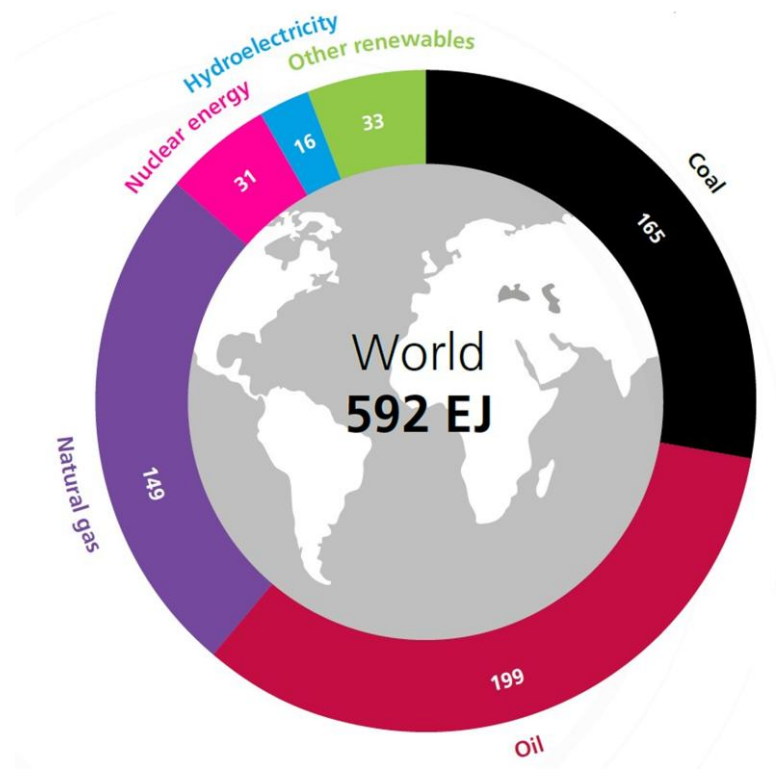


Figure 1. Global total energy production, in EJ (1 EJ = 10^{18} Joules), divided by kind of resource for the year 2024. Adapted from the reference [24].

Besides the distribution of numerous NG reserves worldwide, which allows it to be a global energy source used in homes, factories and as raw material in the chemical industry for hydrogen production [5, 25], its growing adoption is correlated with initiatives to reduce environmental impacts from carbon emissions and greenhouse gases, enabling a gradual transition to less harmful or renewable energy sources [1, 5, 6, 26]. Due to its composition predominantly of hydrocarbons, such as methane (CH_4) [7], the NG emits less carbon compared to widely used non-renewable energy sources like coal [1, 6, 26].

Among the world's leading economic powers, the United States of America (USA) has adopted policies to facilitate the energy transition in the primary sector. In 2016, NG surpassed coal for the first time as the main fuel used for electricity generation [2]. According to data from the *2025 Statistical Review of World Energy*, the four largest producers of GN were the USA, Russia, Iran and China who, together, accounted for 53% of total global production. Also, the liquefied natural gas (LNG) trade remained relatively flat in 2024, with the USA retaining its position as the largest exporter followed closely by Qatar and Australia. Collectively, they accounted for 60% of total global LNG exports, representing a total of 328.9 billion cubic

meters [24]. According to projections from the *Annual Energy Outlook 2019* and the *USA Department of Energy*, global demand for NG is expected to grow at an annual rate of 2.3%, with LNG exports maintaining an upward trajectory and accounting for more than 55% of total USA exports by 2030 [2, 3].

2.1.2. Composition

In order to satisfy the growing global demand for NG consumption, it is necessary to improve production and purification strategies for this fuel, since the quality of the gas is directly related to its composition [3, 27].

NG is primarily formed during the decomposition of organic matter, either through thermal decomposition or the action of methanogenic bacteria, and it appears as a mixture of hydrocarbons, mostly composed of methane (CH_4), ethane (C_2H_6) and propane (C_3H_8) [4, 5]. Besides the presence of hydrocarbons, it also consists of diluent gases such as nitrogen (N_2) and carbon dioxide (CO_2), as well as gases considered contaminants, such as hydrogen sulfide (H_2S) [3–5, 7]. Although its composition varies according to the extraction source of this fuel [4], Table 1 presents an ideal composition of NG [5].

Table 1. Ideal characteristic composition of NG. Data adapted from the reference [5].

Components	Formula	(% v/v)
Methane	CH_4	> 85
Ethane	C_2H_6	3 – 8
Propane	C_3H_8	1 – 5
n-Butane	C_4H_{10}	1 – 2
iso-Butane	C_4H_{10}	< 0.3
n-Pentane	C_5H_{12}	1 – 5
iso-Pentane	C_5H_{12}	< 0.4
Hexane, heptane, octane	$\text{C}_n\text{H}_{2n+2}$	< 2
Carbon dioxide	CO_2	1 – 2
Hydrogen sulfide	H_2S	1 – 2
Oxygen	O_2	< 0.1
Nitrogen	N_2	1 – 5
Helium	He	< 0.5

According to the data presented in Table 1, diluent gases such as oxygen (O_2), nitrogen (N_2), helium (He) and carbon dioxide (CO_2) represent about 8% of the ideal composition of NG and, being non-combustible gases, they could affect the quality of the fuel [4, 5, 27].

These diluent gases are produced by different mechanisms, such as in the degradation processes of organic matter by anaerobic bacteria during sedimentation or by thermal decomposition of carbonates (CO_3^{2-}) at temperatures above 200 °C, as is the case with CO_2 . [4, 5, 25]. The production of N_2 in NG can occur through the bacterial reduction of nitrates (NO_3^-) dissolved in water, present in soils and sediments, as well as through the thermal degradation of organic matter [4, 5]. The constituents that typically represent trace concentrations in NG can be produced by the release of gases from the mantle (the layer between the Earth's crust and outer core) or by the disintegration of radioactive minerals present in the Earth's crust, as is the case with helium (He) [4]. The O_2 commonly found in the composition of NG originates from the gas transportation process, which uses pipelines for gas collection operating at atmospheric pressure [4, 5]. The presence of constituents such as CO_2 , O_2 and water (produced in oil and gas reservoirs) is harmful to the lifespan of pipelines used for NG collection and contributes to their corrosion, damaging gas processing systems [4, 5].

The main constituent considered a contaminant is hydrogen sulfide (H_2S) [4, 5]. This contaminant can be produced by the action of bacteria reducing sulfate ions (SO_4^{2-}) to sulfide ions (S^{2-}) dissolved in water, as well as by the thermal degradation of sulfur-rich substances [4]. Mercury compounds, such as dimethylmercury ($((CH_3)_2Hg)$), mercuric chloride ($HgCl_2$) and arsenic compounds like arsine (H_3As), can also be present in NG composition, typically at parts-per-billion (ppb) concentration levels, exhibiting high toxicity to living beings and the environment [4, 5, 8].

The raw NG extracted from different sources such as oil fields, NG fields and coal deposits has a complex composition due to the presence of diluent gases and contaminants that compromise the energy efficiency of the fuel, as they do not have calorific value during the combustion reaction [4, 5, 27]. Thus, to become a fuel with adequate energy efficiency for different purposes (higher heating value between 34000 and 43000 $kJ \cdot m^{-3}$), raw NG must undergo several processing stages until obtaining the commercial fuel, according to the Brazilian production and import

specifications of resolution number 16 of 2008 from the *National Agency of Petroleum, Natural Gas and Biofuels* (ANP), as indicated in Table 2 [9, 10].

Table 2. NG specifications according to ANP Resolution N°. 16 of 2008. Adapted from the reference [9].

Characteristics	Unit	Regions of the country:		
		North	Northeast	Central-West, Southeast and South
Methane, min.	% mol.	68,0	85,0	85,0
Ethane, máx.	% mol.	12,0	12,0	12,0
Propane, máx.	% mol.	3,0	6,0	6,0
Butanes and heavier, máx.	% mol.	1,5	3,0	3,0
Oxygen, máx.	% mol.	0,8	0,5	0,5
Inerts (N ₂ + CO ₂), máx.	% mol.	18,0	8,0	6,0
Carbon dioxide, máx.	% mol.	3,0	3,0	3,0
Total Sulfur, máx.	mg·m ⁻³	70	70	70
Hydrogen Sulfide (H ₂ S), máx.	mg·m ⁻³	10	13	10

2.1.3. Classical treatment methods

The processing of raw NG aims to purify this fuel in order to comply with the gas quality specifications for pipelines, as well as to allow the combustion of this fuel to be more environmentally clean [4, 8]. During this processing, constituents that impair the use of the gas as fuel, such as N₂ and CO₂, are removed, as well as the separation of valuable components that can be used as raw materials in the petrochemical industry, such as fuels (C₃H₈) or industrial products (C₂H₆ and He), in addition to the liquefaction of the gas (LNG) for transportation or storage purposes [4, 8, 13]. Figure 2 shows a typical processing plant used for the purification of raw NG [5, 13].

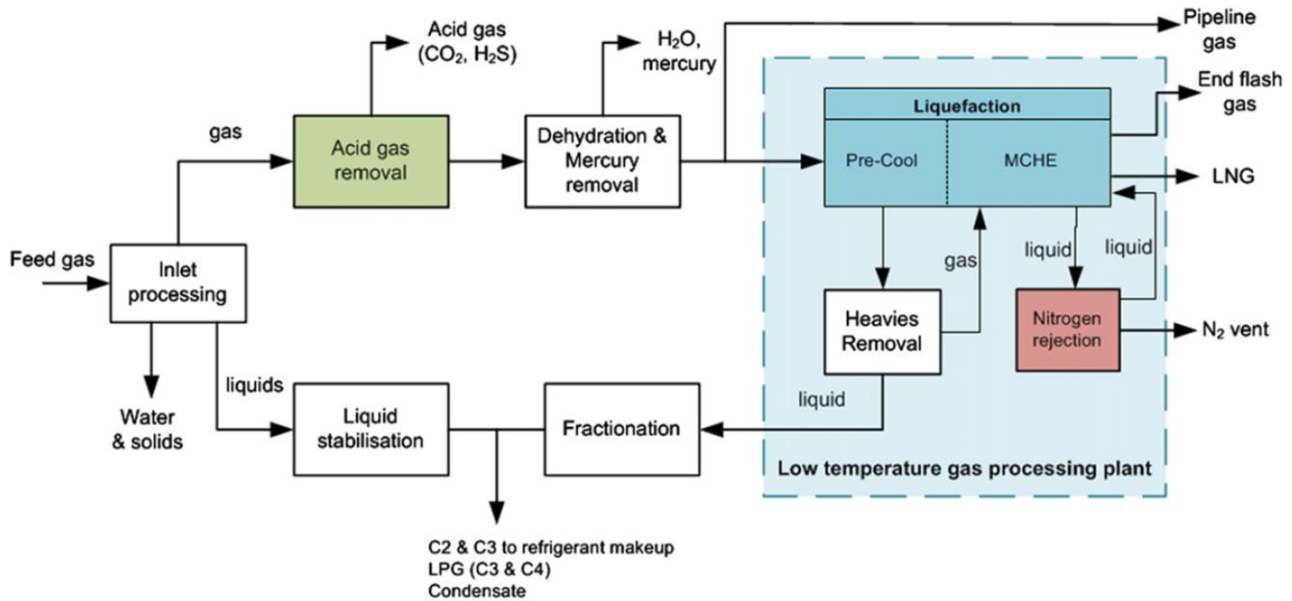


Figure 2. Conventional gas processing operations in a typical NG plant with a cryogenic process for LNG production. Adapted from the reference [13].

Factors such as the type of market in which the fuel will be used, the properties of the raw NG and the specifications of the fuel to be commercialized, along with the flow in which this fuel will be used in the pipelines, will determine the processing steps (Figure 2) required for NG purification [13].

In natural gas fields, it is common for CO₂ concentrations to reach up to 20 vol.% of the raw NG composition [4, 13]. This high concentration of CO₂ makes the commercialization of the gas impractical, as it compromises its calorific value [2, 4, 5, 13, 25, 28]. Therefore, the removal of CO₂ is a common requirement in NG processing facilities. As a result, the standard regulations for gas commercialization establish a maximum limit of 2 vol.% of CO₂ (Table 1) [28].

In conventional NG processing, the removal of CO₂ is generally linked to the elimination of acid components, including H₂S in this category. This removal is carried out through absorption processes based on amines or carbonates [4, 5, 13, 25]. The amine-based absorption process is widely employed in the oil and NG industries and involves the absorption of acid gases into aqueous amine solutions, commonly diethanolamine, at temperatures between 40 and 60 °C and pressures ranging from 20 to 70 atm. After the acid gas components are absorbed, the treated NG exits the absorption unit and proceeds to the next stage of processing (Figure 2) [13, 25]. The amine solution, now rich in absorbed acid gases, is subsequently treated at temperatures between 100 and 140 °C and near-atmospheric pressures (1 to 2 atm).

This step, known as thermal regeneration or stripping, enables the removal of the acid gases from the solvent and allows the amine solution to be reused in the absorption cycle [13, 25]. Although it is a widely accepted technology for CO₂ removal, it has high costs and requires considerable energy consumption [4, 5, 13, 14, 29].

The NG resulting from the absorption process is usually saturated with water, thus requiring dehydration steps before the liquefaction stage. The gas then enters the precooling section of the liquefaction plant, where it is typically compressed to a pressure above 3400 kPa [13]. In this stage, heavier hydrocarbons (longer carbon chains) and aromatics, such as benzene, are removed [4, 5, 13]. Due to the gas liquefaction process, carried out through cryogenic treatment (-161 °C), it is essential to eliminate water, CO₂ and heavy hydrocarbons that can freeze and cause blockages and damage to the equipment [13].

Regarding the presence of N₂ in raw NG, its concentration varies according to its extraction source [4, 5, 13]. Studies conducted in China indicated N₂ concentrations below 5 vol.% in coal-based reservoirs, while concentrations above 20 vol.% were observed in gases extracted from oil fields [5, 30]. In the USA, approximately 14% of raw NG contains N₂ concentrations above 4 vol.% [5, 14], exceeding the maximum indicated value in the ideal concentrations of this gas in NG composition (Table 1) [4, 5]. Similarly to CO₂, N₂ also negatively affects the heating values of NG, as it alters the heat transfer processes during its combustion [5, 7, 31].

The conventional nitrogen removal process occurs through cryogenic distillation and is generally integrated with the gas liquefaction process in NG processing plants (Figure 2) [4, 5, 13]. Typically, this method involves a propane refrigeration circuit that precools the gas before it enters the main distillation column [7, 13]. This distillation column can use a mixture of refrigerants or a cascade of multiple pure refrigerant cycles [13]. The efficiency of this process is based on the boiling point difference between N₂ (-195 °C) and CH₄ (-161 °C). As the mixture cools, CH₄ condenses first, allowing the two gases to be separated [7]. The main disadvantages of this method are the operational costs and the high energy consumption [4, 5, 7, 13]. When the nitrogen removal process is integrated into the NG liquefaction process, it takes place in the step prior to the depressurization of the gas for LNG production (Figure 2) [13].

The industrial stages of NG processing plants for commercial fuel production, although somewhat efficient, face considerable challenges in terms of operational costs and energy consumption [4, 5, 7, 13]. In search of alternatives that provide efficient separations and minimize the issues associated with industrial NG processing, the use of membranes for gas separations has shown promising results in recent decades [5].

2.2. Membranes

Membranes are materials that selectively restrict the movement of different species (molecules and ionic species in liquid or vapor phases), functioning as a thin layer that separates two phases [11]. They can be produced from different classes of materials and are mainly divided into two broad groups: organic membranes, which include polymeric membranes, and inorganic membranes, such as ceramic, glass, zeolite-based, carbon-based and metallic membranes [32].

Membrane-based separation is applicable in various contexts, such as wastewater treatment, desalination and gas separation [11, 32, 33]. Due to these numerous applications, membranes have gained prominence over the past decade, especially in the gas separation sector [11], where they have shown promising results in terms of energy efficiency and large-scale applicability [33]. These materials can exhibit high mass transfer rates, selectivity and permeance, essential characteristics for competing with classical separation processes such as distillation and absorption [11]. In addition to being easy to operate, install and scale up, membranes can operate under mild conditions, resulting in lower energy consumption [5, 11]. They operate continuously, allowing for partial or total recycling of the retained or permeated material. Also, membrane separation can be integrated with other separation processes, making the overall process more efficient in achieving the desired purity levels at a reasonable cost [11, 32, 33].

2.2.1. Separation Mechanisms

In general terms, the separation of a gas mixture occurs through the selective transport of components across a membrane, which can be either dense or porous [11, 32]. The process is driven by the partial pressure gradient, requiring pressure in

the gas feed flow to ensure effective separation [32]. Figure 3 shows some of the mechanisms by which mass transport occurs through a gas separation membrane [34].

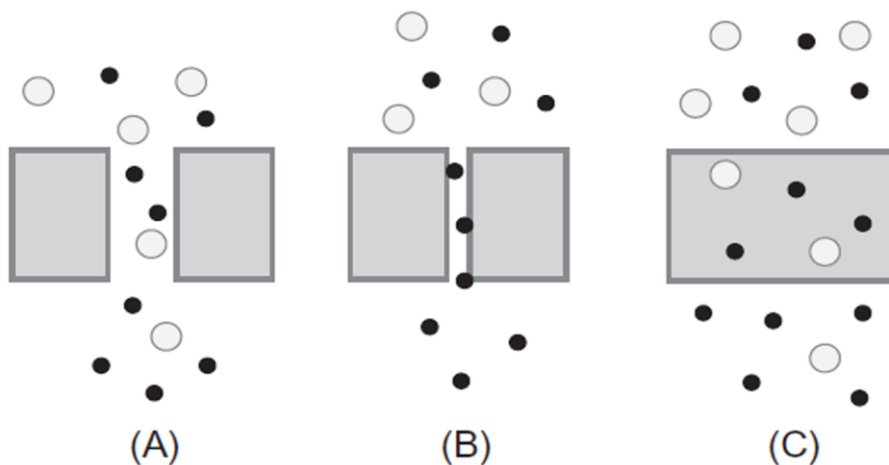


Figure 3. Mass transport mechanisms in gas separation membranes: (A) Selective diffusion through pores; (B) Restricted diffusion through pores; (C) solution-diffusion model through a dense membrane. Adapted from the reference [34].

For porous membranes, the mass transfer model is based on flow through the pores (Figures 3a,b), in which a concentration or partial pressure difference drives the selective diffusion of species through the membrane pores (Figure 3a) [32, 34]. If the membrane pores are small enough to be comparable in size to some of the species in the gas mixture, separation will be optimized due to restricted diffusion, resulting in size exclusion or sieving of larger molecules, as indicated in Figure 3b [34]. In the case of dense (polymeric) membranes, gas permeation is governed by the solution-diffusion (or sorption-diffusion) mass transport model, which consists of the sorption of components from the gas mixture, their diffusion through the membrane and subsequent desorption of these target components into the gas phase (Figure 3c) [34].

Just as both kinetic and thermodynamic aspects govern the separation mechanisms in polymeric membranes, porous membranes also exhibit thermodynamic factors, alongside the kinetic ones described above, that influence the separation of gas mixture components [5]. Therefore, thermodynamic selectivity is based on the strength of interaction (heat of adsorption) between the different components of the mixture and the adsorbent under equilibrium conditions, with

selectivity being mainly determined by the chemical composition of the adsorbent surface [35, 36].

Thermodynamic selectivity is thus established because the separation process occurs through the preferential adsorption of one of the gas mixture components (the one with higher affinity) onto the solid adsorbent (Figure 4). This higher affinity can be attributed to electrostatic interactions related to the polarity and polarizability of the gas molecules (adsorbate). Furthermore, properties such as the type and strength of active sites in the adsorbent contribute to the selective adsorption of the gases to be separated [5, 35–38].

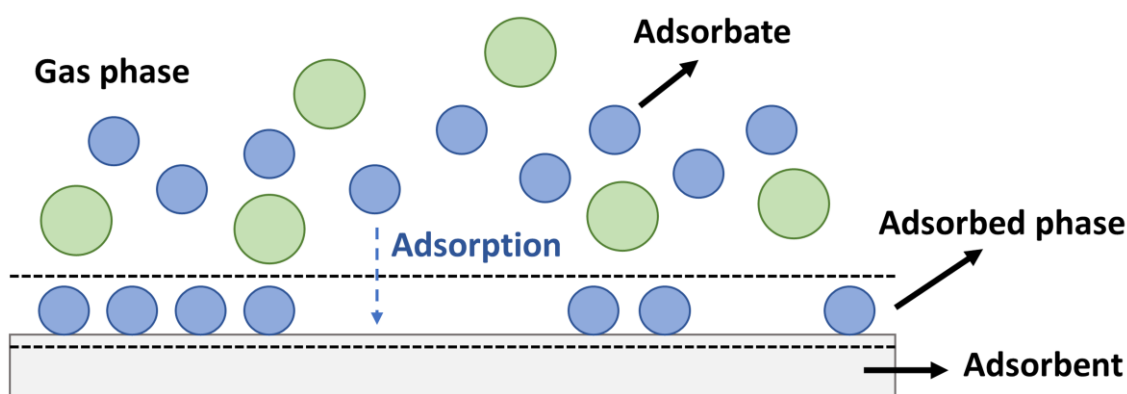


Figure 4. Illustrative diagram of the adsorption process of a gas molecule (adsorbate) on the porous surface of a material (adsorbent).

2.2.2. Permeance, selectivity and adsorption capacity

Through the separation mechanisms provided by porous or dense membranes, it is possible to evaluate their efficiency using two important experimental parameters: permeance and selectivity with respect to a pure gas or a gas mixture [5, 32, 34].

The permeation of a gas through a membrane is related to the path it follows under a pressure gradient [5, 19, 34]. In porous membranes, this process is described by the pore flow model, in which the transport of permeants (adsorbates) occurs due to the pressure difference. The membrane pores act as filters, allowing the selective passage of certain gases and enabling their separation [5, 19]. Therefore, the permeance ($P_{m,i}$) can be mathematically defined as (Equation 1) [19]:

$$P_{m,i} = \frac{Q}{A_m \cdot t \cdot \Delta p_i}$$

(Equation 1)

In which Q is the number of moles of a component i that permeates through a membrane over a time period t (s). A_m is the membrane area and Δp_i is the partial pressure difference of the gas component i at the beginning of the process and after permeating through the membrane ($\Delta p_i = p_{i,f} - p_{i,p}$) [19].

However, when operating in cross-flow mode, the gas feed flows tangentially to the membrane surface, allowing part of the gas to permeate through it while the remainder continues along the surface. This flow reduces the accumulation of rejected components and improves separation efficiency [5, 39]. In this case, permeance should be considered ($p_{m,i}$) as a function of the flux of component i and the pressure difference ($\Delta p_{ln,i}$) caused by this flow, as indicated by Equations 2 and 3 [39]:

$$p_{m,i} = \frac{F_i}{\Delta p_{ln,i}}$$

(Equation 2)

$$\Delta p_{ln,i} = \frac{(p_{f,i} - p_{r,i})}{\ln \left[\frac{p_{f,i} - p_{p,i}}{p_{r,i} - p_{p,i}} \right]}$$

(Equation 3)

In which F_i ($\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) is the gas flux of component i through the membrane; $\Delta p_{ln,i}$ is the logarithmic partial pressure difference for component i . $p_{f,i}$, $p_{r,i}$ e $p_{p,i}$ are the partial pressures of component i in the feed, retentate and permeate gas streams, respectively [39].

Thus, to evaluate the efficiency of different membranes and considering that permeance depends on membrane thickness, permeability ($p_{b,i}$) can be determined by [5, 19, 39]:

$$p_{b,i} = p_{m,i} \cdot \delta$$

(Equation 4)

Where $p_{m,i}$ is the permeance of component i through the membrane and δ is the membrane thickness [5, 39].

In the case of the selectivity parameter, it refers to the membrane's ability to separate different gases based on their physicochemical properties, such as molecular size and solubility [5, 19]. Mathematically, the ideal selectivity ($\alpha_{i/j}^\circ$) can be defined as the ratio between the permeances ($p_{m,i}^\circ$ e $p_{m,j}^\circ$) of two distinct gas components, i and j , measured independently in a single gas system [19]:

$$\alpha_{i/j}^\circ = \frac{p_{m,i}^\circ}{p_{m,j}^\circ}$$

(Equation 5)

And the separation selectivity of the gas mixture can be obtained through the separation factor parameter ($\alpha_{i/j}$), which relates the mole fractions of the gases [5, 19]:

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

(Equation 6)

Where x and y are the mole fractions of the feed gas and the permeate gas, respectively [19].

Regarding adsorption processes, the adsorptive capacity (q_{max}) of a material can be determined using the *Langmuir model*. This model provides a simplified description of the interactions between the adsorbate and the surface of the adsorbent [36].

According to the model, adsorption occurs in a monolayer on well-defined active sites, all of which possess equivalent energy, implying a homogeneous surface of the adsorbent [35, 36]. The adsorbed molecules do not interact with each other and exhibit an equal rate of adsorption and desorption at equilibrium, characterizing a dynamic equilibrium [36].

Based on these assumptions, the maximum adsorption capacity (q_{max}) represents the concentration of adsorbed species on the surface when all available sites have been occupied. Therefore, the *Langmuir isotherm* relates the amount of solute adsorbed to the equilibrium concentration or pressure [36]. Mathematically, the *Langmuir model* is expressed as (Equation 7) [36, 40]:

$$q = \frac{q_{max} * b * P}{1 + bP}$$

(Equation 7)

Where q is the amount adsorbed at equilibrium, q_{max} is the maximum adsorption capacity corresponding to the formation of a monolayer of molecules on the material surface, b is the *Langmuir constant*, related to the adsorption energy and the affinity between the adsorbate and the adsorbent, P is the equilibrium pressure of the gas.

2.2.3. Membranes in NG Processing

The first membrane systems for NG processing were initially introduced in the industry in the 1980s and were primarily focused on the use of polymeric membranes [5]. The use of this type of membrane is related to its simplicity of processing, manufacturing and availability [12]. Among the most commonly used are cellulose acetate and polyimide membranes designed for CO₂ and CH₄ separation, and perfluoropolymers aimed at N₂ and CH₄ separations [5, 12, 14].

Despite the frequent use of polymeric membranes in the gas processing industry, some challenges associated with their use are reported in the literature. Among these is the search for membranes with high selectivity without compromising gas permeability, as observed in the phenomenon of CO₂-induced plasticization in CO₂/CH₄ mixtures [5, 14]. In this case, the high concentration of CO₂ compromises selectivity by reducing the interaction between adjacent segments in the polymer chain, altering the gas permeability throughout the membrane [5, 14, 25]. Other problems include low stability at high temperatures (above 200 °C) and premature aging of the membrane [5, 12, 25, 32]. Therefore, the application of

polymeric membranes is often limited to temperature conditions below 200 °C in separations of chemically inert mixtures with low feed gas flow rates [14, 32].

In this context, over the past two decades, there has been a significant increase in the adoption of inorganic materials for NG processing [5, 14]. This is due to the production of more stable membranes with higher selectivity and permeability compared to polymeric membranes. Inorganic membranes can withstand high pressures, reaching values up to 10 MPa, which allows the feed gas flow to be processed [25]. Additionally, they can be used for the separation of chemically active mixtures and offer the possibility of recycling, as they can be regenerated through cleaning with high temperatures and superheated steam [5, 14, 25, 29].

2.3. Inorganic Membranes

Similar to polymeric membranes, the mass transport properties related to permeation efficiency and separation in inorganic membranes are associated with the microstructure and architectural characteristics of the membranes [15]. In this context, inorganic membranes can be divided into dense (non-porous) and porous membranes [15, 32, 34].

Dense inorganic membranes are characterized by materials composed of solid metal layers, such as membranes made from palladium (Pd) alloys for hydrogen (H₂) separation or membranes made from mixed-conducting oxides for oxygen (O₂) separation [15, 17, 34]. In the case of porous inorganic membranes, they are typically composed of a porous wall or porous top layers, such as metal, oxide or glass, on a porous support made of oxides or metal oxides [15, 32, 34].

As mass transport in separations is directly linked to the porosity of the material, it is crucial to clarify the classifications based on pore diameter (d_p) and the accessibility of these pores to an external flow [17, 41]. According to the International Union of Pure and Applied Chemistry (IUPAC), porous materials can be classified based on the pore size distribution criteria, presented in Table 3 [17, 41, 42].

Table 3. Classification according to the pore diameter (d_p) of porous materials [17, 41, 42].

Pore diameter (d_p):	Classification:
$d_p < 2 \text{ nm}$	Micropores
$2 \text{ nm} < d_p < 50 \text{ nm}$	Mesopores
$d_p > 50 \text{ nm}$	Macropores

Another classification of porous materials is related to the cavities, channels or interstices they contain, which influence their accessibility to external flow [41, 42]. Figure 5 shows several regions that can be classified according to different pore types [41]. Region (a) represents pores that are completely isolated from their neighbors, known as closed pores. This type of pore affects the macroscopic properties of the material, such as density, thermal conductivity and mechanical strength. Regions (b) to (f) represent pores that have a continuous channel of communication with the external surface of the material, referred to as open pores. These pores influence adsorption and mass transport properties. The roughness of porous materials shown in region (g), is classified as a pore only when the surface irregularities exceed their length [41].

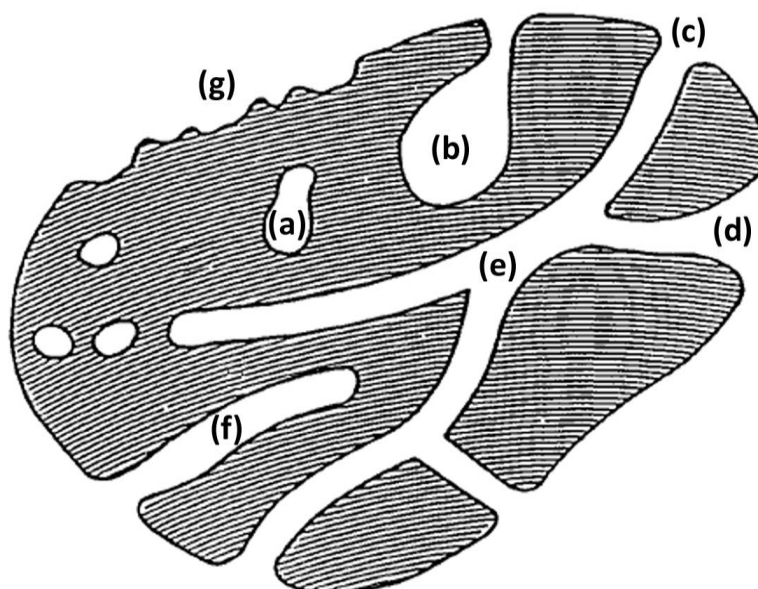


Figure 5. Cross-sectional diagram of a porous material. Adapted from the reference [41].

Regarding the arrangement of the layers that make up a porous inorganic membrane, they can adopt symmetrical configurations, consisting of a single uniformly structured wall that requires a considerable thickness to ensure the

material's mechanical strength [15, 16]. Alternatively, the layers can also be asymmetrical (Figure 6), with a support system featuring a wider pore size distribution and low resistance to the feed gas flow. On this support, layers with gradually decreasing pore sizes are deposited, allowing for efficient separation in large gas flows [15, 17, 34]. The architecture of these systems may vary, including tubular layers, multilayers on porous supports, plates, disks or monoliths [15, 16].

4. Modification of layer (3) to a microporous separation layer

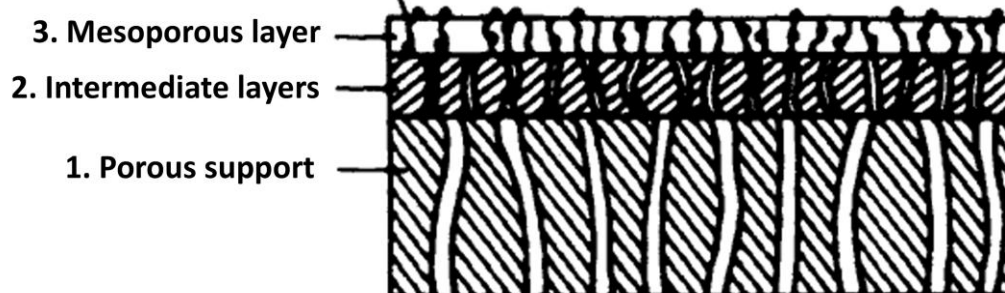


Figure 6. Representative schematic of an asymmetric inorganic (ceramic) membrane: 1. Porous support (pore diameter: 1-15 μm); 2. Intermediate layers (pore diameter: 100-1500 nm); 3. Mesoporous layer (pore diameter: 3-100 nm); 4. Modification of layer (3) to a microporous separation layer (pore diameter: 0.5-2 nm). Adapted from the reference [15].

In this regard, inorganic membranes can be prepared in numerous ways, depending on the porous structure and the type of separation desired [16]. One of the most common methodologies for producing membranes for gas separation is coating deposition [15, 16]. This process involves the formation of a porous support, followed by the preparation of a particle dispersion in a liquid medium (active phase), and subsequent deposition of these particles onto the porous support to form the membrane [16].

2.3.1. Ceramic support

The quality of the produced ceramic support has a direct impact on the overall quality of the membrane. Thus, pores larger than the d_p and irregularities in the support can result in defects (“holes”) in the layers applied over it [15]. Therefore, the choice of support material and the process by which this material is produced

must contribute to the formation of supports with homogeneous surfaces, a relatively uniform d_p distribution and high mechanical strength [15, 16].

2.3.1.1. Alumina (α - Al_2O_3)

Among the classes of materials commonly used as support for gas separation membranes, ceramics stand out, which include metal oxides such as titanium dioxide (TiO_2) and aluminum oxide (Al_2O_3) [15, 17, 32].

Aluminum oxide, also known as alumina (Al_2O_3), is one of the most extensively studied materials as a support for gas separation membranes [20–22, 43–50]. It has a corundum-type crystal structure, being thermodynamically more stable in the alpha phase (α - Al_2O_3) [51]. In this phase, oxygen atoms are arranged in a hexagonal close-packed structure, with trivalent aluminum ions (Al^{3+}) occupying two-thirds of the octahedral sites in the material's structure (Figure 7) [51–53].

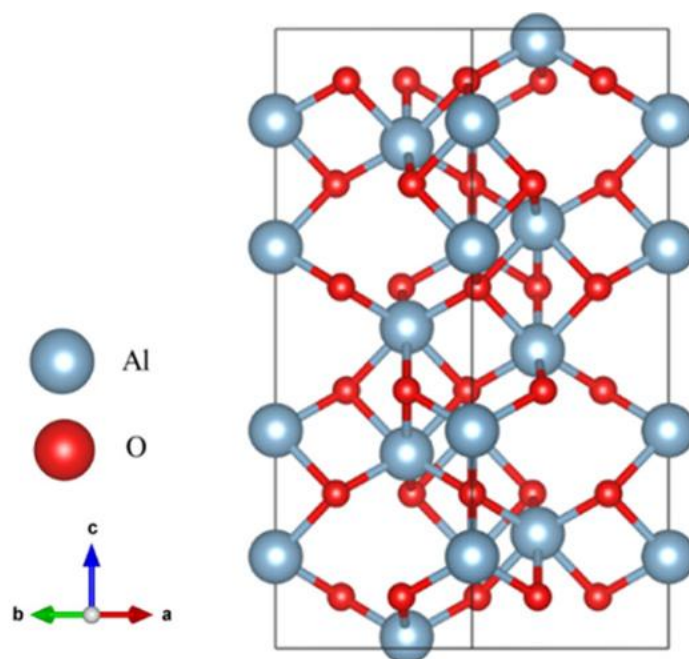


Figure 7. Hexagonal crystal structure of α - Al_2O_3 . Adapted from the reference [52].

This material exhibits numerous characteristics that make it suitable for use in gas separation membranes, such as adequate retention capacity, high permeability, low density, low thermal conductivity, as well as chemical stability and resistance to oxidation and mechanical wear [15, 53].

Changes in the microstructural properties, such as porosity, pore size and pore morphology of porous ceramics, are directly influenced by the processing method used in their production [53–55]. Among the techniques employed for the fabrication of macroporous ceramics, such as α -Al₂O₃, conventional methods like partial sintering, replication and foaming stand out. These processes generally result in a wide porosity range, varying from 40% to 95% and a pore size distribution between 10 μ m and 3 mm [54, 55]. Additionally, macroporous ceramic materials can be produced using the sacrificial materials method [55]. The freeze-casting process, included in this type of ceramic fabrication, has an advantage over other conventional techniques by allowing control over porosity, pore size distribution and pore morphology, factors that are highly important for producing porous supports used in membranes [54].

2.3.1.2. Freeze-casting

The freeze-casting process has become relevant to the scientific community over the past two decades, offering a simplified processing approach that enables the production of materials with complex porous structures, allowing control over porosity, morphology and pore size distribution [54, 56]. This is significant, especially considering that conventional processing routes often face the limitation of being inherently restricted to a narrow range of pore characteristics [57]. Moreover, it is a versatile process not limited to the fabrication of ceramic materials [54, 56, 57], such as aluminum and titanium oxides [58–61]. It can also be applied in the production of metals like porous nickel and titanium [62, 63], polymers such as polymethylsiloxane and chitosan [64, 65], biomaterials like hydroxyapatite [66] and inorganic materials such as silicon carbide [67].

The wide range of materials to which this technique can be applied is related to the fact that freeze-casting consists of a physical freezing process [68]. As outlined in Figure 8, the freeze-casting technique comprises four main steps [54, 56, 57, 69].

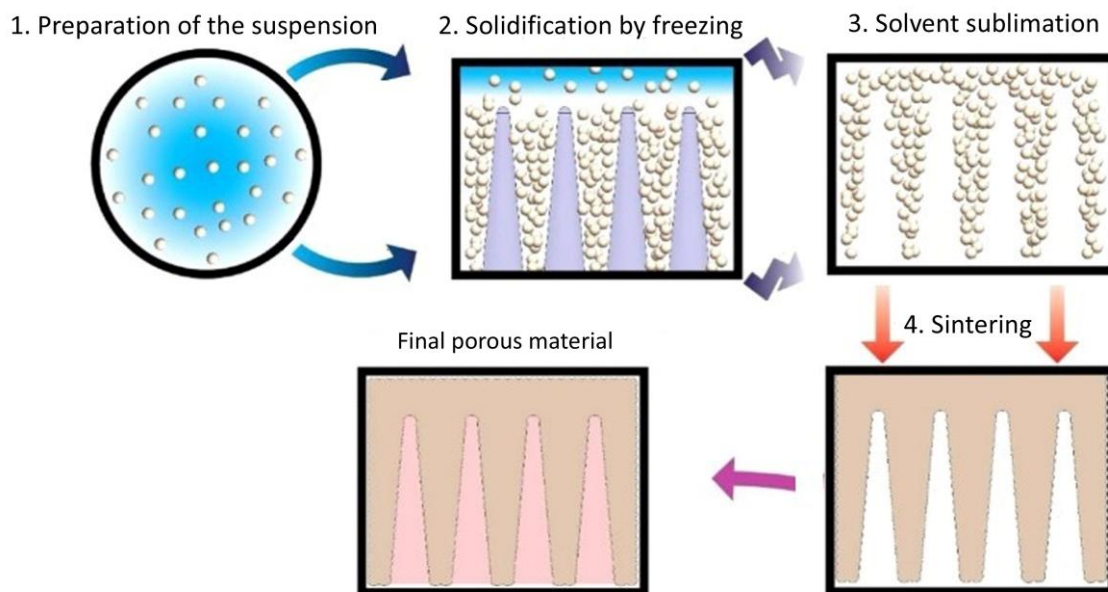


Figure 8. Steps of the freeze-casting process. Adapted from the reference [69].

In the first stage of the process, the suspension is formed by combining a solid load of particles in micrometric or submicrometric sizes with a solvent, which may be aqueous, organic or a mixture of both [56, 57, 68]. This suspension also includes dispersants such as ammonium polymethacrylate [70–73], EFKA FA 4663 (Texafor 963) [60, 61, 74, 75], sodium polyacrylate [76–78], citric acid [58, 59, 75], among others, which serve to reduce particle aggregation by modifying physical properties such as sedimentation and viscosity [57, 68]. In addition, binders such as polyvinyl alcohol (PVA) [71, 74, 75], polyethylene glycol (PEG) [79], among others, are added. Like dispersants, binders influence the viscosity and surface tension of the suspension and, in later stages, contribute to the initial strength of the green body (the formed material that structurally exhibits weak bonds) prior to sintering [57, 68].

The second stage of the freeze-casting process consists of the solidification by freezing of the suspension solvent, which can occur in a unidirectional, bidirectional or radial manner, depending on the type of material (polymeric or metallic) used for the mold [54, 56]. The controlled crystallization of this solvent is fundamental for the formation of the pore structure of the material [57, 68, 69]. Therefore, selecting an appropriate solvent plays a crucial role in achieving the desired porosity. For example, in ceramic materials, the use of water as a solvent result in the formation of lamellar pores, while the organic solvent camphene produces a dendritic pore structure and tert-butyl alcohol (TBA) generates prismatic structures, as illustrated in Figure 9 [57, 69]. Other parameters such as solid loading,

particle size, viscosity, surface tension of the suspension, type of dispersion and freezing temperature will also secondarily influence the pore morphology of the materials [57, 68, 69].

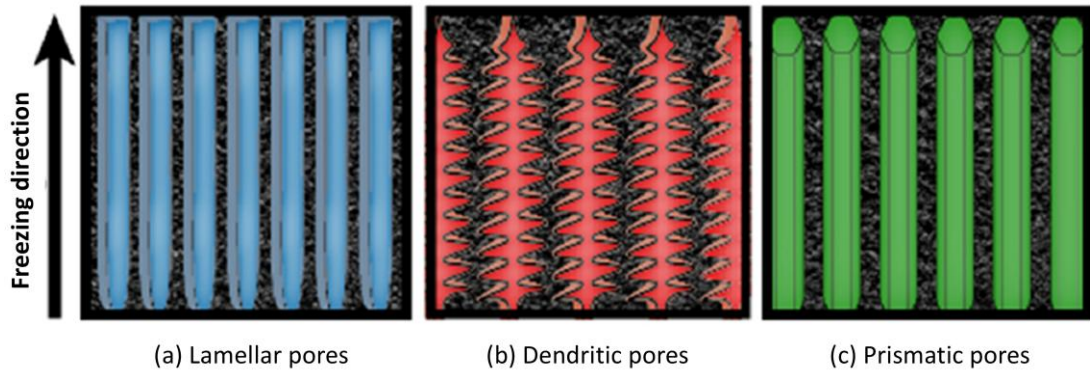


Figure 9. Representative schematic of different pore morphologies obtained through the unidirectional freeze-casting process. Adapted from the reference [69].

Considering the unidirectional (anisotropic) freezing process [64], Figure 10 illustrates the setup of a freeze-casting system. In this type of process, the suspension is poured into a polymeric mold in contact with a metallic surface (copper rod), which is cooled to a controlled temperature. Since the temperature of the metallic surface is below the freezing point of the suspension, a freezing front, defined as the interface between the solid and liquid phases, is established and begins to advance through the sample [57, 68].

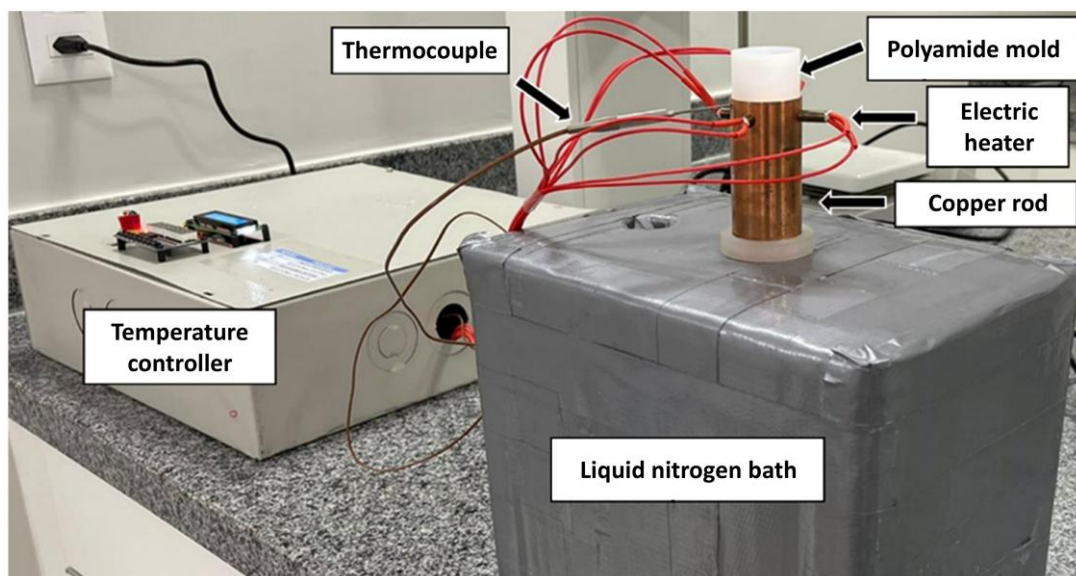


Figure 10. Freeze-casting system of the LMCNano Laboratory, Department of Mechanical Engineering, University of Brasília.

An important parameter related to crystal growth during the solidification process is the freezing front velocity, which determines whether a solid particle in the suspension will be pushed away or trapped by the advancing solid-liquid interface during the process [57, 68, 69]. Another factor to consider is the balance between two opposing forces acting on each particle. A repulsive force keeps the particle in the liquid phase due to the system's resistance to a change in surface energy and an attractive force, caused by viscous drag, pushes the particle toward the solid-liquid interface [57, 68].

Considering the thermodynamics of the process, a suspended particle can only be trapped in the solid portion if the system's free energy ($\Delta\sigma_0$) is negative. Therefore, this condition will be satisfied if the surface energy (σ_{ps}) between the newly formed particle and the solid portion is less than the sum of the surface energies between the particle and the liquid portion (σ_{pl}) and between the solid and liquid portions (σ_{sl}), as indicated in Equation 8 [68].

$$\Delta\sigma_0 = \sigma_{ps} - (\sigma_{pl} + \sigma_{sl}) < 0$$

(Equation 8)

In the liquid phase, considering a spherical particle with radius r , it will be subjected to a repulsive force (F_R) due to the weak molecular interactions present at the solid-liquid interface [68]:

$$F_R = 2\pi r \Delta\sigma$$

(Equation 9)

Where:

$$\Delta\sigma = \Delta\sigma_0 \left(\frac{a_0}{d} \right)^n$$

(Equation 10)

Therefore, $\Delta\sigma$ represents the system's free energy considering the average distance (a_0) between molecules in the liquid phase and the thickness (d) of the liquid layer between the particle and the solid-liquid interface. The exponent n represents a

correction of the repulsive forces acting on the particle, varying from 1 to 4. If this correction is neglected, that is, considering $n = 1$, the repulsive force acting on the particle will be [68]:

$$F_R = 2\pi r \Delta\sigma_0 \left(\frac{a_0}{d} \right)$$

(Equation 11)

The particle also experiences an attractive force resulting from the viscous drag process, following *Stokes' Law*. This law states that a spherical particle with a density different from that of the fluid in which it is immersed will experience a drag force due to its motion. This force depends on the dynamic viscosity (η) of the liquid and the particle's velocity (v). In the specific case where a thin film of the liquid phase fills the space between the solid-liquid interface of the freezing front and the particle, there will be an attractive force (F_η) [68]:

$$F_\eta = \frac{6\pi\eta v r^2}{d}$$

(Equation 12)

From the balance between the repulsive and attractive forces acting on the particle, it is possible to calculate a critical velocity (v_{cr}) of the freezing front at which particle entrapment occurs [68]:

$$v_{cr} = \frac{\Delta\sigma_0 a_0}{3\eta r}$$

(Equation 13)

Therefore, when the freezing front velocities are below this critical value, the particles are pushed (or rejected) by the solid-liquid interface. Otherwise, they will be trapped by the interface, as illustrated in Figure 11 [68].

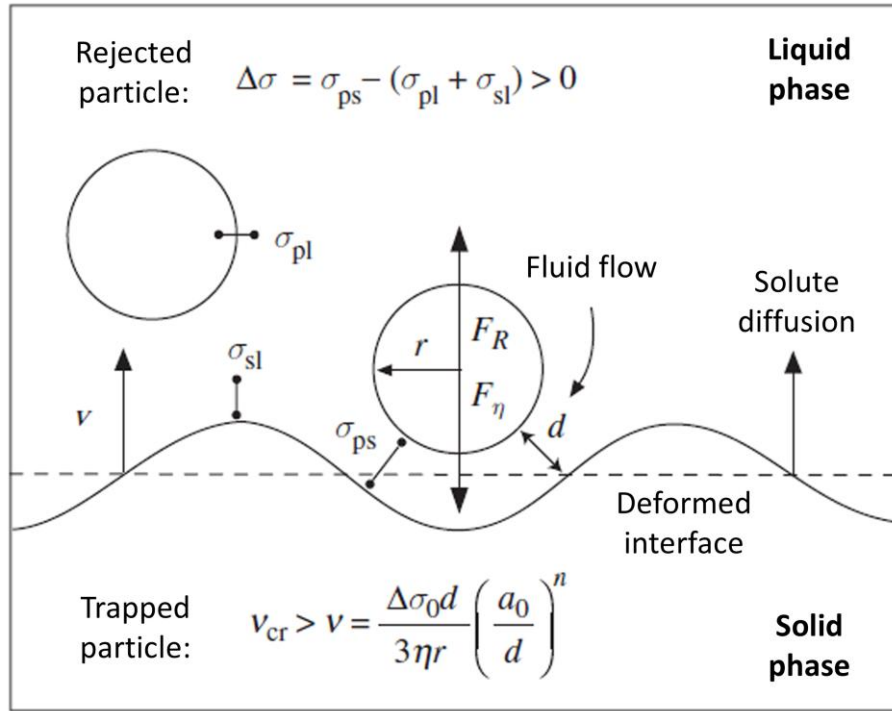


Figure 11. Schematic of particle–freezing front interactions in the freeze-casting process. Adapted from the reference [68].

Due to the differences in thermal conductivity between the particles and the liquid, and assuming a planar freezing front and a velocity below the critical velocity, the particles pushed by this front will form a concentration gradient immediately ahead of the freezing front. As a consequence, there is an increase in particle concentration and a decrease in the freezing point, allowing the formation of a constitutional undercooling zone [68]. When this zone is disrupted, instabilities occur in the system, forming the spacing between solvent crystals [57, 68, 69]. This process alters the velocity of the freezing front along the material, resulting in a temperature gradient that enables the creation of different porosity distribution zones [57, 69]. Therefore, it is crucial to impose a defined temperature gradient during the solidification of the suspension. This allows the solvent crystals to grow along with this gradient, enabling precise control of the porosity in the different regions formed during the process [57]. This phenomenon was demonstrated in the study conducted by Souza et al. [80], which produced cylindrical α -Al₂O₃ samples using TBA as the solvent through the freeze-casting process. Figure 12 shows scanning electron microscopy (SEM) images of the different porous regions (bottom, middle and top) produced in the cylindrical samples of this study after the sintering stage [80].

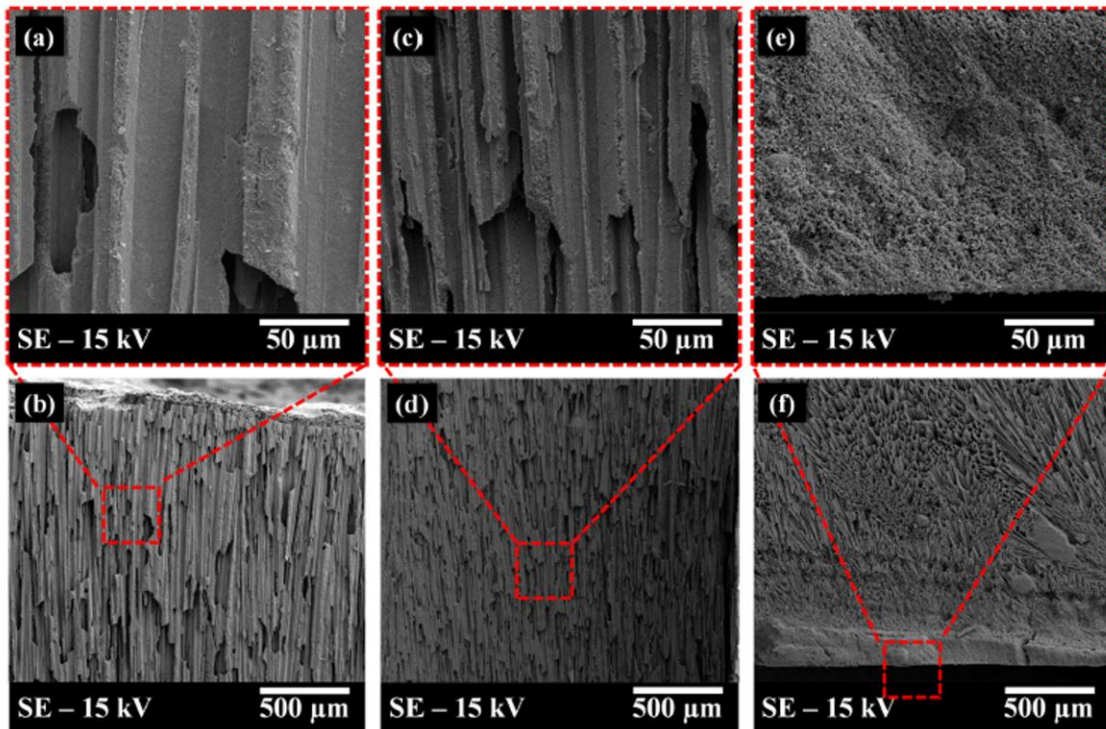


Figure 12. SEM of the surface parallel to the solidification front of the 30 vol.% alumina samples from the study by Souza et al.: (a, b) top region, (c, d) middle region, (e, f) bottom region [80].

The third stage of the freeze-casting technique involves the sublimation of the frozen solvent, which served as a template for pore formation in the material [56, 57, 69]. This sublimation can occur at room temperature, as in the case of ceramics produced using camphene as the solvent [60, 61] or it can be carried out through a lyophilization process, which allows for temperature and pressure control, especially when solvents such as water [76] and TBA [58, 75] are used.

The fourth and final stage involves the sintering of the green body formed during the freeze-casting process. During this step, the decomposition and pyrolysis of the organic additives (dispersant and binder) occur, along with the densification of the material. This stage results in a significant increase in the mechanical strength of the material [56, 57, 69].

In porous ceramic materials, grain boundary diffusion is one of the predominant processes during densification [53]. This phenomenon facilitates the formation and growth of “necks” between interconnected particles, reducing the distance between their centers, as shown in Figure 13. By controlling the movement and growth of these grain boundaries, it is possible to eliminate closed porosity,

increase the thickening of pore walls, and, as a result of densification, define the final porosity of the material [53].

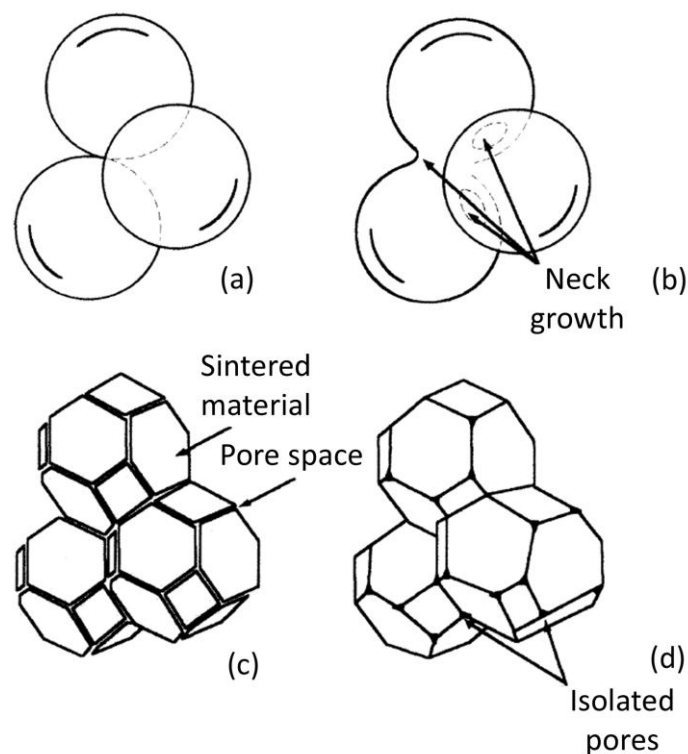


Figure 13. (a) Initial stage of the sintering process represented by spherical particles in contact, (b) neck growth between particles, (c) interconnected pore spaces give rise to the material's porosity, (d) complete densification of the material with the formation of isolated pores. Adapted from the reference [53].

Studies such as those by Souza et al. [59] and Zhu et al. [81] employed the freeze-casting technique to fabricate α -Al₂O₃ supports using TBA as the solvent, aimed at membrane applications, specifically exploring the permeance of gas mixtures and bacterial filtration in aqueous media, respectively. Souza et al. [59] reported that the porous structures obtained in these supports exhibited an arrangement that facilitated diffusion for the permeation of the tested gases (He/CO₂, He/N₂, CO₂/N₂). In the study by Zhu et al. [81], it was possible to create a highly porous ceramic material, which demonstrated a removal efficiency of approximately 80% of bacteria (*Escherichia coli*) in aqueous media at pH 4. These results support the potential of using the freeze-casting process for the production of porous supports.

2.3.2. Active phase

In multilayer asymmetric ceramic membranes, as previously illustrated in Figure 6, the active phase plays a crucial role in the effective separation of the desired components. The thickness of the separation membrane layer and other layers in asymmetric membranes represents a trade-off between the need for high flux, which requires thin layers, and physical integrity and absence of defects, which demand thicker layers [15, 16].

In ceramic membranes intended for gas separation, the thickness of the separation layer can vary considerably depending on the type of material and the manufacturing process applied [15]. Among commonly used materials, zeolites have shown promising results in this field of application. When supported on macroporous α -Al₂O₃ materials, the ideal thickness of the zeolitic active phase ranges between 0.5 and 4 μ m, which falls within the expected thickness range to ensure a high permeate gas flux, potentially resulting in more efficient separation [20, 22, 43–45, 49, 50].

For the production of these zeolitic membranes, growth can occur in situ, with the direct formation of the membrane on the macroporous support, generally without a separate seeding step, using the support itself as the source of elements for film growth [82, 83]. Another production approach is based on secondary growth methods, in which a zeolite layer develops over seeds previously deposited on the support [82]. This approach has proven to be more suitable for producing uniform membranes with a lower incidence of defects, essential characteristics for materials used in gas separation [15, 83, 84].

Among commonly used secondary growth methods, such as spin-coating [85], rub-coating [20, 43] and vacuum seeding [85, 86], the dip-coating technique [20, 44, 45, 85, 87] has stood out in the production of zeolitic membranes due to its simplicity and low cost [82, 83, 87]. This method involves immersing the support in a suspension of zeolite seeds, forming a seed layer on the surface. After deposition, secondary growth occurs by exposing the seeded support to a synthesis solution containing zeolitic precursors under hydrothermal conditions, promoting crystal growth from the seeds and the formation of a continuous and dense layer [20, 44, 45, 83, 85, 87].

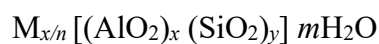
Despite the apparent simplicity of the dip-coating method for producing zeolitic membranes, precise control over the microstructural properties of the films

requires mastery of the multiple factors involved in the process, as well as consideration of specific technical challenges and limitations [83, 85, 87]. Therefore, the quality of the membrane obtained by this secondary growth technique can be influenced by factors such as seed size, uniformity of the seeding layer, synthesis conditions (temperature, time, precursor concentration) and the structural compatibility between the seeds and the growing layer [82, 87].

2.3.2.1. Zeolites

Zeolites are materials with a three-dimensional crystalline structure formed by tetrahedra (TO₄), where the central atom T can be represented by elements such as silicon (Si), aluminum (Al), phosphorus (P), gallium (Ga) among others. These tetrahedra are interconnected through their oxygen atoms, forming the building subunits that compose the zeolitic structures [18, 88, 89]. These three-dimensional structures feature well-defined channels and cavities, and, due to their open microporosity, allow transfer between the crystalline space and the external environment, limited by the pore diameter size of the zeolitic structures, thus providing them with molecular sieve characteristics [88].

The most common zeolites are classified as aluminosilicates, comprising a tetrahedral arrangement with central T atoms represented by silicon and aluminum [18]. Trivalent aluminum (Al³⁺), in the tetrahedra [AlO₄]⁵⁻, generates a negative charge in the structure, which is balanced by counter-ions (Figure 14), typically alkali or alkaline earth metal cations such as sodium ion (Na⁺), potassium ion (K⁺) or calcium ion (Ca²⁺). In addition to these counter-ions, water molecules are also present in the intracrystalline spaces, channels and cavities of these materials [18, 88]. Thus, these zeolites can have their unit cell defined by the following chemical formula [18]:



Where M represents the counter-ion with valence n , m is the number of water molecules and the sum of x e y indicates the number of tetrahedra per unit cell.

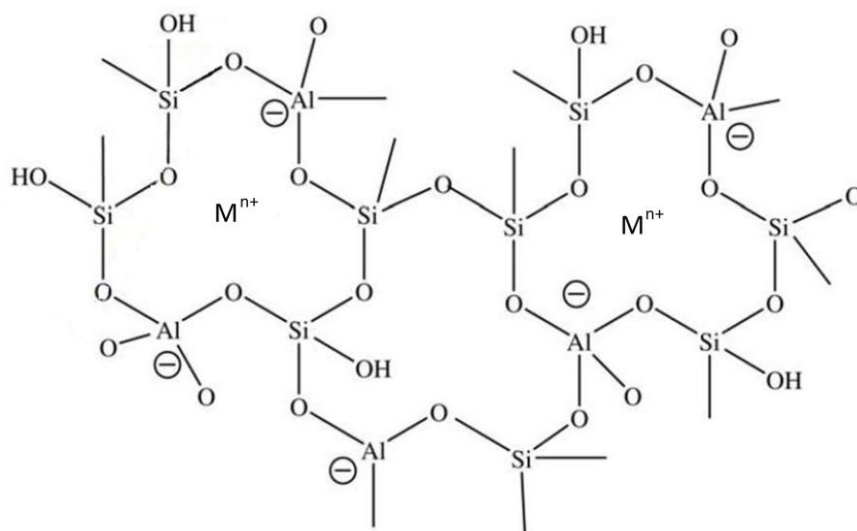


Figure 14. Two-dimensional representation of a zeolitic structure. M^{n+} represents the compensating counter-ions of the structure. Adapted from the reference [88].

Based on the building subunits that compose each zeolitic structure, they generate different topologies that are classified, according to the International Zeolite Association (IZA), by a three-letter uppercase code to refer to a specific structure, regardless of elemental composition (Figure 15) [89–92]. This code is usually related to the mineral name of the zeolite structure, for example, CHA referring to the chabazite zeolite and FAU referring to the faujasite zeolite (Figure 15) [89].

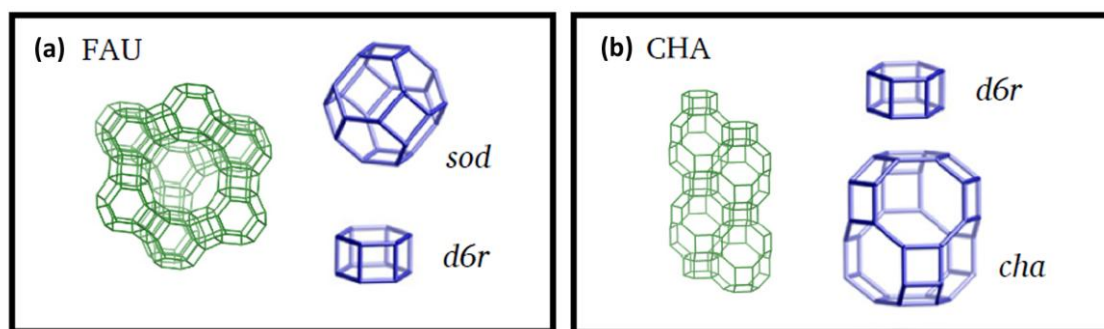


Figure 15. Schematic representation of the topology (in green) of the zeolites (a) FAU and (b) CHA and their respective building subunits. Adapted from the reference [92].

Zeolites are generally synthesized under hydrothermal conditions, in which a gel composed of alkali or alkaline earth metal cations and organic structure-directing agents, such as ammonium cations (R_4N^+), guide the formation of the structure from silicon and aluminum precursors, in the case of aluminosilicates [18, 89, 92, 93].

Additionally, mineralizing agents such as hydroxide (OH^-) and fluoride (F^-) ions, and solvents like water are used. The synthesis gel, formed by mixing the reagents, is heated in a stainless-steel autoclave lined with polytetrafluoroethylene (PTFE) under autogenous pressure conditions at a temperature below 250 °C for a certain period [89, 92].

Although conventional hydrothermal synthesis is widely used, several other methods have been explored to improve zeolite synthesis, often aiming to reduce reaction (crystallization) time or production costs [92, 94].

In this context, techniques such as seed-assisted synthesis, which accelerates nucleation and significantly reduces crystallization time [46, 92, 93, 95–97] and steam-assisted crystallization (SAC), which uses water vapor to promote crystallization, allowing for lower reagent amounts and shorter synthesis times stand out [20, 92, 98]. Additionally, microwave-assisted synthesis has proven effective in accelerating nucleation and zeolite crystal growth rates, resulting in smaller particles and shorter reaction times [92, 96, 99, 100]. Other methods investigated include two steps crystallization synthesis, zeolitic interconversion, synthesis without organic structure-directing agents and dry gel conversion, all aimed at reducing synthesis costs without compromising process efficiency [92, 101–103].

In this context, many synthetic factors influence zeolite formation, such as the reagents used, the type and amount of solvent, the organic structure-directing agent, gel composition, pH, temperature and crystallization time [18, 89, 92]. Table 4 shows some molar ratios between the synthesis reaction components and their effect on the final material structure [18].

Table 4. Molar ratios between the synthesis reaction components and their effect on the final material structure. Adapted from the reference [18].

Molar ratio:	Effect on structure:
$\text{SiO}_2/\text{Al}_2\text{O}_3$	Structural composition
$\text{H}_2\text{O}/\text{SiO}_2$	Crystallization rate and mechanism
OH^-/SiO_2	Degree of silicate oligomerization and OH^- concentration
M^+/SiO_2	Structure and cation distribution
$\text{R}_4\text{N}^+/\text{SiO}_2$	Amount of structural aluminum

To understand the zeolite synthesis process, it is essential to clarify the concepts related to crystallization in solution, especially the stages of nucleation and crystal growth [18, 95, 104]. Nucleation refers to the formation of the smallest recognizable entity presenting a crystalline atomic structure, which can occur via a single or multiple associated mechanism. On the other hand, crystal growth in solutions involves the increase in size of these nuclei, requiring the transport of dissolved solutes to the nucleus surface. The application of mechanical actions, such as stirring, vibration or ultrasound, helps maintain a uniform concentration gradient around the crystal, facilitating its proper growth [95].

In the zeolite synthesis process, oligomeric precursors dissolve into smaller units and more reactive reagents are provided in the liquid phase to assist in the formation of nuclei, which will grow into definitive zeolite crystals (Figure 16) [18, 94, 95, 104]. Nucleation in this type of synthesis can occur homogeneously, without the interference of external agents, or heterogeneously, with the intervention of such agents. The difference between the atoms present in the critical nucleus formed in the early stages of the crystal and those in the solution lies in the fact that, in the liquid, only short-range atomic ordering occurs, while in the critical nucleus, long-range ordering follows the characteristic unit cell of the zeolite. When the atoms in the crystal are more stable than those in the solution, the microscopic ordering of the nuclei induces the incorporation of atoms from the solution, promoting crystal growth and formation [95].

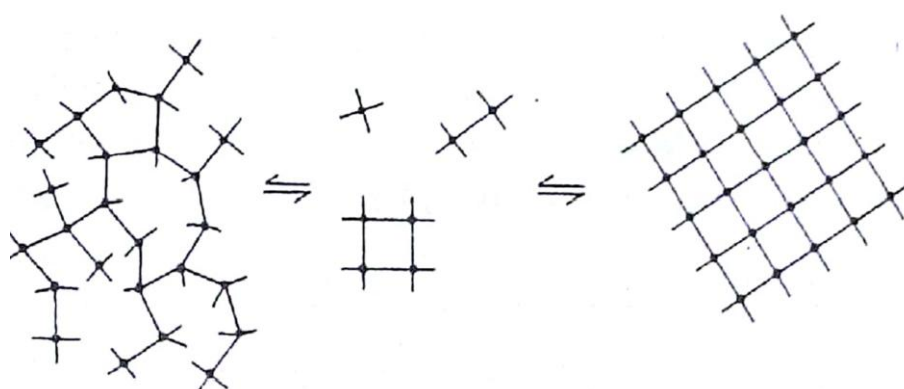


Figure 16. Crystallization in the liquid phase of the gel. Adapted from the reference [18].

In general, due to their three-dimensional crystalline structures, zeolites exhibit characteristics such as high surface area, competitive adsorption capacity, the presence of acidic sites, chemical resistance under high-temperature conditions and

molecular sieving properties that enable differences in the diffusivity of components within their structures [18, 88, 89]. These properties ensure their application in numerous industrial processes in the fields of catalysis, adsorption and separation [18, 88, 91, 105].

2.3.2.2. SSZ-13

Initially developed in 1985 by Stacey I. Zones, SSZ-13 is a synthetic aluminosilicate with a characteristic chabazite (CHA) topology and a high silica content ($\text{Si}/\text{Al} > 5$). Its structure is composed of double six-ring (d6r) and chabazite (cha) building subunits, arranged in four-, six- and eight-membered rings (MR), which form a three-dimensional architecture with perpendicular channels (Figure 17) [23, 92, 104, 106, 107]. The CHA structure has pore openings of approximately $3.8 \times 3.8 \text{ \AA}$, an ellipsoidal cavity size of $6.7 \times 10 \text{ \AA}$ and a framework density of $15.1 \text{ T}/1000 \text{ \AA}^3$ [23, 92, 106].

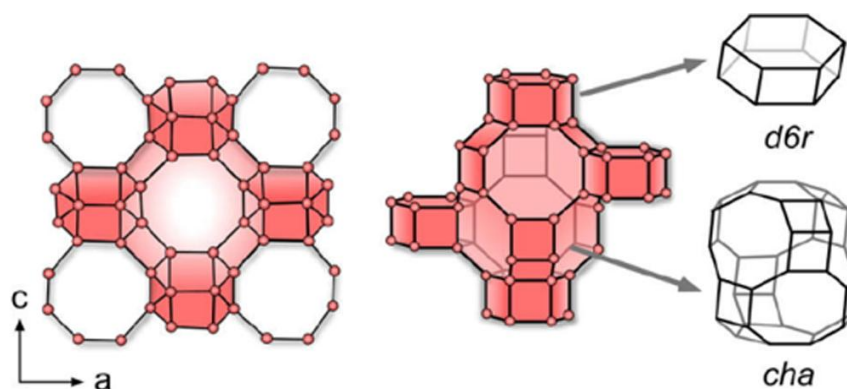


Figure 17. Structure of the SSZ-13 zeolite. Adapted from the reference [104].

Since its development, SSZ-13 zeolite has attracted considerable attention from both the academic community and industry due to its outstanding performance in heterogeneous catalysis [92, 106, 107]. This includes applications such as selective catalytic reduction of NO_x [108, 109], methanol-to-olefins conversion [110, 111] and ethylene-to-propylene transformation [101, 112], as well as its remarkable gas adsorption and separation capabilities [21–23, 43, 44, 113]. In this latter field, this zeolite emerges as a promising alternative for NG purification, given that its micropores have dimensions similar to the kinetic diameters of CH_4 ($3.8 \text{ \AA}$), N_2 ($3.6 \text{ \AA}$) and CO_2 ($3.3 \text{ \AA}$), which make up this mixture [19, 23, 43, 92].

2.3.3. Applicability of SSZ-13 zeolite and SSZ-13/ α -Al₂O₃ Inorganic Membranes

The SSZ-13 zeolite has been extensively studied and recognized as a promising material for various gas adsorption processes, particularly for the separation of gas mixtures such as CH₄/N₂, CO₂/CH₄ and CO₂/N₂. Its microporous structure enables efficient molecular sieving, making it suitable for selective gas adsorption [114]. This zeolite has shown outstanding performance in CO₂ separation, especially in post-combustion capture (CO₂/N₂ mixtures) and biogas or NG purification (CO₂/CH₄ mixtures) [38].

In the study by Shang et al. [115], the CH₄ adsorption capacity of CHA-type zeolites (Chabazite-K, SAPO-34 and SSZ-13) was investigated for CH₄/N₂ mixtures (CH₄ < 20%) at 10 bar and 298 K. Among them, SSZ-13 exhibited the highest CH₄ adsorption capacity (1.381 mmol·g⁻¹), approximately 97% and 88% higher than those of Chabazite-K and SAPO-34, respectively. This superior capacity was attributed to its larger pore volume and surface area, which are crucial for CH₄ recovery.

Similarly, Wang et al. [114] evaluated the dynamic breakthrough adsorption performance of Li-SSZ-13 compared with Na-SSZ-13 and Li-Na-SSZ-13. The directly synthesized Li-SSZ-13 exhibited a high CO₂ adsorption capacity of 4.48 mmol·g⁻¹ at 1 bar and 273 K, representing 45.0% increases compared to Na-SSZ-13 and 24.8% compared to Li-Na-SSZ-13, respectively. These results indicate that Li-SSZ-13 has great potential for efficient CO₂ capture from flue gas.

In another study, Thompson et al. [116] investigated Na-SSZ-13 for CO₂/CH₄ separations in the presence of impurities such as C₂H₆ and H₂S, simulating real NG conditions. The ability of Na-SSZ-13 to separate CO₂ from sulfur-containing species suggests a broader applicability for NG purification compared to high-aluminum zeolites, which may be limited by equilibrium reactions with sulfur contaminants.

Overall, these studies highlight the considerable adsorption performance of SSZ-13 compared to other CHA-type structures, reinforcing its potential for advanced gas separation applications.

Given the notable adsorption properties of SSZ-13 zeolites discussed above, considerable research has focused on their incorporation into inorganic membranes. Studies involving SSZ-13/ α -Al₂O₃ composite membranes highlight their remarkable separation performance, primarily attributed to restricted molecular diffusion within the microporous framework. Moreover, different approaches to the synthesis of SSZ-13/ α -Al₂O₃ membranes have enabled the investigation and improvement of permeance and selectivity parameters for the gas mixtures under study, CO₂/CH₄, N₂/CH₄ and CO₂/N₂ [20–23, 43, 44].

In the study conducted by Gui et al. [23], SSZ-13/ α -Al₂O₃ membranes were produced using conventional hydrothermal synthesis followed by acid treatment. The results indicated that, under a pressure of 20 bar (2 MPa) and a temperature of 298 K, the acid treatment negatively affected the permeance and selectivity parameters for equimolar mixtures of N₂/CH₄ and CO₂/N₂. Specifically, the N₂ gas permeance was reduced by up to 82% in the N₂/CH₄ mixture. However, for CO₂/CH₄ mixtures, the CO₂ permeance did not show significant variation, while its selectivity increased by up to three times with the acid treatment.

In comparison to the study by Wu et al. [20], which was conducted under similar experimental conditions for permeance and selectivity tests, the SSZ-13/ α -Al₂O₃ membrane was produced using the steam-assisted conversion method. The results indicated that increasing the synthesis duration from 4 to 8 days led to an increase in the membrane thickness, which negatively affected N₂ permeability in N₂/CH₄ mixtures. For membranes synthesized over 6 days, with an active layer thickness of 3.0 μ m, N₂ permeance values of $1.4 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ and a selectivity of 15.2 were obtained. These values were found to be optimized when compared to the study by Gui et al. [23], which reported, for the same active layer thickness, N₂ permeability values of $8.8 \times 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ and a selectivity of 5 for the N₂/CH₄ mixture.

The studies conducted by Li et al. [21] addressed the production of SSZ-13/ α -Al₂O₃ membranes using the hydrothermal method over a period of 3 days, with a special focus on controlling the concentration of SSZ-13 seeds in the synthesis gel. In addition, they investigated membrane calcination conditions in three different atmospheres: static air, oxygen atmosphere and ozone/oxygen atmosphere. The results of this study enabled the fabrication of membranes with a 1.2 μ m thick active

layer, showing the best N₂ performance of $8.5 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ and a selectivity of 13.5 for the equimolar N₂/CH₄ mixture, under temperature and pressure conditions similar to the previously described studies. These results were achieved with a seed concentration of 0.7 mg per gram of synthesis gel and calcination performed at low temperatures (473 K) in an ozone atmosphere.

Studies evaluating the separation efficiency of SSZ-13 membranes for CO₂/CH₄ mixtures have also been reported by Qiu et al. [44] and Tang et al. [45]. In the work by Qiu et al. [44], ultrathin SSZ-13 membranes (0.4 - 0.7 μm) were synthesized hydrothermally at low temperatures (353 - 373 K), achieving outstanding performance with a CO₂ permeance of $4.8 \times 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ and a CO₂/CH₄ selectivity of 153 for an equimolar mixture at 140 bar (0.14 MPa). Tang et al. [45] developed an innovative hot-dipping method for ultrafast synthesis (less than 1.5 h), producing SSZ-13 membranes with a CO₂ permeance of $2.86 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ and a CO₂/CH₄ selectivity of 180 under the same conditions.

Based on the studies mentioned above, it is evident that variations in the synthesis parameters employed in the production of SSZ-13/ α -Al₂O₃ inorganic membranes directly influence the permeance and selectivity properties of these materials. In all reported cases, the membranes demonstrated promising capabilities for separating CO₂/CH₄, N₂/CH₄ and CO₂/N₂ gas mixtures, which are relevant for NG purification processes [20, 21, 23]. These results highlight the importance of precise control over synthesis parameters to obtain membranes with optimized performance for specific gas separation applications.

In the work by Silva et al. [5], different SSZ-13-based materials had their selectivity and permeance values for the separation of the N₂/CH₄ and CO₂/CH₄ mixtures compared to values obtained for different types of materials, as shown in Figure 18. This comparison was performed within the context of the *Robeson plot*, which establishes the empirical upper bound between these properties, allowing for the evaluation of the materials' performance relative to the best membranes developed to date [5, 117].

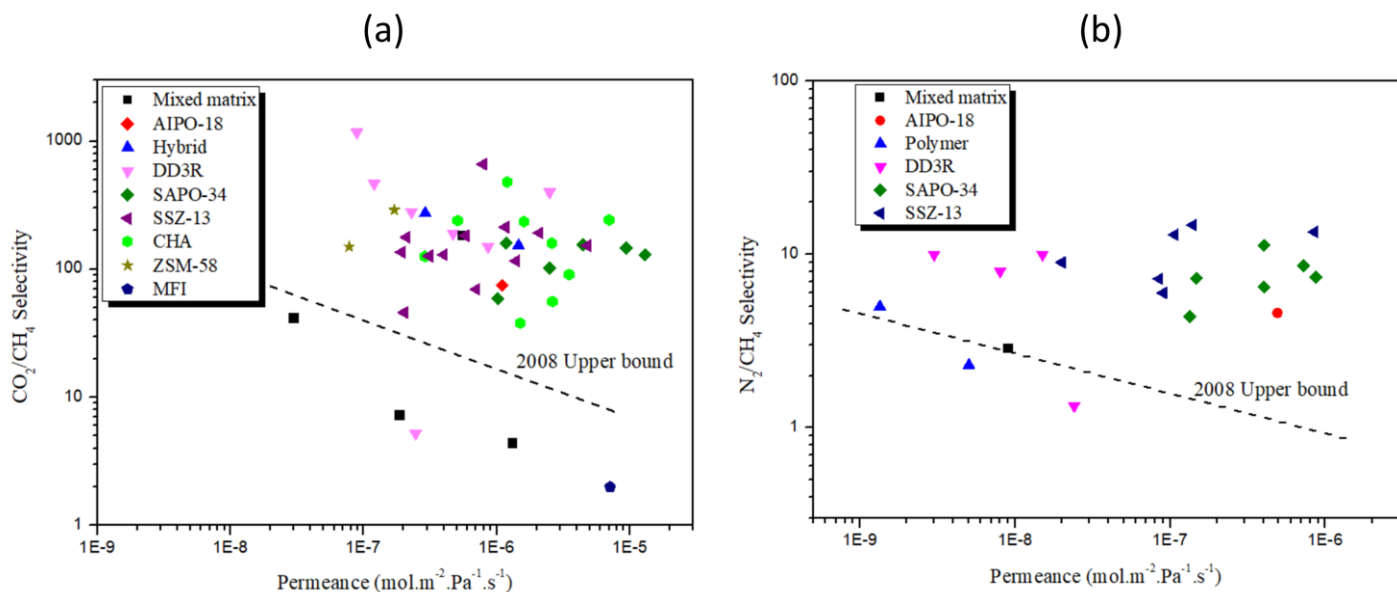


Figure 18. Robeson plots the main separation results for: (a) CO₂/CH₄ and (b) N₂/CH₄ mixtures across different types of materials. A membrane thickness standard of 1 μm was considered to plot the Robeson upper bound for polymeric membranes. Adapted from the reference [5].

The Robeson Plot for CO₂/CH₄ separation (Figure 18a) shows that zeolitic membranes, including SSZ-13, significantly demonstrate superior performance compared to polymeric membranes, exceeding the 2008 upper bound limit. Also, the Robeson Plot for N₂/CH₄ separation (Figure 18b) indicates that, in particular, SSZ-13 membranes demonstrated the highest selectivity and permeance for N₂/CH₄ separation. However, N₂/CH₄ selectivities remain lower than those achieved for CO₂/CH₄. This difference arises because N₂ (3.64 Å) and CH₄ (3.80 Å) have very similar kinetic diameters, making their separation considerably more challenging and primarily governed by molecular sieving rather than adsorption effects [5].

In this context, the present work aims at the production of SSZ-13/ α -Al₂O₃ inorganic membranes for future gas separation applications. The study initially involves the production of the ceramic support via the freeze-casting process and its characterization, followed by the synthesis of the SSZ-13 zeolite (active phase) through both the hydrothermal and microwave-assisted methods, along with their characterization. Subsequently, the steps of membrane production and characterization of the SSZ-13/ α -Al₂O₃ membrane will be carried out. This approach aims to develop membranes with optimized properties tailored to the specific requirements of gas separation, thereby contributing to advances in NG purification technology.

3. Experimental Section

This chapter presents the materials and methods employed in the development of this thesis. Initially, the list of reagents used is described, followed by the methodology adopted for the production of ceramic supports through the freeze-casting process. Subsequently, the procedures for the synthesis of the SSZ-13 zeolite by hydrothermal methods, using different counter-ions (Na^+ and K^+), are detailed, as well as the synthesis of SSZ-13 via a microwave-assisted route, employing seeds obtained by hydrothermal synthesis and different synthesis times.

Then, the production of the membranes is described, involving the use of $\alpha\text{-Al}_2\text{O}_3$ ceramic supports, the deposition of an intermediate silica layer and the application of zeolite seeds by dip-coating, followed by the growth of the SSZ-13 zeolitic layer by a hydrothermal method. Finally, the structural and textural characterization techniques of the materials are presented, along with the theoretical adsorption studies performed for the most promising SSZ-13 seed used in the formation of SSZ-13/ $\alpha\text{-Al}_2\text{O}_3$ membranes.

3.1. Materials List

The following reagents were used for the production of alumina ceramic monoliths and tubes:

- The ceramic source, alumina powder - $\alpha\text{-Al}_2\text{O}_3$, *Almatix* CT 3000 LS SG, 99.8%;
- The solvent, tert-butyl alcohol - TBA, *Sigma-Aldrich*, 99.5%;
- The dispersants, EFKA FA 4663 – EFKA, *Cognis*, Southampton Hampshire, United Kingdom; and citric acid - CA, *Sigma-Aldrich*, 90%;
- The binder, polyvinyl alcohol - PVA, *Sigma-Aldrich*, 90%;
- Liquid nitrogen, N_2 , purity $\geq 99.998\%$, *White Martins*.

The following reagents were used for the synthesis of SSZ-13 zeolite seeds and membrane fabrication:

- Silicon source, colloidal silica – SiO_2 , Ludox AS 40, *Sigma-Aldrich*, $\geq 50\%$;
- Aluminum source, aluminum hydroxide - $\text{Al}(\text{OH})_3$, *Sigma-Aldrich*, 98% which may be present in the composition 52.2% de Al_2O_3 ;
- Mineralizing agents and structure counter-ions, sodium hydroxide – NaOH , *Sigma-Aldrich*, 99%; and potassium hydroxide – KOH , *Sigma-Aldrich*, 99%;
- Organic structure-directing agent N,N,N-trimethyladamantyl-1-ammonium hydroxide – TMAdaOH, *Chem. Scene* (CAS 53075-09-5), $\geq 98\%$;
- Ultrapure deionized water (resistivity of $18.2 \text{ M}\Omega \text{ cm}^{-1}$), model Aurium mini plus – *Sartorius*;
- Solvent, ethyl alcohol - $\text{C}_2\text{H}_6\text{O}$, *Dinâmica Química Contemporânea Ltda.*, 95%;
- Solvent, isopropanol - $\text{C}_3\text{H}_8\text{O}$, *Dinâmica Química Contemporânea Ltda.*, 99.5%;
- Solvent, acetone – $\text{C}_3\text{H}_6\text{O}$, *Êxodo Científica*, 99.5%;
- Commercial $\alpha\text{-Al}_2\text{O}_3$ tubes from *Tecnicer Ceramica*, with an internal diameter of 8 mm and external diameter of 12 mm.

For the adsorption study (isotherms) from IAST methodology, the following pure gases were used:

- Nitrogen gas (N_2), Methane gas (CH_4) and carbon dioxide gas (CO_2), purity $\geq 99.998\%$, *White Martins*.

3.2. Sample Synthesis

3.2.1. Synthesis of the supports of $\alpha\text{-Al}_2\text{O}_3$

Figure 19 illustrates the scheme used according to the methodology established by our research group [75]. The suspensions, composed of $\alpha\text{-Al}_2\text{O}_3$, the binder PVA, the dispersant (CA or EFKA) in TBA solvent, were prepared by mechanical stirring using the *IKA T25 ULTRARRAX* disperser at 8000 rpm, at 30°C for 5 minutes to ensure proper mixing of the components and to disperse any solid

material agglomerates present in the suspensions. The solid loading of $\alpha\text{-Al}_2\text{O}_3$ tested was 20% by volume, while the concentrations of dispersant (CA or EFKA) and binder (PVA) were 2% and 1% by weight relative to the mass of $\alpha\text{-Al}_2\text{O}_3$, respectively. After preparation, the suspension was poured into polyamide molds (13 mm in height x 22 mm in diameter), supported on the surface of a copper rod partially immersed in a liquid nitrogen bath. A type T thermocouple was positioned around the copper rod, while four electric resistances were connected to an on-off controller to adjust the copper surface temperature at the bottom of the mold. The upper temperature of the copper rod was controlled with an accuracy of $\pm 2\text{ }^\circ\text{C}$, with the temperatures set to $-170\text{ }^\circ\text{C}$, $-150\text{ }^\circ\text{C}$ and $-130\text{ }^\circ\text{C}$. The molds were previously lubricated with silicone to facilitate removal of the monoliths, while the top part of the mold remained open under ambient temperature and pressure conditions to allow unidirectional freezing of the solvent. After solidification of the suspensions, the samples were subjected to a freeze-drying process in a lyophilizer (*Terroni model, LS E 3000*) for 24 hours at a pressure of $1\text{ }\mu\text{mHg}$. Subsequently, the freeze-dried material was sintered in a muffle furnace (*Nabertherm*) at a heating rate of $2\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ until reaching a temperature of $1500\text{ }^\circ\text{C}$, held for 2 hours. The monoliths were then cooled at a rate of $2\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ to room temperature.

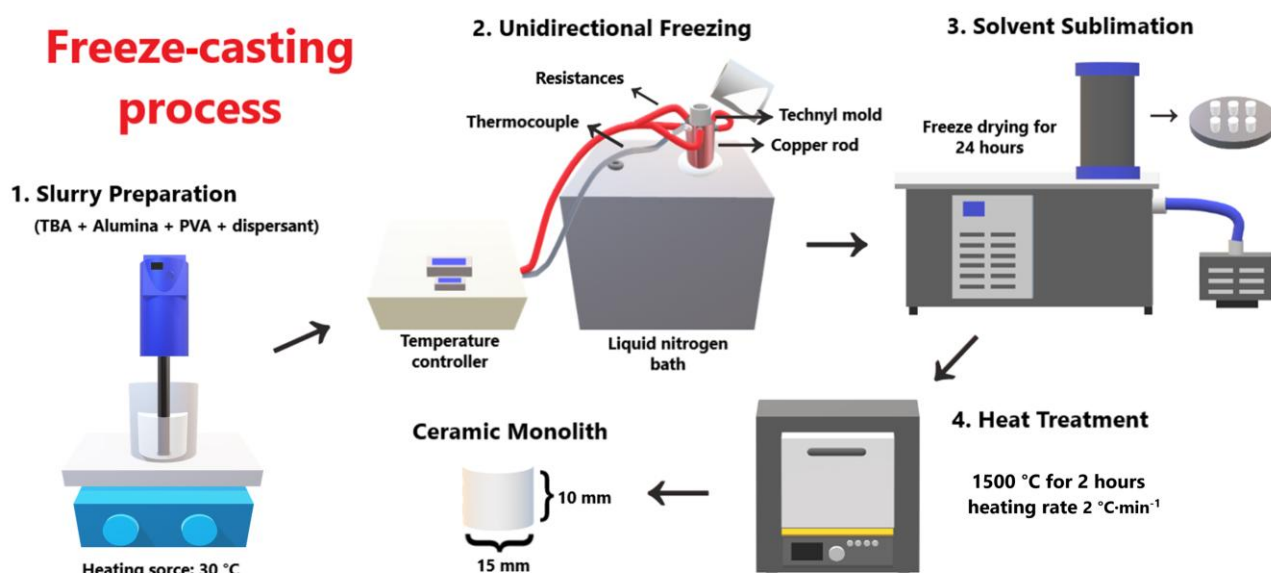


Figure 19. Schematic illustration of the production of ceramic monoliths. Adapted from the reference [75].

The freeze-casting methodology shown in Figure 19 was also adapted for the production of cylindrical α -Al₂O₃ samples (tubes), aiming to facilitate the subsequent step of SSZ-13 membrane fabrication on this substrate. The method used to produce the tubes was similar to that employed for the monoliths, differing only in the freezing stage. In this step, a copper rod, with temperature control, immersed in a liquid nitrogen bath was also used. At the center of this rod, a cavity was made to accommodate the *Technyl* mold (polyamide mold), into which the suspension was poured for freezing at the controlled temperature of -130 °C (Figure 20). The remaining steps were carried out as previously described for production of the monoliths.

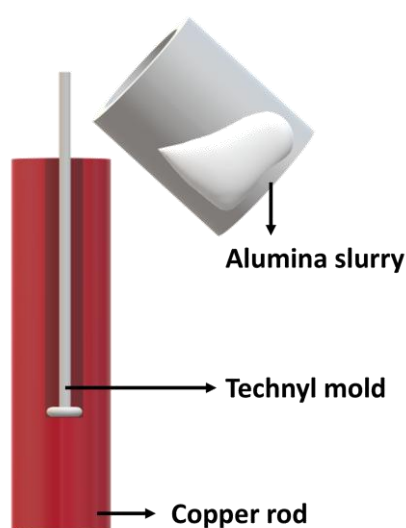


Figure 20. Simplified scheme illustration of the copper rod and mold used for the production of ceramic tubes (the resistances connected to the copper rod were not illustrated).

3.2.2. Hydrothermal Synthesis of SSZ-13 Zeolite

Figure 21 shows the synthesis scheme of SSZ-13 zeolite by the hydrothermal method. This methodology, based on the studies by Aydani et al. [43], was adapted with some specific modifications to meet the needs of the present work. The molar ratio of the produced zeolite seeds was 20 SiO₂: 4 NaOH or KOH: 1 Al(OH)₃: 16 TMAOH: 750 H₂O. Initially, in a heating plate and a 100 mL borosilicate beaker, deionized water and sodium hydroxide (NaOH) or potassium hydroxide (KOH) were added. With magnetic stirring, this solution was mixed until the mineralizing agent was completely dissolved, which took approximately 5 minutes. Then, aluminum hydroxide (Al(OH)₃) was added and the mixture was stirred for

24 hours at 600 rpm. In the next step, the structure-directing agent N,N,N-trimethyladamantyl-1-ammonium hydroxide (TMAdaOH) was added, and stirring was maintained for another hour. Subsequently, using a Pasteur pipette, colloidal silica was added dropwise to the suspension, which continued stirring at 600 rpm for an additional 3 hours. After this period, 34 mL of the suspension were transferred to a Teflon (PTFE) vessel with a capacity of 50 mL. The vessel was then placed in an autoclave, sealed and kept under static conditions in an oven (*Tecnal model TE-393/80L*) for periods ranging from 1 to 4 days at 160 °C. After removing the autoclave from the oven, it was immersed in an ice bath for 5 minutes. The resulting product was washed by vacuum filtration with deionized water until neutral pH was reached. Then, the material was dried in an oven at 100 °C for 24 hours. After drying, the material was ground and calcined in a muffle furnace (*Nabertherm*) at 600 °C for 6 hours, with a heating ramp of 1 °C · min⁻¹. The final powder showed a white color.

Syntheses for studying material crystallization (section 4.4.2 - change in the H₂O/SiO₂ molar ratio) were also carried out with the molar ratio of 20 SiO₂: 4 KOH: 1 Al(OH)₃: 16 TMAdaOH: 375 H₂O.

Hydrothermal synthesis

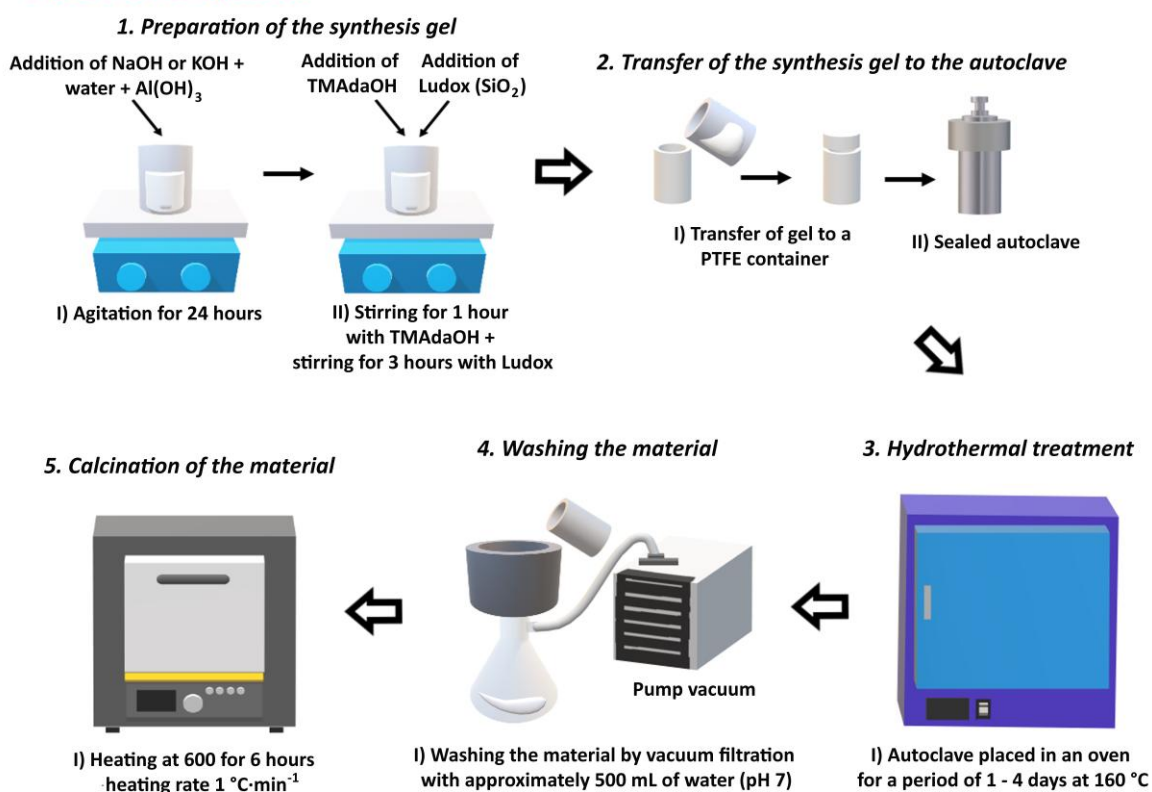


Figure 21. Illustrative scheme of SSZ-13 zeolite synthesis by the hydrothermal method.

3.2.3. Microwave-Assisted Synthesis and Seeding of SSZ-13 Zeolite

Figure 22 presents the synthesis scheme of SSZ-13 zeolite using microwave methods and SSZ-13 seeding. This methodology, based on the studies by Aydani et al [43] and Khan et al. [96], was adapted with specific modifications to meet the needs of the present work. The molar ratio of the produced zeolite seeds was 20 SiO₂: 4 KOH: 1 Al(OH)₃: 16 TMAdaOH: 750 H₂O. Initially, in a heating plate and a 100 mL borosilicate beaker, deionized water and KOH were added. With magnetic stirring, this solution was mixed until the mineralizing agent was completely dissolved, which took approximately 5 minutes. Then, Al(OH)₃ was added, and the mixture was stirred for 24 hours at 600 rpm. In the next step, the structure-directing agent TMAdaOH was added, and stirring was maintained for another hour. Subsequently, using a Pasteur pipette, colloidal silica was added dropwise to the suspension. SSZ-13 seeds were also added to the suspension, corresponding to 5% by weight of the colloidal silica mass, produced after 4 days of hydrothermal synthesis. This suspension continued stirring at 600 rpm for an additional 3 hours. After this period, 12 mL of the suspension were transferred to a borosilicate glass vessel coated with a Teflon lining, with a capacity of 35 mL. The vessel was then placed into the microwave equipment chamber (*Discover 2.0 Microwave Digester by CEM*), sealed, and the synthesis process was initiated for periods ranging from 15 to 60 minutes at 170 °C. After the reactions, the obtained product was washed by centrifugation (*Hermle model Z327 centrifuge*) with deionized water until the pH of the washing water was approximately 7, using 4 cycles of 5 minutes at 11000 rpm. Then, the material was dried in an oven at 100 °C for 24 hours. After drying, the material was ground and calcined in a muffle furnace (*Nabertherm*) at 600 °C for 6 hours, with a heating ramp of 1 °C · min⁻¹. The final powder presented a white color.

Microwave-Assisted Synthesis and Seeding of SSZ-13 Zeolite

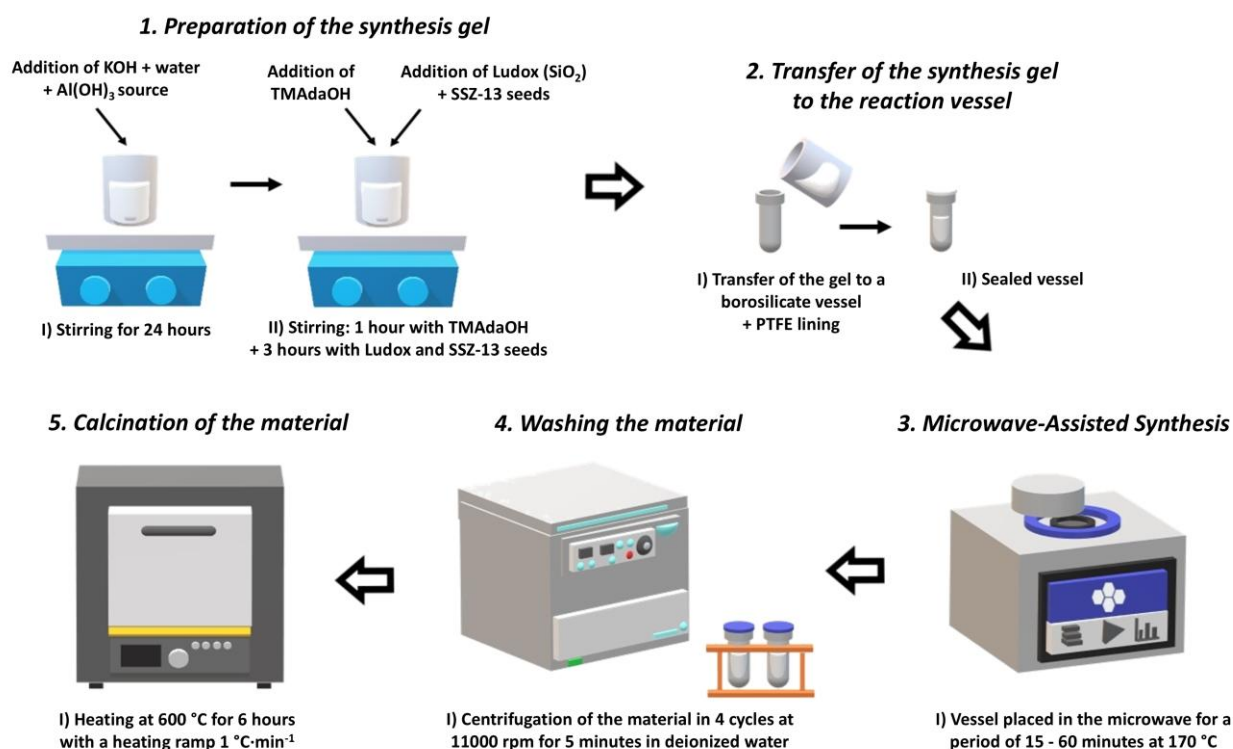


Figure 22. Illustrative scheme of microwave-assisted synthesis and seeding of SSZ-13 zeolite.

3.2.4. Production of SSZ-13 Membranes

Figure 23 presents the schematic of the production of SSZ-13 ceramic membranes. This methodology, based on the studies by Aydani et al. [43] and Athayde et al. [118], was adapted with specific modifications to meet the needs of the present work.

Initially, the commercial tubes and those obtained by freeze-casting were cut into 4.5 cm long segments (*IsoMet™ 1000 Precision Saw, Buehler*), sanded, and cleaned in an ultrasonic bath (*SSBu 15L model, Solid Steel*) for 20 minutes using different solvents (isopropyl alcohol, acetone and deionized water). After the cleaning and drying stage (100°C for 24 hours), the second step of the process was carried out, involving the deposition of the silica layer. This step aimed to ensure that the zeolite film (active layer) could later be deposited, via dip-coating, on the tubes more uniformly, minimizing the formation of incrustations. This second step was performed by depositing two layers of a 3.0% by weight suspension of Ludox AS 40 in ethyl alcohol. The suspension was subjected to magnetic stirring for 15 minutes, followed by 10 minutes in an ultrasonic bath before each deposition. These

depositions were carried out using a dip-coater (*KSV NIMA – Single vessel small model, Biolin Scientific*) with immersion speeds of $30 - 90 \text{ mm} \cdot \text{min}^{-1}$ and an immersion time of 30 seconds. Between each deposition, the produced film was allowed to dry at room temperature for 20 minutes, followed by drying at 70°C for 2 hours. At the end of the final drying, the tubes were calcined at 400°C for 3 hours with a heating and cooling rate of $0.5^\circ\text{C} \cdot \text{min}^{-1}$.

In the third stage of the process (Figure 23), an aqueous suspension containing 1% by volume SSZ-13 zeolite seeds (produced by hydrothermal synthesis and via microwave method) was subjected to the same stirring and deposition conditions previously described for the silica depositions, except for the immersion speed, which was fixed at $90 \text{ mm} \cdot \text{min}^{-1}$. After the drying stage of the final zeolite layer (1 - 3 depositions), the tubes were subjected to a hydrothermal treatment, as described in section 3.3.2. for periods of 6 - 24 hours, using a synthesis gel with the molar ratio of $20 \text{ SiO}_2 : 4 \text{ KOH} : 1 \text{ Al(OH)}_3 : 8 \text{ TMAdaOH} : 750 \text{ H}_2\text{O}$. Subsequently, the tubes with deposited active layer were washed with deionized water, dried at 100°C for at least 12 hours, and then calcined at 550°C for 10 hours, with a heating and cooling rate of $0.5^\circ\text{C} \cdot \text{min}^{-1}$, to obtain the final SSZ-13 membrane.

Production of SSZ-13 Membranes

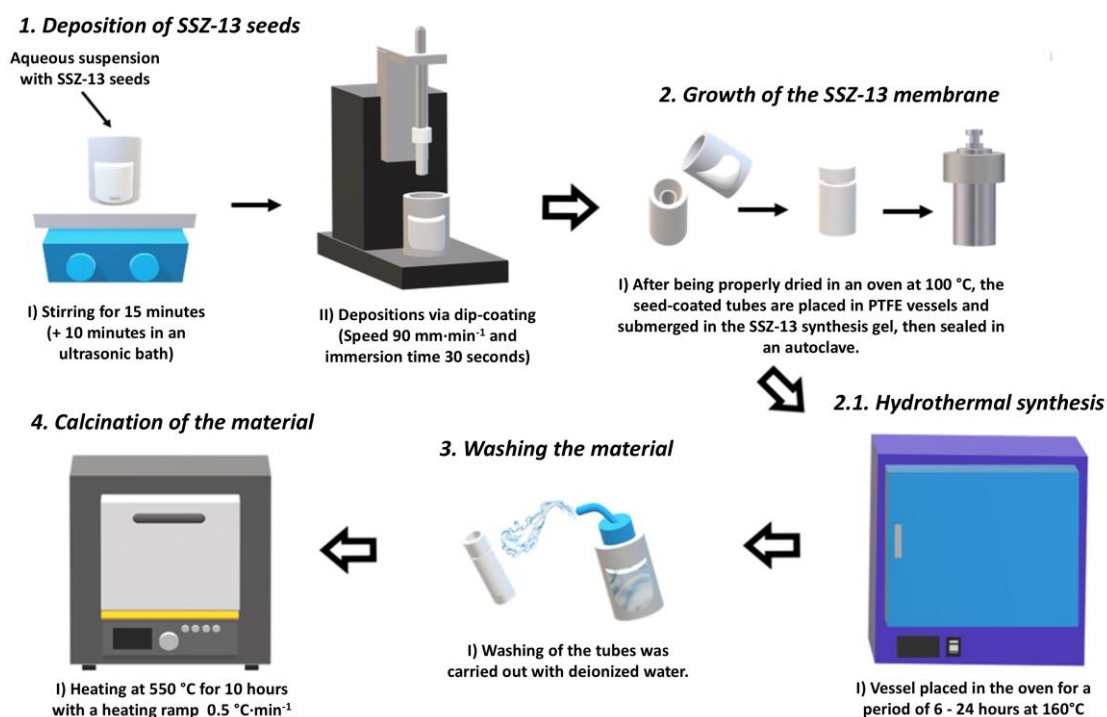


Figure 23. Illustrative diagram of the production of SSZ-13 ceramic membranes.

3.3. Sample Identification

The freeze-cast ceramic samples were identified with the codes AM_CA(T) and AM_EFKA(T), where AM stands for alumina monolith; CA and EFKA are abbreviations for citric acid and EFKA FA 4663, respectively, and T corresponds to the temperature used in the freezing process (-170, -150 or -130 °C). The alumina tube produced by the freeze-casting method was named FCT.

The SSZ-13 zeolite samples produced were identified with the codes Na⁺_SSZ-13_Hn e K⁺_SSZ-13_Hn, where Na⁺ e K⁺ represent the framework counter-ion used (K⁺ or Na⁺), H stands for hydrothermal synthesis, and *n* indicates the number of days (1-4) of synthesis. For samples with a change in the H₂O/SiO₂ molar ratio, the number 375 was added at the end of the code, K⁺_SSZ-13_Hn_375. In the case of samples synthesized by the microwave (MW) method, they were identified as SSZ-13_MW*m*, where *m* represents the time of the synthesis in minutes (15 - 60 minutes). All microwave syntheses were performed using potassium (K⁺) as the counter-ion.

The SSZ-13 membranes produced in this study were designated as HM_*h*, and MWM_*h*, corresponding respectively to the membrane synthesized with the best SSZ-13 seed via the hydrothermal method and the one synthesized with the best seed obtained through microwave synthesis. The letter *h* represents the time of the synthesis (membrane growth) in hours. All synthesis were grown on commercial α-Al₂O₃ tubes. And the SSZ-13 membrane produced (with the most promising seed) on freeze-cast tubes was designated as FCM.

3.4. Characterization Techniques

3.4.1. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy analyses were conducted at the Laboratory of Nanostructured Ceramic Materials (LMCNano) of the Department of Mechanical Engineering, Darcy Ribeiro campus, University of Brasília. The infrared spectra of the lyophilized ceramic samples, for quantifying the structure and interactions of dispersants in the green body, were obtained using a *Nicolet iS50* spectrometer from *Thermo Fisher* in attenuated total reflectance mode (ATR). The spectra of the

lyophilized samples were collected under transmittance conditions, with 64 scans at a resolution of 4 cm^{-1} over the range of 3500 to 400 cm^{-1} . The spectra of the SSZ-13 zeolite samples, for structural quantification, were obtained under the same conditions, varying only the analysis range from 1400 to 400 cm^{-1} . The software used to process the data and generate graphs were *Microsoft Excel* from *Office 365* and *OriginPro 2018* from *OriginLab Corporation*.

3.4.2. Scanning Electron Microscopy (SEM)

Micrographs of the ceramic samples (monoliths) were acquired at the Laboratory of Geodynamic, Geochronological and Environmental Studies (LEGGA) at the Darcy Ribeiro campus of the University of Brasília. Microscopy images were obtained using a *QUANTA 450* microscope from *FEI*, equipped with a low vacuum secondary electron detector (LFD - Large Field Detector), operating at 20 kV and magnifications ranging from 100 to 1000x. The samples were coated with a layer of carbon and mounted on a carbon tape. Subsequently, image processing was performed to analyze pore morphology, $\alpha\text{-Al}_2\text{O}_3$ wall thickness and grain size counting (with a minimum count of 500 grains per sample) referring to the central region of the monoliths, located approximately 6 mm from the copper surface, using *ImageJ* software (version 1.53e) from the *National Institutes of Health* (NIH) and *OriginPro 2018* from *OriginLab Corporation*.

Microscopy of the SSZ-13 zeolite samples was performed at the Microscopy Center on the Pampulha campus of the Federal University of Minas Gerais (UFMG). Microscopy images were obtained using a *QUANTA 200 FEG* microscope from *FEI*, equipped with a high vacuum backscattered secondary electron detector (ETD - Everhart-Thornley Detector), operating at 15 kV and magnifications ranging from 5000 to 20000x. The powder samples were mounted on carbon tape attached to a sample holder (stub) and coated with a carbon layer. Image processing was carried out using *ImageJ* software, as well as the images of the ceramic supports, to quantify morphology and particle size counting (with a minimum count of 300 particles per sample), and were also analyzed using *OriginPro 2018* from *OriginLab Corporation*.

Additionally, microscopy of the SSZ-13 membranes, zeolites and freeze-casting tubes was also performed at the Scanning Electron Microscopy and Confocal Laser Laboratory (LMEVCL), located in the Mechanical Engineering

Laboratory, SG-9 building, at the Darcy Ribeiro campus of the University of Brasília. Microscopy images were obtained using a *JSM 7100F* microscope from *JEOL*, equipped with a secondary electron detector (LED - Low Energy Detector) under high vacuum, operating at 15 kV and magnifications ranging from 250 to 20000x. Sample preparation and image processing were similar to those described in the previous paragraphs, however, gold coating was used instead of carbon.

3.4.3. Porosity measurement via the Archimedes' Principle

Porosity analyses of the ceramic materials using Archimedes' Principle were carried out at the Laboratory of Nanostructured Ceramic Materials (LMCNano) of the Department of Mechanical Engineering, Darcy Ribeiro campus, University of Brasília. The porosity of the ceramic samples was measured according to Archimedes' Principle, following the ASTM B962-13 standard [119, 120]. This principle states that an object immersed in a fluid is buoyed up by a vertical force equal to the weight of the fluid it displaces, which allows for the determination of the sample volume and, consequently, its porosity. Accordingly, the sintered ceramic monolith (or tube) was weighed to obtain its dry mass (m_s). The mass while immersed in distilled water (m_i) was obtained using the apparatus described in reference [120]. Next, the sample was removed from the liquid and immediately wiped with moistened cotton to remove the surface liquid film. The ceramic monolith (or tube) was then weighed to obtain the wet mass (m_w). The measured values were used to calculate the total volume of the samples (V_T), the open pore volume (V_O), and the solid volume (V_S) using Equations 14, 15 and 16, respectively.

$$V_T = \frac{m_w - m_i}{\rho_{H2O}}$$

(Equation 14)

$$V_O = \frac{m_w - m_s}{\rho_{H2O}}$$

(Equation 15)

$$V_s = \frac{m_s}{\rho_s}$$

(Equation 16)

Where ρ_{H_2O} is the density of water ($0.998 \text{ g} \cdot \text{cm}^{-3}$) and ρ_s is the density of the solid ($\alpha\text{-Al}_2\text{O}_3 = 3.97 \text{ g} \cdot \text{cm}^{-3}$). Subsequently, the total (P_T) and open (P_O) porosity percentages were determined according to Equations 17 and 18:

$$P_T = \frac{V_T - V_s}{V_T} \cdot 100$$

(Equation 17)

$$P_O = \frac{V_O}{V_T} \cdot 100$$

(Equation 18)

The data were processed using *Microsoft Excel* from *Office 365* and *OriginPro 2018* from *OriginLab Corporation*.

3.4.4. Helium Pycnometry

The pycnometry analysis was carried out at the Laboratory of Nanostructured Materials (LMN) on the Pampulha campus of the Federal University of Minas Gerais (UFMG). The measurements of the density of the ceramic samples were performed using the helium gas displacement method in a density analyzer (ρ_r), model *AD 200*, from *ACP Instruments*. The measurement process is automatic, with 10 repetitions and a maximum deviation of $0.005 \text{ g} \cdot \text{cm}^{-3}$. This procedure was performed in triplicate for each ceramic monolith. In simplified terms, the measurements are based on *Archimedes' principle* of fluid displacement and *Boyle's Law* to determine the volume, according to Equation 19 [119, 120]:

$$V_s = \frac{V_b + V_c}{\left(\frac{P_2}{P_3}\right)}$$

(Equation 19)

Where V_s is the volume of the solid sample, V_b is the volume of helium gas that occupies the solid at ambient pressure, V_c is a known volume at ambient pressure, P_2 is the pressure above ambient after the pressurization step of the system, and P_3 is the pressure generated when the pressurized system is connected to the known gas volume V_c .

Once the volume V_s is obtained, it is substituted into Equation 20, where m_s is the mass of the solid, and the density (ρ_r) of the material is calculated:

$$\rho_r = \frac{m_s}{V_s}$$

(Equation 20)

The data was processed using *Microsoft Excel* from *Office 365*.

3.4.5. X-ray Microcomputed Tomography (μ -CT)

X-ray microcomputed tomography analyses of the ceramic materials were conducted at the Laboratory of Nanostructured Ceramic Materials (LMCNano) of the Department of Mechanical Engineering, Darcy Ribeiro campus, University of Brasília. The micro-CT images were acquired using a *HeliScan mk1 μ -CT scanner* from *FEI*, operated through the *Qrumba software* (version 1.1.2.231), under conditions of 100 kV voltage, 70 μ A current, 1 x 1 camera and a maximum voxel size of 6.6 μ m. The *Pymango software* was used for data processing and 3D reconstruction of the ceramic sample's images. To evaluate the three-dimensional morphology and the distribution of pore size and total porosity, the reconstructed images were processed using *Avizo 3D* and *OriginPro 2018* from *OriginLab Corporation*. Aspects such as absolute permeability and hydraulic tortuosity of the materials were assessed using the *XPoreNetworkModeling* (PNM) model, which considers *Poiseuille flow* and assumes that the porous network is completely filled with a single phase [121, 122].

3.4.6. Mechanical Testing

Mechanical compression tests of the ceramic samples were conducted at the Nuclear Technology Development Center (CDTN), performed by the Mechanical

Testing Laboratory (LABMEC) located on the Pampulha campus of the Federal University of Minas Gerais (UFMG). The tests were carried out uniaxially on cylindrical ceramic samples (with 7 measurements per sample group) using an *Instron universal testing machine*, model 5882, equipped with a 5 kN load cell, at a rate of $0.5 \text{ mm} \cdot \text{min}^{-1}$. For the calculation of material strength, the maximum load corresponding to the first fracture of the material was considered, in accordance with the NBR 5739 standard [123]. The data was processed using *Microsoft Excel* from *Office 365* and *OriginPro 2018* from *OriginLab Corporation*.

3.4.7. X-ray Diffraction (XRD)

X-ray diffraction analyses of the SSZ-13 zeolite samples were performed at the Laboratory of Nanostructured Ceramic Materials (LMCNano) using equipment from the Department of Mechanical Engineering, located in the SG-9 building, Darcy Ribeiro campus, University of Brasília. The diffractograms of the samples were obtained using a *Shimadzu* diffractometer, model *Lab XRD-600*, with $\text{CuK}\alpha$ radiation ($\lambda = 0.15409 \text{ nm}$). The scan was conducted at $0.5^\circ \cdot \text{min}^{-1}$ with a step size of 0.02° over the 2θ range of 5 to 40° . The crystallite size (C_s) of the samples was calculated using the *Scherrer equation* indicated in Equation 21 [124]:

$$C_s = \frac{K \lambda}{\beta \cos \theta}$$

(Equation 21)

Where K is a constant related to the shape of the crystallites of the analyzed phase, with a value of 0.94; λ is the wavelength; and β is the full width at half maximum (FWHM) of the 100 reflection of the rhombohedral-type structure phase of the SSZ-13 zeolite (obtained by fitting the signal as a *psd-Voigt* peak). The relative crystallinity (C_R) of the samples was determined using a method adapted from reference [125], which calculates the sum of the areas of the crystalline portions (peaks) relative to the total area of the diffractogram, encompassing both the crystalline and amorphous areas of the material (Equation 22).

$$C_R(\%) = \frac{\Sigma(\text{peak area})}{\text{total area}} \cdot 100$$

(Equation 22)

The data were processed using *Microsoft Excel* from *Office 365* and *OriginPro 2018* from *OriginLab Corporation*.

3.4.8. Solid-State Nuclear Magnetic Resonance Spectroscopy with Magic Angle Spinning (MAS NMR)

The MAS NMR spectra of the SSZ-13 zeolite samples in the solid state were acquired at the Analytical Center of the Institute of Chemistry, Darcy Ribeiro campus, University of Brasília. The analyses were performed on a *Bruker* spectrometer, model *Magneto Ascend 600 Console Avance III HD*, operating at a magnetic field of approximately 14 T and equipped with a 4 mm probe. All solids were packed in zirconia rotors. For the ^{29}Si (119.24 MHz), the conditions used were: magic angle spinning (MAS) at a speed of 10 kHz and heteronuclear decoupling, pulse duration of 4.25 μs , 20 s delay between pulses and 512 scans. The ^{29}Si spectra were referenced to the external standard tetramethylsilane (TMS, $\delta = 0$ ppm). For the ^{27}Al (156.39 MHz), the conditions used were: magic angle spinning (MAS) at 10 kHz and heteronuclear decoupling, pulse duration of 0.40 μs , 1 s delay between pulses and 512 scans. The ^{27}Al spectra were referenced to the external standard of 0.1 M aqueous solution of hexahydrate aluminum chloride ($[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$, $\delta = 0$ ppm). The spectra were processed using *SpecManager software* (version 10.8) from *ACD/Labs* and *OPUS* (version 3.1) from *Bruker*. They were deconvoluted using *OMNIC software* (version 8.0.342) from *Thermo Fisher* and modeled through the *Voigt* mathematical function.

For the SSZ-13 zeolite samples, the molar percentages of silicon and aluminum species in the materials (based on their areas) and their $\text{Si}/\text{Al}_{\text{framework}}$ ratio were calculated using the simplified formulas of Equations 23 and 24, respectively [18, 126]:

% Si(*n*Al) or Al^{*x*}

$$= \frac{\text{Area of the specie's Si}(n\text{Al})\text{ or Al}^x\text{ resonance peak}}{\sum \text{Area of all detected } (n\text{Al}) \text{ or Al}^x \text{ peaks}} \cdot 100$$

(Equation 23)

$$\text{Si/Al}_{\text{framework}} = \frac{\sum_{n=0}^4 I_{\text{Si}(n\text{Al})}}{\sum_{n=0}^4 \frac{n}{4} (I_{\text{Si}(n\text{Al})})}$$

(Equation 24)

Where the terms Si(*n*Al) or Al^{*x*} refer to the species associated with the different chemical environments of silicon or aluminum in the SSZ-13 samples. I_{Si(*n*Al)} corresponds to the peak intensity related to the environment of Si bonded to *n* Al atoms. Since the peak intensity is proportional to the number of Si atoms in each chemical environment, the total amount of Si is proportional to the sum of all chemical environments. According to *Loewenstein's rule*, each Al is surrounded by four Si atoms in the zeolite framework, therefore, each Si(*n*Al) group corresponds to ¼ of an Al atom [18].

As for the ²⁹Si MAS NMR discussion in section 4.2.3, the Q⁴/ΣSi(OAl)_{*n*} ratio and the proportion of Si(OAl)_{*n*} were calculated with Equations 25 and 26, adapted from reference [93]:

$$\frac{Q^4}{\sum \text{Si(OAl)}_n \text{ ratio}} = \frac{\text{Area of the } -110 \text{ ppm peak}}{\sum \text{Area of the } -105 \text{ ppm and } -100 \text{ ppm peaks}}$$

(Equation 25)

Proportion of Si(OAl)_{*n*}

$$= \sum \text{Area of the } -105 \text{ ppm and } -100 \text{ ppm peaks}$$

(Equation 26)

The software used to obtain the final graphs was *OriginPro 2018* from *OriginLab Corporation*.

3.4.9. Textural Analysis

The textural properties of the zeolitic materials were obtained at the Laboratory of Nanostructured Ceramic Materials (LMCNano) of the Department of Mechanical Engineering, Darcy Ribeiro campus, University of Brasília. The N₂ gas adsorption isotherms were obtained using a *Quantachrome Instruments analyzer*, model 7 *Autosorb IQ*. In this analysis, the first step involved degassing the material (weighed mass between 40 and 60 mg) through heating under vacuum for approximately 5 hours at 350 °C with a heating rate of 2.5 °C · min⁻¹. In the second step of the procedure, a flow of N₂ gas was passed over the sample at a temperature of -196 °C, with the aim of allowing the gas to be physisorbed by the material under study.

The specific surface area was calculated from the obtained isotherms using the *Brunauer-Emmett-Teller* (BET) method in the relative pressure range of P/P₀ de 0.02 a 0.10 (Equation 27) [127]:

$$\frac{P/P_0}{n(1-P/P_0)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} \left(P/P_0 \right)$$

(Equation 27)

Where n is the specific amount adsorbed at the relative pressure P/P₀, n_m is the specific monolayer capacity, and the parameter C is exponentially related to the adsorption energy of the monolayer [127].

The quantification of the microporous area, micropore volume and external surface area was obtained using the *t*-plot method with the *Boer equation*, in the relative pressure range of P/P₀ from 0.15 a 0.50 (Equation 28) [127, 128]:

$$t(\text{\AA}) = \left(\frac{13,99}{\log P_0/P + 0,034} \right)^{1/2}$$

(Equation 28)

The calculation of t assumes that the thickness of a single molecular layer of N₂ is 3.5 Å [128]. The pore size was estimated using Density Functional Theory

(DFT) based on zeolitic/silica materials with spherical/cylindrical pores. The calculation model used was NLDFIT (non-local density functional theory) through the *AsiQwin software* provided by *Quantachrome Instruments*. The software used to obtain the final graphs was *OriginPro 2018* from *OriginLab Corporation*.

3.5. Applicability of the materials

3.5.1. Adsorptive properties of the SSZ-13 zeolite

The experiments to obtain the ideal adsorptive properties of the SSZ-13_MW60 sample were carried out at the Laboratory of Nanostructured Ceramic Materials (LMCNano), Department of Mechanical Engineering, Darcy Ribeiro Campus, University of Brasília. These properties were determined from the adsorption isotherms of different pure gases (CH₄, CO₂ and N₂) at 298 K and pressures ranging from 0.1 to 0.9 bar. The sample preparation methodology and the adsorption isotherm acquisition followed a procedure similar to that described in Section 3.4.9., using a *Quantachrome Instruments analyzer*, model 7 *Autosorb IQ*.

From the adsorption isotherms obtained for the different gases, it was possible to fit the experimental data to the *Langmuir isotherm* model that assumes the adsorbent surface is energetically homogeneous and that no lateral interactions occur between adsorbed molecules. This model allows the determination of the maximum adsorption capacity (q_{max}) and the *Langmuir* affinity constant (b) parameters. Equation 7 used for the calculations was described in section 2.2.2.

The separation efficiency of an adsorbent is often evaluated by its selectivity, which, at low pressures (where the isotherm exhibits an approximately linear behavior) is proportional to the ratio between the *Henry's constants* (K_H) of the different gases. *Henry's selectivity* (S_H) is defined as (Equation 29) [129, 130]:

$$S_{H\,gas1/gas2} = \frac{K_{H\,gas1}}{K_{H\,gas2}} = \frac{q_{max-gas1} * b_{gas1}}{q_{max-gas2} * b_{gas2}}$$

(Equation 29)

Where S_H is *Henry's selectivity* between two gases and K_H is *Henry's constant* for each gas. The software used to obtain the final graphs (*Langmuir Isotherms*) was *OriginPro 2018* from *OriginLab Corporation*.

3.5.2. Ideal adsorbed solution theory (IAST) gas selectivity

Based on the adsorption isotherm data of the single gases (section 3.5.1.), it was possible to predict the adsorption equilibrium of multicomponent gas mixtures using the Ideal Adsorbed Solution Theory (IAST) [40]. This theory is based on the premise that the adsorbed phase, that is, the gas mixture on the adsorbent surface, behaves as an ideal solution [40, 130]. From this assumption, the model uses the adsorption isotherm data of the pure components to predict the adsorption selectivity when these components are present in a mixture.

The selectivity for the preferential adsorption of component i over component j in a binary mixture can be defined as (Equation 30) [129, 131]:

$$S_{ads} = \frac{x_i/x_j}{y_i/y_j}$$

(Equation 30)

Where S_{ads} is the adsorption selectivity, defined as the ratio between the molar fractions of the components in the adsorbed phase (x_i, x_j) and those in the gas phase (y_i, y_j).

For the fitting of the adsorption isotherms and the calculation of IAST selectivity, the software *GraphIAST* was used. Within this software, the *Dual-Side Langmuir* model was employed for fitting, which can be understood as an extension of the classical *Langmuir model* (Equation 7), developed to account for the heterogeneity of the adsorbent surface [35]. In this fitting model, the total adsorption is considered as the sum of the contributions from two types of adsorption sites (each with different adsorption energies) present in the sample [35, 114, 129].

The data were processed using *Microsoft Excel* from *Office 365* and *OriginPro 2018* from *OriginLab Corporation*.

4. Results and Discussion

4.1. Ceramic Support

In this first section of the discussion, the results obtained in the production of the α -Al₂O₃ ceramic support are presented. The aim of this study was to evaluate, at three different freezing temperatures in the freeze-casting process, two dispersants: citric acid (CA), commonly used in freeze-casting processes employing the solvent tert-butyl alcohol (TBA), and EFKA FA 4663 (EFKA), used for the first time in this type of slurry. The data produced and discussed in this section, which are part of this thesis, were published in reference [75].

4.1.1. Dispersant - α -Al₂O₃ Particle Interaction in the Freeze-Casting Process

To obtain suitable support for the gas separation process, it is essential that it exhibits structural properties that allow efficient mass transport and ensure mechanical strength for the membrane [15]. In this regard, it is crucial to ensure proper dispersion of the α -Al₂O₃ particles during the suspension preparation stage in the freeze-casting process.

Initially, the dispersion of the components in the suspension is influenced by Van der Waals forces between the particles, which favor their agglomeration due to collisions caused by Brownian motion. However, as the particles increase in size, these forces become less significant on a microscopic scale and the agglomerates become more affected by gravity [132, 133]. This results in higher sedimentation rates for larger particles, with the coalescence phenomenon further accelerating their settling. Therefore, the choice of an appropriate dispersant for the freeze-casting process can improve sedimentation time in suspensions and prevent the formation of agglomerates [132–134], promoting an adequate pore structure formation at the end of the process.

Citric acid (CA) is a carboxylic acid widely used as an anionic dispersant due to the presence of carboxyl groups ($-\text{COOH}$) in its structure, which enable electrostatic interaction and stabilization of the $\alpha\text{-Al}_2\text{O}_3$ particles present in suspensions (Figure 24a) [59, 134]. On the other hand, EFKA FA 4663 (formerly known as Texaphor 963 [135]) belongs to the class of polyelectrolytes and consists of a solution composed of 50% of an electrically neutral salt of a polycarboxylic acid containing amine derivatives in a hydrocarbon solution [135, 136]. This polyelectrolyte dispersant provides anti-sedimentation properties, which confer stability to the suspension mainly through steric interaction forces due to the size of the carbon chain (Figure 24b).

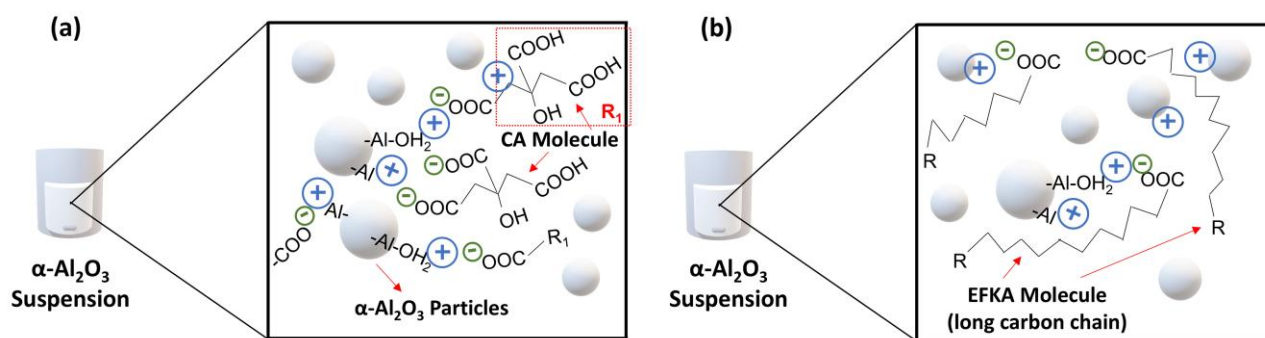


Figure 24. Illustrative scheme of the interaction between $\alpha\text{-Al}_2\text{O}_3$ particles with different dispersants: (a) Citric acid and (b) EFKA FA 4663. Adapted from the reference [75].

These interactions can be observed in the infrared spectra of Figure 25, for the lyophilized samples (after the solvent sublimation step) of AM_CA(-170) and AM_EFKA(-170), which were compared with the standards of $\alpha\text{-Al}_2\text{O}_3$, polyvinyl alcohol (PVA), CA and EFKA. The spectra for the other freezing temperatures are presented in Appendix A (Figures A1 and A2).

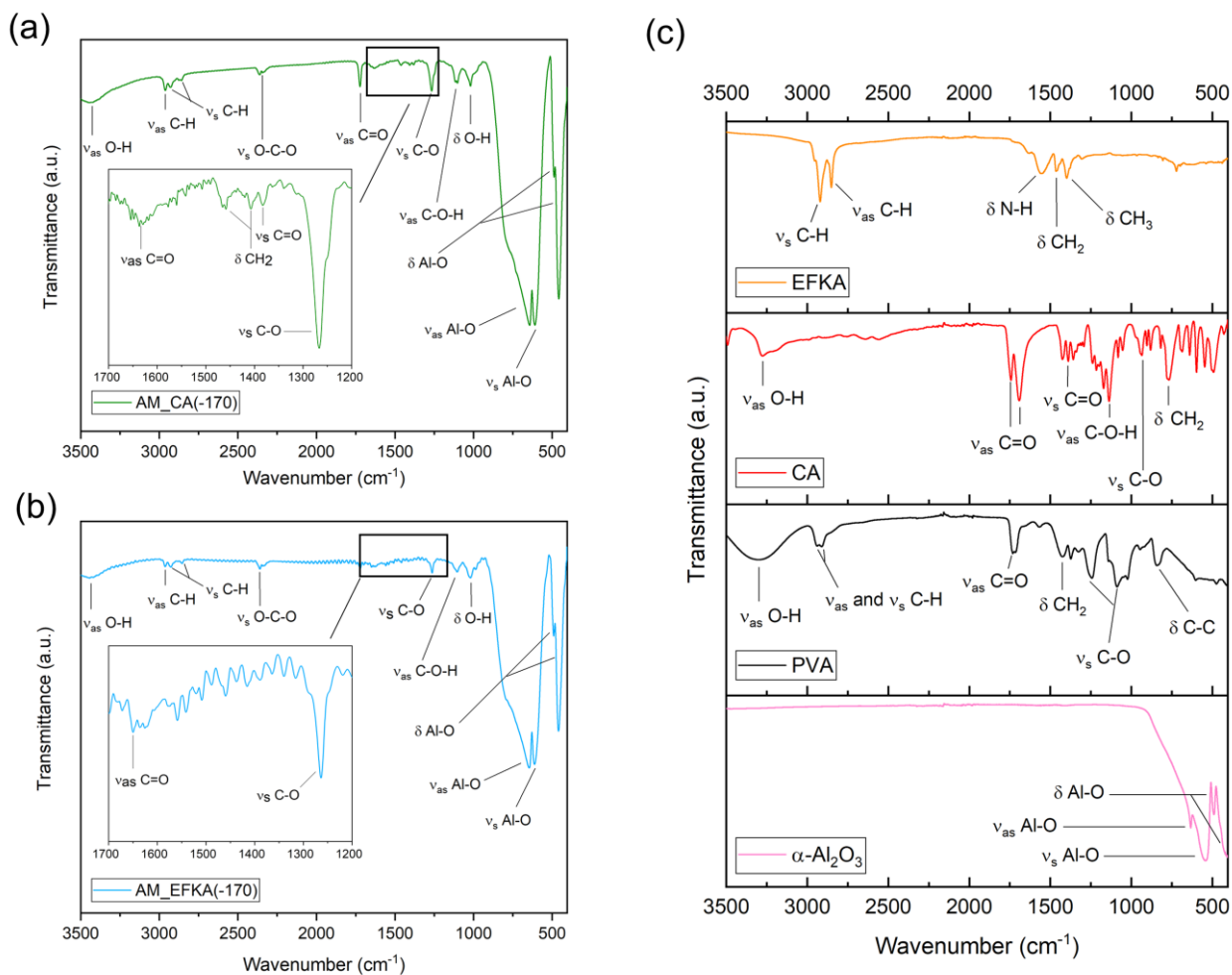


Figure 25. Infrared spectra for the samples (a) AM_CA(-170); (b) AM_EFKA(-170); (c) standards of α -Al₂O₃, PVA, CA and EFKA. Product of the thesis published and adapted from the reference [75].

As observed in Figures 25a and 25b, the spectra of the lyophilized samples showed similar behavior with respect to the presented bands, regardless of the type of dispersant and the temperature at which the suspensions were frozen (Figure 25, A1 and A2). This similar behavior is mainly due to the presence of α -Al₂O₃ particles, since this substance is the most abundant in the analyzed samples. The characteristic bands of the α -Al₂O₃ structure (Figure 25c) present in these spectra are in the transmittance regions around 638, 560, 426 and 496 cm⁻¹ represent the symmetric and asymmetric stretching and bending vibrations of Al-O from the octahedral AlO₆ species [60, 61, 137]. These bands highlight the presence of the α -Al₂O₃ structure in the monoliths after the freezing and TBA solvent sublimation process.

In the case of the lyophilized monolith spectra for AM_CA (Figures 25a, A1a and A2a), the carboxylate ions (R-COO⁻) in the structure also exhibited shifts in the characteristic bands of this group. A change was observed from 1695 to 1633 cm⁻¹,

suggesting possible complexation of the α -Al₂O₃ particles by these ions [138–140]. This interaction may result in an increase in the reduced mass of the atom bonded to the ion, in the mathematical relationship of a harmonic oscillator representing a chemical bond, altering its vibration frequency and leading to a decrease in the wavenumber [138]. In addition, the AM_CA monoliths exhibited characteristic bands at 2861, 1726, 1382 and 1112 cm⁻¹ corresponding to the contribution of the symmetric stretching of the CH₂ group and the asymmetric stretching of the C=O and C-OH bonds of the carboxylic group, respectively [138–140]. The remaining bands (Figure 25a) are associated with the presence of the PVA ligand at 2967, 2930 and 1410 cm⁻¹, indicating the asymmetric and symmetric stretching and bending, respectively, of the CH₂ group. Furthermore, the bands at 1264 and 1020 cm⁻¹ correspond to the C-O stretching and O-H bending vibrations. The band at 3426 cm⁻¹, possibly corresponds to the overlap of the O-H stretching bands from the PVA ligand at 3298 cm⁻¹ (Figure 25c) and the O-H stretching band of the carboxyl group from the CA dispersant at 3282 cm⁻¹ [141, 142].

In the case of the lyophilized monolith spectra for AM_EFKA (Figures 25b, A1b and A2b), the characteristic bands of the EFKA compound (Figure 25c) at 2919 and 2824 cm⁻¹, corresponding to the symmetric and asymmetric C-H stretching and the bands at 1556, 1457 and 1402 cm⁻¹ corresponding to N-H bending, CH₂ bending and CH₃ bending, were not clearly observed in the lyophilized ceramic samples. The bands at 3444, 2854 and 1101 cm⁻¹ are possibly derived from the polycarboxylic group of the molecule, but they may also include contributions from the vibrational modes of the PVA molecule (Figure 25c) [138, 141, 142].

In the spectra, the increase in the shoulder intensity in the 1000 to 600 cm⁻¹ region (Figures 25a,b) may be associated with the contributions of the bands at around 762 cm⁻¹, corresponding to the CH₂ rocking and at 829 cm⁻¹, related to the symmetric stretching of the C-C bond, from the CA and PVA compounds (Figure 25c), which were overlapped by the characteristic bands of α -Al₂O₃ [61, 140–142]. The bands around 2356 cm⁻¹ in the spectra may be associated with the symmetric stretching of atmospheric CO₂, which may have been adsorbed on the sample surfaces during analysis [138].

The infrared analysis indicated the contributions of the interactions between the dispersants and the α -Al₂O₃ particles. The results suggest that the electrostatic interaction of the CA dispersant was attributed to the interaction of carboxylic groups

with the α -Al₂O₃ particles. In the case of the EFKA dispersant, no interactions involving the carboxylic and amine groups of the structure were observed. However, given that it is a polyelectrolyte dispersant [135, 136], it is reasonable to assume that the stabilization of the dispersion involves a significant contribution through steric effect.

4.1.2. Microstructure of the Monoliths

Based on the different types of dispersants used, CA and EFKA, the influence of this change on the formation process of the final structure of the ceramic monoliths was investigated. This investigation was motivated by the fact that structural modifications are typically expected when manipulating parameters such as the solid loading ratio used in the freeze-casting process or when adjusting variables related to the sintering time and temperature of the samples [56, 57]. However, as discussed in the study by Lasalle et al. [143], which examined particle interactions during the freezing of α -Al₂O₃ suspensions using water as the solvent and various types of dispersants, changes in the nature of the dispersion can influence the redistribution of α -Al₂O₃ particles in the frozen suspension. This, in turn, may affect the green body density, the sample obtained after the solvent sublimation step, and contribute to changes during the sintering stage of the ceramic materials. In this regard, the surface tension of the TBA solvent plays an important role in the relative proportion of macropores, which are generated by pure TBA crystals, and micropores, which are formed by the concentrated particle regions between the pure TBA crystals (interparticle spaces) [143–145].

In this context, and based on the SEM images, it was possible to quantify the grain size distribution found in the ceramic samples produced, as shown in Figure 26.

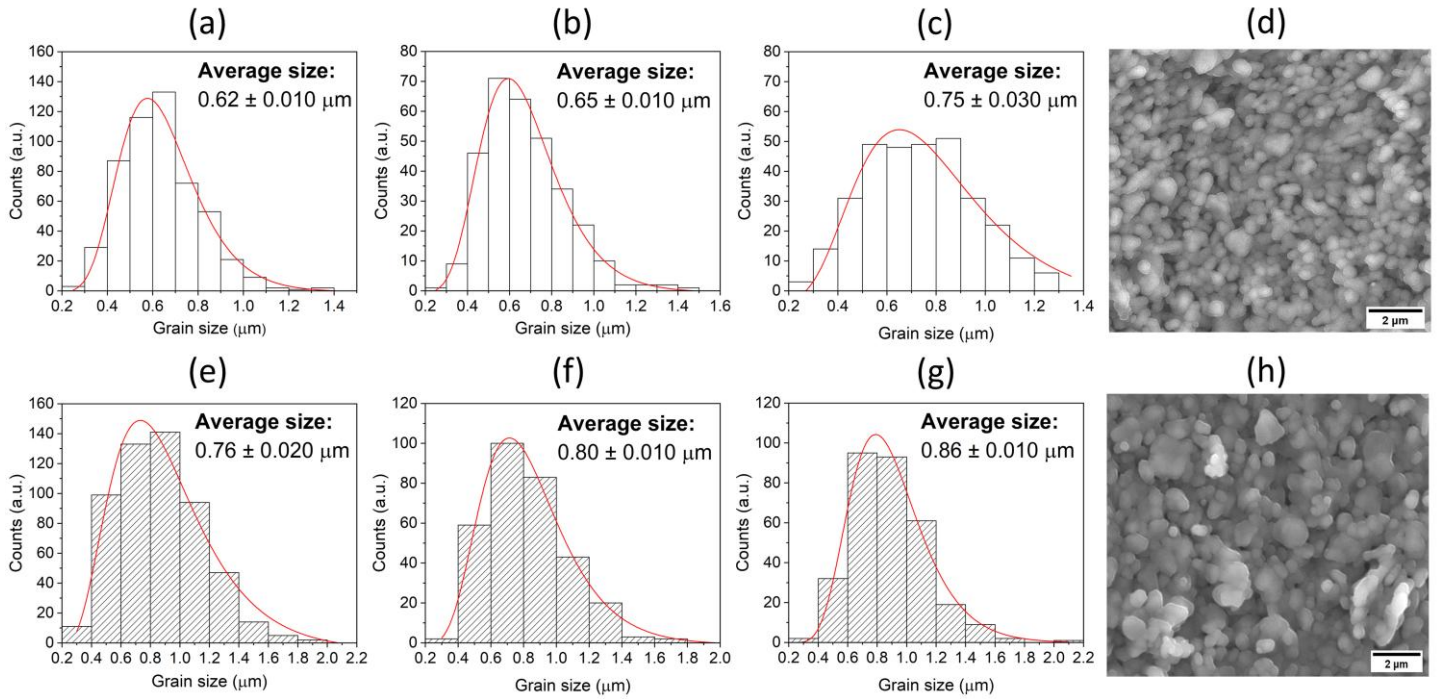


Figure 26. Grain size distributions for the different ceramic samples: (a) AM_CA(-170), (b) AM_CA(-150), (c) AM_CA(-130), (e) AM_EFKA(-170), (f) AM_EFKA(-150) and (g) AM_EFKA(-130). Micrographs of the cross-section at the center of the monoliths from samples (d) AM_CA and (h) AM_EFKA. Product of the thesis, published and adapted from reference [75].

The average grain size values, as shown in Figure 26, exhibited a relative increase between 14.7% and 23.1% in the AM_EFKA samples compared to the AM_CA samples, regardless of the freezing temperature used. This trend can be attributed to the fact that, according to the infrared analysis, the interaction of the CA dispersant was primarily mediated by electrostatic interactions between the carboxylic groups and the $\alpha\text{-Al}_2\text{O}_3$ particles. In contrast, the interaction of the polyelectrolyte dispersant EFKA with the $\alpha\text{-Al}_2\text{O}_3$ particles may involve dispersion through steric effects. These different natures of interaction likely altered the distribution of $\alpha\text{-Al}_2\text{O}_3$ particles during the freezing of the suspension, slightly modifying the green body density, which resulted in a slight change in the curvature of the solid/solid and solid/vapor interfaces during the diffusion process in the sintering stage [53, 144, 145].

Another important point to highlight in this grain size analysis is the influence of the variation in the freezing front velocity, which proved capable of causing a slight change in grain size, as shown in Figure 26. It was observed that, with the increase in temperature from -170°C to -130°C , both AM_CA and AM_EFKA

samples exhibited a relative increase in grain size of 21% and 13.2%, respectively. This behavior can be attributed to changes in the growth kinetics of TBA crystals as the solidification front velocity is altered [143, 146, 147]. Such variation in solidification velocity can affect parameters such as the surface tension and osmotic pressure of the solvent, potentially leading to changes in the green body density by altering the proportions of macropores and micropores. These changes, in turn, influence the grain growth and densification processes that occur during the sintering stage of the materials [53, 72, 144, 145].

The microscopy technique also enabled the visualization of the pore morphology of the materials, as shown in Figure 27 for the AM_CA and AM_EFKA samples at different freezing temperatures. Regardless of the dispersant used in the preparation of the freeze-casting suspensions, the pore morphology of the materials exhibited a prismatic type, with unidirectional pore growth. This morphology is characteristic of the use of TBA as the solvent in unidirectional freeze-casting processes [58, 78, 80, 81, 148, 149].

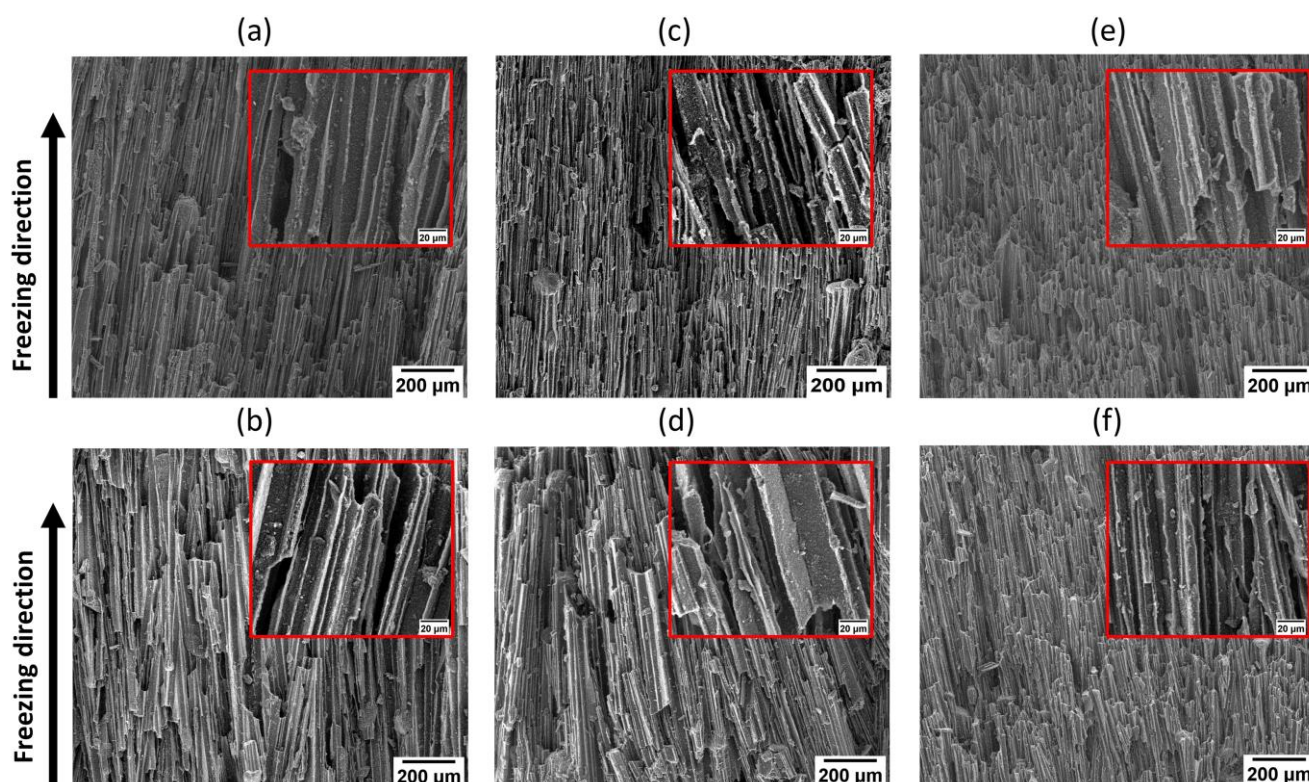


Figure 27. Cross-sectional micrographs of the monolith centers, parallel to the freezing front, at different magnifications (100x and 1000x – red square) for the samples: (a) AM_CA(-170), (b) AM_EFKA(-170), (c) AM_CA(-150), (d) AM_EFKA(-150), (e) AM_CA(-130) and (f) AM_EFKA(-130). Product of the thesis, published and adapted from the reference [75].

During the freezing stage of the freeze-casting process, the suspension, when poured into the mold in direct contact with the cooled copper surface, initiates the solidification process. This phenomenon is triggered by the advancement of the freezing front, enabling the growth of pore channels perpendicular to the freezing direction [57, 58, 72]. Such growth is caused by the crystallization of TBA into six-membered rings, promoting the formation of hexagonal layer packing (Figure 28) [58]. Under unidirectional freezing conditions, this structure facilitates the growth of aligned pore channels in the materials.

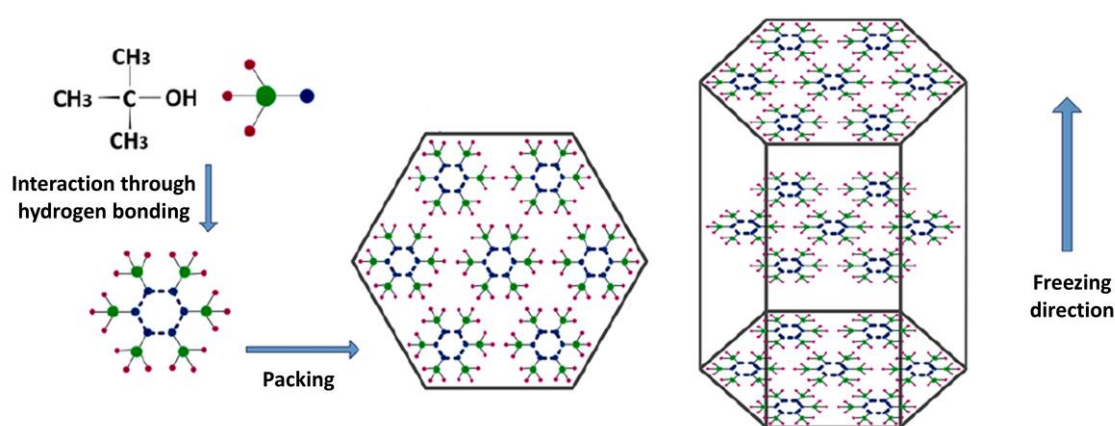


Figure 28. Illustrative scheme of the crystallization of TBA molecules in the freeze-casting process. Adapted from the reference [58].

However, even with the suspension subjected to a controlled freezing rate, due to the thermal inertia of the newly solidified layer (at the base of the mold), the velocity of the solid–liquid interface decreases as it moves away from the cooling surface [72]. Therefore, the organization of the sample morphology obtained by freezing is modified along the cooling direction, since TBA crystals can grow both perpendicular to the temperature gradient (freezing front) and in the direction of interfacial energies. Given that these directions differ, the crystals may exhibit a slight angle in their growth direction at higher freezing front velocities [72, 121, 145]. This phenomenon is consistent with the improved pore alignment observed for the two dispersants when the freezing temperature was changed from $-170\text{ }^{\circ}\text{C}$ para $-130\text{ }^{\circ}\text{C}$ (Figure 27).

Another aspect observed, still regarding pore morphology, is that the variation in freezing temperature during the freeze-casting process resulted in different pore

wall thicknesses in the materials. These results are shown in Figure 29 and Table 5, which present the average pore wall thickness distribution and the density of the AM_CA and AM_EFKA materials at temperatures of -170 and -130 °C (the pore wall thickness distribution graphs are found in Figure A3, in Appendix A).

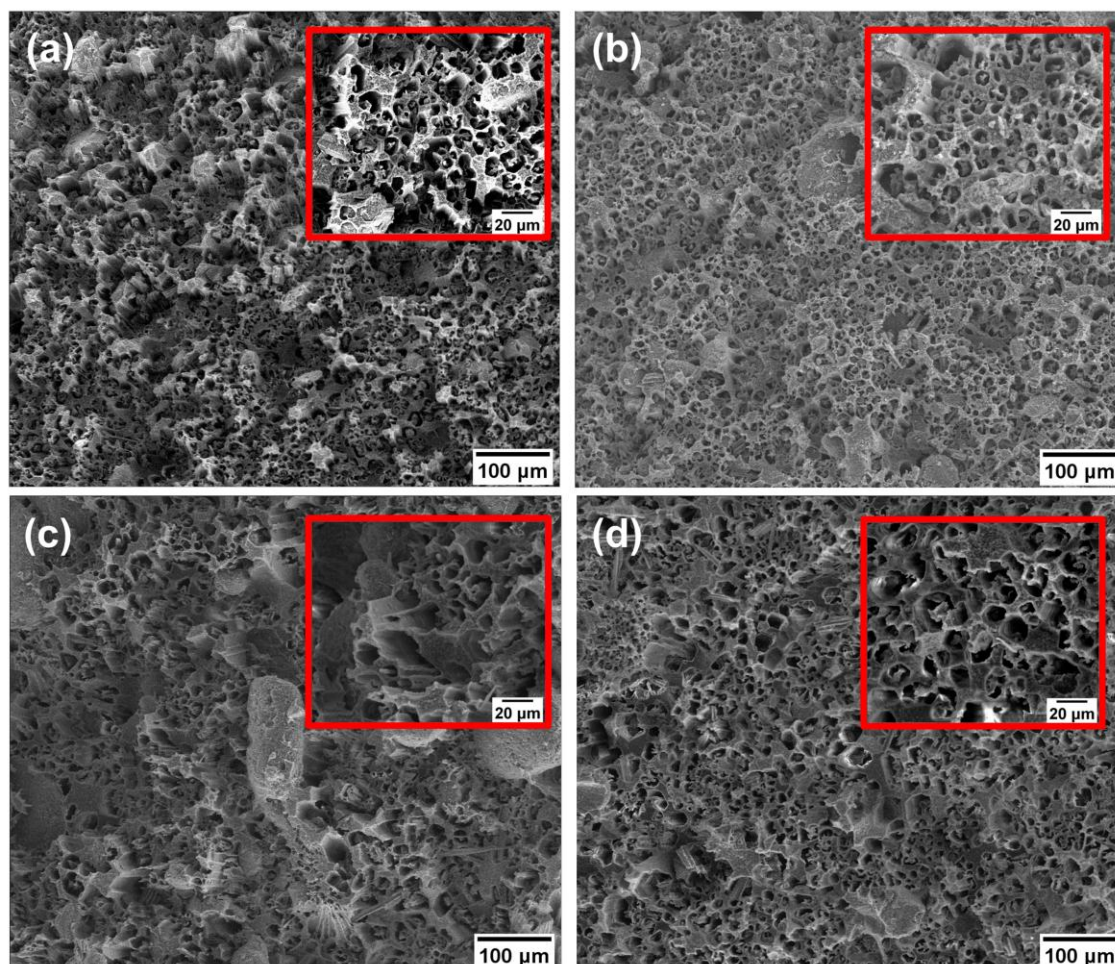


Figure 29. Cross-sectional micrographs perpendicular to the freezing front at the center of the monoliths, with magnifications of 200x and 1000x (red square): (a) AM_CA(-170) and (c) AM_EFKA(-170); (b) AM_CA(-130) and (d) AM_EFKA(-130). Product of the thesis, published and adapted from the reference [75].

Table 5. Density and average pore wall thickness of the monoliths. Product of the thesis, published and adapted from the reference [75].

Samples	Density (g·cm ⁻¹)	Average pore wall thickness (μm)
AM_CA(-170)	3.87 ± 0.06	3.15 ± 0.10
AM_EFKA(-170)	3.74 ± 0.09	3.44 ± 0.10
AM_CA(-130)	3.98 ± 0.16	3.67 ± 0.10
AM_EFKA (-130)	3.85 ± 0.07	4.63 ± 0.15

As evidenced in Table 5, despite the assumed change in the green body density obtained after the solvent sublimation step, the density of the materials did not show considerable variation ($> 4\%$) with changes in temperature and dispersant type, indicating that the produced monoliths exhibit densities close to that of the $\alpha\text{-Al}_2\text{O}_3$ raw material used. However, as observed in the study by Sun et al. [58], who fabricated $\alpha\text{-Al}_2\text{O}_3/\text{TiO}_2$ samples using TBA as the solvent and varied the freezing temperature between $-10\text{ }^\circ\text{C}$ and $-90\text{ }^\circ\text{C}$, as the freezing temperature decreased, the resulting samples exhibited reductions in both pore wall thickness and pore size, without significant changes in their final densities.

This same behavior regarding pore wall thickness and real density was observed in the $\alpha\text{-Al}_2\text{O}_3$ monoliths produced in this study when the freezing temperature varied from $-130\text{ }^\circ\text{C}$ (Figures 29b,d) to $-170\text{ }^\circ\text{C}$ (Figures 29a,c). The variation in freezing front velocity resulted in a more organized prismatic pore morphology and thickening of the pore walls at $-130\text{ }^\circ\text{C}$ (Figures 29b,d), with a relative increase of 16.5% for the AM_CA samples and 34.6% for the AM_EFKA samples. On the other hand, for monoliths produced at $-170\text{ }^\circ\text{C}$, the higher freezing front velocity likely prevented adequate growth of the TBA crystals in the suspension [58, 78], leading to the formation of small agglomerates of $\alpha\text{-Al}_2\text{O}_3$ within the structure and hindering the formation of a proper pore morphology (Figures 29a,c).

To complement the results presented by the micrographs and to elucidate parameters such as pore size distribution, pore interconnection and total porosity in the different samples, 3D reconstruction images obtained through μCT were processed using the *XPoreNetworkModeling* (PNM) model in *Avizo* software (Figure 30).

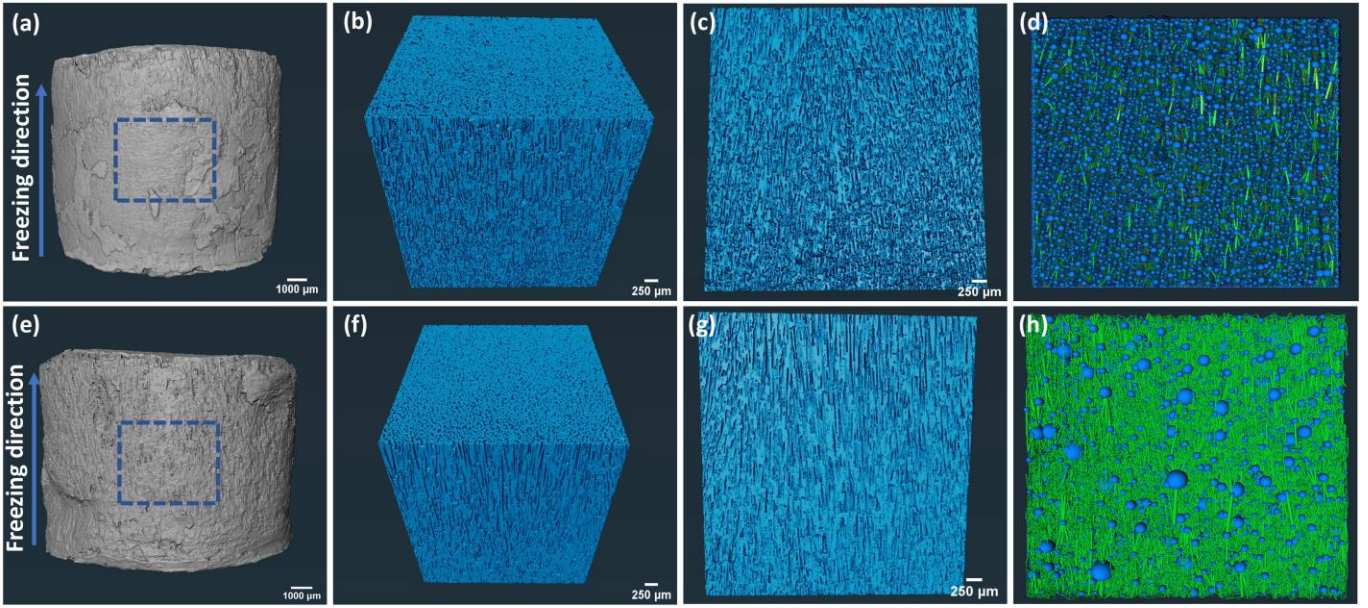


Figure 30. 3D reconstruction of the monoliths (a) AM_CA(-170) and (e) AM_EFKA(-170), with the marked region from which the subvolume was extracted. Representative central subvolume of the porosity in (b) AM_CA(-170) and (c) its frontal view; and (f) AM_EFKA(-170) and (g) its frontal view. Use of PNM on the subvolumes: (d) AM_CA(-170) and (h) AM_EFKA(-170), where the blue spheres represent the pores and the connections between them are represented by the green rods. Product of the thesis, published and adapted from reference [75].

Just like the micrographs presented in Figure 27, the reconstructions shown in Figure 30 demonstrated the unidirectional growth of porosity in the AM_CA and AM_EFKA samples. Furthermore, through the PNM model, it was observed that the AM_CA sample (Figure 30d) exhibited a uniform pore size distribution and adequate connectivity between pores, with an estimated hydraulic tortuosity in the range of 1.2 to 1.3 (where 1 indicates perfectly aligned porosity [121, 122]) and an absolute permeability of $179.7 \mu\text{m}^2$ at a freezing temperature of -170°C . On the other hand, the AM_EFKA sample (Figure 30h) showed a PNM with a variable pore size distribution but better connectivity between pores. The estimated hydraulic tortuosity for this sample was within the same range as that of the AM_CA sample, and its absolute permeability was $370.1 \mu\text{m}^2$ at the same freezing temperature of -170°C . These results are consistent with reports in the literature for ceramic matrices similar to the materials in this study, indicating an appropriate permeability range in the samples [150–152].

Although the tortuosity of the samples falls within the same range, the absolute permeability estimated by the model was doubled for the AM_EFKA sample compared to the AM_CA sample. This difference may be related to the better

connectivity observed by the PNM model in the AM_EFKA sample, suggesting a pore size distribution that allows superior fluid transport performance in this material [121, 122]. In this context, pore size distributions were obtained from the reconstructed 3D images, as shown in Figure 31a. Additionally, the total porosity (P_T) present in these samples was evaluated and compared with the open porosity (P_O) and total porosity values obtained by *Archimedes' principle*, as illustrated in Figure 31b and Table 6.

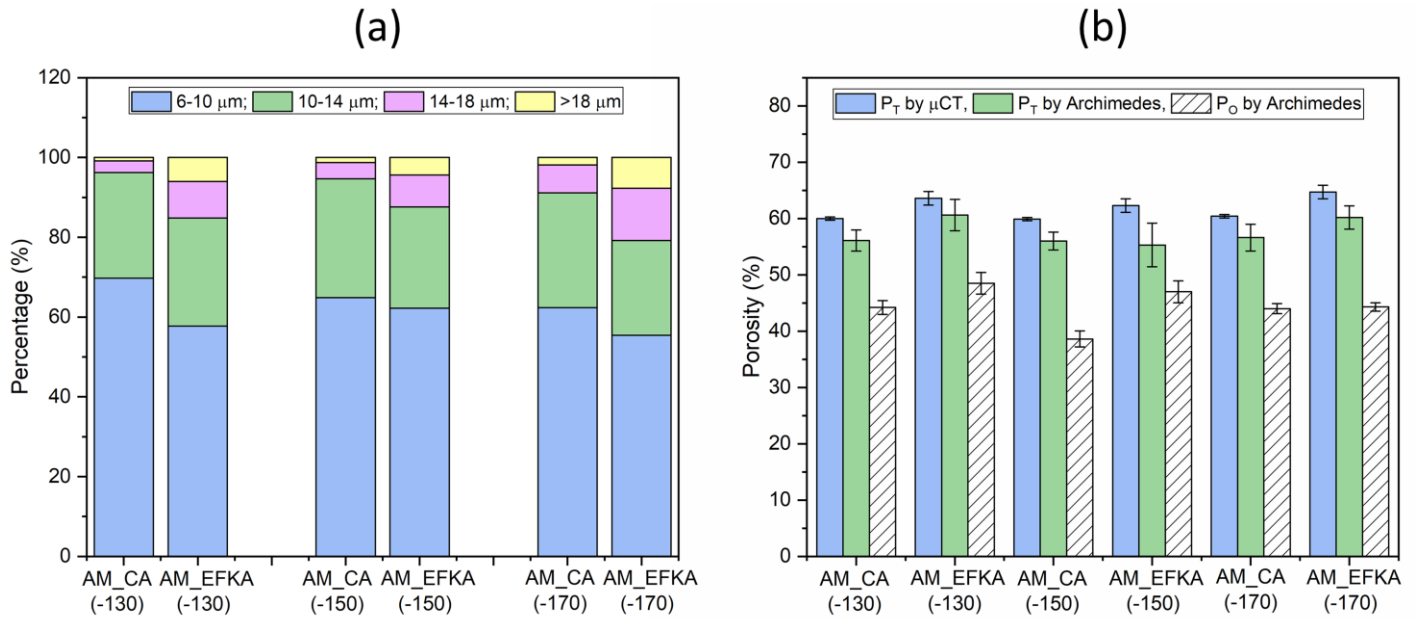


Figure 31. (a) Pore size distribution and (b) porosities of $\alpha\text{-Al}_2\text{O}_3$ monoliths. P_T represents the total porosity and P_O the open porosity of the materials. Published thesis product and adapted from the reference [75].

Table 6. Average pore size, total porosity (P_T) by μCT , total porosity and open porosity (P_O) by the *Archimedes' principle*. Published thesis product and adapted from reference [75].

Samples:	Average pore size (μm):	P_T μCT (%):	P_T Archimedes (%):	P_O Archimedes (%):
AM_CA(-170)	7.07 ± 0.06	60.4 ± 0.3	56.6 ± 2.4	44.0 ± 0.9
AM_EFKA(-170)	9.23 ± 0.05	64.7 ± 1.2	60.2 ± 2.1	44.3 ± 0.8
AM_CA(-150)	7.62 ± 0.03	59.9 ± 0.3	56.0 ± 1.6	38.6 ± 1.4
AM_EFKA(-150)	9.45 ± 0.06	62.3 ± 1.2	55.3 ± 3.9	47.0 ± 1.9
AM_CA(-130)	7.82 ± 0.02	60.0 ± 0.3	56.1 ± 1.9	44.2 ± 1.2
AM_EFKA(-130)	9.95 ± 0.03	63.6 ± 1.2	60.6 ± 2.8	48.5 ± 1.9

As illustrated in Figure 31a, regardless of the freezing temperature used, an increase was observed in the percentages of the larger pore size ranges (14 - 18 μm and $>18 \mu\text{m}$) when comparing AM_CA samples to AM_EFKA samples. The AM_CA sample showed a relative increase between 4.2% and 20.8% in the 6 - 10 μm pore size range and a relative increase between 17.4% and 21.2% in the 10 - 14 μm range compared to the AM_EFKA sample, regardless of the freezing temperature applied. On the other hand, the AM_EFKA sample exhibited a relative increase between 88.2% and 214% in the 14 - 18 μm pore size range and a relative increase of up to 306% in the $>18 \mu\text{m}$ range compared to the AM_CA sample. Similarly to the average grain size (Figure 26), the average pore size varied depending on the dispersant used (Table 6). This result suggests that changes in the chemical interaction between the dispersants and $\alpha\text{-Al}_2\text{O}_3$ particles, in the suspensions prepared during the first step of the freeze-casting process, may lead to different pore size distributions throughout the samples, thereby altering the material's permeability [121, 150, 151].

In the case of temperature variation, it was observed that the lowest average pore sizes were obtained at a freezing temperature of -170°C . This is because, as faster crystal growth is induced in the direction of the temperature gradient, lateral growth becomes increasingly limited, resulting in thinner prisms with reduced pore structure diameters [57, 58, 72, 153]. However, the change in solidification front velocity when varying the temperature from -130°C to -170°C did not indicate a significant change in the average pore size (a relative increase of 7.8% for AM_EFKA samples and 10.6% for AM_CA samples) when compared to the effect of using different dispersants at the same temperature (relative increase between 24% and 30.5%). It is believed that this change in freezing front velocity, when using the same dispersant, did not significantly affect the surface tension of the TBA solvent during the solidification stage, minimizing its impact on the green body density and the density of the final materials produced (Table 5), and consequently, on the average pore size property [144, 145].

Another parameter to be evaluated is the total porosity of the samples, as shown in Figure 31b and Table 6. It is observed that the total porosity calculated using the *Archimedes' principle* [119] was very similar to the values obtained through porosity calculations based on 3D reconstructed images, showing an average variation of 4% for AM_CA samples and 4.8% for AM_EFKA samples. The total

porosity obtained from the 3D reconstructed images reached values of up to $64.7 \pm 1.2\%$ for AM_EFKA samples and up to $60.4 \pm 0.3\%$ for AM_CA samples. In the case of porosities calculated by the Archimedes' principle, the AM_EFKA samples exhibited a total porosity of up to $60.6 \pm 2.8\%$ and an open porosity of up to $48.5 \pm 1.9\%$, while the AM_CA samples showed a total porosity of up to $56.6 \pm 2.4\%$ and an open porosity of up to $44.2 \pm 1.2\%$. These results are consistent with those reported in the literature for the exclusive use of TBA as a solvent [80, 148] and similar results have been found for mixed water/TBA samples [58, 78, 81, 149].

From Figure 31b and Table 6, it can be observed that at a temperature of $-170\text{ }^{\circ}\text{C}$ there was a relative increase of 6.36% in total porosity and 0.68% in open porosity for the AM_EFKA samples compared to the AM_CA samples. A similar behavior was observed at $-130\text{ }^{\circ}\text{C}$, with a relative increase of 8.02% in total porosity and 9.70% in open porosity for the AM_EFKA sample compared to the AM_CA sample. The change in dispersant combined with a slight variation in temperature may possibly alter the surface tension generated by the TBA solvent. It is believed that the reduction in surface tension promotes better dispersion of the $\alpha\text{-Al}_2\text{O}_3$ particles, leading to improved packing and a higher fraction of micropores in the green body, which are more easily eliminated during the densification process (sintering stage), and tend to enhance the removal of closed porosity in the material [53, 144, 145]. This argument can be supported by the slight decrease in total porosity and increase in open porosity (Table 6) for the samples produced at $-130\text{ }^{\circ}\text{C}$ with the two dispersants, features caused by the slight increase in final density shown by the materials produced at this temperature (Table 5).

4.1.3. Influence of Microstructural Properties on the Mechanical Strength of the Monoliths

One of the essential parameters for a gas separation membrane support is its ability to withstand the pressures imposed by the gas flow through the membrane. Therefore, it is crucial that the produced materials offer sufficient robustness to be effectively used in the separation process [15, 32, 34]. Figure 32 presents the results of the compressive strength test of the $\alpha\text{-Al}_2\text{O}_3$ monoliths prepared with different dispersants, in order to assess their mechanical strength.

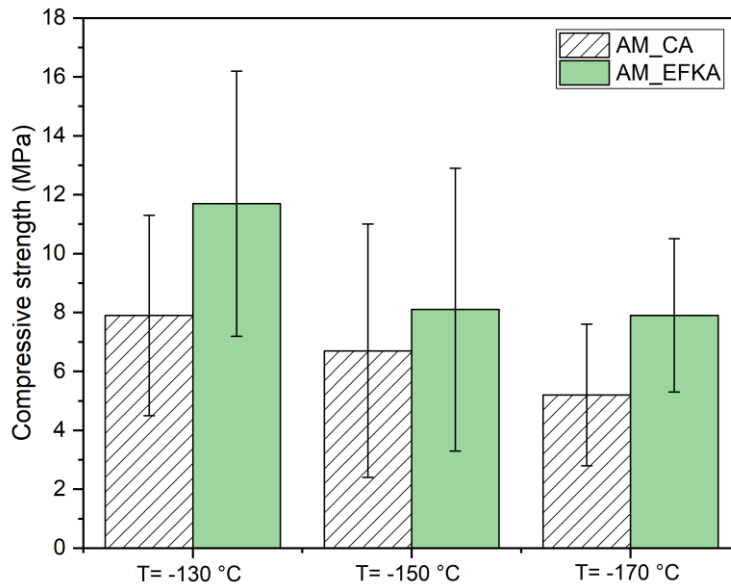


Figure 32. Compressive strength (parallel to the solidification front) of AM_CA and AM_EFKA samples at different freezing temperatures. Published thesis product and adapted from the reference [75].

When the monolith is subjected to uniaxial stress, the sizes and morphologies of the grains and pores that compose it are important factors in determining the flow and fracture resistance of the ceramic material [53]. During the freezing process, the cooling conditions dictate the growth characteristics of TBA crystals and, consequently, the final porosity of the materials [56, 57]. The results shown in Figure 32 revealed that the AM_EFKA monoliths exhibited higher strength compared to the AM_CA monoliths, with a relative increase of 51.9% for the samples obtained at -170 °C and 48.1% for those obtained at -130 °C. This behavior contrasts with the general trend reported in the literature, where, for a given porosity, finer pores are typically associated with thinner structures that are able to withstand higher mechanical stresses [57, 72]. Although the AM_EFKA samples display a larger average pore size (as shown in Table 6) and more pronounced pore connectivity compared to the AM_CA samples (as evidenced in Figure 30), it is believed that the steric effect, provided by the EFKA dispersant contributed to the thickening of the α -Al₂O₃ walls (as indicated in Figure 29 and Table 5) in these samples. This thickening enabled the materials to exhibit higher compressive strength, due to the symmetry of the hexagonal pores resulting from TBA crystallization. In this way, the produced materials possess a specific internal architecture that allows the necks, formed by the densification of α -Al₂O₃ grains during the sintering stage, to be

uniformly located between the pores, thereby distributing the load across the material (Figure 33), improving the strength of the monoliths and preventing premature structural collapse [57, 58, 78, 80].

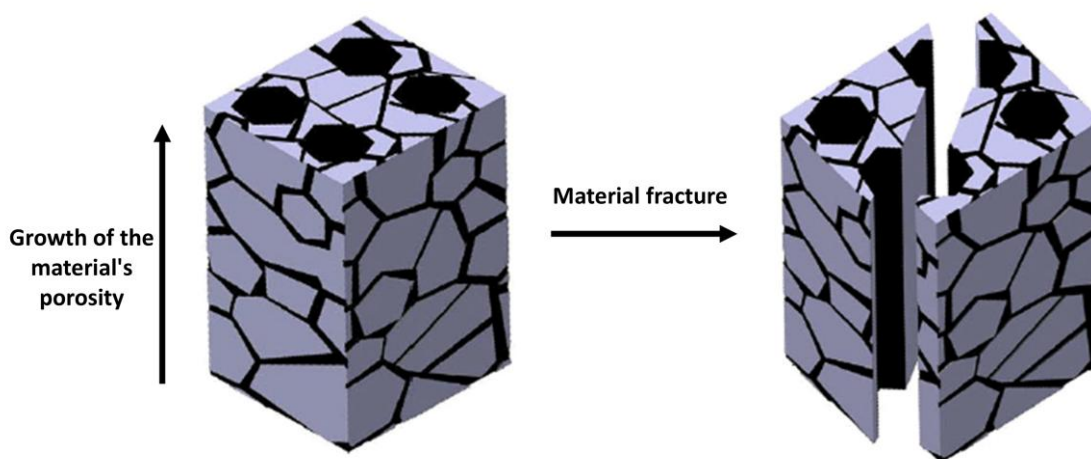


Figure 33. Illustrative diagram of the fracture of a ceramic material produced with TBA solvent by the freeze-casting process. Adapted from the reference [58].

Therefore, the compressive strength obtained in the studied samples falls within the range reported in the literature for materials that use only TBA as a solvent [80, 148], and is consistent with the pore morphology geometry of the produced materials [56–58, 78, 81, 149].

The discussions developed in section 4.1. revealed that the difference in dispersion provided by the CA and EFKA dispersants had a direct impact on the physical properties of the produced materials [75]. The dispersion via electrostatic interaction promoted by the CA dispersant contributed to improved densification of the monoliths, resulting in materials with smaller pore sizes compared to the monoliths produced with EFKA. On the other hand, the dispersion achieved through steric effect, provided by the EFKA dispersant, allowed for the formation of larger pores, leading to a slight increase in open porosity and a permeability twice as high as that of the AM_CA samples. Furthermore, the EFKA dispersant contributed to the thickening of the pore walls, providing greater strength to the materials.

4.1.4. Tubular ceramic samples

In applications as supports for gas separation membranes, the tubular shape of ceramic components offers a more efficient distribution of gas flow, as well as a larger surface area for the permeation of the mixture to be separated, compared to flat geometries such as monoliths. This shape also facilitates integration into commercial membrane modules, favoring the industrial scale-up of the process [15, 84].

Based on preliminary studies conducted on simplified ceramic components (monoliths), it was possible to evaluate the influence of different dispersants on the microstructural properties of the samples. Although the monoliths prepared with the polyelectrolyte dispersant EFKA at -130 °C showed promising characteristics for gas separation applications, the high viscosity of the resulting slurry prevented its use in the freeze-casting process with tubular geometries. Therefore, the samples produced with the CA dispersant at -130 °C were selected as the most suitable condition. These conditions also showed promising results for use as ceramic supports in gas permeation membranes. Among the temperatures evaluated, -130 °C favored a more efficient formation of the prismatic structure in the materials, resulting in a compressive strength of 7.9 MPa, significantly higher than the range typically required for gas permeation tests reported in the literature, which operates under pressures of 0.2 to 0.3 MPa [20, 21, 23].

In this context, Figure 34 presents SEM images and the grain size distribution of the tubular α -Al₂O₃ sample (FCT).

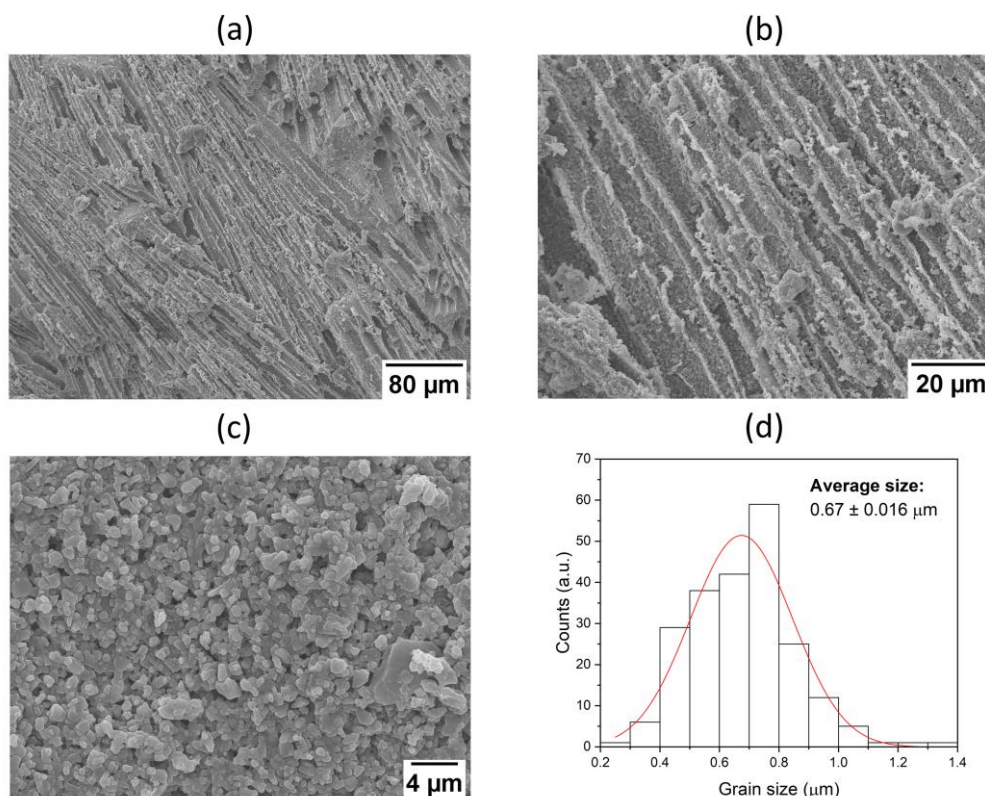


Figure 34. Cross-sectional micrographs of the ceramic tube (FCT) at different magnifications: (a) 250x, (b) 1000x, (c) 3500x and (d) grain size distribution.

As shown in Figures 34a and 34b, the pore morphology is determined by the crystalline structure of the solvent. Thus, the prismatic shape of the pores obtained in the tubes remained characteristic of the use of TBA as a solvent [58, 78, 80, 81, 148, 149]. However, due to the use of a copper mold, which exhibits a thermal conductivity of approximately $400 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, significantly higher than that of the polyamide mold ($0.23 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$), a radial solidification front of the prismatic pores was observed. This front promoted the growth of prismatic pores oriented perpendicular to the mold surface [58, 74, 76], with the TBA crystal growth direction occurring from the outer to the inner surface of the tube. The radial freezing front, however, promoted small junctions or bridges between the prismatic pores (Figure 34a).

These structural connections may have influenced the variation in porosity observed experimentally. As shown in Table 7, the total and open porosity values, obtained using the *Archimedes' principle*-based technique, were similar for the FCT and AM_CA(-130) samples. A similar behavior for total porosity (P_T) was reported

by Faria et al. [74], who produced alumina monoliths using camphene as a solvent and different molds (technyl, copper and technyl/copper).

Table 7. Total porosity (P_T) and open porosity (P_O) by the Archimedes' principle from sample FCT.

Samples:	P_T Archimedes (%):	P_O Archimedes (%):
FCT	58.6 ± 0.6	48.0 ± 0.6

Although a decrease in open porosity (P_O) was expected due to the higher efficiency of the freezing front in the metallic mold, an 8.6% increase in this property was actually observed for the FCT sample compared to the AM_CA(-130) sample ($44.2 \pm 1.2 \mu\text{m}$). This result suggests that the radial solidification induced by the copper mold can modify pore connectivity through the formation of junctions between prismatic pores, which may enhance the interconnection of the porous network and, consequently, increase open porosity. In parallel, a 10.7% reduction in the average grain size ($0.67 \pm 0.016 \mu\text{m}$, Figure 34d) was observed in comparison with the AM_CA(-130) monolith ($0.75 \pm 0.03 \mu\text{m}$). This behavior is consistent with the faster cooling rate imposed by the copper mold, which restricts grain growth during sintering [58, 74, 76, 143].

Despite the structural junctions observed in the tubes produced by freeze-casting, these samples exhibited porosity and average grain size values similar to those of the AM_CA(-130) monolith. Therefore, the tubular ceramic support will be evaluated in the subsequent stages of SSZ-13 membrane production.

4.2. SSZ-13 zeolite

In this second section of the discussion, the results obtained from the hydrothermal synthesis of the active phase to be used later in the membrane production will be presented. The aim of this study was to evaluate the influence of two different counter-ions (Na^+ and K^+) on the structure of the SSZ-13 zeolite. Additionally, the $\text{H}_2\text{O}/\text{SiO}_2$ molar ratio parameter was also later evaluated for the samples synthesized with the K^+ counter-ion in their structure.

As the final stage in the study of SSZ-13 seeds, the effect of crystallization was investigated by combining two synthesis methods, microwave-assisted and seed-assisted, for samples synthesized with the K^+ counter-ion.

4.2.1. Influence of counter-ion on the structural properties of SSZ-13 samples.

SSZ-13 zeolite is frequently produced through hydrothermal synthesis, in which the sodium counter-ion (Na^+) is commonly used along with the organic structure-directing agent N,N,N-trimethyladamantane-1-ammonium hydroxide (TMAdaOH) [154]. Studies by Iorio et al. [155, 156] have shown that the variation in the $\text{Na}^+/\text{TMAda}^+$ ratio is directly related to the number of paired aluminum (Al) sites within the six-membered rings (6-MR) characteristic of the SSZ-13 zeolite structure. However, modifying the counter-ion used can influence nucleation processes and the distribution of Al sites in the framework [154–156].

Among the counter-ions that can replace Na^+ , potassium (K^+) has shown promising properties in stabilizing pore channels during the synthesis of ZSM-5 zeolite [157] and in acting as a structure-directing agent in the synthesis of zeolite L [103]. When used together with TMAda^+ , the K^+ ion allows for the presence of only one Al site within the 6-MR structure (with a radius of 1.3 Å) of the SSZ-13 zeolite (Figure 35). This is due to the difference in ionic radius between K^+ (1.52 Å) and Na^+ (1.16 Å), which gives K^+ a greater affinity for positioning within the eight-membered rings (8-MR, radius of 1.9 Å). This positioning affects the system's energy for co-occlusion with the structure-directing agent TMAda^+ , resulting in different Al pairing configurations in the 6-MR and 8-MR units, thus influencing the stabilization of the final structure [155, 156]. It is believed that this change in Al pairing may alter the catalytic or adsorptive properties of different SSZ-13 zeolites with similar compositions, which could be advantageous for their application as the active phase in inorganic membranes for gas separation [5, 16, 19].

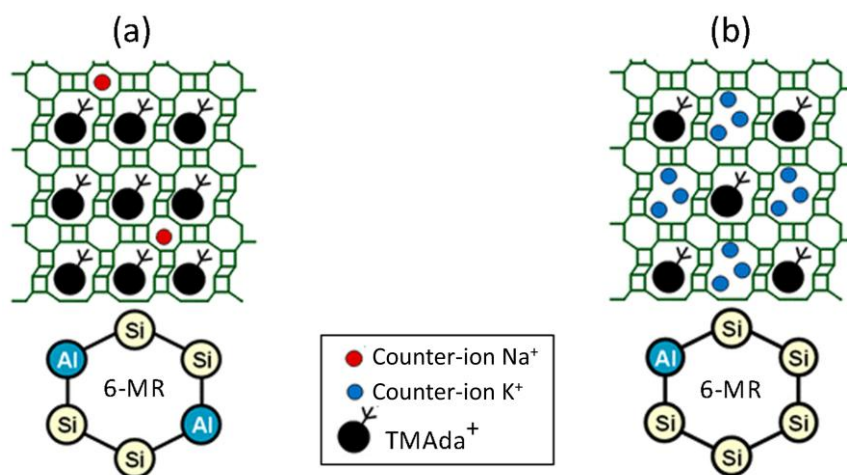


Figure 35. Arrangement of Al in the SSZ-13 structure using the counter-ion (a) Na^+ and (b) K^+ . Adapted from the reference [155].

Thus, the structural influences of using different counter-ions, Na^+ and K^+ , in the synthesis of SSZ-13 zeolite were investigated. As shown in Figure 36, the diffractograms of SSZ-13 zeolite synthesized with Na^+ and K^+ counter-ions at different synthesis times are presented.

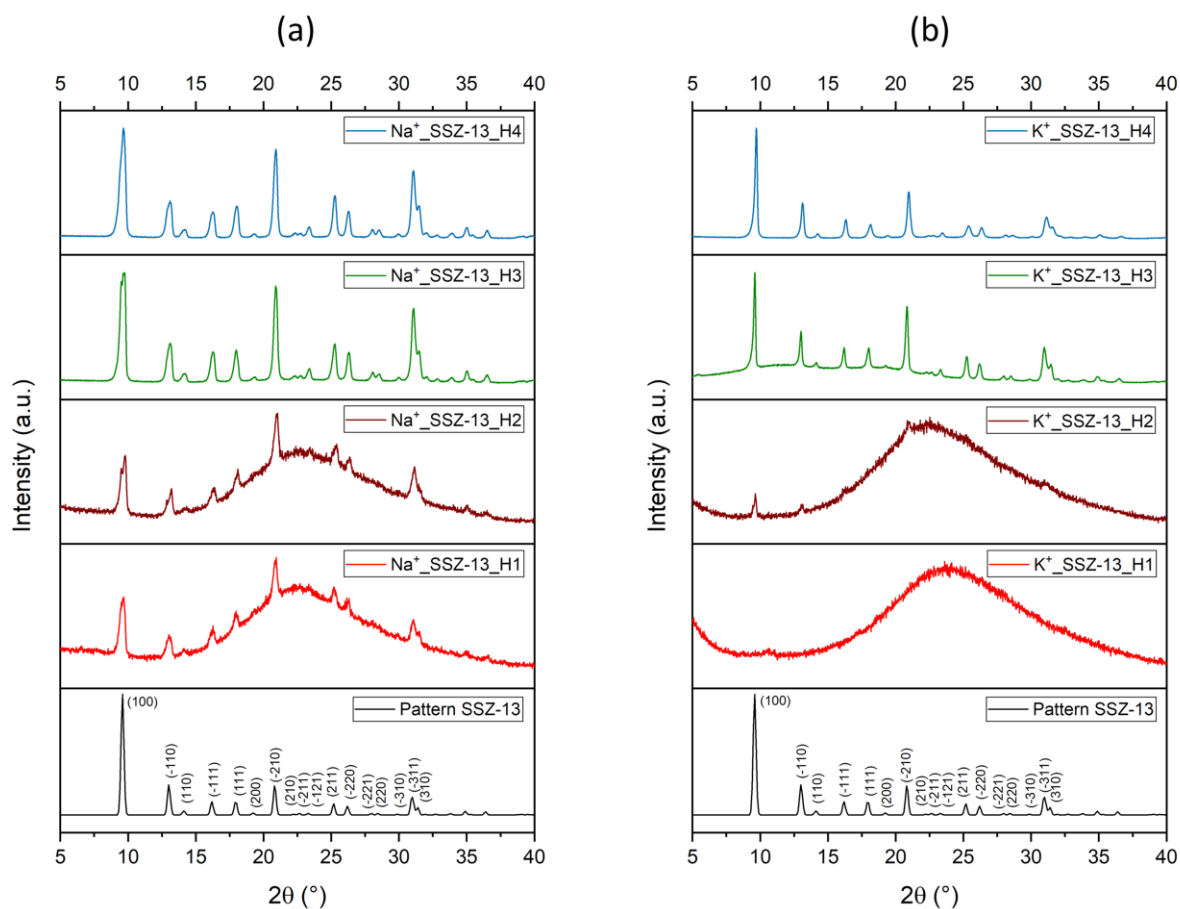


Figure 36. X-ray diffraction of samples (a) Na^+ SSZ-13 and (b) K^+ SSZ-13 at different synthesis times (H1 = 1 day; H2 = 2 days; H3 = 3 days and H4 = 4 days).

From the diffractograms, it was possible to observe that the characteristic peaks of the CHA structure of SSZ-13 (Inorganic Crystal Structure Database (ICSD) – Code#84255) [158] are present in the samples synthesized after 1 day of synthesis for the Na⁺_SSZ-13 samples and after 3 days of synthesis for the K⁺_SSZ-13 samples. These same peaks are consistent with the characteristic peaks described in the literature [21, 23, 43–45, 154, 159–161] for the SSZ-13 zeolite, approximately at $2\theta = 9.6^\circ; 13.1^\circ; 16.2^\circ; 18^\circ; 20.9^\circ; 25.3^\circ; 26.2^\circ; 31.1^\circ$, corresponding to the rhombohedral crystallographic structure of space group *R-3m* [22, 158, 162]. This result indicates that the CHA structure, typical of the SSZ-13 zeolite, was successfully produced under the conditions proposed in this study, regardless of the change in the counter-ion of the structure.

From the diffractograms, parameters such as relative crystallinity and crystallite size of the SSZ-13 samples were also obtained, as shown in Table 8.

Table 8. Relative crystallinity (%) and crystallite size for the Na⁺_SSZ-13 and K⁺_SSZ-13 samples.

Samples:	Relative crystallinity (%):	Crystallite size (nm):
Na ⁺ _SSZ-13_H1	9.94	17.60 ± 0.01
Na ⁺ _SSZ-13_H2	10.5	16.90 ± 0.02
Na ⁺ _SSZ-13_H3	60.3	17.30 ± 0.01
Na ⁺ _SSZ-13_H4	93.5	16.30 ± 0.01
K ⁺ _SSZ-13_H3	39.1	46.600 ± 0.001
K ⁺ _SSZ-13_H4	97.9	39.200 ± 0.001

The data presented in Table 8, supported by the diffractogram in Figure 36, suggests that the Na⁺_SSZ-13 samples likely underwent a faster crystallization process. However, the K⁺_SSZ-13_H4 sample exhibited slightly higher crystallinity, indicated by sharp and well-defined peaks, with a preferred growth plane at $2\theta = 9.6^\circ$, which may have contributed to the reduction of the other peaks observed in the diffractogram [124]. Furthermore, for these more crystalline samples obtained after 4 days of synthesis, the crystallite size of K⁺_SSZ-13_H4 was twice as large as that of the Na⁺ sample.

The micrographs in Figure 37, together with the data presented in Table 9, reveal the influence of the counter-ion and the number of days of crystallization on the morphology obtained.

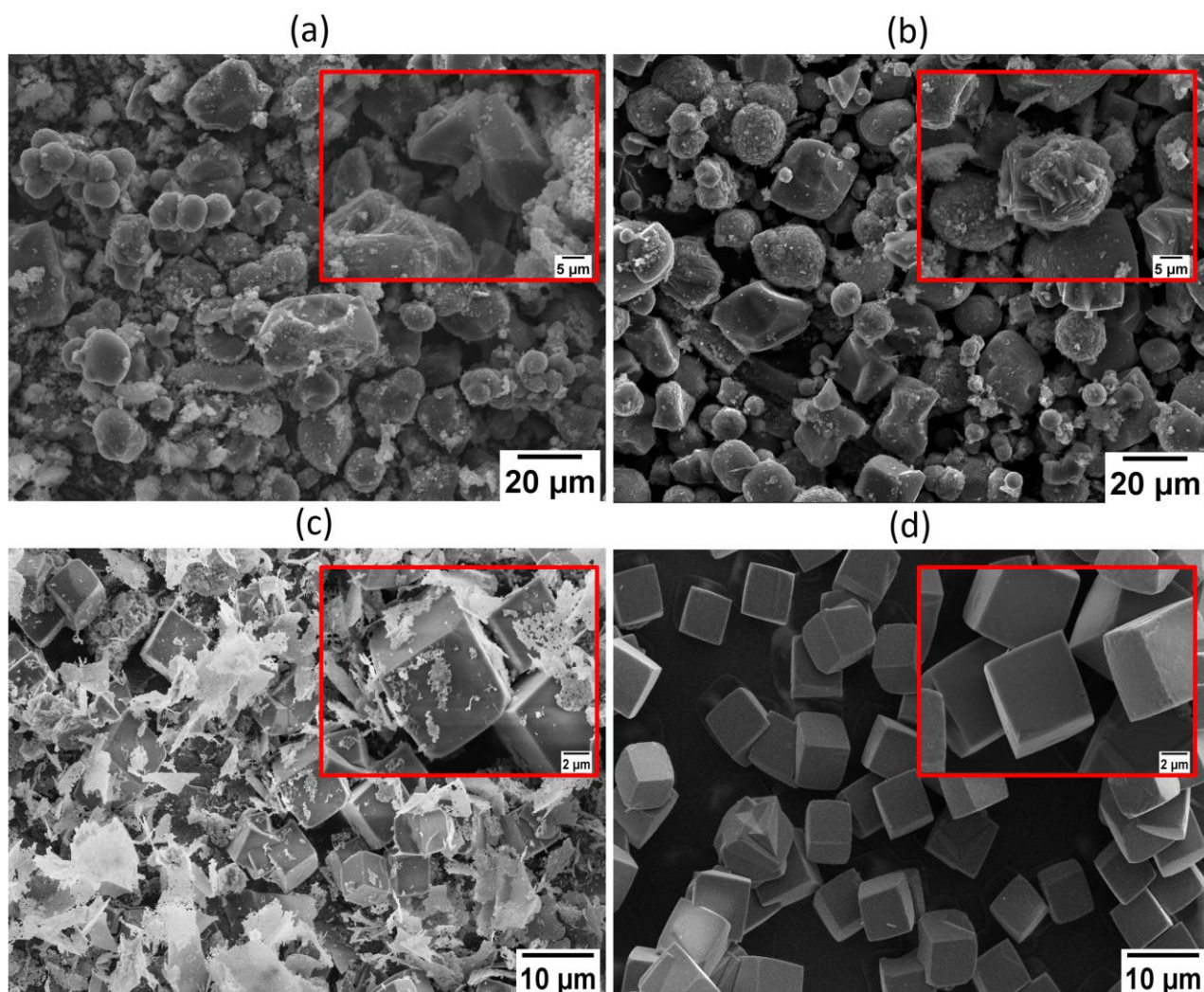


Figure 37. Micrographs of the samples: (a) Na^+ _SSZ-13_H3 and (b) Na^+ _SSZ-13_H4 at 650x magnification and 2000x zoom (red square); and samples (c) K^+ _SSZ-13_H3 and (d) K^+ _SSZ-13_H4 at 5000x magnification and 20000x zoom (red square).

Table 9. Average particle size based on the micrographs of the Na^+ _SSZ-13 and K^+ _SSZ-13 samples.

Samples:	Average particle size (μm):
Na^+ _SSZ-13_H3	15.6 ± 0.51
Na^+ _SSZ-13_H4	16.0 ± 0.97
K^+ _SSZ-13_H3	5.19 ± 0.17
K^+ _SSZ-13_H4	5.67 ± 0.07

As observed in the micrographs (Figure 37a,b), the Na⁺SSZ-13 samples synthesized over 3 and 4 days exhibited rounded (spheroidal) shapes, with some crystals showing lamellar growth and no distinct facets, as highlighted in the magnified view in Figure 37b. In contrast, the K⁺SSZ-13 samples produced over the same periods (Figure 37c,d) showed the formation of well-defined cubic crystals, which are characteristic of the SSZ-13 zeolite structure [20, 21, 44, 45, 92, 93, 98, 154, 159, 160].

As shown in Table 9, and in agreement with the diffractogram data (Figure 36), it can be inferred that the threefold increase in the average particle size of the Na⁺SSZ-13 samples compared to the particles of the K⁺SSZ-13 samples may be related to the reaction pathway induced by each counter-ion during the synthesis of SSZ-13. According to the study by Kumar et al. [104], considering that the reaction solution consists of silica, alumina, aluminosilicate molecules and amorphous precursors, there are two common crystallization pathways in the synthesis of SSZ-13 zeolite. The first involves crystal growth through the direct addition of molecules, which are soluble species generated from the amorphous precursors, following a layer-by-layer mechanism that typically results in well-defined crystals (classical pathway I in Figure 38). The second mechanism considers that the growth of nucleated SSZ-13 crystals is mediated by the attachment and subsequent rearrangement of amorphous precursors, leading to the formation of crystals with rough surfaces and irregular morphologies (non-classical pathway II in Figure 38).

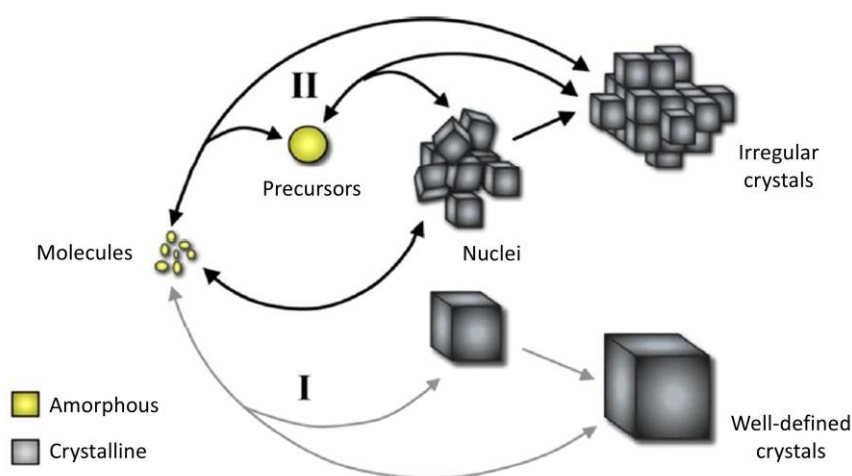


Figure 38. Illustration of the potential crystallization pathways, classical (I) and non-classical (II), of the SSZ-13 zeolite. Amorphous precursors and molecules (soluble species) highlighted in yellow represent possible growth units. Adapted from reference [104].

In this context, it is plausible to consider that the K^+ counter-ion favored the formation of the SSZ-13 crystalline structure by following the classical crystallization pathway. This crystallization process proved to be slower, as it involves the dissolution of molecules derived from the reaction precursors, as evidenced by the progression of relative crystallinity (Table 8) for the K^+ _SSZ-13 samples during the 1 to 3 days synthesis period. However, on the fourth day of synthesis, higher crystallinity was observed, resulting in smaller and well-defined particles, due to the layer-by-layer growth mechanism, in which the generated layers have thicknesses proportional to the dimensions of the crystal unit cell [92, 104].

On the other hand, it is believed that for the samples produced with the Na^+ counter-ion, the predominant crystallization mechanism was the non-classical pathway. This pathway was shown to induce faster crystallization, as indicated by the progression of relative crystallinity over short periods of 1 and 2 days (Table 8), compared to the K^+ _SSZ-13 samples for the same synthesis period. Furthermore, this crystallization pathway leads to the formation of larger particles (Table 9), characterized by crystals without distinct facets and spheroidal shapes, resulting from the direct addition of amorphous precursors during the SSZ-13 particle growth process [92, 104].

To investigate whether the different crystallization mechanisms affect the structural arrangement of the SSZ-13 zeolite, analyses were conducted using infrared spectroscopy. Figure 39 shows the infrared spectra of the Na^+ _SSZ-13 and K^+ _SSZ-13 samples at different synthesis days.

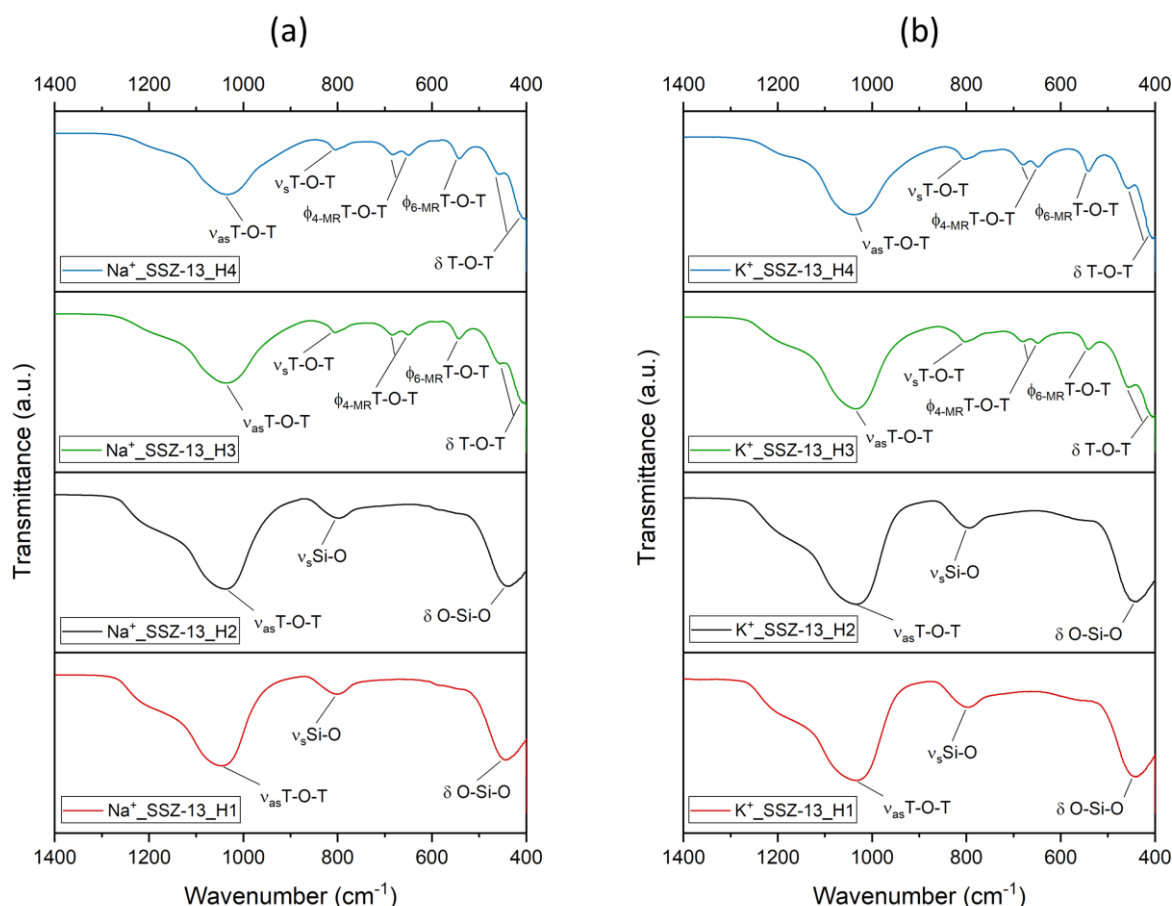


Figure 39. Infrared spectra of the samples: (a) Na⁺_SSZ-13 and (b) K⁺_SSZ-13 at different synthesis times (H1 = 1 day; H2 = 2 days; H3 = 3 days and H4 = 4 days).

Although crystallization in the samples produced with the Na⁺ counter-ion is faster, as indicated by the diffractograms (Figure 36), the characteristic bands of the SSZ-13 zeolite appear only in the samples synthesized after 3 days, as shown in the infrared spectra in Figure 39.

The spectra of the samples synthesized after 3 and 4 days, regardless of the counter-ion used, exhibit bands at approximately 1036 - 1037 cm⁻¹ corresponding to the asymmetric stretching, related to the transverse and longitudinal planes of the T-O-T bonds (T = Si or Al). In the region around 807 - 808 cm⁻¹, the bands correspond to symmetric stretching, while those at approximately 457 - 458 and 411 cm⁻¹ are associated with angular deformations (bending) of the T-O-T bonds [107, 163]. Additionally, weak intensity bands at around 684 - 687 and 650 cm⁻¹ correspond to T-O-T vibrations of the zeolite framework rings, attributed to the presence of four-membered rings (4-MR), while the band at 544 cm⁻¹ corresponds to the double six-membered rings (6-MR) characteristic of chabazite-type (CHA) structures, the zeolite family to which SSZ-13 belongs [107, 164, 165].

The absence of nearly all bands in the 1000 - 400 cm^{-1} region in the samples synthesized after 1 and 2 days, regardless of the counter-ion used, indicates a significant presence of amorphous silica in the composition of these samples. These observations are supported by the bands at 799 cm^{-1} , related to the symmetric stretching of the Si-O and at 447 cm^{-1} , corresponding to the bending of the O-Si-O bond [163].

As the infrared spectra indicated similar behavior regarding the presence of the characteristic bands of the SSZ-13 structure, MAS NMR analyses were carried out, as shown in Figures 40 and 41.

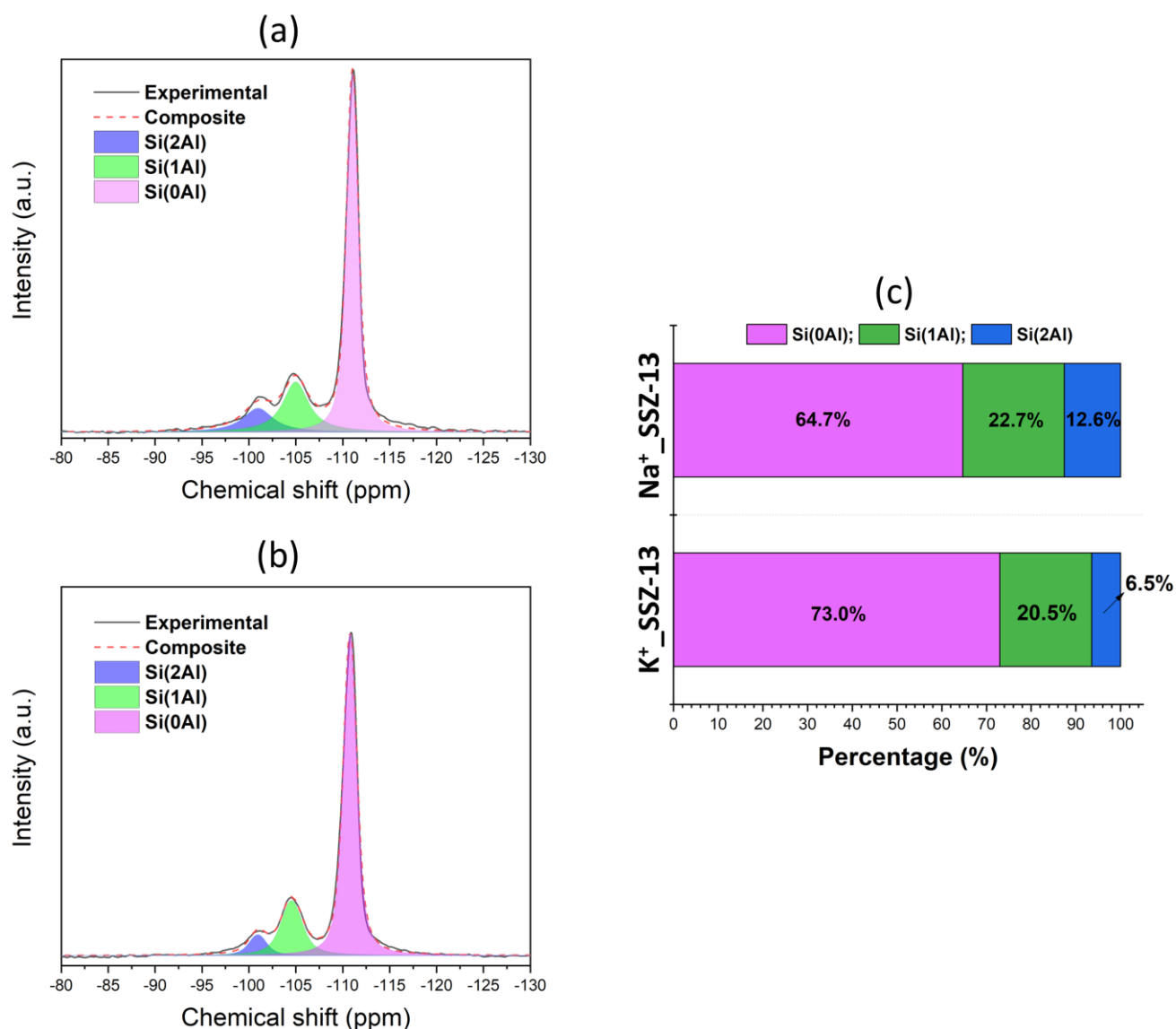


Figure 40. Deconvoluted (Composite) ^{29}Si MAS NMR spectra of the samples: (a) Na^+ SSZ-13_H4, (b) K^+ SSZ-13_H4 and (c) the molar percentages of the different silicon species present. Where Si(0Al) = $\text{Si}(\text{OSi})_4$; Si(1Al) and Si(2Al), corresponding to $\text{Q}^n\text{Si}(\text{OSi})_{4-n}(\text{OAl})_n$ species (with $n = 1$ and 2), respectively.

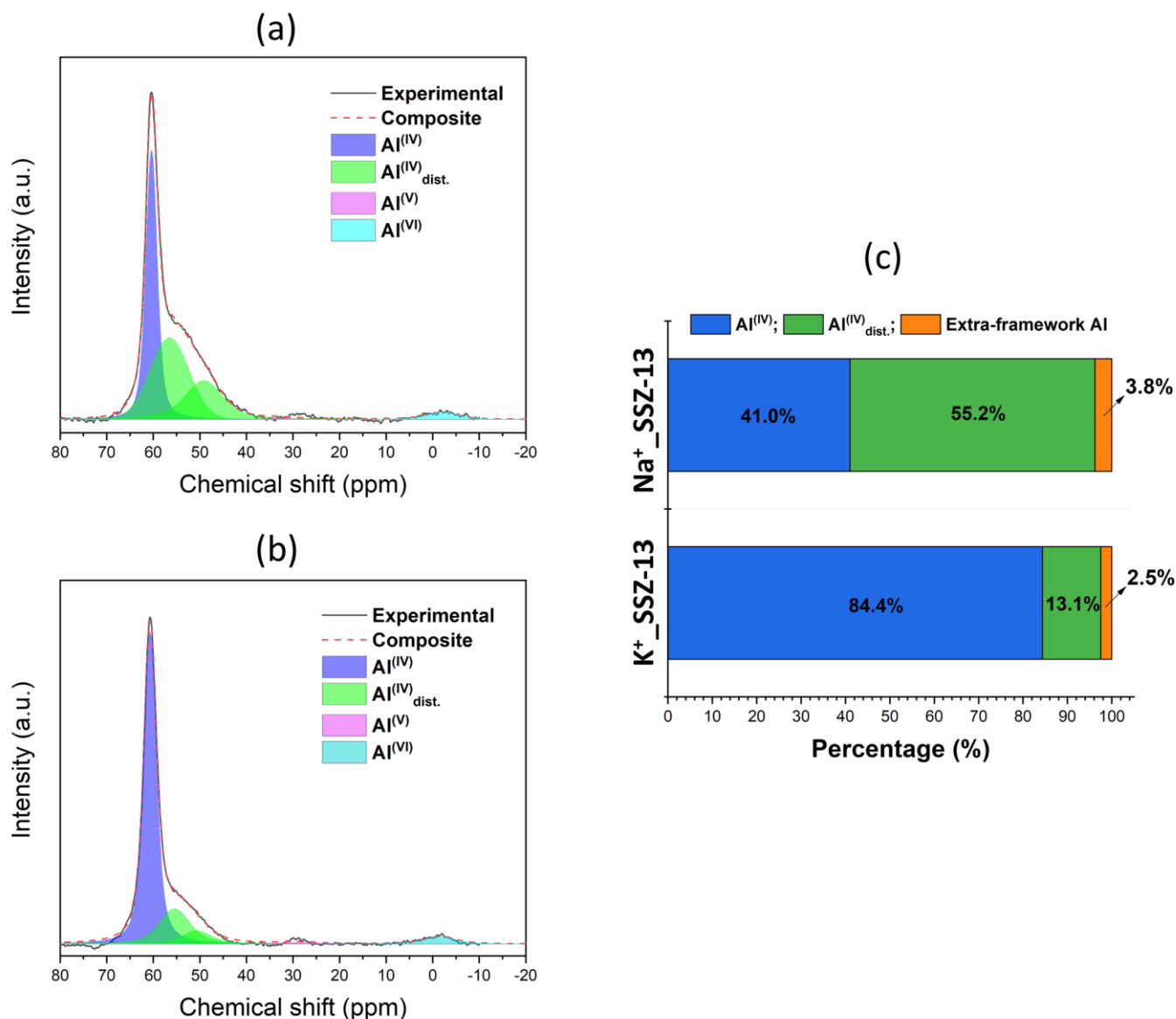


Figure 41. Deconvoluted (Composite) ^{27}Al MAS NMR spectra of the samples: (a) Na^+ _SSZ-13_H4, (b) K^+ _SSZ-13_H4 and (c) the molar percentages of the different aluminum species present. Where (Al^{IV}) is tetra-coordinated aluminum; ($\text{Al}^{\text{IV}}_{\text{dist.}}$) distorted tetrahedral aluminum species; and penta- (Al^{V}) and hexa-coordinated aluminum (Al^{VI}) corresponding to extra-framework structures.

The MAS NMR ^{29}Si and ^{27}Al nuclei of the Na^+ _SSZ-13_H4 and K^+ _SSZ-13_H4 samples were analyzed to clarify the chemical environments present in the zeolite structures, as well as to calculate the molar ratios of the $\text{Si}(n\text{Al})$ and Al^x species in these different chemical environments and, consequently, their $\text{Si}/\text{Al}_{\text{framework}}$ ratio.

The MAS NMR technique analyzes the spin transition frequency of atomic nuclei, induced by a magnetic field, which is related to the crystalline structure and conformation of a given molecule in a medium [166]. In the case of the ^{29}Si nucleus,

the chemical shift signals observed in its spectra are associated with the silicate species present in the structure. These signals represent the degree of polymerization of the SiO_4 tetrahedra, indicated by the substitution of Si atoms with other elements (Figure 42) and by the Si-O-T (T = Si or Al) [166, 167].

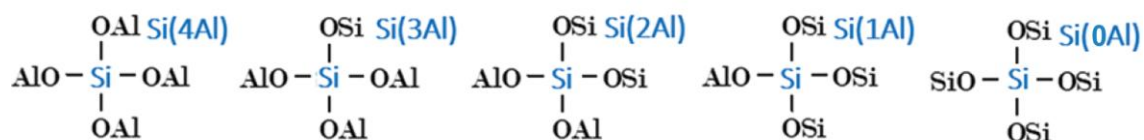


Figure 42. Different chemical environments in which tetrahedral ^{29}Si species may be found within zeolite structures. Adapted from the reference [167].

As shown in Figure 40, the chemical shift magnitude of the ^{29}Si nucleus is influenced by the number of neighboring Al atoms, serving as a parameter for elucidating the ordering of these atoms within the structure [126, 168]. The chemical shifts (δ) observed at approximately -111, -105 and -101 ppm are attributed to $\text{Si}(0\text{Al})$, associated with siloxane species ($\text{Q}^4 - \text{Si}(\text{OSi})_4$), and to $\text{Si}(1\text{Al})$ and $\text{Si}(2\text{Al})$, corresponding to $\text{Q}^n\text{Si}(\text{OSi})_{4-n}(\text{OAl})_n$ species (with $n = 1$ and 2), respectively [90, 93, 126, 169]. These signals are characteristic of the crystalline SSZ-13 structure, that form the 4-, 6-, 8- and double six-membered rings (d6r) in the CHA framework [93, 126].

The $\text{Si}(0\text{Al})$ species ($\text{Q}^4 - \text{Si}(\text{OSi})_4$) corresponds to the most intense peak in the spectrum at -111 ppm, indicating the presence of silicon tetrahedra in the structure. This species is abundant in the SSZ-13 samples produced with different counter-ions, showing a higher percentage in the K^+ _SSZ-13_H4 samples (73%) compared to the Na^+ _SSZ-13_H4 samples (64.7%). Another observed aspect was the slight increase in the proportion of $\text{Si}(1\text{Al})$ species, $\text{Q}^1\text{Si}(\text{OSi})_3(\text{OAl})$, and a significant increase in the $\text{Si}(2\text{Al})$ species, $\text{Q}^2\text{Si}(\text{OSi})_2(\text{OAl})_2$, in the Na^+ _SSZ-13_H4 sample. This phenomenon indicates, as described in the study by Iorio et al. [155, 156], that the Na^+ counter-ion preferentially promotes the conformation of two paired Al atoms within the double 6-membered rings (d6r), unlike the K^+ counter-ion, which favors the presence of only one Al atom in the same type of ring. Therefore, the significant increase of the $\text{Si}(2\text{Al})$ species in the Na^+ _SSZ-13_H4 sample is consistent with the expected SSZ-13 structures reported in the literature [93, 126, 155, 156, 169].

In this context, the study by Prasad et al. [126] analyzed the Al distribution in a Si-rich Na^+ _SSZ-13 structure (with a Si/Al ratio between 11 and 17). In that study (Figure 43), the double 6-membered ring (d6r) was considered a basic repeating unit of the chabazite structure, and therefore an ideal model for understanding Al distribution. As in the spectrum obtained in this thesis, the same characteristic peaks for the ^{29}Si nucleus were observed, indicating the possible presence of one or two paired Al atoms in the d6r structure, as shown in Figure 40. This result is consistent with the data analyzed for the Na^+ _SSZ-13_H4 and K^+ _SSZ-13_H4 structures in this work, which exhibited $\text{Si}/\text{Al}_{\text{framework}}$ ratios of 17.7 and 16.4, respectively.

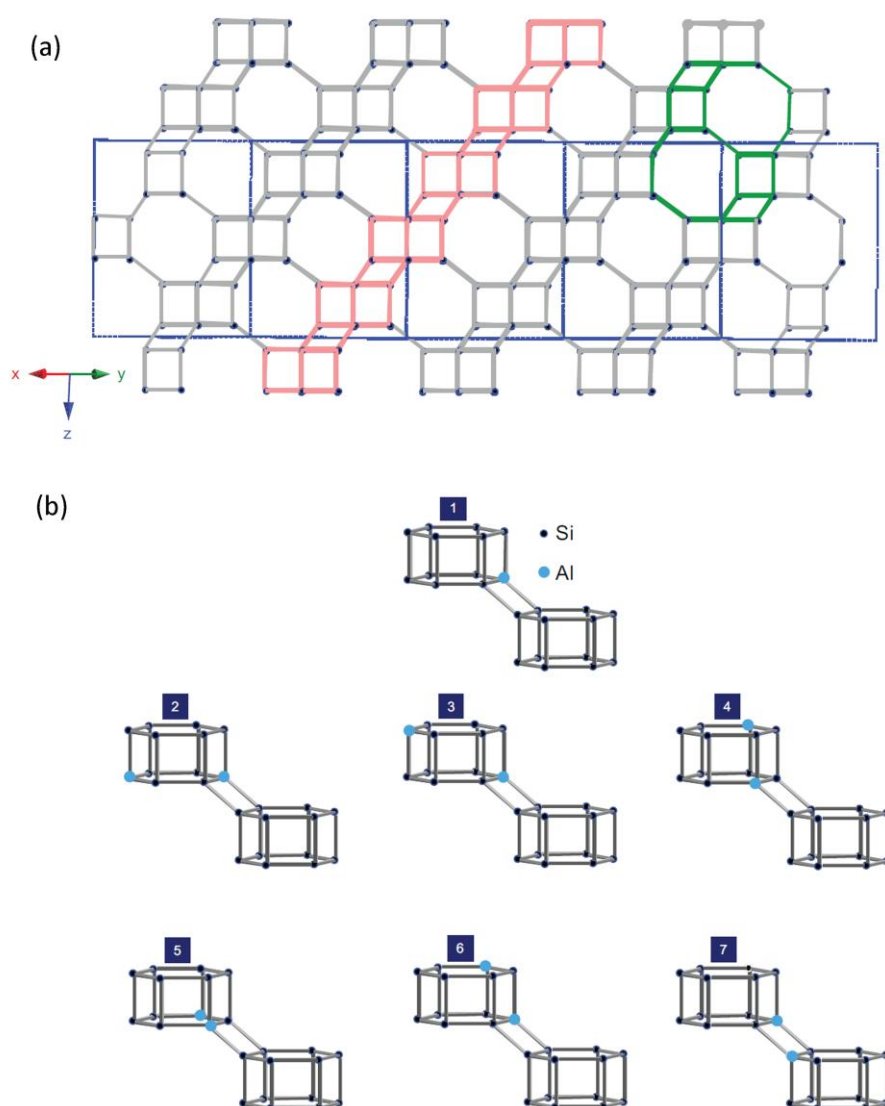


Figure 43. (a) Connectivity of the d6r units (highlighted in pink) resulting in the formation of cages with 8-MR windows and the CHA cage structure (highlighted in green). (b) Illustrative scheme of the distribution of one or two Al atoms as predicted by the model within the arrangement of the d6r double rings. Adapted from reference [126].

Based on the ^{27}Al in Figure 41, it is possible to obtain information regarding the coordination of these atoms, allowing the identification of species located within or outside the zeolite framework [90, 167, 169, 170]. In these spectra, the presence of four main Al coordination environments in the zeolite structure can be observed. The peak at approximately 60 ppm corresponds to tetra-coordinated aluminum (Al^{IV}) within the zeolite framework, associated with the $\text{AlO}_4(4\text{Si})$ species. The signals in the regions of 56 - 55 and 50 ppm correspond to distorted tetrahedral aluminum species ($\text{Al}^{\text{IV}}_{\text{dist.}}$) [93, 169, 170]. This distortion of the tetrahedral site may have been caused during synthesis by the reaction between the octahedral $\text{Al}(\text{OH})_3$ species and the framework through Si-O(H)-Al bonding, leading to the formation of distorted tetrahedral AlOH^{2+} sites [126, 168]. The signal at approximately 30 ppm is attributed to $\text{Al}(\text{OH})_2^+$ species with penta-coordinated aluminum (Al^{V}), while the final signals near 0 ppm, specifically at -2 and -1 ppm, indicate the presence of hexa-coordinated aluminum (Al^{VI} , AlO_6). These last two signals are associated with extra-framework aluminum species [93, 167, 169, 170].

Accordingly, it is observed that the K^+ _SSZ-13_H4 sample exhibited an increase in the percentage of Al^{IV} species within the zeolite framework compared to the Na^+ _SSZ-13_H4 samples (Figure 41). The higher contribution of $\text{Al}^{\text{IV}}_{\text{dist.}}$ and other extra-framework species in the Na^+ _SSZ-13_H4 sample is consistent with the slight increase in the $\text{Si}/\text{Al}_{\text{framework}}$ ratio and the slight decrease in relative crystallinity observed for this sample when compared to the K^+ _SSZ-13_H4 sample. This change in the proportion of Al species may indicate that, under the same synthesis time, the zeolite K^+ _SSZ-13_H4 exhibited better incorporation and structuring of Al species within the CHA framework compared to the Na^+ _SSZ-13_H4 sample [166–168].

Another aspect to be discussed concerns the textural properties of the materials. Characteristics such as specific surface area, microporous area and pore diameter (d_p) are of great importance for the application of this zeolite as an active phase in gas separation membranes [5, 18]. Accordingly, Figure 44 presents the N_2 adsorption–desorption isotherms of the Na^+ _SSZ-13 and K^+ _SSZ-13 materials synthesized over periods of 3 and 4 days.

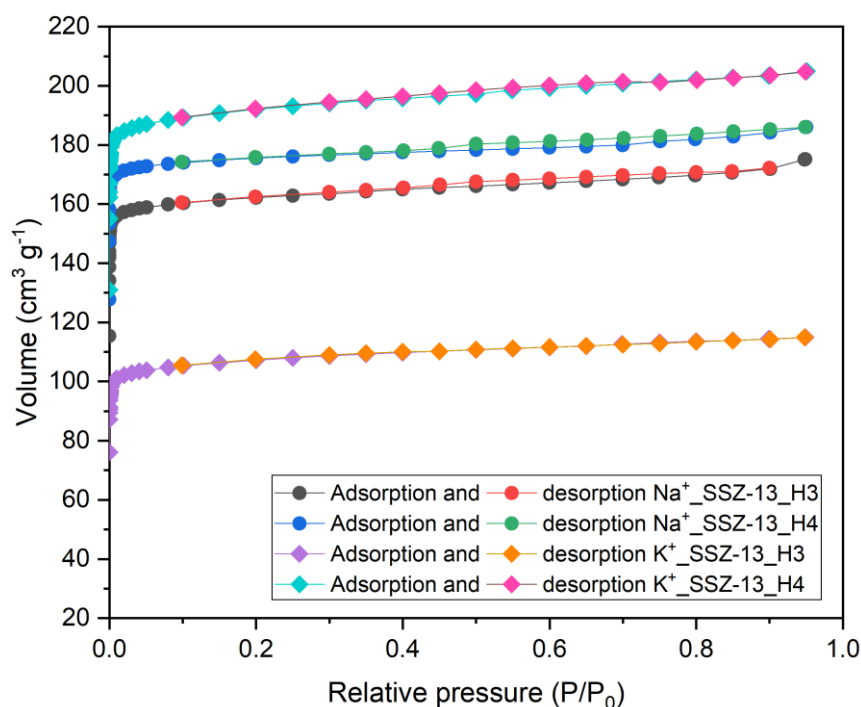


Figure 44. N₂ adsorption and desorption isotherms of the Na⁺SSZ-13 e K⁺SSZ-13 samples synthesized over 3 and 4 days.

According to the IUPAC classification, all materials exhibited type I isotherms, characterized by reaching saturation at low relative pressures, while at high relative pressures, the pores are filled by the adsorbate (N₂ gas), either adsorbed or condensed, leading to a plateau. This behavior is typical of microporous materials, such as zeolites [127, 128]. Additionally, the Na⁺SSZ-13 samples exhibited a type IV hysteresis loop, which is characteristic of micropore filling in aggregated zeolite crystals or may indicate the presence of mesoporosity in zeolites [127]. This hysteresis was possibly observed due to the increase in Al^{IV}_{dist.} and extra-framework Al species, as indicated by the MAS NMR analysis for the Na⁺SSZ-13_H4 sample, which may have caused “defects” (mesoporosity) in the microporous structure of these zeolites.

From these isotherms (Figure 44), it was possible to determine the specific surface area (S_{BET}), external surface area (S_{EXT}) and microporous surface area (S_{MICRO}), as well as the pore volume (V_p), micropore volume (V_μ) and pore diameter (d_p) of the materials, as shown in Table 10.

Table 10. Textural properties of the Na⁺_SSZ-13 and K⁺_SSZ-13 samples.

Samples	S _{BET} (m ² ·g ⁻¹)	S _{EXT} (m ² ·g ⁻¹)	S _{MICRO} (m ² ·g ⁻¹)	V _μ (cm ³ ·g ⁻¹)	V _p (cm ³ ·g ⁻¹)	d _p (nm)
Na ⁺ _SSZ-13_H3	674.3	30.9	643.4	0.238	0.266	0.942
Na ⁺ _SSZ-13_H4	734.7	21.8	712.9	0.263	0.286	0.942
K ⁺ _SSZ-13_H3	436.8	27.7	409.0	0.154	0.177	0.982
K ⁺ _SSZ-13_H4	792.8	40.5	752.3	0.280	0.316	0.942

As shown in Figure 44 and supported by the data in Table 10, the K⁺_SSZ-13_H3 sample exhibited lower N₂ gas adsorption, possibly due to having the highest percentage of amorphous area among the samples analyzed. The presence of amorphous content resulted in a relative decrease of 44.9% in the specific surface area compared to the K⁺_SSZ-13_H4 sample, which was synthesized with one additional day.

The other samples exhibited high specific surface areas, typical of SSZ-13 zeolite, which generally range between 500 and 700 m²·g⁻¹ [92, 101, 169]. Furthermore, these samples showed significant microporous surface area values, representing more than 90% of the total surface area of the materials, while the pore volume corresponded to approximately 88% of the total pore volume of the material. These results indicate that the materials produced, regardless of the counter-ion used in the synthesis, possess promising characteristics for gas separation applications due to their high surface and microporous areas, which may contribute to the selectivity of the materials [5, 19, 92]. It is observed that the Al^{IV}_{dist.} and extra-framework Al species, although possibly causing hysteresis in the isotherms of the materials synthesized with the Na⁺ counter-ion, did not result in significant changes in the surface and microporous areas of these materials.

However, the N₂ gas used in this experiment is not the ideal molecule for textural quantification of microporous materials such as zeolites. For this type of material, argon (Ar) gas is more suitable [127, 128]. This is because the quadrupolar nature of the N₂ molecule leads to specific interactions with surface functional groups, affecting the micropore filling pressure. Moreover, pre-adsorbed N₂ molecules can block micropore entrances and interact with functional groups in the zeolite structure, complicating the interpretation of adsorption isotherms. On the

other hand, Ar gas does not exhibit these specific interactions with surface functional groups, which simplifies the interpretation of the isotherms. At 87 K, Ar fills narrow micropores at higher pressures than N₂ at 77 K, allowing for higher-resolution measurements and a more direct correlation between pore filling pressure and confinement effects [127]. Therefore, the use of Ar could likely reduce the overestimation of pore diameter values as indicated by the results in Table 10. The overestimated value of 0.942 nm corresponds to gas adsorption in the interconnected elliptical cages of the CHA structure ($0.67 \times 1.1 \text{ nm}^2$ or $6.7 \times 11 \text{ \AA}^2$), which are indeed measured, rather than the true pore diameter of the materials, which should be in the range of 0.38 nm (3.8 Å) [169].

Based on the data analyzed, the choice of different counter-ions influenced the synthesis mechanisms and the properties of the resulting materials. Although the zeolites produced with Na⁺_SSZ-13 exhibited a faster crystallization process, they showed spheroidal morphology and larger particle sizes. Additionally, the structure synthesized over 4 days displayed increased formation of extra-framework species, which could potentially cause defects and mesoporosity in this zeolite, possibly reducing its selective properties for gas separation applications. On the other hand, the K⁺_SSZ-13 samples showed promising results, especially for the synthesis over 4 days. They exhibited smaller particle sizes, well-defined cubic morphology, high crystallinity and a decrease in extra-framework Al species. Thus, the K⁺_SSZ-13_H4 zeolite demonstrated the most promising results for application as an active phase in membranes for gas separation.

4.2.2. Influence of the H₂O/SiO₂ molar ratio on the crystalline properties of SSZ-13 samples

The molar ratio of water in the synthesis of SSZ-13 zeolite plays a key role, as it serves as the medium in which the transformation from the amorphous phase to the crystalline phase responsible for zeolite formation occurs [18, 94]. Its mineralizing effect is crucial for the dissociation of the synthesis hydroxides, resulting in an increased concentration of available hydroxyl anion species (-OH⁻), which in turn promote the breaking of Si-O-Si and Si-O-Al bonds, followed by the polymerization of these species into the crystalline phase [18, 94]. Therefore, modifying the molar ratio of water can influence the concentrations of silica (SiO₂)

and alumina (Al_2O_3), and potentially affect the pH of the reaction medium. All these factors directly alter the reaction kinetics of zeolite formation [18, 94, 102].

Given that the SSZ-13 zeolite produced with the K^+ counter-ion showed better characteristics for its application as an active phase in inorganic membranes for gas separation, the influence of water ratio variation on the crystallization process of this sample was investigated. Thus, the $\text{H}_2\text{O}/\text{SiO}_2$ ratio was adjusted from 37.5 (molar ratio used in the synthesis described in section 4.2.1) to 17.5, aiming to improve the crystallization rate of this material. Figure 45 presents the XRD and infrared spectra for the K^+ _SSZ-13_375 samples at different synthesis times. Table 11 shows the relative crystallinity and the crystallite size obtained for these samples.

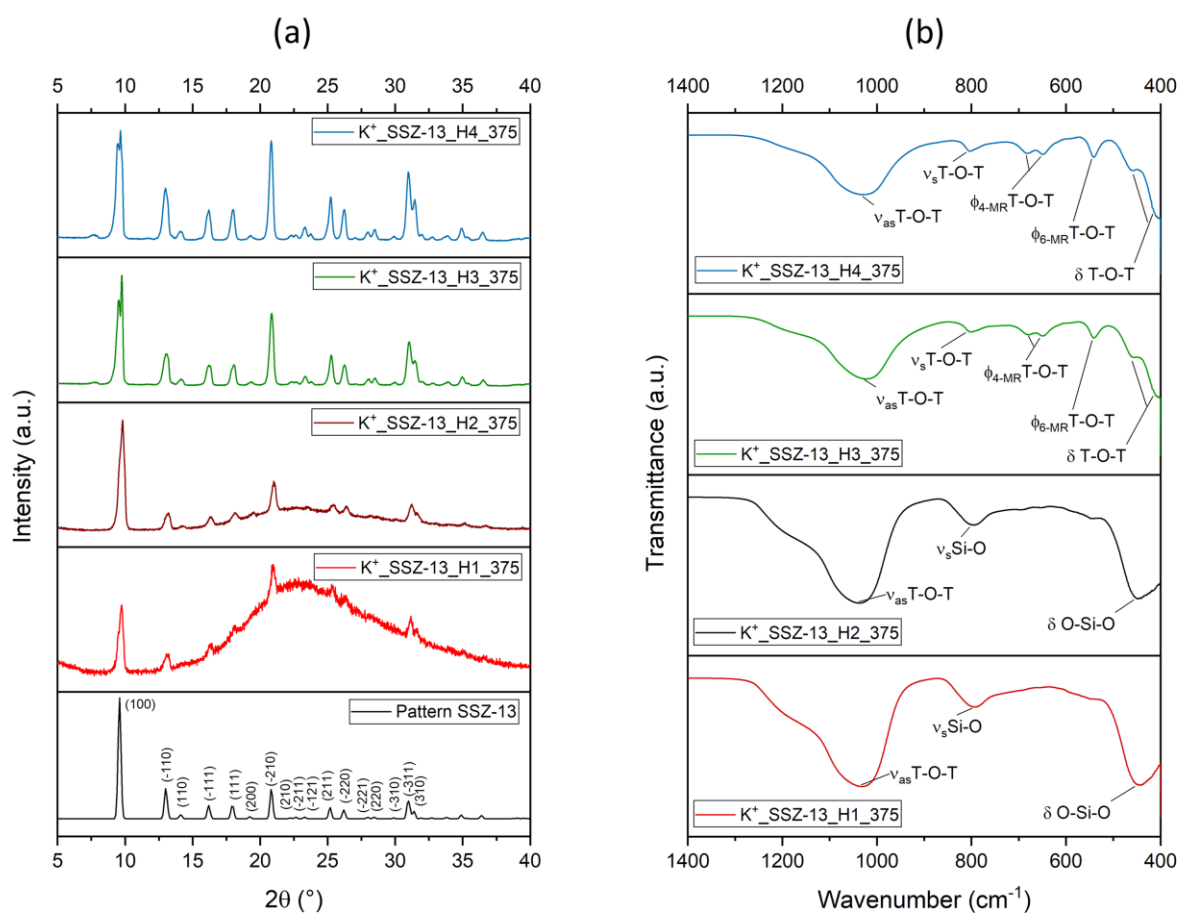


Figure 45. (a) X-ray diffraction and (b) infrared spectra of K^+ _SSZ-13_375 samples produced at different synthesis times (H1 = 1 day; H2 = 2 days; H3 = 3 days and H4 = 4 days).

Table 11. Relative crystallinity (%) and crystallite size of K⁺SSZ-13_375 samples at different synthesis times.

Samples:	Relative crystallinity (%):	Crystallite size (nm):
K ⁺ SSZ-13_H1_375	6.06	19.10 ± 0.02
K ⁺ SSZ-13_H2_375	29.9	17.50 ± 0.01
K ⁺ SSZ-13_H3_375	92.2	16.10 ± 0.02
K ⁺ SSZ-13_H4_375	98.0	15.60 ± 0.01

As observed for syntheses with an H₂O/SiO₂ molar ratio of 37.5 (section 4.2.1, samples K⁺SSZ-13), based on the diffractograms of the synthesized K⁺SSZ-13_375 samples (Figure 45a), the characteristic peaks of the CHA structure [158] were identified starting from the 1-day synthesis period. These peaks mostly agree with the characteristic signals described in the literature [21, 23, 44, 45, 93, 154, 159–161] for SSZ-13 zeolite, corresponding to the rhombohedral crystal structure with space group *R-3m* [22, 158, 162]. However, the samples synthesized after 3 and 4 days, while showing a reduction in the amorphous region between 15 and 30° in 2θ, also exhibited peak splitting around 9.6° and the initial appearance of a peak at 7.8° in 2θ. These peaks are believed to indicate the onset of the formation of silicalite-1 species [171]. A similar behavior was observed in the study by Valtchev et al. [172], who varied several parameters (time, temperature and water molar ratio) in the hydrothermal synthesis of zeolite A. When modifying the water molar ratio parameter (H₂O/SiO₂ < 100), the purity of the crystalline solid was affected, resulting in the formation of both zeolite A and hydroxysodalite species.

Regarding the infrared bands indicated (Figure 45b), these behaved similarly to the samples previously described in section 4.2.1, exhibiting asymmetric and symmetric stretching bands, as well as T-O-T bending vibrations at 1036, 807 cm⁻¹ and in the regions of 459 and 411 cm⁻¹, respectively [107, 163]. The other bands indicated the presence of double six-membered rings (6-MR or d6r) at 544 cm⁻¹ and four-membered rings (4-MR) at 685 and 650 cm⁻¹, characteristic of the SSZ-13 zeolite structure produced after 3 and 4 days of synthesis [107, 164, 165].

Analyzing the data in Table 11, which are consistent with the diffractograms presented in Figure 45a, it is observed that by reducing the H₂O/SiO₂ molar ratio, the K⁺SSZ-13_375 samples exhibited higher relative crystallinity and smaller crystallite size compared to the K⁺ samples prepared with an H₂O/SiO₂ ratio of 37.5

(Figure 36b and Table 8). Despite these results indicating optimization in the crystallization kinetics, the cubic morphology obtained for the K^+ _SSZ-13_H3_375 and K^+ _SSZ-13_H4_375 samples (Figure 46) were similar to that observed for the K^+ _SSZ-13_H3 and K^+ _SSZ-13_H4 samples (Figure 37c,d).

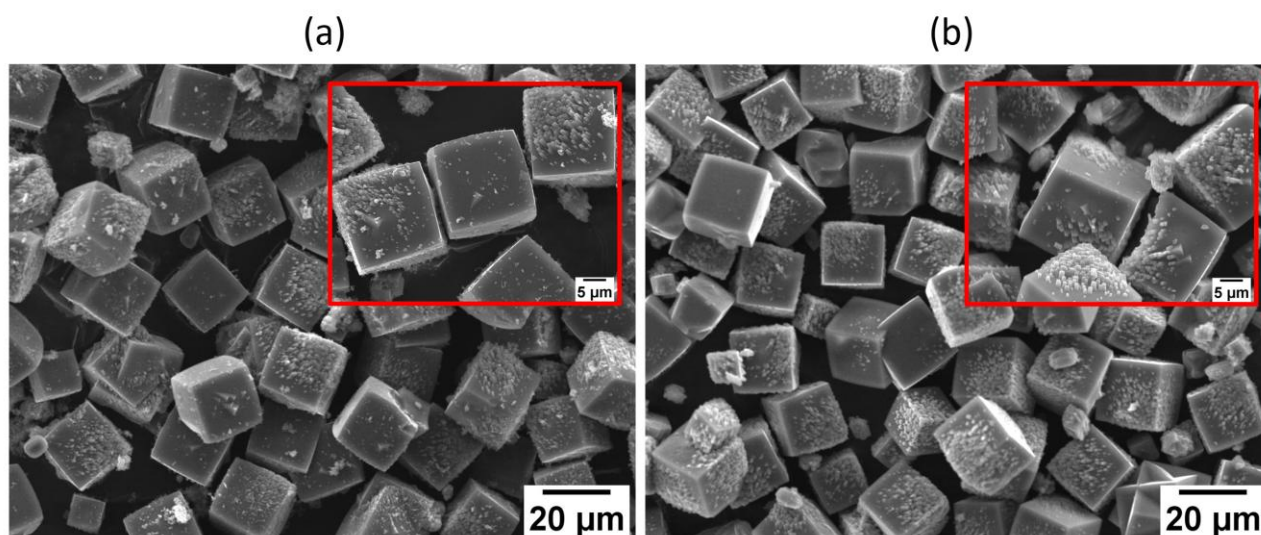


Figure 46. Micrographs of the samples (a) K^+ _SSZ-13_H3_375 and (b) K^+ _SSZ-13_H4_375 at 650x magnification and 2000x zoom (red square).

Table 12. Average particle size obtained from the micrographs of the K^+ _SSZ-13_375 samples.

Samples:	Average particle size (μm):
K^+ _SSZ-13_H3_375	16.8 ± 0.20
K^+ _SSZ-13_H4_375	17.0 ± 0.21

As evidenced by the micrographs in Figure 46 and the data in Table 12, although the crystal morphology exhibits well-defined shapes, as expected from the classical crystallization mechanism of SSZ-13 zeolite (Figure 38), there was an increase in the average particle size compared to the synthesis of the K^+ _SSZ-13 samples prepared with a higher water molar ratio (Table 9).

A reduction in the water ratio is expected to result in lower availability of hydroxide ions (OH^-) in the reaction medium [102]. However, in the molar ratio of 20 SiO_2 : 4 KOH : 1 $\text{Al}(\text{OH})_3$: 16 TMAdaOH : 375 H_2O used in the synthesis of this section, it is believed that the decrease in water quantity did not significantly affect the concentration of OH^- ions. On the contrary, despite the reduction in the molar ratio of water, this amount was still sufficient to promote the dissociation of these

ions from the hydroxides, resulting in an increased concentration of OH^- ions and, consequently, an increase in the basicity of the reaction medium ($\text{pH} < 14$). In the presence of OH^- ions, silica and alumina species dissociate into aluminate and silicate anions, allowing their subsequent oligomerization and formation of the zeolite structure [18, 94]. Due to the higher concentration of OH^- , both the solubility and dissolution of silica and alumina species are enhanced [18]. Thus, it is possible that the increased concentration of these Al and Si species, which are precursors of the zeolite structure, alters the reaction kinetics of the process, leading to an increased crystal growth rate [18, 94], as indicated by the increase in average particle size observed in the K^+ _SSZ-13_H4_375 sample (Table 12) compared to the K^+ _SSZ-13_H4 sample (Table 9).

In aluminosilicate solutions, such as those used in the synthesis of SSZ-13 zeolite, silicate and aluminate species also coexist in equilibrium. An increase in pH to values close to 14 results in an increase in the concentration of aluminate monomers, indicated by the presence of $\text{Al}(\text{OH})_4^-$ species. Regarding silicates, at pH 9, the formation of monomeric $(\text{Si}(\text{OH})_4)$, is observed, while at higher pH values, such as 11 and >13.5 , the monomers exist as mono-dissociated $(\text{SiO}(\text{OH})_3^-)$ and bi-dissociated $(\text{SiO}_2(\text{OH})_2^{2-})$ species, respectively [18]. Therefore, increasing the pH, while keeping the silica concentration constant, results in a decrease in the formation of species with higher polymerization potential, such as $\text{Si}(\text{OH})_4$, whereas the concentration of $\text{Al}(\text{OH})_4^-$ remains constant with the pH change. This behavior may promote the incorporation of more aluminate monomer species into the zeolite structure [18, 94]. Hence, it is believed that the $\text{Si}/\text{Al}_{\text{framework}}$ ratios would be lower in the K^+ _SSZ-13_375 samples at the same synthesis time, compared to the ratio of 16.4 found in the K^+ _SSZ-13_H4 sample based on the MAS NMR data. Furthermore, the presence of the initial formation of the silicalite-1 phase is confirmed by the micrographs in Figure 46, when compared with the micrographs of silicalite-1 obtained under hydrothermal conditions (Figure 47) [171]. This behavior may have occurred possibly due to the presence of a larger number of mono- and bi-dissociated silicate monomers in solution, which by the crystallization kinetics, could have induced the onset of silicalite-1 growth instead of the SSZ-13 zeolite structure.

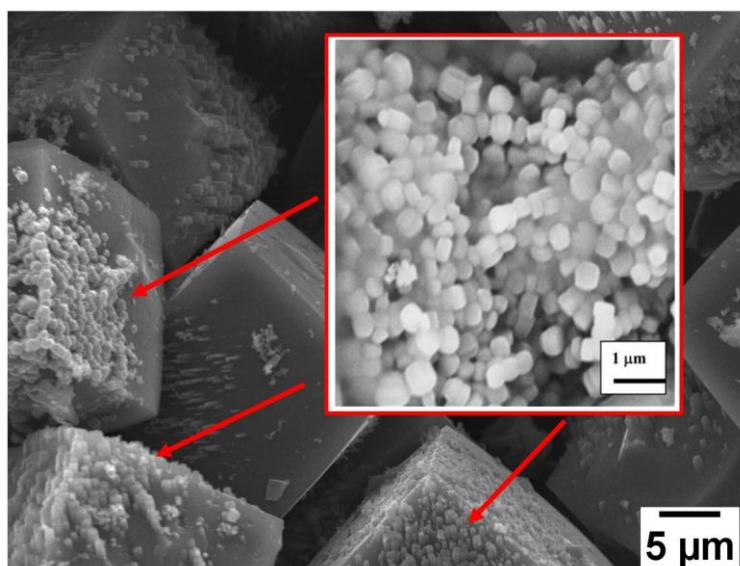


Figure 47. K^+ _SSZ-13_H3_375 sample showing the presence of silicalite-1 phase within the SSZ-13 crystals and a zoomed-in view (red square) of the silicalite-1 structure produced via hydrothermal synthesis, adapted from reference [171].

To investigate the textural characteristics of the crystalline K^+ _SSZ-13_375 materials produced after 3 and 4 days of synthesis, N_2 adsorption and desorption isotherms were analyzed, as shown in Figure 48.

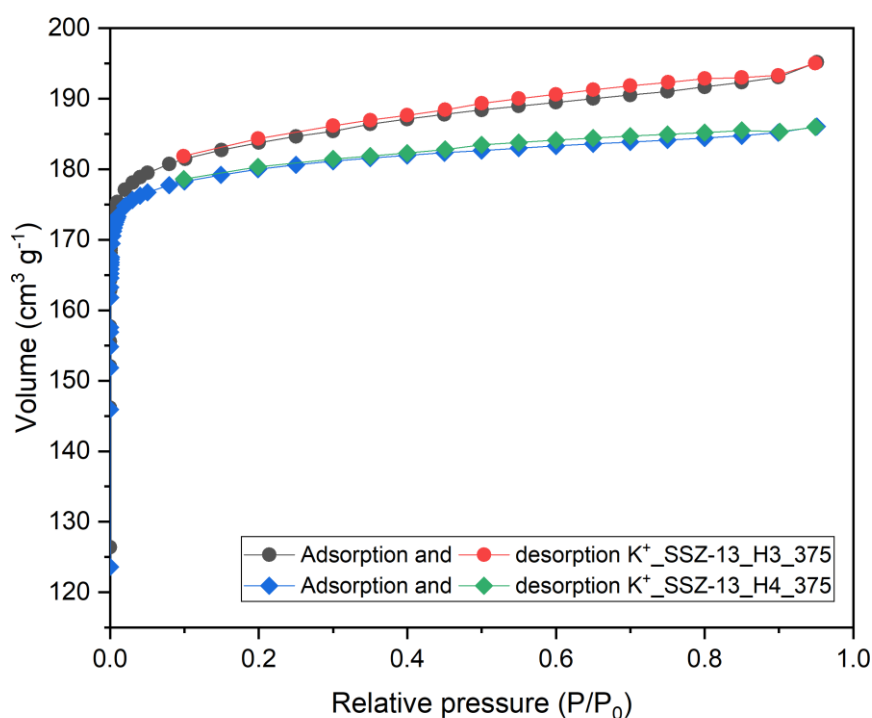


Figure 48. N_2 adsorption and desorption isotherms of the K^+ _SSZ-13_H3_375 and K^+ _SSZ-13_H4_375 samples.

As evidenced in the analysis of the isotherms of the materials in section 4.2.1, the K⁺_SSZ-13_375 samples exhibited the typical profile of microporous materials, with type I isotherms [127, 128]. In contrast to the K⁺_SSZ-13 (section 4.2.1), the K⁺_SSZ-13_375 samples showed behavior similar to the isotherms of the Na⁺_SSZ-13 materials, with type IV hysteresis loops [127]. This behavior may suggest that the increased crystallization kinetics of the material, besides compromising the purity of the obtained material, may have contributed to the increase in the percentages of Al^{IV}_{dist.} and extra-framework Al species, which can lead to “defects” (mesoporosity) in the zeolite structure, as observed in the Na⁺_SSZ-13 samples [18, 94, 95].

From these isotherms (Figure 48), it was possible to determine the specific surface area (S_{BET}), external surface area (S_{EXT}) and microporous surface area (S_{MICRO}), as well as the total pore volume (V_p) micropore volume (V_μ) and pore diameter (d_p) of the materials, as shown in Table 13.

Table 13. Textural properties of the K⁺_SSZ-13_375 samples.

Samples	S_{BET} (m ² ·g ⁻¹)	S_{EXT} (m ² ·g ⁻¹)	S_{MICRO} (m ² ·g ⁻¹)	V_μ (cm ³ ·g ⁻¹)	V_p (cm ³ ·g ⁻¹)	d_p (nm)
K ⁺ _SSZ-13_H3_375	759.1	36.5	722.6	0.270	0.299	0.982
K ⁺ _SSZ-13_H4_375	749.8	21.6	728.2	0.270	0.287	0.942

The data in Table 13 showed similar behavior to that observed in Table 10 for the Na⁺_SSZ-13 and K⁺_SSZ-13 samples in section 4.2.1. Due to the faster crystallization observed in the K⁺_SSZ-13_375 samples, an improvement in the specific surface area was noted for the sample synthesized in 3 days, increasing by approximately 74% compared to the K⁺_SSZ-13_H3 sample from section 4.2.1. Although they are similar, the surface area of the K⁺_SSZ-13_H4 sample was greater than that of the K⁺_SSZ-13_H4_375 sample which supports the hypothesis that in samples with higher crystallization rates and larger particle sizes, there is a likely formation of more Al^{IV}_{dist.} and extra-framework aluminum species, which may impair their textural properties and efficiency in applications such as gas separation membranes [5, 18, 19, 94, 95].

Therefore, despite the accelerated crystallization process, the change in the molar water ratio in the K^+ _SSZ-13 synthesis hindered its formation as a pure crystalline phase, resulting in an increase in particle size and possibly contributing to the production of extra-framework species, as observed in the Na^+ _SSZ-13 sample in section 4.2.1. Thus, to improve the synthesis process of SSZ-13 zeolite, new changes in the synthesis routes are needed to optimize the process, including parameters such as reducing the synthesis time and the particle size obtained.

4.2.3. Influence of SSZ-13 Crystallization in Microwave- and Seed-Assisted Synthesis

In the previous sections, it was observed that among the variations carried out in the synthesis of the SSZ-13 structure, the hydrothermal synthesis using potassium (K^+ _SSZ-13) as the counter-ion presented the most promising results for the objectives of this study. However, in order to improve parameters such as synthesis time and particle size, an alternative approach to SSZ-13 production became necessary.

Microwave radiation is a form of electromagnetic wave capable of promoting dielectric heating through two main mechanisms: dipole rotation and ionic conduction. In the first case, polar molecules, which possess permanent or induced dipoles, align with the oscillating electric field of the microwaves. This continuous realignment leads to intense molecular motion, generating heat through molecular friction and dielectric losses. In ionic conduction, ions present in the reaction mixture oscillate and collide with neighboring molecules under the influence of the microwave field, also producing heat through friction. These mechanisms make microwave heating efficient and fast, allowing for a significant reduction in synthesis time [99, 173, 174].

Thus, the microwave-assisted synthesis method, combined with the use of seeds, was chosen with the aim of accelerating the crystallization process and, consequently, obtaining zeolites with high crystallinity and smaller particle sizes. These characteristics are advantageous for its application as the active phase in gas separation membranes, since smaller crystals imply shorter diffusion paths for the molecules, favoring gas transport through the membrane [83, 96]. In addition,

microwave-assisted synthesis may contribute to the production of thinner and more compact SSZ-13 layers, which would allow for higher permeation fluxes, one of the desirable aspects for improving the efficiency of the gas separation process [83, 100, 173].

In this context, Figure 49 presents the X-ray diffraction and infrared spectra of the samples obtained through microwave-assisted synthesis with the use of seeds, considering the different synthesis times employed. All SSZ-13_MW samples used K^+ as the counter-ion.

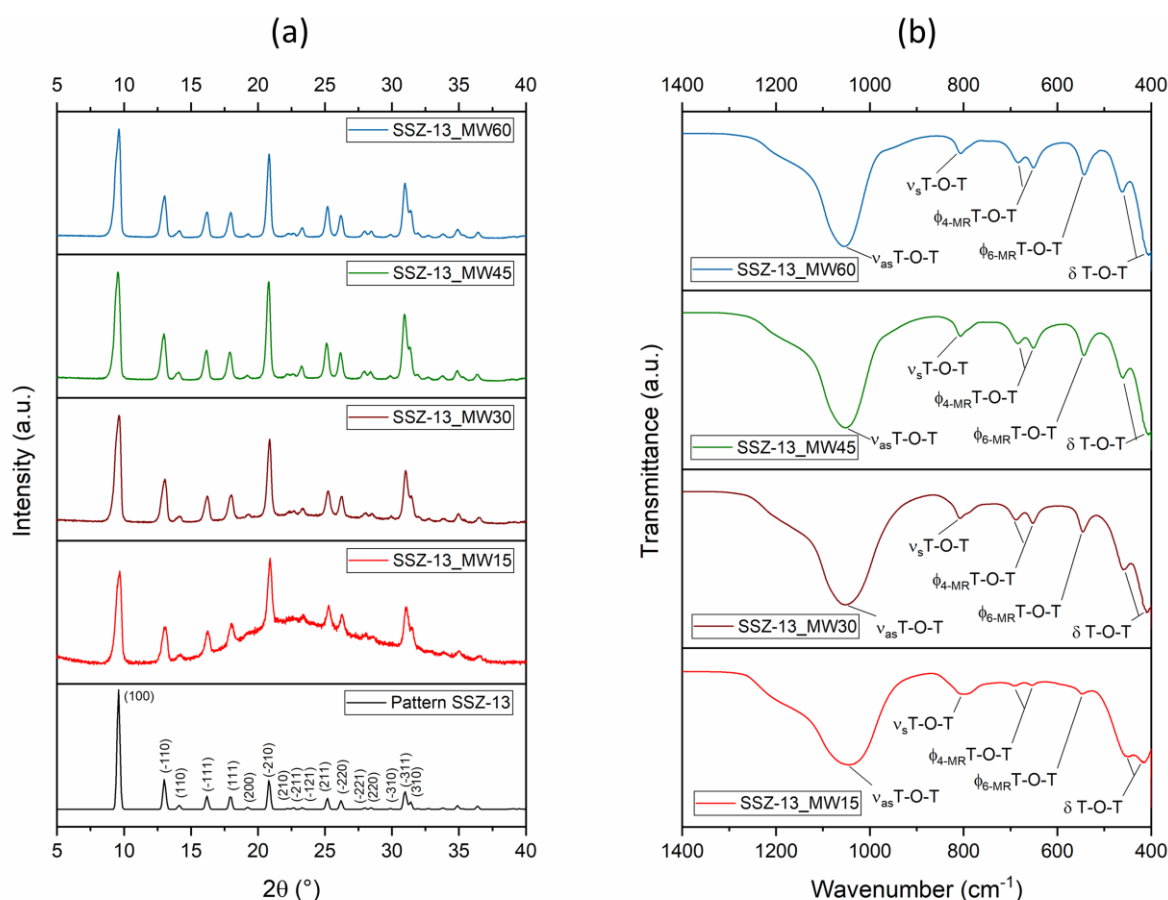


Figure 49. (a) X-ray diffraction and (b) infrared spectra of SSZ-13_MW samples synthesized over different times (MW15 = 15 minutes; MW30 = 30 minutes; MW45 = 45 minutes and MW60 = 60 minutes).

As indicated in Figure 49a, the analysis of the X-ray diffraction confirms the presence of the characteristic peaks of the CHA structure of SSZ-13 zeolite in the synthesized samples [158]. As described in sections 4.2.1 and 4.2.2, the observed peaks are consistent with those reported in the literature [21, 23, 44, 45, 93, 154, 159–161] for SSZ-13, located approximately at $2\theta = 9.6^\circ$; 13.1° ; 16.2° ; 18° ; 20.9° ; 25.3° ;

26.2° and 31.1°, corresponding to the rhombohedral crystal structure of space group *R-3m* [22, 158, 162]. Furthermore, it is observed that increasing the synthesis time from 15 to 60 minutes leads to an increase in crystallinity and a reduction in the amorphous fraction of the materials, as shown in Table 14.

Table 14. Relative crystallinity (%) and crystallite size of SSZ-13_MW samples at different synthesis times.

Samples:	Relative crystallinity (%):	Crystallite size (nm):
SSZ-13_MW15	23.7	16.20 ± 0.01
SSZ-13_MW30	69.1	16.02 ± 0.01
SSZ-13_MW45	89.6	16.78 ± 0.01
SSZ-13_MW60	97.0	16.89 ± 0.01

The samples obtained through microwave-assisted synthesis exhibited high crystallinity percentages (Table 14), even with a significantly reduced synthesis time, allowing the formation of SSZ-13 zeolite in just 30 minutes. This performance is attributed to the uniform heating provided by microwave radiation, which enhances reagent dissolution and intensifies nucleation rates, resulting in the fast formation of small and homogeneous particles [96, 99, 100, 173]. Although seeds from hydrothermal synthesis were used, with crystallite sizes on the order of 39.200 ± 0.001 nm, the samples synthesized via microwave showed significantly smaller crystallites (approximately 16 nm). This result is associated with the predominance of nucleation over crystal growth, favored by the rapid and energetic conditions of the microwave-assisted synthesis [96, 99, 100, 173, 175].

In agreement with the XRD results, the infrared spectroscopy analysis presented in Figure 49b reveals the characteristic bands of SSZ-13 zeolite. The bands in the range of $1052 - 1054 \text{ cm}^{-1}$ are attributed to the asymmetric stretching vibrations of T-O-T bonds (T = Si or Al) in both transverse and longitudinal planes. In the region of $808 - 810 \text{ cm}^{-1}$, symmetric stretching vibrations are observed, while the bands around $459 - 460 \text{ cm}^{-1}$ and 411 cm^{-1} correspond to angular deformations (bending) of the tetrahedral framework [107, 163]. Additionally, the low-intensity bands between 686 cm^{-1} and 651 cm^{-1} are associated with T-O-T vibrations of the zeolite ring network, related to the presence of four-membered rings (4-MR). The band at $545 - 547 \text{ cm}^{-1}$ is characteristic of double six-membered rings (6-MR), which are typical of chabazite (CHA)-type frameworks, the structural class to which SSZ-13

belongs [107, 164, 165]. The SSZ-13_MW15 sample exhibited slight band shifts, possibly due to the presence of amorphous silica in the structure.

Another aspect directly influenced by the high nucleation rate and rapid crystallization is the particle size obtained during synthesis. This effect is evident in the scanning electron microscopy images of the SSZ-13_MW samples (Figure 50) and Table 15.

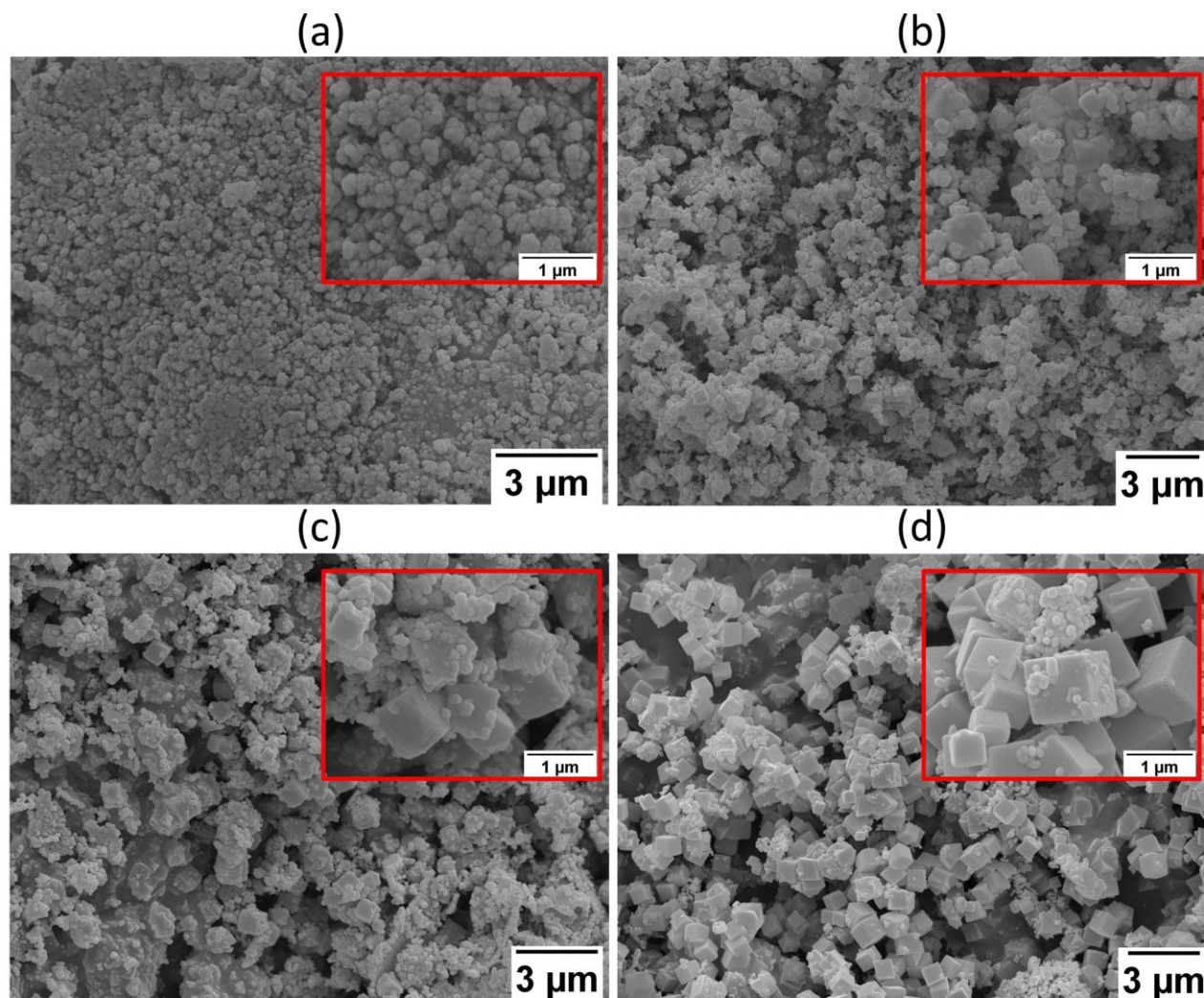


Figure 50. Micrographs of the samples (a) SSZ-13_MW15, (b) SSZ-13_MW30, (c) SSZ-13_MW45 and (d) SSZ-13_MW60 at 5000x magnification and zoomed-in views (red square) at 20000x/30000x magnification.

Table 15. Average particle size determined from the micrographs of the SSZ-13_MW samples.

Samples:	Average particle size (μm):
SSZ-13_MW15	0.221 ± 0.002
SSZ-13_MW30	0.480 ± 0.005
SSZ-13_MW45	0.560 ± 0.013
SSZ-13_MW60	0.645 ± 0.016

At synthesis times of 15 and 30 minutes (Figures 50a,b), the formation of crystals with a more rounded morphology is observed. For longer synthesis times of 45 and 60 minutes (Figures 50c,d), these rounded crystals tend to agglomerate and evolve into a cubic morphology, which is characteristic of the SSZ-13 zeolite structure [20, 21, 44, 45, 92, 93, 98, 154, 159, 160].

Unlike what was observed in section 4.2.1, where the K^+ _SSZ-13 sample synthesized via hydrothermal method exhibited a classical growth mechanism, the samples obtained through microwave-assisted synthesis (and SSZ-13 seeds addition) followed a non-classical growth pathway. In this mechanism, amorphous precursors, initially spheroidal aggregates, attach directly to the surface of pre-nucleated SSZ-13 crystals, leading to the initial formation of particles with irregular morphology and rough surfaces [92, 93, 104], as observed in the SSZ-13_MW15 sample (Figure 50a). As the synthesis progresses, a disorder-to-order transition occurs after attachment, which may involve solid-state rearrangements or solution-mediated processes. This transition results in smoother surfaces and more well-defined edges and corners, ultimately yielding well-developed cubic structures [92, 93, 104], as observed from the 30-minute synthesis time (Figure 50b - d).

The rapid heating provided by microwave irradiation creates “hot spots” that promote the fast dissolution of reagents and the intense nucleation of the product. This high nucleus density, combined with the quick consumption of reactants, leads to the formation of smaller and more homogeneous particles in significantly shorter synthesis times [92, 96, 173]. This phenomenon is clearly evidenced by the drastic reduction in particle size for the sample synthesized via microwave heating for 60 minutes (SSZ-13_MW60, $0.645 \pm 0.016 \mu\text{m}$) compared to the 4 days hydrothermally synthesized sample (K^+ _SSZ-13_H4, $5.67 \pm 0.07 \mu\text{m}$).

Therefore, to clarify the chemical environments and the synthesis mechanism followed by the SSZ-13_MW samples, Figures 51 and 52 show the deconvoluted MAS NMR spectra of ^{29}Si and ^{27}Al nuclei, respectively.

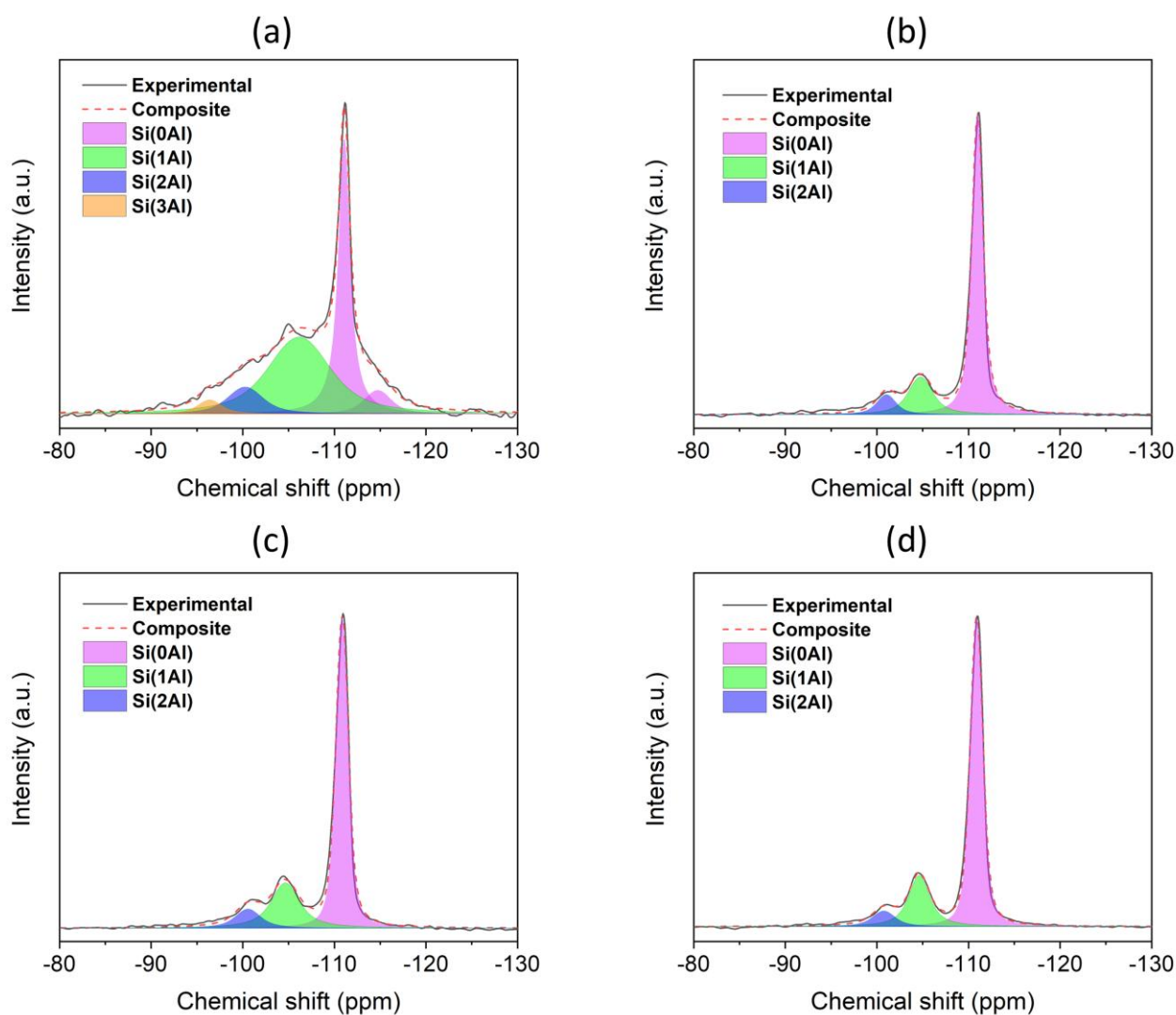


Figure 51. Deconvoluted ^{29}Si MAS NMR spectra of the samples: (a) SSZ-13_MW15, (b) SSZ-13_MW30, (c) SSZ-13_MW45, and (d) SSZ-13_MW60. Where Si(0Al) = Si(OSi)₄; Si(1Al) and Si(2Al), corresponding to QⁿSi(OSi)_{4-n}(OAl)_n species (with $n = 1$ and 2), respectively; and Si(3Al) can be attributed to Si(OSi)(OAl)₃ species units.

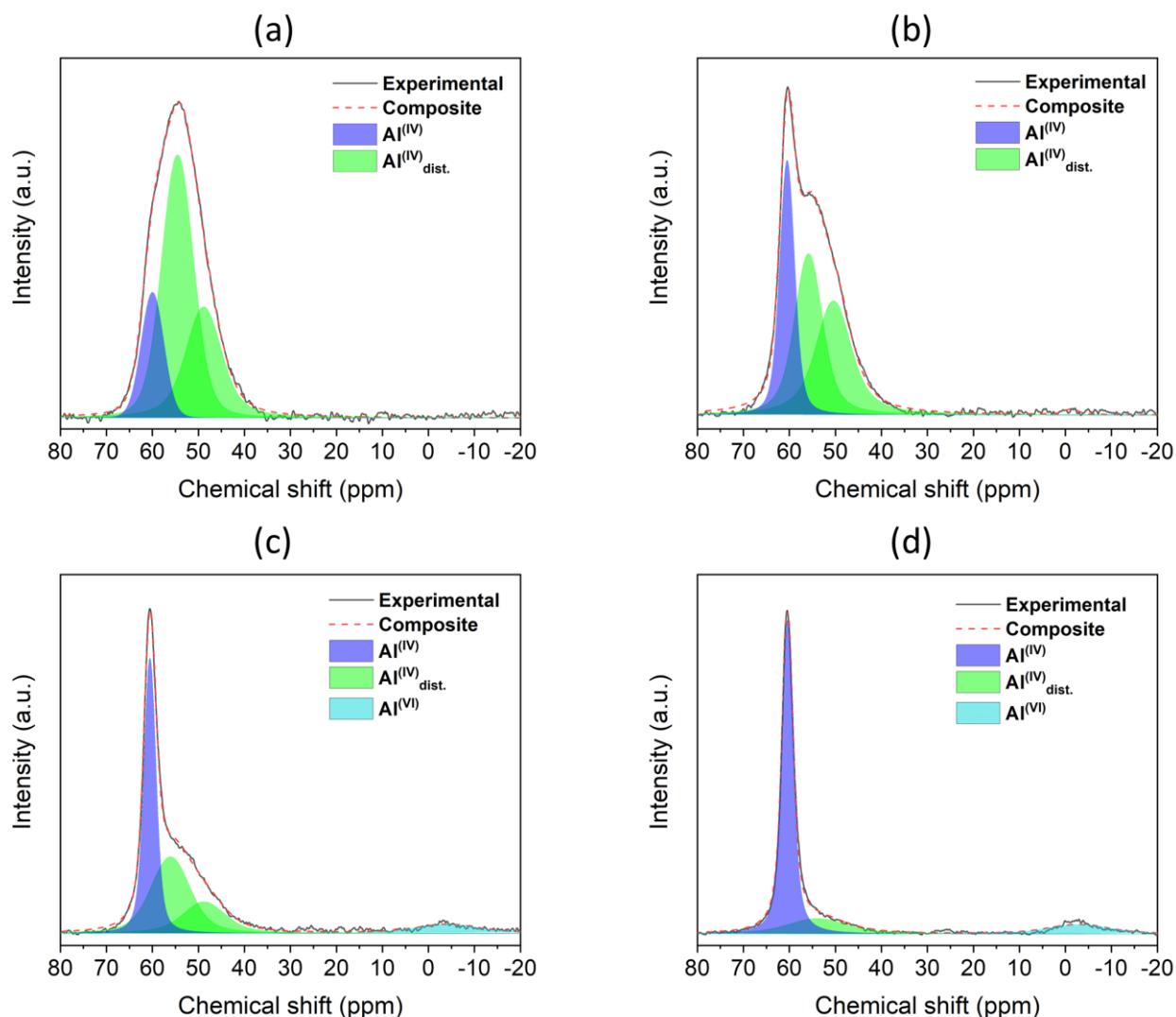


Figure 52. Deconvoluted ^{27}Al MAS NMR spectra of the samples: (a) SSZ-13_MW15, (b) SSZ-13_MW30, (c) SSZ-13_MW45 and (d) SSZ-13_MW60. Where (Al^{IV}) is tetra-coordinated aluminum; ($\text{Al}^{\text{IV}}_{\text{dist.}}$) distorted tetrahedral aluminum species; and hexa-coordinated aluminum (Al^{VI}) corresponding to extra-framework structures.

Based on the information provided by the ^{29}Si NMR spectrum (Figure 51), it is observed that at the beginning of the synthesis, when the particles exhibit a more rounded morphology and a higher amorphous content as in the case of the SSZ-13_MW15 sample, broader and overlapping signals are present (Figure 51a). Among the chemical shifts (δ) described in section 4.2.1 as typical for the CHA structure of SSZ-13 zeolite, the signals around -111 ppm are attributed to $\text{Si}(0\text{Al})$ environments associated with siloxane species ($\text{Q}^4 - \text{Si}(\text{OSi})_4$), while the signals at -105 and -101 ppm correspond to $\text{Si}(1\text{Al})$ and $\text{Si}(2\text{Al})$, respectively, related to $\text{Q}^n\text{Si}(\text{OSi})_{4-n}(\text{OAl})_n$ species (with $n = 1$ or 2) [90, 93, 126, 169]. Additionally, atypical

signals at -96 ppm ($\text{Si}(3\text{Al})$) and -115 ppm were observed, suggesting the presence of incompletely crystallized particles. The signal at -96 ppm can be attributed to $\text{Si}(\text{OSi})(\text{OAl})_3$ species units or terminal silanol groups ($\text{Si}(\text{OSi})_3\text{OH}$), while the signal at -115 ppm is associated with highly distorted siloxane groups [93, 126]. The remaining samples (Figure 51b - d) showed similar behavior, with a high degree of similarity among them and with a high percentage (above 65%) of siloxane species ($\text{Si}(\text{OSi})_4$) around -111 ppm.

The ^{27}Al NMR spectra (Figure 52) indicates that, at the initial synthesis times of 15 and 30 minutes (Figures 52a,b), there is a significant presence of broad peaks attributed to distorted tetrahedral aluminum species ($\text{Al}^{\text{(IV)}_{\text{dist.}}}$) observed at approximately 56 - 55 and 50 ppm [93, 169, 170]. The presence of these signals suggests aluminum sites within the framework exhibiting structural defects or less ideal coordination, typically associated with a lower degree of structural order [93, 126]. As the microwave synthesis time increases to 45 and 60 minutes (Figures 52c,d), there is an improvement in peak intensity and narrowing at around 60 ppm, corresponding to tetra-coordinated aluminum ($\text{Al}^{\text{(IV)}}$) incorporated into the zeolite framework, specifically associated with $\text{AlO}_4(4\text{Si})$ species. However, these samples still exhibit a slight signal beyond 0 ppm, specifically between -2 and -4 ppm, indicative of the presence of hexa-coordinated aluminum ($\text{Al}^{\text{(VI)}}$, AlO_6), related to extra-framework aluminum species [93, 167, 169, 170].

From the deconvoluted spectra (Figures 51 and 52), it was possible to obtain quantitative data regarding the ratio between well-defined tetrahedral species and other framework aluminosilicate species ($\text{Q}^4/\Sigma\text{Si}(\text{OAl})_n$), the relative percentage of different aluminum species, and better comprehend the particle growth evolution in terms of the aluminosilicate species, involved in the process of SSZ-13 zeolite under microwave conditions over synthesis times ranging from 15 to 60 minutes, as shown in Table 16 and Figure 53.

Table 16. Quantitative results of the ^{29}Si and ^{27}Al NMR data showing the ratios of the areas estimated by deconvolution of the NMR spectra and the $\text{Si}/\text{Al}_{\text{framework}}$ ratio of the SSZ-13_MW samples.

Samples:	$\text{Q}^4/\Sigma\text{Si}(\text{OAl})_n$ ratio:	$\Sigma\text{Si}(\text{OAl})_n$ (%):	$\text{Si}/\text{Al}_{\text{framework}}$ ratio:
SSZ-13_MW15	0.706	58.6	9.60
SSZ-13_MW30	2.62	27.6	18.5
SSZ-13_MW45	1.91	34.4	17.9
SSZ-13_MW60	2.37	29.7	18.1

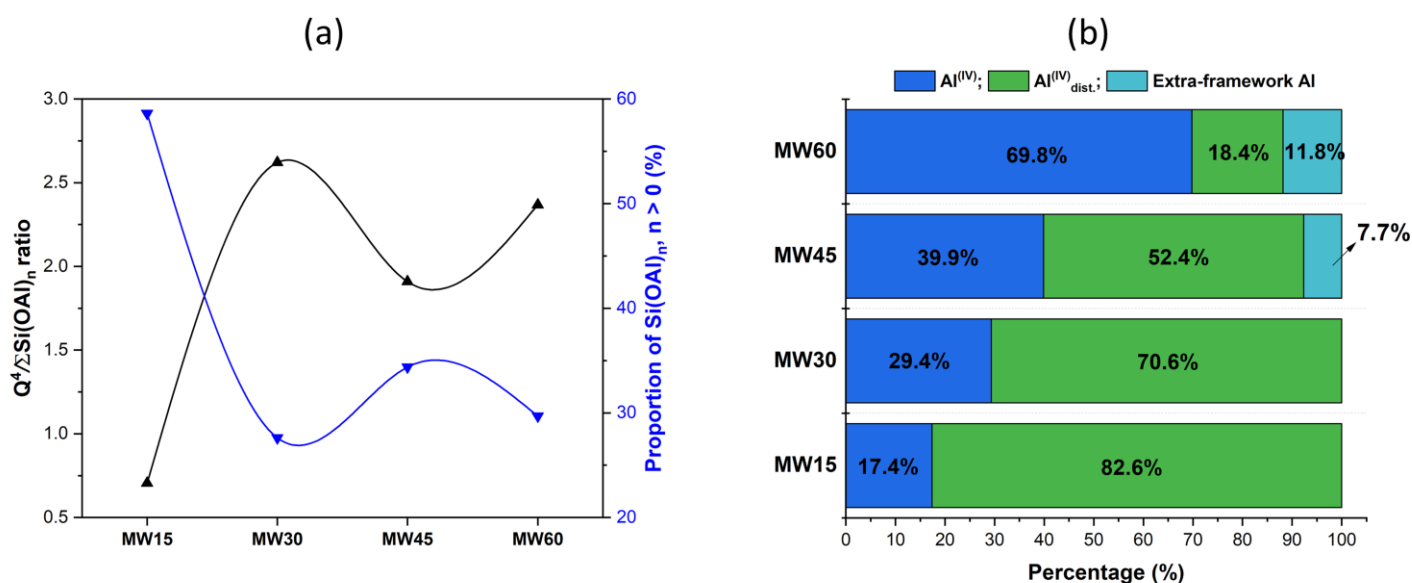


Figure 53. Quantitative analysis obtained by the deconvolution of ^{29}Si and ^{27}Al MAS-NMR data, showing: (a) the ratio between the Q^4 silanol groups ($\text{Si}(\text{OSi})_4$) and all Q^n aluminosilicate groups and the proportion of $\text{Si}(\text{OAl})_n$ groups for and (b) The bar graphs details further the contribution of each aluminum species for SSZ-13_MW samples.

From Table 16 and Figure 53a, it is possible to observe that the variation in the $\text{Q}^4/\Sigma\text{Si}(\text{OAl})_n$ ratio was significant at the initial synthesis times of 15 and 30 minutes, increasing from 0.706 to 2.62 as a consequence of the decrease in the proportion of aluminosilicate species (from 58.6% to 27.6%, respectively). At 45 minutes, the $\text{Q}^4/\Sigma\text{Si}(\text{OAl})_n$ ratio decreased to 1.91, accompanied by an increase in aluminosilicate species to 34.4%. However, at 60 minutes, the ratio increased again to 2.37, while the proportion of aluminosilicate species decreased to 29.7%. This behavior suggests that the first SSZ-13 crystals to form were likely rich in aluminum. As the synthesis progressed, disorder-to-order transition mechanism occurred [92, 93, 104], leading to greater incorporation of silicon into the framework and a

structure enriched in siloxane groups, as indicated by the increase in the Si/Al_{framework} ratio from 9.6 at 15 minutes to 18.1 at 60 minutes of synthesis.

Analysis of the relative percentage of aluminum species over the course of the synthesis time (Figure 53b) reveals a significant increase of 69.0% in the tetrahedral aluminum (Al^(IV)) fraction between 15 and 30 minutes of hydrothermal treatment. As the synthesis continues to 45 and 60 minutes, this increase still occurs, although less markedly, at 35.7% and 57.2%, respectively. Furthermore, starting at 45 minutes, a decrease in distorted tetrahedral aluminum species (Al^(IV)_{dist.}) is observed, along with the appearance of extra-framework aluminum species, indicating a restructuring process among the aluminum species within the CHA zeolite framework. This behavior supports the hypothesis of an internal reorganization mechanism, involving the gradual conversion of distorted species into more ordered ones [92, 93, 104]. Although the presence of extra-framework aluminum is commonly associated with amorphous or defective structures, small amounts of such species may still appear even in highly crystalline zeolites, especially as byproducts of the calcination process. This thermal treatment can induce the hydrolysis of aluminum atoms and their subsequent migration to extra-framework sites, as observed in the H-form of the SSZ-13 zeolite [93, 126].

As previously discussed, microwave irradiation, when combined with the use of seeds, significantly accelerates nucleation and crystal growth, resulting in smaller and more homogeneous particles [92, 96, 173, 174]. Compared to conventional hydrothermal synthesis, this method follows a distinct crystallization mechanism, characterized by the fast formation of multiple nuclei and accelerated gel consumption [92, 99]. This behavior is associated with a growth process dominated by particle aggregation in the early stages, differing from the layer-by-layer growth typical of slower, classical mechanisms. The high nucleation rate promoted by microwave-assisted synthesis is, therefore, consistent with characteristics of a non-classical growth mechanism [92, 104].

Overall, based on the NMR spectra (Figures 51 and 52), Table 16 and Figure 53, it can be concluded that this non-classical growth governs the formation of SSZ-13 zeolite under microwave irradiation and use of seeds. The data indicates the occurrence of dynamic solid-state rearrangements cycles throughout the synthesis studied, consistent with a disorder-to-order mechanism in which SSZ-13 crystallizes

through the aggregation of molecules onto previously formed particles [92, 93]. This hypothesis is also further supported by the SEM micrographs (Figure 50).

To also investigate the textural characteristics of the crystalline SSZ-13_MW materials produced between 15 and 60 minutes of synthesis, N₂ adsorption and desorption isotherms were analyzed, as shown in Figure 54.

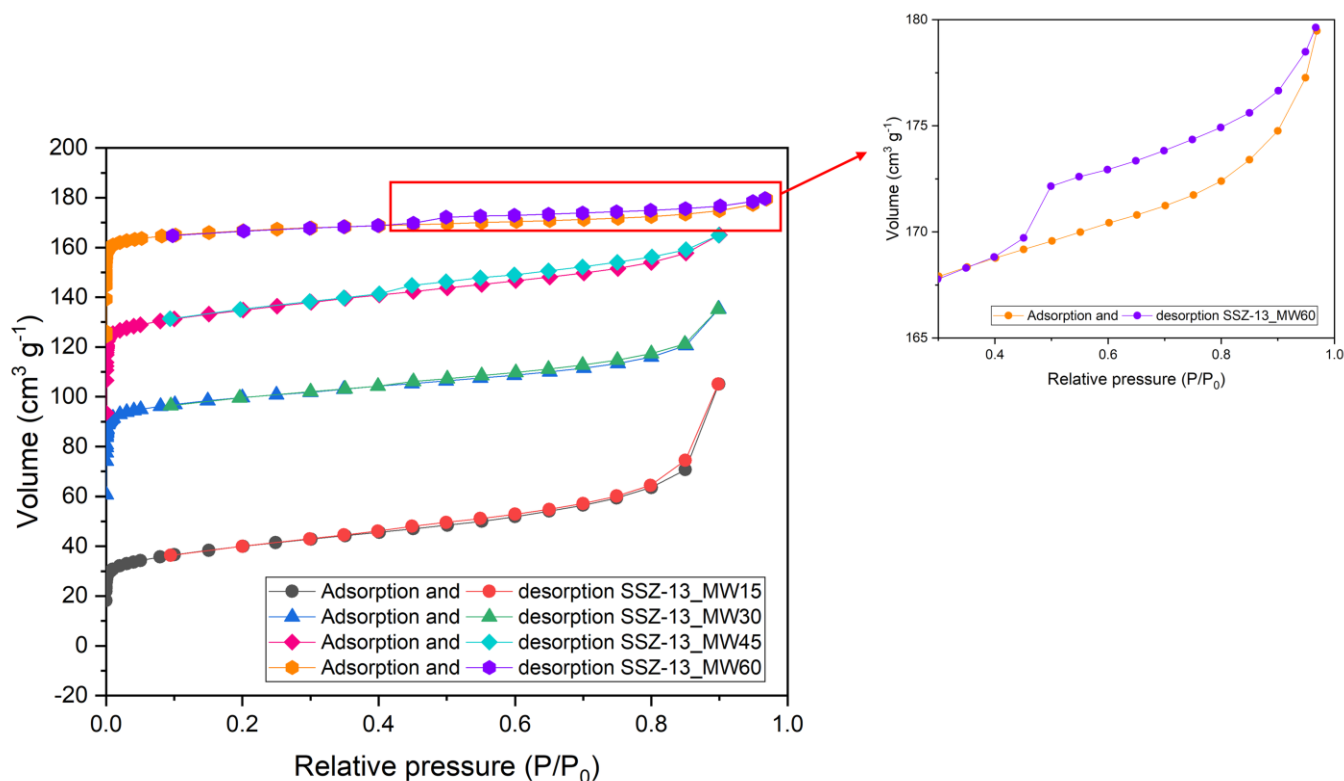


Figure 54. N₂ adsorption and desorption isotherms of the SSZ-13_MW samples with a detailed view of the hysteresis of the SSZ-13_MW60 sample.

As evidenced by the isotherm analysis presented in sections 4.2.1 and 4.2.2, the SSZ-13_MW samples exhibited a typical microporous behavior, characterized by type I isotherms [127, 128]. Unlike the K⁺SSZ-13_H4 sample, all SSZ-13_MW samples showed isotherms profiles similar to those of the Na⁺SSZ-13 and K⁺SSZ-13_375 materials, displaying possibly a mixture of type II and IV hysteresis loops [127]. This behavior may indicate that the enhanced crystallization kinetics associated with microwave-assisted synthesis contributed to higher proportions of extra-framework aluminum species, which can induce structural “defects” such as mesoporosity in the zeolite framework [18, 94, 95]. Also, the ability of microwave radiation to promote rapid and uniform crystallization, leading to the formation of nanocrystals and altering crystal growth conditions, may favor the development of

mesoporosity, either through direct mechanisms related to microwave heating or indirectly via the formation of intercrystalline mesopores resulting from the aggregation of smaller particles [92, 96, 173].

From these isotherms (Figure 54), it was possible to determine the specific surface area (S_{BET}), external surface area (S_{EXT}) and microporous surface area (S_{MICRO}), as well as the total pore volume (V_{p}), micropore volume (V_{μ}) and pore diameter (d_{p}) of the materials, as shown in Table 17.

Table 17. Textural properties of the SSZ-13_MW samples.

Samples	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	S_{EXT} ($\text{m}^2\cdot\text{g}^{-1}$)	S_{MICRO} ($\text{m}^2\cdot\text{g}^{-1}$)	V_{μ} ($\text{cm}^3\cdot\text{g}^{-1}$)	V_{p} ($\text{cm}^3\cdot\text{g}^{-1}$)	d_{p} (nm)
SSZ-13_MW15	142.6	64.3	78.34	0.034	0.110	0.982
SSZ-13_MW30	397.9	51.6	346.3	0.132	0.187	0.982
SSZ-13_MW45	541.5	68.0	473.5	0.179	0.245	0.942
SSZ-13_MW60	694.9	22.6	672.3	0.249	0.949	0.942

The data presented in Table 17 revealed a behavior consistent with that observed in the previous sections. As the synthesis time increases from 15 to 60 minutes, there is a significant rise in specific surface area, which is accompanied by corresponding increases in microporous surface area and pore volume. For the most crystalline material obtained after 60 minutes, 96.7% of its total specific surface area was composed of micropores. When compared to the zeolite synthesized via the hydrothermal method (K^+ _SSZ-13_H4) discussed in section 4.2.1, this sample showed a relative decrease in specific surface area of approximately 12.3%. This result suggests that, although microwave radiation enables a drastic reduction in synthesis time, it may also lead to the possible formation of intercrystalline mesoporosity resulting from the aggregation of smaller particles [92, 96, 173]. This effect could potentially reduce the efficiency of the material in applications such as gas separation membranes [5, 18, 19, 94, 95].

Nevertheless, despite the possible formation of intercrystalline mesoporosity, the samples synthesized via microwave irradiation combined with seed addition and a synthesis time of 60 minutes (SSZ-13_MW60) are considered promising candidates for permeation tests. Overall, this sample exhibited high crystallinity, reduced particle size (compared to conventional hydrothermal synthesis), a high degree of

ordering of the tetrahedral species forming the CHA framework and a large specific surface area.

In this context, along with the K⁺SSZ-13_H4, the SSZ-13_MW60 sample exhibit promising properties for use as the active phase in gas separation membranes. These samples will be employed as seeds for the fabrication of SSZ-13 membranes, which will be presented in the following section.

4.3. SSZ-13 Ceramic Membrane

In this section, the data regarding the characterization of the SSZ-13 ceramic membranes will be discussed. First, the intermediate silica layer will be analyzed, along with the different SSZ-13 membranes produced on commercial α -Al₂O₃ tubes and by freeze-casting, using the distinct seeds selected in the study described in section 4.2.

4.3.1. Characterization of the silica layer

In the fabrication of SSZ-13 ceramic membranes, an intermediate silica layer was introduced between the ceramic tubular substrate and the zeolite active layer. This layer plays a crucial role in enhancing membrane performance for gas separation [176–178]. It provides a gradual pore-size transition between the macroporous support and the microporous zeolite layer, offers a uniform surface for zeolite seed deposition and acts as a barrier that prevents zeolite intrusion into the support [177, 179]. Additionally, the silica layer improves adhesion between the substrate and the zeolite, while potentially reducing aluminum leaching from the support during secondary growth. This contributes to a more uniform deposition of the active phase, thereby enhancing the selectivity and stability of the membranes [177–179].

In this context, Figure 55 shows the SEM images of the intermediate silica layer produced on commercial α -Al₂O₃ tubes at different deposition rates using the dip-coating technique.

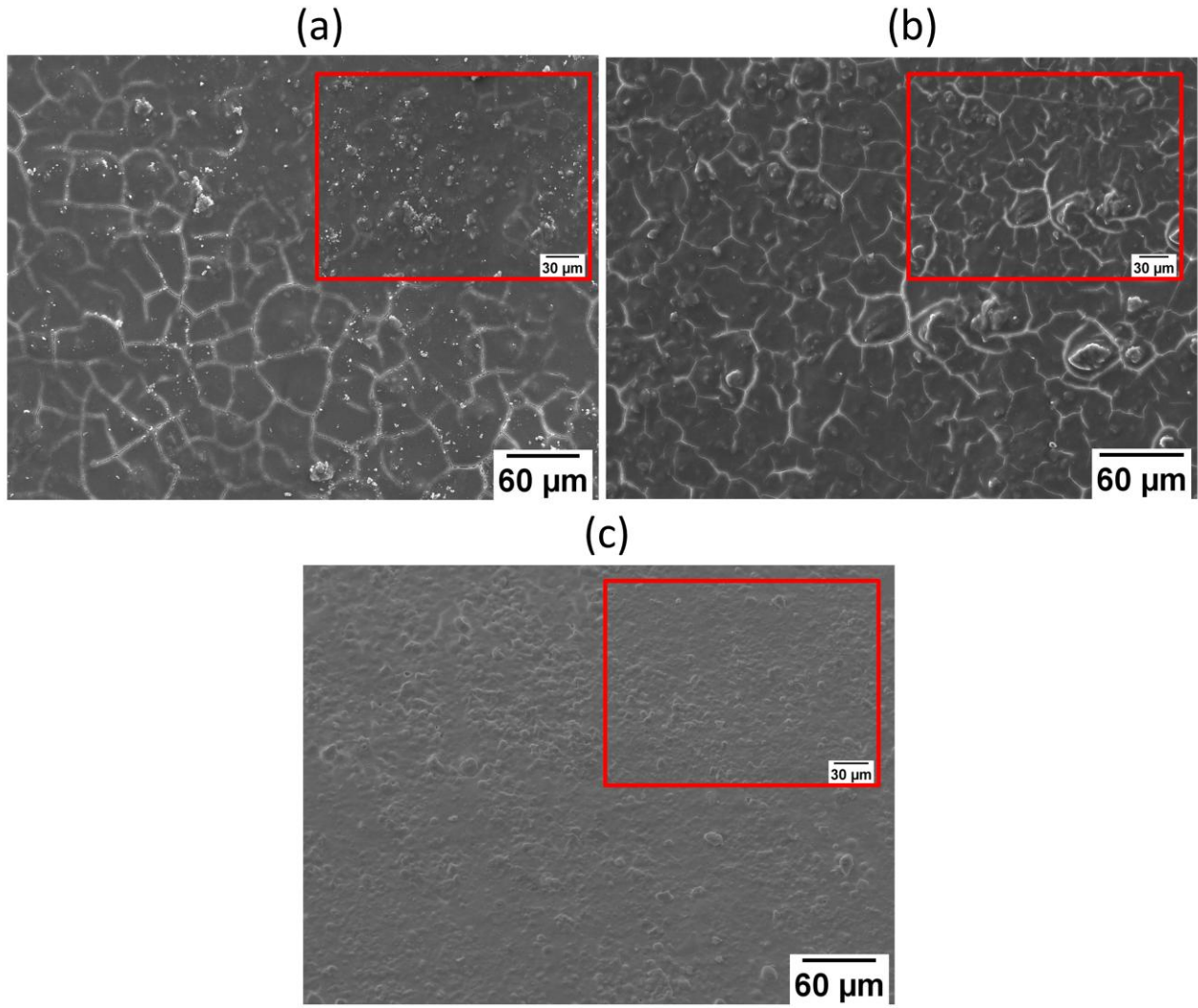


Figure 55. SEM images of the surface of the commercial α - Al_2O_3 tube at different silica layer deposition rates: (a) $30 \text{ mm} \cdot \text{min}^{-1}$, (b) $60 \text{ mm} \cdot \text{min}^{-1}$ and (c) $90 \text{ mm} \cdot \text{min}^{-1}$ at 250x magnification, with a zoom-in (red square) at 500x.

As observed in Figure 55, different dip-coating speeds affected the coverage of the ceramic substrate. At $30 \text{ mm} \cdot \text{min}^{-1}$ (Figure 55a), the coating was uniform but showed cracking and surface agglomerates. At $60 \text{ mm} \cdot \text{min}^{-1}$ (Figure 55b), the coating remained uniform, yet some fissures persisted. At $90 \text{ mm} \cdot \text{min}^{-1}$, the coating was uniform and free of cracks (Figure 55c).

The superior performance at $90 \text{ mm} \cdot \text{min}^{-1}$ can be explained by the dip-coating process, which involves three key stages: immersion and dwell time, deposition and drainage and evaporation [87]. The immersion speed influences wetting and liquid-substrate interactions, while the withdrawal speed plays a critical role in film formation [87, 118]. According to the *Landau–Levich* equation, which relates film thickness to the withdrawal speed raised to the $2/3$ power, higher

withdrawal speeds generally yield thicker films. At lower speeds (typically between 60 and 600 $\text{mm} \cdot \text{min}^{-1}$), uneven liquid distribution and capillary effects can occur, as the film thickness is governed by the balance between viscous drag and liquid-vapor surface tension [87]. Increasing the withdrawal speed to 90 $\text{mm} \cdot \text{min}^{-1}$ likely resulted in a thicker and more homogeneous silica film, allowing for more efficient stress distribution during drying and calcination and significantly reducing surface cracking [87, 118].

Using the optimal coating condition, achieved at a dip/withdrawal speed of 90 $\text{mm} \cdot \text{min}^{-1}$, the thickness of the layer was measured, as shown in Figure 56.

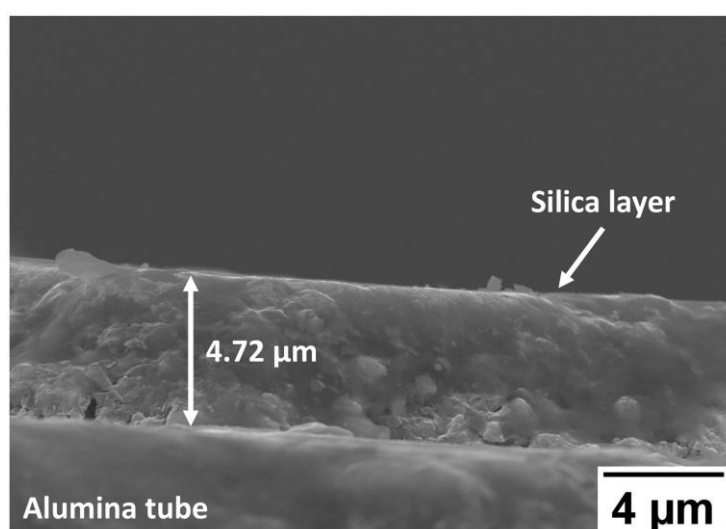


Figure 56. SEM image of the thickness of silica layer deposited at a dip/withdrawal speed of 90 $\text{mm} \cdot \text{min}^{-1}$ on commercial $\alpha\text{-Al}_2\text{O}_3$ tubes at 5000x magnification.

As indicated in Figure 56, the average thickness obtained for the intermediate silica layer was $4.72 \pm 0.07 \mu\text{m}$. Considering that the total resistance of a membrane is directly proportional to its thickness and, according to *Darcy's Law* for porous membranes, the permeance (flux normalized by the pressure difference) is inversely proportional to membrane resistance [180]. Thus, a thicker layer implies higher resistance and, consequently, lower permeate flux. Although the intermediate silica layer plays a relevant functional role in optimizing the adhesion and quality of the zeolite selective layer, it is not selective for the separation of small gas molecules [177, 180]. Therefore, when a non-selective layer is excessively thick, it only adds unnecessary resistance to mass transport, reducing flux without providing any separation benefit [5, 118, 180]. Hence, the thickness of $4.72 \mu\text{m}$ obtained in the

silica deposition can be considered adequate, as it does not represent a significant barrier to permeation, thereby minimizing negative effects on membrane performance.

Using the optimal silica deposition condition established for the commercial α -Al₂O₃ tubes, the coating was applied to the tube produced by freeze-casting, and the results are shown in the SEM images in Figure 57.

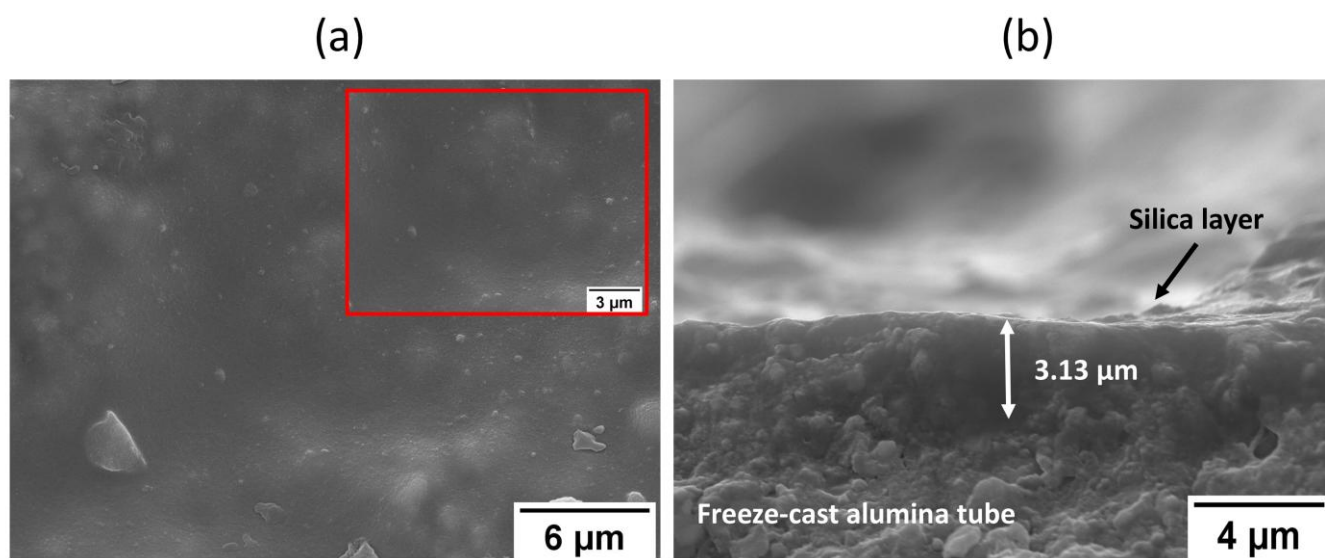


Figure 57. SEM images of (a) the surface and (b) the thickness of silica layer deposited at a dip/withdrawal speed of $90 \text{ mm} \cdot \text{min}^{-1}$ on freeze-cast α -Al₂O₃ tube at 4000 - 6000x magnification, with a zoom-in (red square) at 7000x.

As observed for the commercial α -Al₂O₃ tubes, the freeze-cast tube (FCT) also exhibited a uniform coating along the tube surface under the optimal conditions of $90 \text{ mm} \cdot \text{min}^{-1}$. Furthermore, the average thickness of the silica intermediate layer was approximately $3.13 \pm 0.04 \text{ } \mu\text{m}$ (Figure 57b), a value lower than that obtained for the silica layer deposited on commercial tubes (Figure 56).

The difference in thickness between the films deposited on freeze-cast α -Al₂O₃ substrates ($3.13 \text{ } \mu\text{m}$) and commercial substrates ($4.72 \text{ } \mu\text{m}$), under identical dip-coating conditions, could be attributed to the distinct porous morphologies of the supports [87, 118]. Freeze-cast substrates exhibit a high open porosity (approximately, 48%) with macropores distribution, possibly in the $6\text{-}14 \text{ } \mu\text{m}$ range, which could facilitate the infiltration and retention of silica within the ceramic matrix. In contrast, commercial substrates, with smaller pores (around 200 nm or $0.2 \text{ } \mu\text{m}$) [22], restrict infiltration and concentrate the deposition on the external surface.

Consequently, although the total amount of deposited silica may be comparable or even greater in freeze-cast supports, the superficial layer detectable by SEM appears thinner, since a portion of the material is distributed within the macropores. While the silica layer improves film-substrate adhesion [118], its intrusion within the macropores of the freeze-cast substrate may be detrimental for the intended gas separation application. The SSZ-13 zeolite layer, responsible for gas separation, requires a homogeneous and well-defined surface for continuous growth [5]. Irregularities caused by silica embedding in the macropores increase the risk of defects, compromising membrane selectivity when separating gases with closely similar kinetic diameters [5, 83].

Therefore, SSZ-13 seed deposition will initially be carried out on commercial α -Al₂O₃ substrates, with the best-performing conditions subsequently applied to the freeze-cast support.

4.3.2. Characterization of SSZ-13 Membranes

To produce a high-quality zeolite membrane, especially for gas separations, it is essential to consider a combination of structural characteristics and synthesis conditions that optimize both permeance and selectivity. An ideal membrane should have a thin selective layer, typically in the order of nanometers to a few micrometers [177]. Thinner membranes, such as SSZ-13 with thicknesses of approximately 3.5 - 6.0 μm , result in higher fluxes (permeances), since the total resistance of the membrane is directly proportional to its thickness [22]. However, very thin films may be more susceptible to defects. Beyond thickness, the layer must be continuous, homogeneous and composed of well-intergrown crystals to ensure an effective selective pathway for the permeate [5, 22, 83].

In this context, Figure 58 shows the SEM images of the SSZ-13 (HM) membrane produced with the hydrothermal seed synthesized over 4 days (K⁺_SSZ-13_H4).

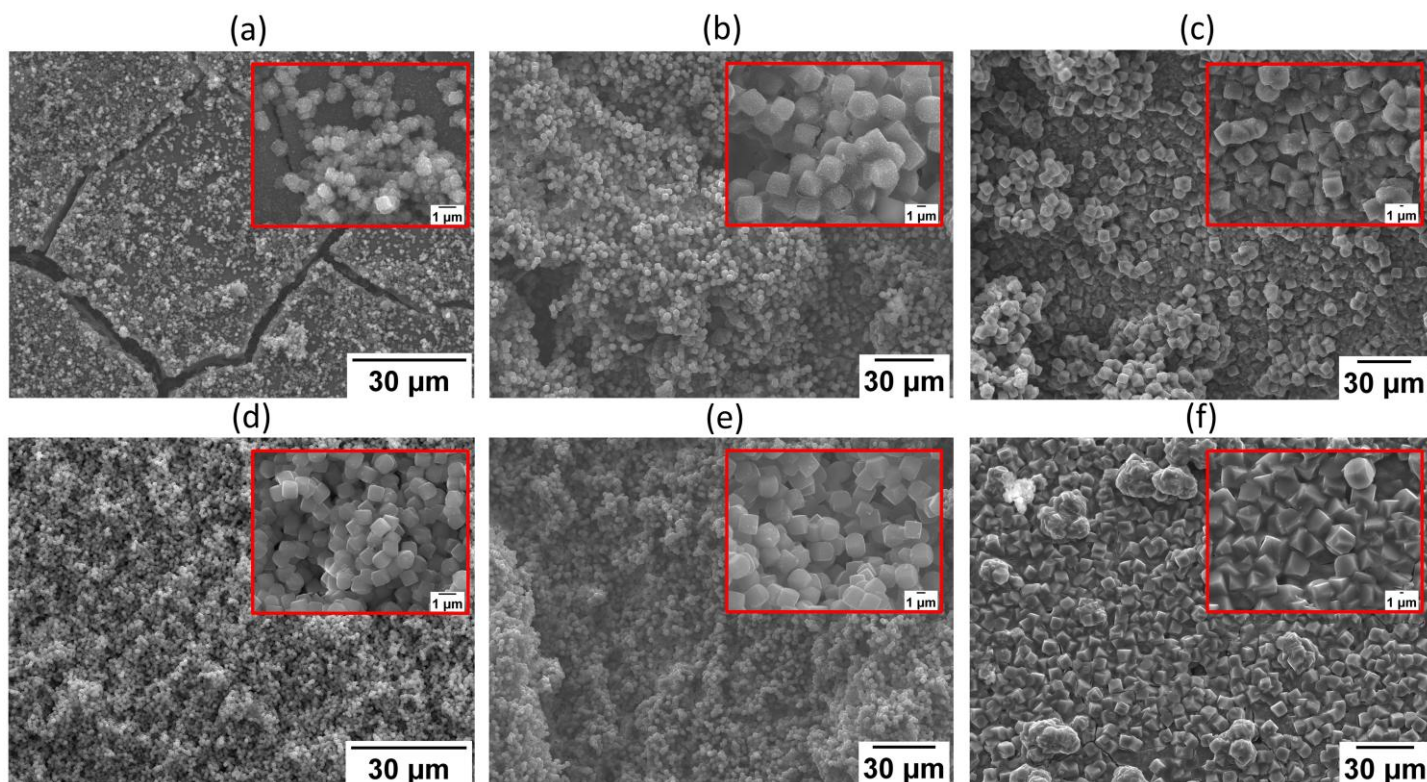


Figure 58. Micrographs of SSZ-13 membranes using hydrothermal seed (HM) with two and three depositions, respectively: (a) and (d) HM_6h; One and two depositions respectively: (b) and (e) HM_12h; (c) and (f) HM_24h at 500 - 10000x magnification, with a zoom-in (red square) at 2000 -5000x.

Figure 58 illustrates the influence of different seed layer depositions followed by hydrothermal growth on the formation of the zeolitic layer. For the 6-hour synthesis (Figures 58a,d), three successive seed depositions were required to obtain a uniform and well-distributed zeolitic layer (Figure 58d). In the membrane prepared with two seed depositions (Figure 58a), continuous cracks were observed, extending from the membrane support through the zeolitic layer, fragmenting it into pieces a feature that would have a significantly negative impact on selectivity .

In contrast, for the 12-hour synthesis (Figures 58b,e), a single seed deposition was sufficient to produce a dense layer, although some agglomerates were observed during membrane growth (Figure 58b). A similar trend was found for the 24-hour synthesis (Figures 58c,f), where a single zeolite deposition also resulted in homogeneous surface coverage, again with the presence of agglomerates. This homogeneous layer exhibited vacancy formation, which may be related to mesoporous defects [83]. These defects likely arise from imperfect intergrowth between crystals during synthesis, leading to intercrystalline pores that can

compromise the selectivity of the material (Figures 58b,e). Discontinuous cracks were also observed within the zeolitic crystals (Figures 58c,f), representing another factor that can impair the performance of this membrane in gas separation applications [5, 83].

Although the membrane produced with 24 hours of hydrothermal growth (Figures 58c,f) exhibited a seemingly continuous layer with well-intergrown crystals, features that could provide an effective selective pathway for permeation [22], it also presented cracks, voids and agglomerates of SSZ-13 within the zeolitic layer. Such defects can impair mass transport, reduce selectivity and compromise performance under humid conditions [5, 82]. They generate larger voids that enable non-selective gas permeation, weakening the membrane's ability to discriminate between gases [5, 22]. Under humid environments, water adsorption within the cracks can block transport pathways, decreasing permeance and overall efficiency. Furthermore, these defects may arise from incomplete layer formation or thermal stresses, ultimately undermining the membrane's long-term mechanical stability [5, 22, 82, 177].

It was also possible to quantify the distribution of average thicknesses in the SSZ-13 membranes produced at synthesis times of 6-hours (three seed layer depositions, HM_6h), 12-hours (one seed layer deposition, HM_12h) and 24-hours (one seed layer deposition, HM_24h), as shown in the SEM images in Figure 59.

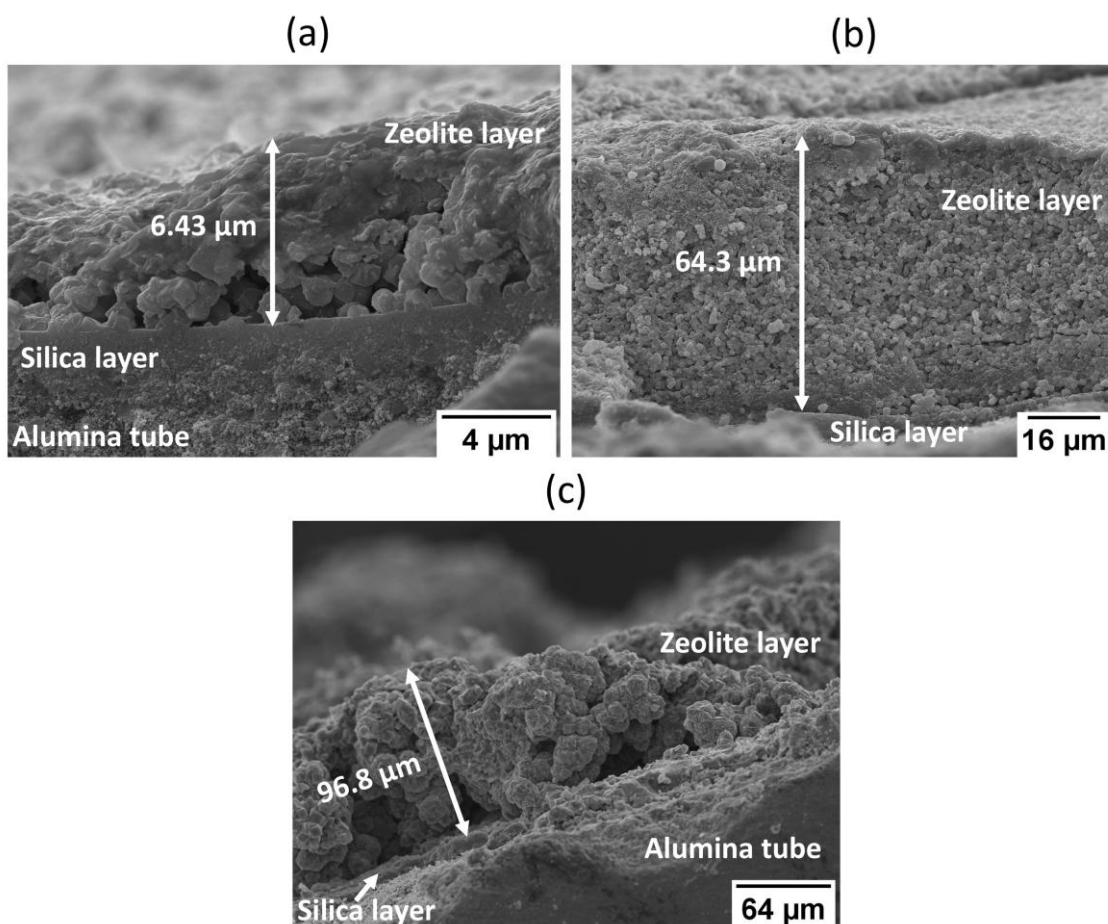


Figure 59. SEM images of the average thickness obtained for the SSZ-13 membranes (HM): (a) 6 hours - three seed layer depositions, (b) 12 hours - one seed layer deposition and (c) 24 hours - one seed layer deposition. Approximations between 350x and 6000x.

As expected, increasing the synthesis time for SSZ-13 membrane growth also led to an increase in membrane thickness [5, 83]. The HM_6h membrane (Figure 59a) exhibited the lowest average thickness of 6.43 μm , which approximately falls within the range reported in the literature for SSZ-13 membranes used in gas separation [20, 22, 43–45, 49, 50]. Moreover, the high surface coverage and well-defined cubic crystals observed at this growth time indicate that this membrane is promising for gas separation process, as it can result in higher fluxes (permeances), given that the total resistance of the membrane is directly proportional to its thickness [22].

In the case of the HM_12h membrane (Figure 59b), although high surface coverage was achieved, the membrane thickness of 64.3 μm would likely result in high resistance to permeate flow, reducing the membrane's efficiency in gas separation [5, 22, 82, 177]. The HM_24h membrane (Figure 59c) exhibited an even

greater thickness of 96.8 μm and the formation of agglomerates, which generated defects throughout the structure. These defects are expected to decrease both the selectivity and the permeance of the membrane when applied to gas separation process [5, 22, 82, 177].

The same SEM image analysis was performed for the membrane (MWM) produced using microwave-synthesized seeds (SSZ-13_MW60), as shown in Figure 60.

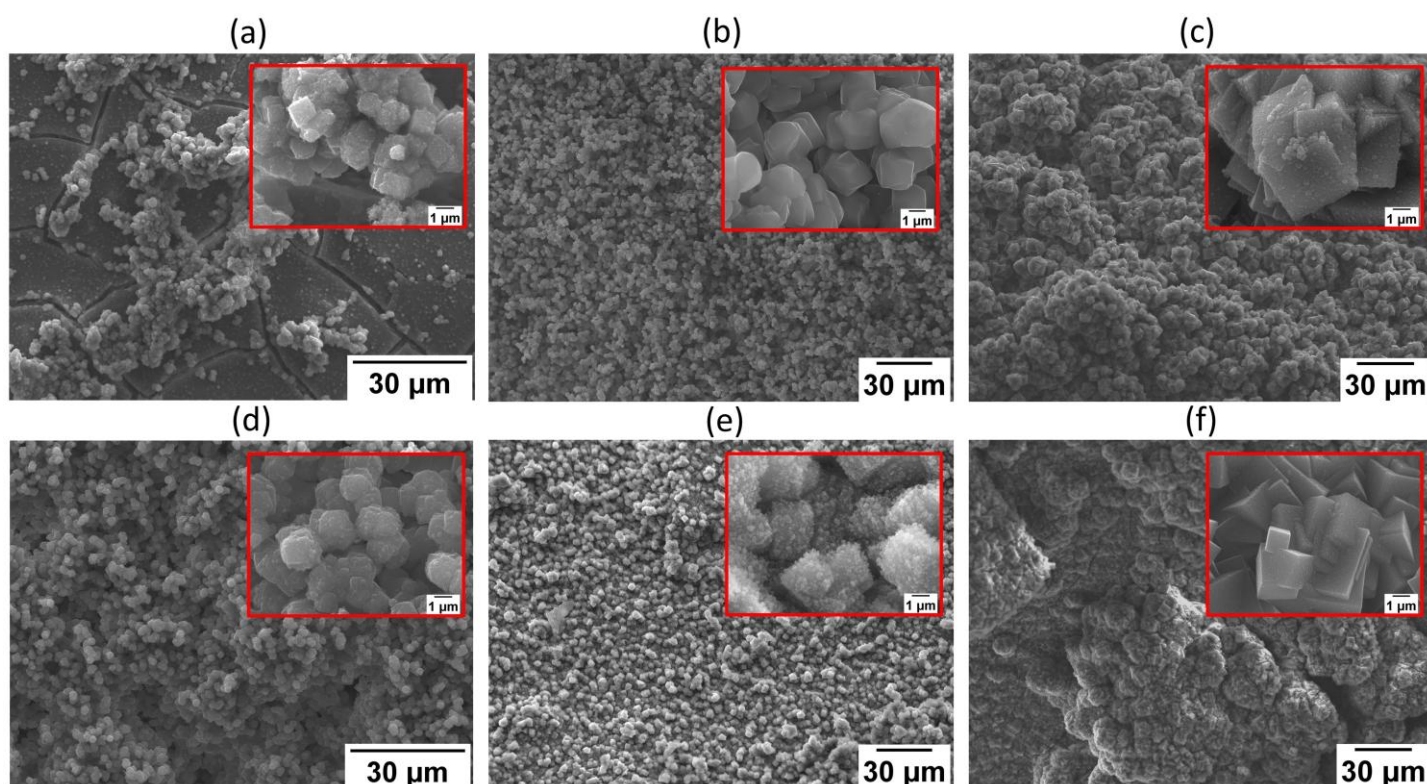


Figure 60. Micrographs of SSZ-13 membranes using microwave seed (MWM) with two and three depositions, respectively: (a) and (d) MWM_6h; One and two depositions, respectively: (b) and (e) MWM_12h; (c) and (f) MWM_24h at 500-1000x magnification, with a zoom-in (red square) at 10000x.

Although the seed used for the production of the MWM membrane (average size, $0.645 \pm 0.016 \mu\text{m}$) was significantly smaller than that used for the HM membrane (average size, $5.67 \pm 0.07 \mu\text{m}$), it exhibited a behavior similar to the HM membrane. For the 6-hour synthesis (Figures 60a,d), three successive seed layer depositions were required to obtain a uniform and well-distributed zeolitic layer (Figure 60d). As observed for the HM_6h membrane (Figure 58a), also two

depositions were insufficient to achieve complete coverage, resulting in continuous cracks throughout the membrane surface (Figure 60a).

In the case of the 12-hour synthesis (Figures 60b,e), a single deposition was sufficient to produce a dense and uniform layer (Figure 60b). However, for the 24-hour synthesis (Figures 60c,f), one zeolite deposition led to homogeneous surface coverage but with non-uniform growth. This non-uniformity is likely due to the smaller seed size, which favors the formation of agglomerates during deposition, and combined with the extended growth time, resulted in more pronounced crystal growth in some regions than in others [82, 83, 92].

It was also quantified the distribution of the average thicknesses of the SSZ-13 membranes produced at synthesis times of 6-hours (three seed layer depositions, MWM_6h), 12-hours (one seed layer deposition, MWM_12h) and 24-hours (one seed layer deposition, MWM_24h), as shown in the SEM images in Figure 61.

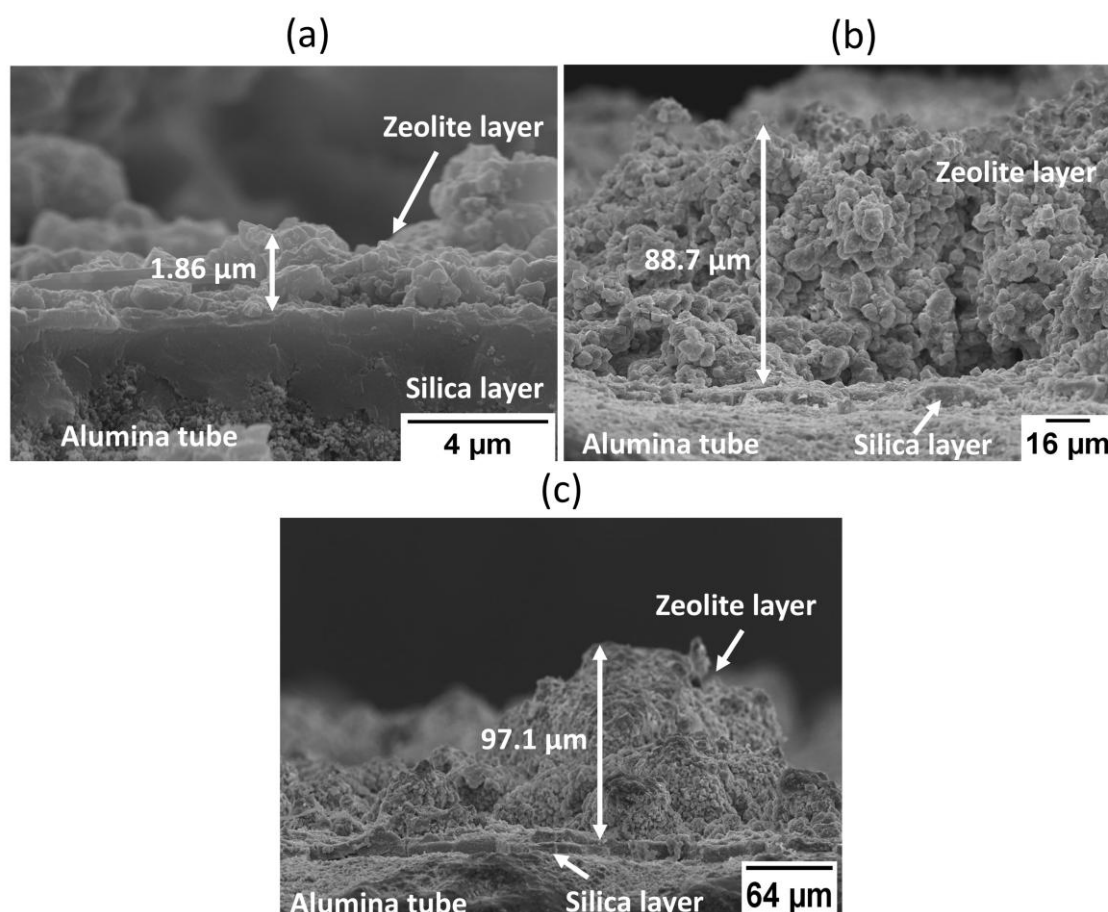


Figure 61. SEM images of the average thickness obtained for the SSZ-13 membranes (MWM): (a) 6 hours - three seed layer depositions, (b) 12 hours - one seed layer deposition, and (c) 24 hours - one seed layer deposition. Approximations between 300x and 8000x.

Although exhibiting behavior similar to that observed in the HM membranes, the MWM_6h membrane (Figure 61a) showed a reduction in average thickness, measuring 1.86 μm . This thin layer may be ideal, as it does not impose significant resistance to permeate flow while potentially presenting high selectivity in gas mixture separation applications [5, 82, 83, 180]. Despite the dense layer formed with only a single deposition in the MWM_12h membrane (Figure 61b), it resulted in a zeolitic layer with considerable thickness and the presence of defects along the membrane. A similar behavior was observed for the MWM_24h membrane (Figure 61c), which exhibited even greater non-uniform growth along the intermediate silica layer, features that are undesirable for its use as a gas separation membrane [5, 83].

Based on the optimization of membrane formation parameters in commercial $\alpha\text{-Al}_2\text{O}_3$ tubes, the best seed and deposition conditions were applied to the tubes produced via freeze-casting (FCT). In this case, the FCM membrane was grown using SSZ-13_MW60 with 3 seed deposition steps and 6 hours of synthesis. The SEM results for this FCM membrane are shown in Figure 62.

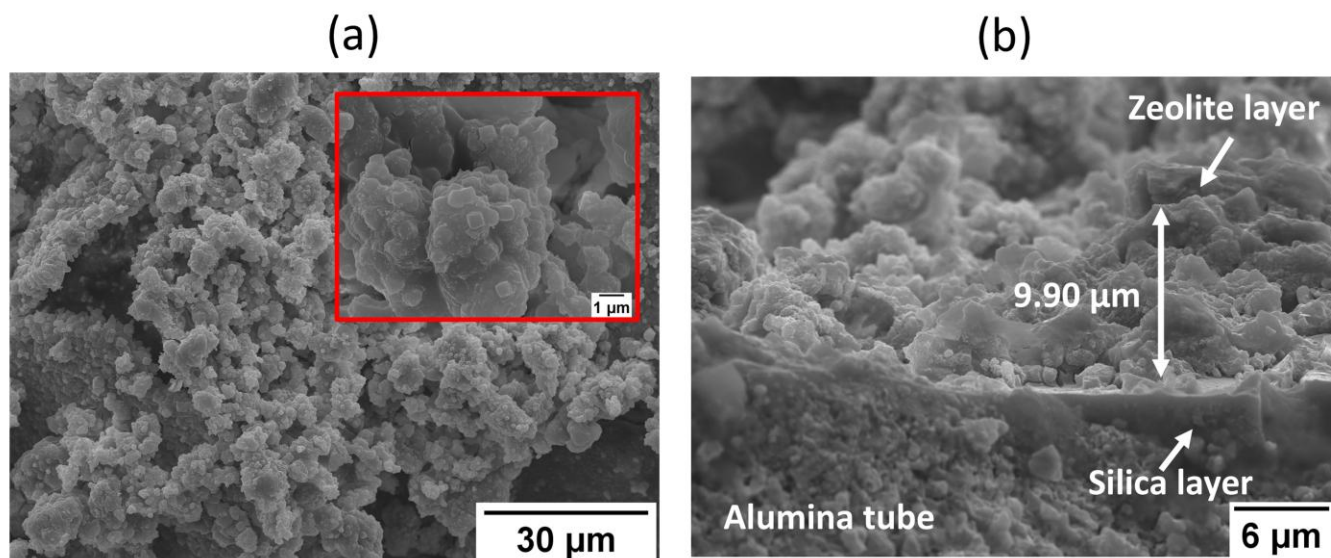


Figure 62. SEM images showing (a) the surface and (b) the average thickness of the SSZ-13 membranes (FCM) at 1000x magnification, with a zoom-in (red square) at 10000x.

As shown in Figure 62a, the FCM membrane exhibited the growth of SSZ-13 layer characterized by the formation of aggregates composed of numerous interconnected cubic crystals. Irregularities along the zeolitic layer can also be

observed, most likely influenced by the preliminary deposition of the silica layer on the freeze-cast α -Al₂O₃ substrate. Figure 62b shows that the average thickness of the zeolite layer is approximately $9.90 \pm 0.26 \mu\text{m}$, a value significantly higher than that observed for the MWM membrane ($1.86 \pm 0.05 \mu\text{m}$), which used the same seeding material (SSZ-13_MW60) for zeolite layer formation. As previously discussed, the increased average thickness and structural irregularities, observed in the FCM membrane, may lead to significant reductions in selectivity and efficiency during gas separation process [5, 22, 82, 177].

Therefore, membranes synthesized on commercial α -Al₂O₃ tubes for 6 hours (HM_6h and MWM_6h) are considered more promising, due to their high coverage and average zeolitic layer thickness between 1.8 - 7 μm . In the case of the FCM membrane, whose substrate was produced via freeze-casting, it may exhibit reduced selectivity and efficiency in the gas separation process due to irregularities in the deposited SSZ-13 layer. Therefore, optimization of the tubular substrate (FCT) production is necessary to achieve better coverage and formation of the zeolitic film on its surface.

4.4. Applicability of the materials

In this section, the adsorption properties obtained from the *Langmuir isotherm* and Ideal Adsorbed Solution Theory (IAST) methods will be discussed for the SSZ-13_MW60 seed using different single gases (CH₄, N₂ and CO₂) at various pressures (0.1 to 0.9 bar). Subsequently, these results will be compared with literature data on SSZ-13 membrane for the separation of NG components.

4.4.1. Adsorptive properties of the SSZ-13_MW60 zeolite

As indicated in Figure 63 and Table 18, the *Langmuir isotherms* were used to predict the theoretical maximum adsorption capacity per unit mass of the SSZ-13_MW60 zeolite in the presence of different gases present in the NG composition.

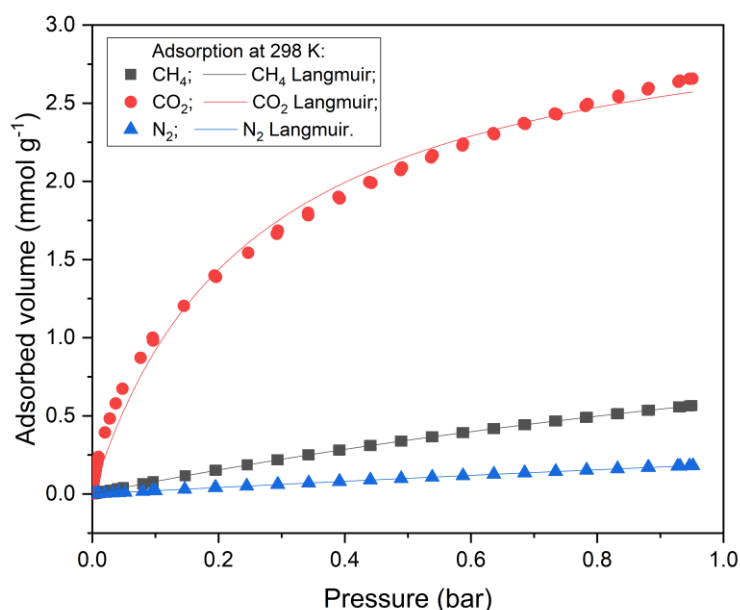


Figure 63. Adsorption isotherms for different pure gases at 298 K for the SSZ-13_MW60 sample.

Table 18. *Langmuir isotherm* regression parameters for different gases adsorbed on the SSZ-13_MW60 sample.

Single gas:	$q_{\max}$ (mmol · g ⁻¹):	b (bar ⁻¹):	R^2 :	K_H (mmol · g ⁻¹ · bar ⁻¹)
CH ₄	1.951 ± 0.005	0.429 ± 0.002	0.999	0.837
CO ₂	3.260 ± 0.053	3.933 ± 0.197	0.996	12.82
N ₂	1.620 ± 0.026	0.133 ± 0.002	0.999	0.215

Observing the maximum adsorption capacity ($q_{\max}$) values, it can be noted that CO₂ is adsorbed more strongly on the zeolite surface than the other gases, as it exhibited a $q_{\max}$ value 67% higher than that for CH₄ and twice the value for N₂. This parameter indicates that CO₂ is more easily adsorbed than the other components due to the stronger interaction between CO₂ molecules and the zeolite, which occurs because of its higher polarizability ($\alpha_{\text{CO}_2} = 27.60 \times 10^{25} \text{ C} \cdot \text{m}^2 \cdot \text{V}^{-1}$) [181] and quadrupole moment ($Q_{\text{CO}_2} = 13.4 \times 10^{-40} \text{ C} \cdot \text{m}^2$) [182], favoring interactions with polar groups or charged surfaces. This result is consistent with SSZ-13 zeolite (CHA topology), which is recognized for its high performance in CO₂ capture/separation [38, 181].

The other gases, being more nonpolar molecules, have a less significant interaction with the zeolite surface. However, due to the higher polarizability of the CH₄ molecule compared to the N₂ molecule ($\alpha_{\text{CH}_4} = 25.93 \times 10^{25} \text{ C} \cdot \text{m}^2 \cdot \text{V}^{-1}$ and $\alpha_{\text{N}_2} = 17.40 \times 10^{25} \text{ C} \cdot \text{m}^2 \cdot \text{V}^{-1}$) [115, 130, 181], it exhibited a slightly higher q_{max} (20.4% greater) than the N₂. This behavior suggests that zeolite may be efficient for CH₄ enrichment from CH₄/N₂ mixtures [115, 181].

Regarding the parameter b , shown in Table 18, it measures the gas affinity for the surface [36, 40]. As observed in Figure 63, there is an increase in gas adsorption as pressure increases, with this phenomenon being more prominent for CO₂, consistent with its higher b value. As previously mentioned, this preferential affinity is related to the strong quadrupole moment and high polarizability of the CO₂ molecule [129, 130], which interacts strongly with the electrostatic field of the cations in the zeolite structure [181].

Another aspect to consider is the possibility of determining the adsorption selectivity (*Henry's selectivity* – S_{H}) of gases on the zeolite surface, at low pressures, from the *Henry constant* (K_{H}) [129, 130], as shown in Table 18. The high thermodynamic selectivity indicated by CO₂ is evidenced by its considerable adsorption capacity and affinity compared to the other gases. When comparing the K_{H} values for CO₂/CH₄ and CO₂/N₂, S_{H} of 15.3 and 59.6 are observed, respectively. This goods adsorption selectivities further confirms the strong potential for CO₂ separation from gas mixtures, such as in natural gas purification (CO₂/CH₄) and carbon capture from flue gases (CO₂/N₂) [114, 129, 130].

Regarding the adsorptive selectivity of CH₄/N₂, it has a value of 3.89, indicating a preferential adsorption of the CH₄ molecule. This preferential adsorption, as mentioned earlier, is related to the polarizability of the CH₄ molecule, which, being higher than that of the N₂ molecule, facilitates stronger interactions with the adsorbent surface [35, 115, 181]. Relating this behavior to the adsorption capacity (q_{max}) obtained for CH₄ (1.951 mmol·g⁻¹), it can be observed that this value was higher than those reported for CHA-type molecular sieves in the study by Shang et al. [115], which showed q_{max} values around 1.38 mmol·g⁻¹. This result reflects a thermodynamic advantage for CH₄ adsorption on the SSZ-13 produced in this work for the CH₄/N₂ mixture.

4.4.2. Ideal adsorbed solution theory (IAST) gas selectivity of the SSZ-13_MW60 zeolite

In the previous section, based on the adsorption isotherms of different pure gases on the SSZ-13_MW60 material, the adsorption capacity ($q_{\max}$) and *Henry's selectivity* (S_H) were determined, serving as preliminary criteria for discussing the adsorbent's performance. However, to deepen this analysis, the theoretical IAST model aims to predict the equilibrium adsorption behavior of bicomponent gas mixtures [130, 131], providing the separation selectivity (S_{IAST}) for different gas ratios in the NG composition and under different pressures.

In this context, Figure 64 shows the S_{IAST} for the gas mixtures N_2/CH_4 and CH_4/N_2 (Figure 64a,b). When analyzing the selectivity behavior of the N_2/CH_4 mixture (Figure 64a), it is observed that for low N_2 proportions (10/90, 20/80 and 30/70), the increase in pressure initially leads to a reduction in selectivity. However, for pressures above 0.6 bar, selectivity starts to increase again. For mixtures richer in N_2 , the increase in pressure results in a decrease in the sample's selectivity. In the case of the CH_4/N_2 mixture (Figure 64b), it is verified that for CH_4 proportions between 10/90 and 60/40, selectivity increases with increasing pressure. For CH_4 concentrations above 60%, an initial increase in selectivity is observed up to approximately 0.6 bar, followed by a decrease at higher pressures, indicating a decline in mixture selectivity for the SSZ-13 sample.

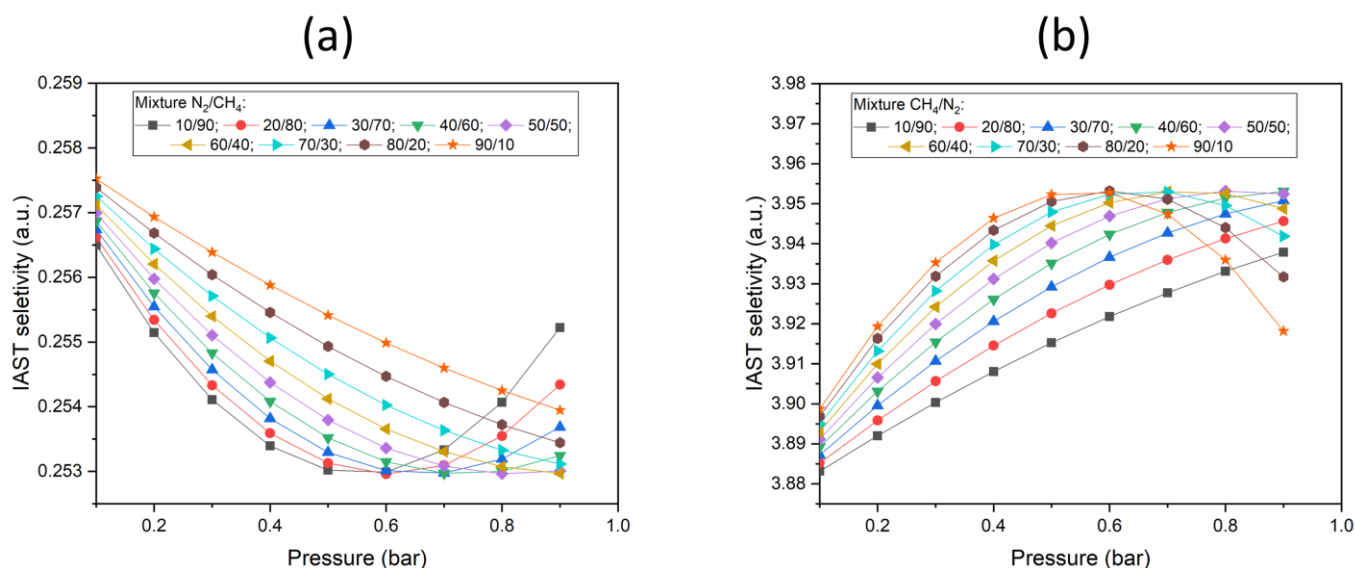


Figure 64. IAST selectivity (S_{IAS}) for N_2/CH_4 and CH_4/N_2 gas mixtures at different molar ratios and pressures.

As indicated in the previous section, the SSZ-13 zeolite acts as a selective adsorbent for CH_4 due to the higher polarizability of this gas compared to N_2 , which favors its adsorption in the micropores of the structure, even in mixtures with low CH_4 concentrations [115, 130, 181]. The low selectivity observed (values below 0.258) for the N_2/CH_4 gas mixture and the higher selectivity (values between 3.88 and 3.95) for the CH_4/N_2 mixture confirms this adsorption preference for CH_4 .

Under low-pressure conditions (up to 0.6 bar), the most energetic sites, with higher affinity, are preferentially occupied by CH_4 molecules, which limits the adsorption of N_2 . As the pressure increases above 0.6 bar and the CH_4 proportion exceeds 70%, the selectivity changes, since the high-energy sites are already saturated with the preferential gas. Thus, adsorption begins to occur at lower-energy sites, where the difference in affinity between the molecules still favors CH_4 , although in a more balanced manner. Consequently, as the pressure increases, N_2 gas is also adsorbed, reducing the relative ratio between the adsorbed quantities and, therefore, the CH_4/N_2 selectivity, as the system approaches a more balanced saturation regime between the two gases. It can thus be concluded that gas adsorption on the zeolite surface is initially governed by site affinity (in the range of 0.1 to 0.6 bar), and later by micropore filling capacity at higher pressures (0.6 to 0.9 bar) [35, 38, 115].

In the study conducted by Shang et al. [115], it was observed that for low CH₄ concentrations (around 20%) and pressures close to 10 bar, the SSZ-13 zeolite with a Si/Al ratio of 30 exhibited an S_{IAST} of 2.5 for the CH₄/N₂ mixture. This value is lower than the one obtained for the SSZ-13_MW60 zeolite synthesized in this work, which has a Si/Al ratio of 18.1 and an S_{IAST} of 3.94 (Figure 64b). Although the zeolite reported by Shang et al. presented a higher specific surface area (704.6 m²·g⁻¹) and micropore volume (0.32 cm³·g⁻¹) compared to the SSZ-13_MW60 sample (694 m²·g⁻¹ and 0.249 cm³·g⁻¹, respectively), the higher IAST selectivity of the latter is believed to be associated with the Si/Al ratio of the samples. At higher Si/Al ratios, the zeolite framework is more electrically neutral. However, as this ratio decreases toward values similar to that of the zeolite synthesized in this study (Si/Al = 18), a greater number of compensating cations (K⁺) are introduced to balance the negative charge of the aluminosilicate framework. This enhances the interaction strength between the zeolite and the more polarizable CH₄ molecules, thereby increasing the CH₄/N₂ S_{IAST} [115].

Another gas mixture of interest for NG purification is the CO₂/CH₄ and CH₄/CO₂ mixture, whose S_{IAST} results are shown in Figure 65.

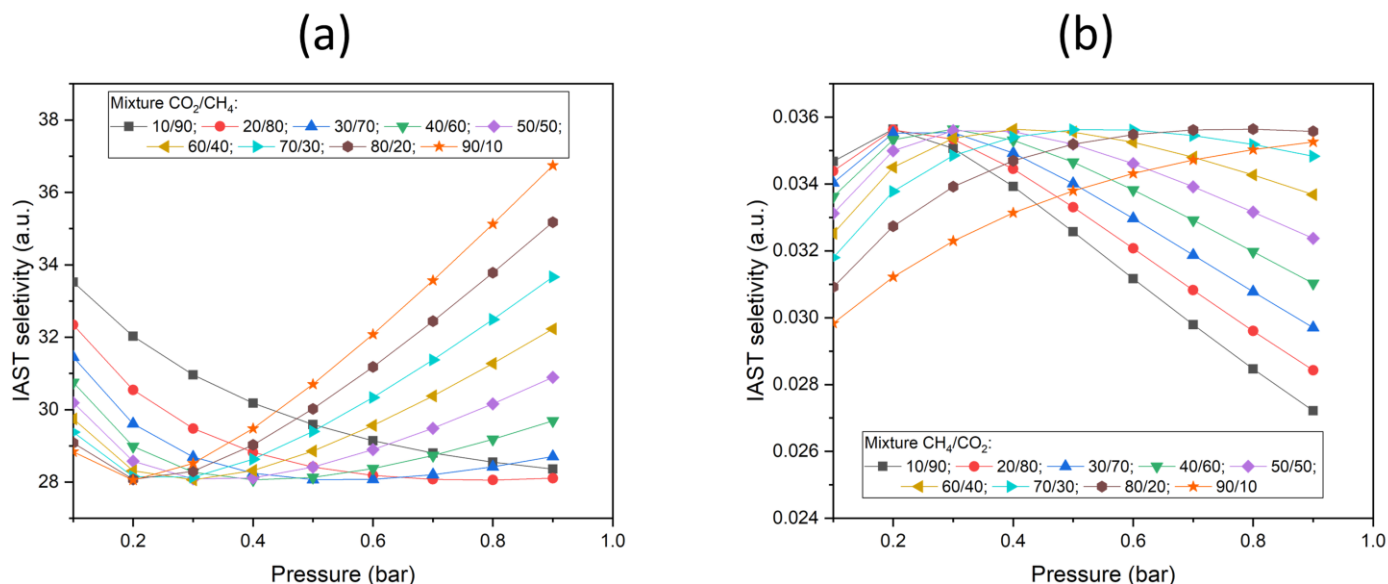


Figure 65. IAST selectivity (S_{IAST}) for CO₂/CH₄ and CH₄/CO₂ gas mixtures at different molar ratios and pressures.

In the previous section, it was shown that the CO₂ gas molecule exhibits an adsorptive capacity 67% higher than that of the CH₄ molecule with respect to

adsorption on the SSZ-13_MW60 zeolite. This higher affinity of CO₂ for SSZ-13_MW60 is confirmed by the considerably higher S_{IAST} values for the CO₂/CH₄ mixture (ranging from 28 to 37) compared to the CH₄/CO₂ mixture (values below 0.034).

The S_{IAST} range for the CO₂/CH₄ mixture (Figure 65a) indicates that, for the 10/90 and 20/80 ratios, selectivity decreases as pressure increases from 0.1 to 0.9 bar. The other compositions show similar behavior, with an initial drop in selectivity followed by an increase as pressure rises. This initial decrease becomes progressively less pronounced, and the subsequent increase more significant, as the CO₂ molar proportion in the mixture increases. The same behavior is consistent with that observed in Figure 65b for the CH₄/CO₂ mixture, where compositions with higher CH₄ concentrations (between 90/10 and 70/30) exhibited an increase in selectivity with increasing pressure. For the remaining proportions, the pressure increase resulted in an initial rise followed by a decrease in selectivity, with this reduction becoming more gradual as the CH₄ fraction in the mixture increased.

Analogous to the reasoning applied in the analysis of CH₄/N₂ mixture selectivities, the CO₂ molecule, due to its higher polarizability and quadrupole moment compared to CH₄, is preferentially adsorbed at high-energy sites at low pressures, resulting in high selectivity within the micropores of the zeolitic structure. As pressure increases, these sites become saturated with CO₂ molecules, and adsorption occurs at lower-energy sites, reducing the affinity difference between CO₂ and CH₄ and, consequently, the selectivity, a behavior observed in mixtures with lower CO₂ concentrations. Thus, as the CO₂ concentration in the mixture increases, the initial decrease becomes less pronounced, followed by a more evident increase in selectivity with rising pressure. In CO₂-rich fractions, the more strongly adsorbable molecules predominate, intensifying micropore occupancy under a saturation regime, which diminishes the contribution of CH₄ adsorption and, consequently, increases the selectivity of the CO₂/CH₄ mixture [35, 38, 130, 182].

In the work of Pérez-Botella et al. [37], low S_{IAST} values were reported for equimolar CO₂/CH₄ mixtures at 1 bar in pure-silica zeolites (Si-CHA), reaching values around 5. This is considerably lower than the value obtained under the same conditions for SSZ-13_MW60 (approximately 31). Pure-silica zeolites contain no aluminum in their framework and therefore lack charge-compensating cations. In such materials, adsorption relies mainly on dispersion forces and confinement effects

within the microporous structure [35]. Although Si-CHA exhibits slightly higher affinity for CO₂ than for CH₄, since CO₂ possesses greater polarizability and a higher quadrupole moment as discussed previously, the absence of charged sites severely limits selectivity [35, 37]. Hence, the Si/Al ratio in SSZ-13_MW60 is believed to be at an optimal level, where the presence of K⁺ active sites enables more selective interactions with CO₂, resulting in an S_{IAST} more than four times higher than that observed for Si-CHA.

The S_{IAST} was also calculated for the CO₂/N₂ and N₂/CO₂ mixtures, as shown in Figure 66.

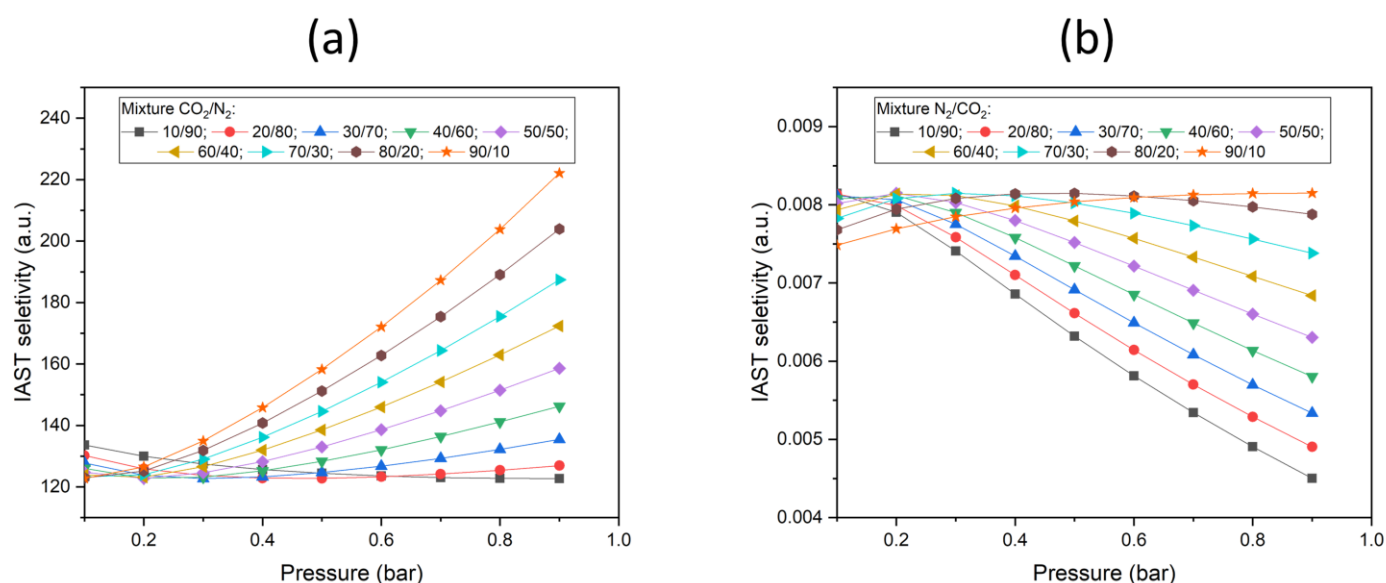


Figure 66. IAST selectivity (S_{IAST}) for CO₂/N₂ and N₂/CO₂ gas mixtures at different molar ratios and pressures.

As shown in Figure 66a, in summary, the S_{IAST} of the CO₂/N₂ mixture increases with rising pressure, exhibiting the highest selectivity values among the analyzed mixtures, ranging from 120 to 220. In contrast, the selectivity obtained for the N₂/CO₂ mixture (Figure 66b) tends toward zero and decreases as pressure increases. This analysis highlights that the adsorption capacity and affinity for the zeolite's microporous sites are significantly higher for the CO₂ molecule, indicating that the SSZ-13_MW60 exhibits excellent performance in adsorbing this gas, a behavior expected for this class of materials [35, 38, 114, 182].

Although it shows a trend similar to S_{IAST}, *Henry's selectivity*, reported in the previous section, represents only the initial behavior (intrinsic affinity) of gas adsorption [35, 129]. In contrast, S_{IAST}, by simulating the competitive behavior of the

mixture under a bicomponent equilibrium regime, results in higher values, as observed for the CO₂/N₂ mixture, due to the predominance of CO₂ adsorption at the available sites, especially when increased pressure favors partial saturation of the micropores [35].

In the study by Hudson et al. [182], S_{IAST} values between 72 and 74 were reported for H_SSZ-13 and Cu_SSZ-13 zeolites with a Si/Al ratio of 6 under a 20/80 CO₂/N₂ mixture at 1 bar. These values are lower than that obtained for the SSZ-13_MW60 sample in this work, which reached a selectivity of 127 at 0.9 bar for the same gas composition. In aluminosilicate zeolites, CO₂/N₂ selectivity is primarily driven by strong electrostatic interactions between the high quadrupole moment of CO₂ and the compensating K⁺ cations balancing the negatively charged framework [114]. The SSZ-13 structure features 8-MR windows of approximately 3.8 Å, where K⁺ ions preferentially reside. This strategic positioning near the pore openings can impose a subtle steric or kinetic restriction, since the kinetic diameter of N₂ (3.6 Å) is slightly larger than that of CO₂ (3.3 Å), the presence of K⁺ can hinder N₂ diffusion while allowing easier CO₂ passage [38, 155, 156, 182]. This “trapdoor” or molecular gating effect, previously documented in K-exchanged CHA zeolites, results in highly discriminative gas separation [35]. Therefore, the high selectivity observed for SSZ-13_MW60 likely arises from the combined influence of enhanced electrostatic interactions (due to Si/Al = 18) and a strong kinetic sieving effect associated with K⁺ counter-ions positioned at the pore apertures.

In general, as discussed previously, the IAST model predicts the thermodynamic equilibrium selectivity of gas mixtures but neglects kinetic effects such as diffusion rates through the zeolitic framework [115]. This limitation can lead to misinterpretations when comparing IAST predictions with experimental permeation data, particularly for N₂/CH₄ mixtures, where the separation mechanism is primarily governed by molecular diffusion (molecular sieving) rather than adsorption [20, 21]. In these cases, N₂ diffuses more rapidly through the SSZ-13 pores than CH₄, even though CH₄ is preferentially adsorbed. This diffusion-dominated mechanism results in N₂-selective behavior, with reported permeation selectivities by Li et al. [21] and Wu et al. [20], ranging from 11.6 to 15.2 for equimolar N₂/CH₄ mixtures at 278 K and pressures between 20 and 30 bar. Therefore, the dynamic performance of N₂/CH₄ separation is governed by both

adsorption capacity and diffusion kinetics rather than by thermodynamic selectivity only.

Thus, the IAST is a valuable theoretical approach for predicting separations, provided that adsorption plays the dominant role in understanding the separation mechanism of the gas mixture in question. This is evidenced in the work of Aydani et al. [43], who studied highly selective SSZ-13 membranes. For equimolar CO₂/CH₄ mixtures at 2 bar, the CO₂ permeance was nearly identical to that of single gas CO₂, while CH₄ permeance decreased by about 75%. Consequently, the ideal CO₂/CH₄ selectivity prediction of 60 increased to 183 in the mixture. This remarkable enhancement was attributed to both kinetic diffusion effects and a blocking phenomenon, in which strongly adsorbed CO₂ molecules hinder CH₄ transport through the zeolitic channels.

For CO₂/N₂ separation, the IAST-predicted selectivity is typically very high, reflecting the strong affinity of CO₂, due to its large quadrupole moment and electrostatic interactions with framework cations, compared to N₂ [182]. Similarly, Aydani et al. [43] observed that in SSZ-13 membranes, the CO₂ permeance in an equimolar CO₂/N₂ mixture was comparable to that of single gas CO₂, while N₂ permeance was significantly reduced. As a result, the mixed-gas CO₂/N₂ selectivity doubled relative to the ideal value, confirming the blocking effect of adsorbed CO₂, analogous to the CO₂/CH₄ separation mechanism. Nonetheless, the CO₂/N₂ selectivity achieved experimentally (approximately, 32) remained well below the IAST-predicted value at near-atmospheric pressure.

Overall, the SSZ-13_MW60 zeolite exhibited excellent adsorption performance for the gases studied. Although the predominant mechanism in some mixtures is more strongly influenced by kinetic rather than thermodynamic factors, the material demonstrates significant potential for application as an active phase in gas separation processes. Furthermore, as discussed previous, its incorporation into ceramic matrices was successful, with zeolite-layer thicknesses ranging from 1.86 to 6.43 μm, values comparable to those reported by Li et al. [21] (1.2 μm), Wu et al. [20] (1.2 - 3.0 μm) and Aydani et al. [43] (3.0 μm), who achieved promising results for gas separation, indicating that SSZ-13-based membranes are strong candidates for the separation of gases present in NG.

5. Conclusions and perspectives

5.1. Conclusions

The study on the production of ceramic support indicated that the different dispersion mechanisms promoted by the EFKA and CA dispersants in the α -Al₂O₃/TBA suspensions during the freeze-casting process enabled the refinement of the microstructural properties of the ceramic materials. The AM_EFKA monoliths, due to steric hindrance, exhibited increases in the average grain size (up to 23.1%) and pore size (up to 30.5%), as well as greater pore connectivity compared to the AM_CA samples. This behavior resulted in an absolute permeability approximately twice as high for the AM_EFKA sample. In contrast, the electrostatic dispersion in the AM_CA samples likely influenced the distribution of α -Al₂O₃ particles within the suspension during freezing, contributing to changes during the sintering stage. Consequently, a reduction in pore size and a slight decrease in total porosity were observed. Despite the larger average pore size and higher connectivity observed in the AM_EFKA monoliths, these materials exhibited higher mechanical strength, reaching values up to 11.7 MPa. This result is attributed to the effect of α -Al₂O₃ particle distribution promoted by the EFKA dispersant, which enhanced the densification of the pore walls, leading to an increase of up to 20.3% in their average thickness compared to the AM_CA samples. However, the AM_CA samples also achieved adequate compressive strength values of up to 7.9 MPa. The variation in freezing temperature (-170 °C to -130 °C) had an effect similar to or smaller than that of the dispersant change on the microstructural properties, indicating better ordering of the prismatic structures at -130 °C.

When applying this freeze-cast methodology to the production of tubular supports (FCT), the CA dispersant and a freezing temperature of -130 °C were selected, since the viscosity of the slurry prepared with EFKA was too high to allow its use in the tube-forming process. The resulting tube exhibited radial growth and a prismatic pore morphology, in which the meeting of the prisms generated discontinuities along the porous structure. Nevertheless, the total and open porosities

obtained by the *Archimede's principle* were similar to those of the AM_CA(-130) sample. Therefore, the FCT produced could be a suitable substrate for gas separation membrane applications, as it presented grain size and porosity properties comparable to those of its analogous monolith. However, the tube production methodology still requires further study and characterization for optimization.

The study on the synthesis of SSZ-13 zeolite evaluated the influence of the structure-directing counter-ion and synthesis time by comparing the Na⁺_SSZ-13 and K⁺_SSZ-13 samples. Although both samples exhibited the characteristic SSZ-13 zeolite framework regardless of the counter-ion used, distinct synthesis mechanisms were observed. The Na⁺_SSZ-13 samples were formed through a non-classical mechanism, resulting in faster crystallization but without a well-defined morphology, with crystal sizes reaching up to $16.0 \pm 0.97 \mu\text{m}$. In contrast, the K⁺_SSZ-13 samples followed a classical crystallization pathway, leading to slower formation but achieving high crystallinity after 4 days (97.9%), with well-defined cubic crystals up to $5.67 \pm 0.07 \mu\text{m}$ in size. Results from the MAS NMR analysis indicated that both samples synthesized over 4 days exhibited high Si/Al_{framework} ratios, ranging from 16.4 to 17.7. Moreover, this analysis revealed that the K⁺_SSZ-13_H4 sample showed a more homogeneous distribution of Si and Al atoms compared to the Na⁺_SSZ-13_H4 sample, with a high percentage of Si(0Al) (73%) and Al^{IV} (84.4%), tetrahedral species that constitute the zeolitic framework. These findings were consistent with the high specific surface area ($792.8 \text{ m}^2 \cdot \text{g}^{-1}$) and micropore area ($752.3 \text{ m}^2 \cdot \text{g}^{-1}$) measured for the K⁺_SSZ-13_H4 sample, suggesting highly selective structural properties. Therefore, the K⁺_SSZ-13_H4 sample demonstrated more promising characteristics for application as the active phase in gas separation membranes.

To improve the crystallization of the K⁺_SSZ-13 samples, the molar ratio of water was modified by reducing the H₂O/SiO₂ ratio from 37.5 to 17.5. The samples produced with this adjustment showed enhanced crystallization between 1 and 4 days of synthesis. However, they exhibited larger average particle sizes (up to $17.0 \pm 0.21 \mu\text{m}$) and similar crystallinity compared to the K⁺_SSZ-13_H4 sample synthesized in 4 days. Furthermore, the increased crystallization rate promoted the onset of silicalite-1 formation, indicating the presence of a mixed-phase structure. It is believed that this phase mixture and the increase in average particle size, compared to the K⁺_SSZ-13_H4 samples, led to the formation of

extra-framework aluminum species, as the syntheses conducted under these conditions (K⁺_SSZ-13_375) exhibited behavior similar to that of the Na⁺_SSZ-13 samples. This assumption is supported by the slight decrease observed in the specific surface and micropore areas of these materials.

Additionally, to further improve reaction kinetics and synthesize SSZ-13 zeolites with reduced crystal sizes, a microwave-assisted synthesis was performed with the addition of SSZ-13 seeds. The samples synthesized via microwave irradiation exhibited dynamic solid-state rearrangements cycles throughout the process, consistent with a disorder-to-order non-classical mechanism, drastically reducing the synthesis time to between 30 and 60 minutes. Although microwave radiation allows for such a drastic reduction in synthesis time (4 days to 60 minutes), it may also induce the formation of intercrystalline mesoporosity resulting from the aggregation of smaller particles. Nevertheless, the samples synthesized under microwave irradiation with seed addition and a synthesis time of 60 minutes (SSZ-13_MW60) showed highly promising properties for permeation testing, exhibiting high crystallinity (97%), reduced particle size ($0.645 \pm 0.016 \mu\text{m}$), a high degree of ordering of the tetrahedral species forming the CHA framework and a large specific surface area ($694.9 \text{ m}^2 \cdot \text{g}^{-1}$).

The most promising seeds (K⁺_SSZ-13_H4 and SSZ-13_MW60) were used for the fabrication of SSZ-13/ α -Al₂O₃-type membranes. Initially, studies carried out on commercial α -Al₂O₃ tubes allowed the determination of optimal deposition conditions, based on the efficient coating and adequate thickness of the formed zeolitic layer. The best conditions, 3 seed depositions and 6 hours of synthesis, resulted in high coverage and thin zeolitic layers with thicknesses of 1.86 μm and 6.43 μm for the MWM and HM membranes, respectively. Such a thin layer is ideal for minimizing gas flow resistance, thus ensuring efficient permeance and contributing to the high selectivity of the materials. The formation of this thin zeolitic layer was facilitated by the efficient preliminary deposition of a silica interlayer, which provided suitable interaction between the support and the zeolitic phase, leading to high coverage and uniform membrane formation. In the case of membranes produced via the freeze-casting technique, the SSZ-13_MW60 seed was used to form the active phase. However, the resulting FCM membrane exhibited coating defects and a relatively high thickness (approximately 10 μm). This behavior is likely related to the roughness of the silica layer, deposited prior to the zeolitic phase, which may

have hindered zeolite deposition and consequently will affect the performance of the membrane in gas separation applications.

The theoretical adsorption study (IAST) was conducted using only the SSZ-13_MW60 seed, which produced the most promising membrane (MWM) in terms of coating quality and active layer thickness. The SSZ-13_MW60 zeolite exhibited excellent adsorption performance for the studied gas mixtures (CO_2/N_2 , CO_2/CH_4 and CH_4/N_2), showing the highest selective adsorption for CO_2 due to its greater quadrupole moment and polarizability compared to the other molecules. Although the IAST model does not account for kinetic factors, predominant in some NG separations such as N_2/CH_4 , it provides a theoretical assessment of adsorptive selectivity, a parameter of relevance for CO_2/CH_4 and CO_2/N_2 separations. Therefore, the SSZ-13_MW60 zeolite shows great potential for application as an active phase in gas separation processes, particularly for CO_2 capture, in which it exhibited the highest IAST selectivity at pressures up to 1 bar.

Therefore, the main objective of this work was achieved, with the successful fabrication of SSZ-13/ α - Al_2O_3 membranes derived from seeds exhibiting high affinity for CO_2 and promising potential for the separation of mixtures such as N_2/CH_4 . The optimized synthesis and deposition conditions yielded membranes with thin and homogeneous zeolitic layers. Thus, the results presented in this thesis contribute to the advancement of selective zeolitic membranes, promising materials for future applications in gas separation processes.

5.2. Perspectives

For future developments of this study, it is expected to optimize the production of tubular supports obtained by freeze-casting, aiming to improve surface uniformity and increase the mechanical strength of the material.

Further optimization of SSZ-13 membrane synthesis through different secondary growth strategies is also planned, in order to enhance the results already achieved via dip-coating.

Due to unforeseen circumstances that limited the experimental application of the membranes produced in this work, it is intended to evaluate their performance using different gas mixtures (N_2/CH_4 , CO_2/CH_4 and CO_2/N_2) under various pressure and temperature conditions. These studies will enable the assessment of membrane efficiency in gas separation processes, as well as the investigation of possible mechanisms governing each type of separation.

Finally, the preparation of new scientific papers and the presentation of results at conferences are expected, expanding the dissemination and impact of the contributions achieved in this research.

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Appendix A: Figures and Tables

Figures A1 and A2 refer to the infrared spectra of the AM_CA and AM_EFKA samples at temperatures of -150 and -130 °C, respectively.

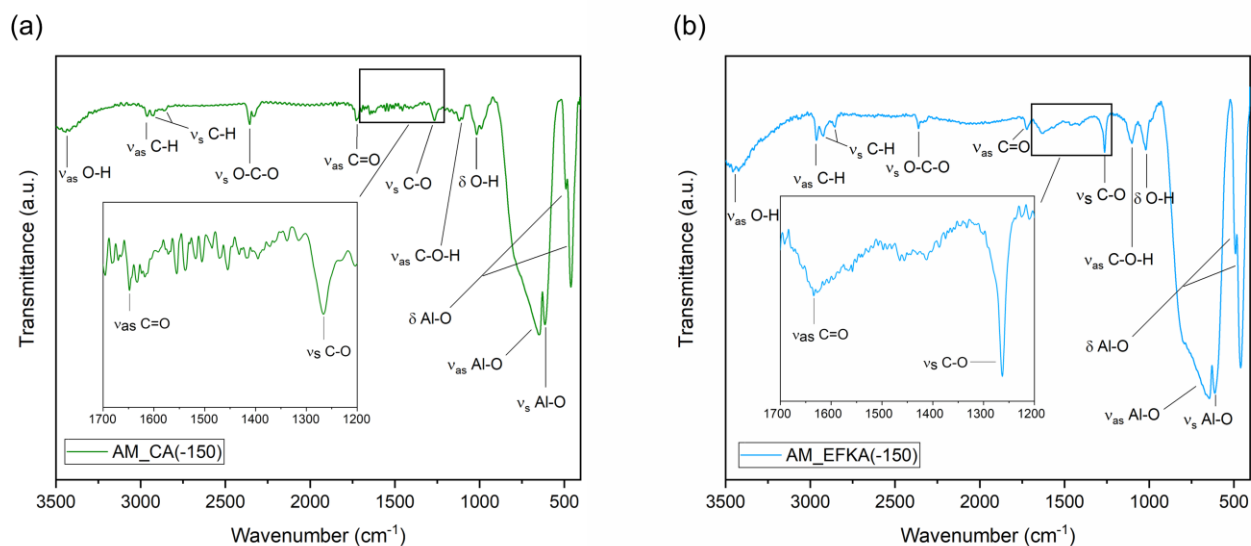


Figure A 1. Infrared spectra for the samples (a) AM_CA(-150) and (b) AM_EFKA(-150). Product of the thesis published and adapted from the reference [75].

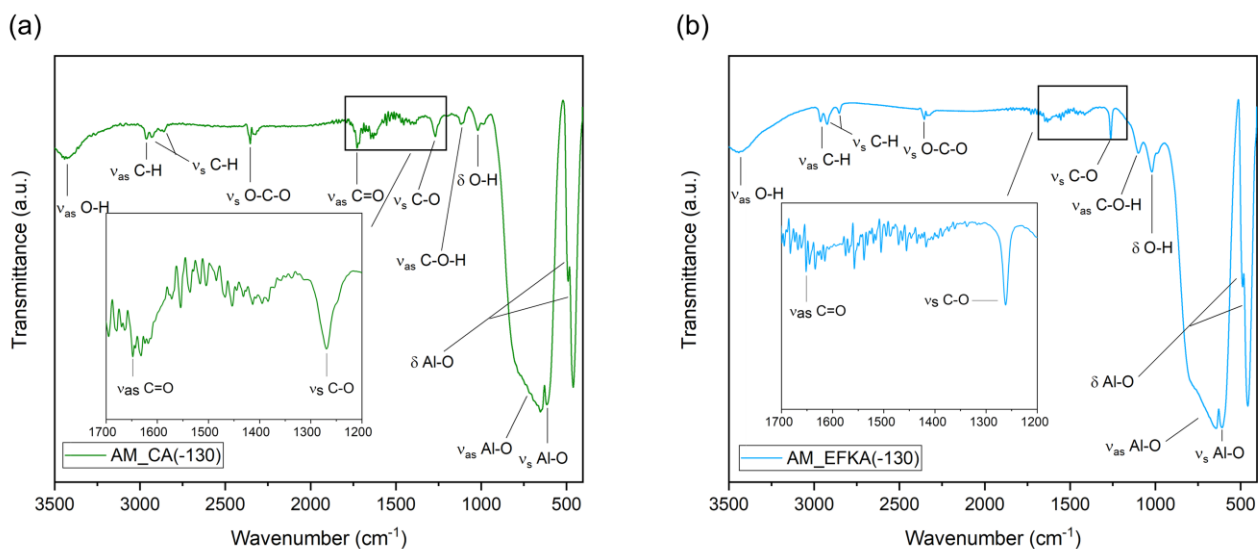


Figure A 2. Infrared spectra for the samples (a) AM_CA(-130) and (b) AM_EFKA(-130). Product of the thesis published and adapted from the reference [75].

Figure A3 refers to the pore wall thickness distribution of the AM_CA and AM_EFKA samples at freezing temperatures of -170 and -130 °C.

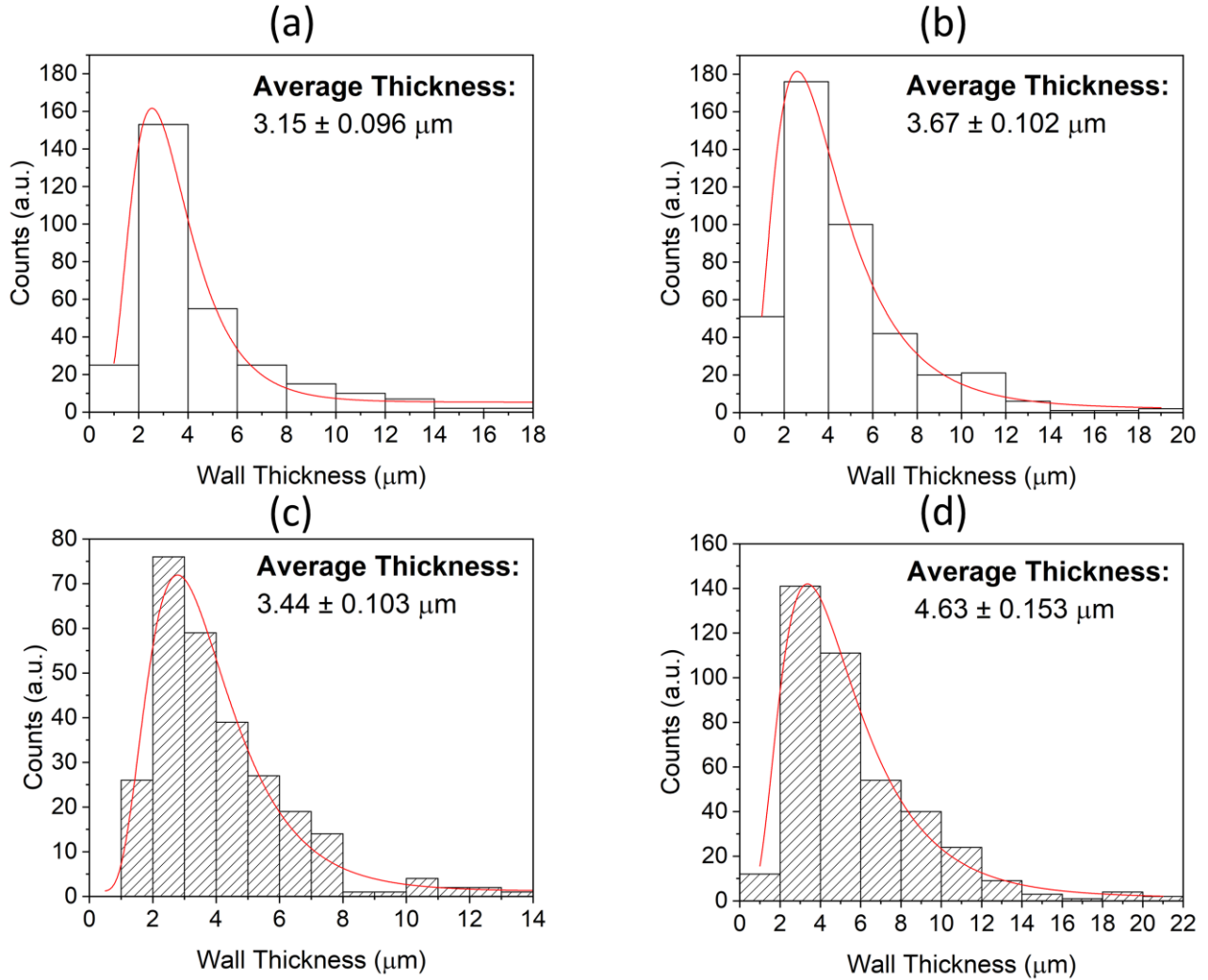


Figure A 3. Pore wall thickness distribution of the samples: (a) AM_CA(-170), (b) AM_CA(-130), (c) AM_EFKA(-170), and (d) AM_EFKA(-130). Adapted from the reference [75].

Figure A4 refers to the particle size distribution of the Na⁺_SSZ-13 and K⁺_SSZ-13 samples.

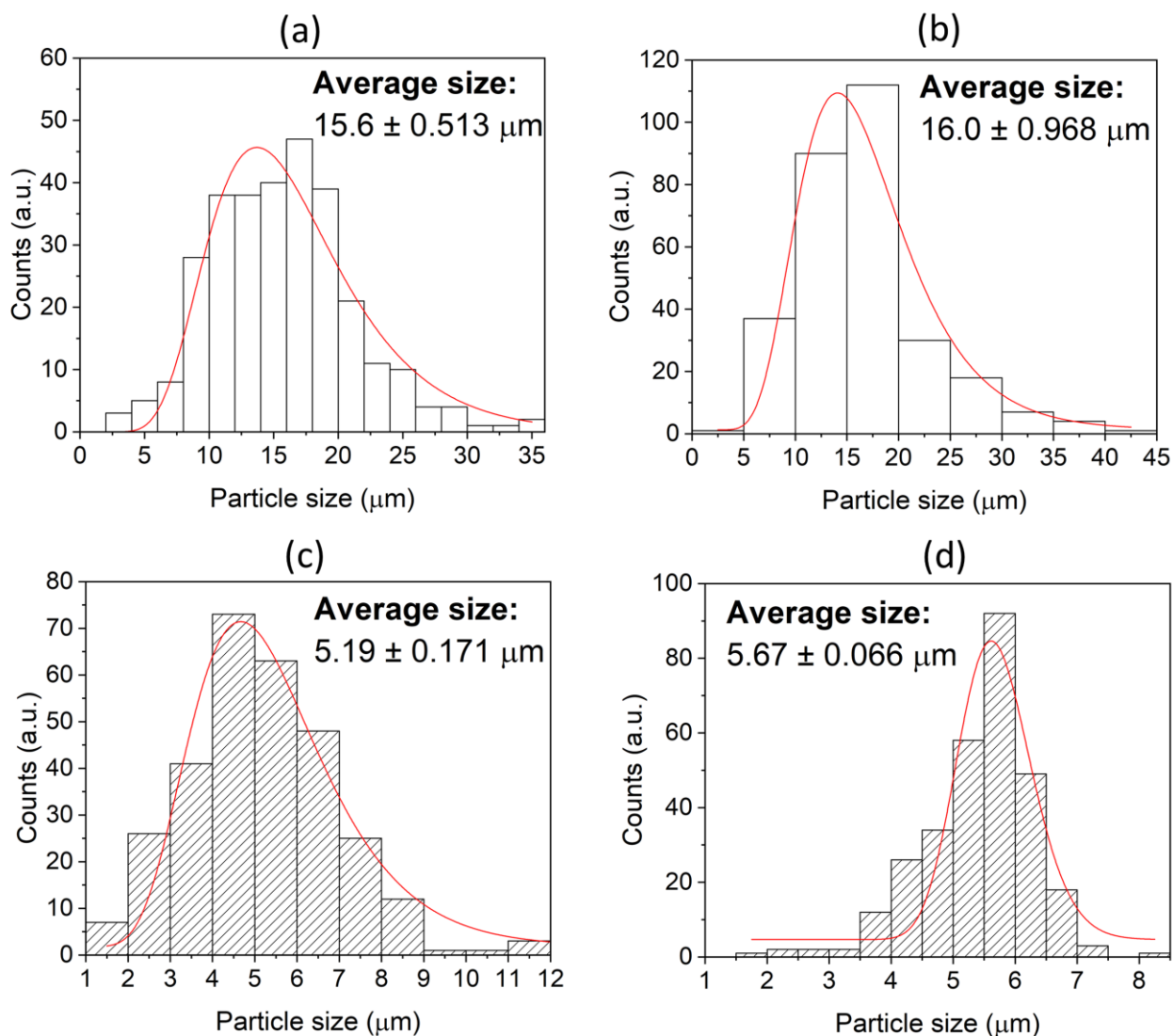


Figure A 4. Particle size distribution of the samples (a) Na⁺_SSZ-13_H3, (b) Na⁺_SSZ-13_H4, (c) K⁺_SSZ-13_H3 and (d) K⁺_SSZ-13_H4.

Figure A5 refers to the *t*-plot graph obtained from the N₂ isotherm analysis of the Na⁺_SSZ-13 and K⁺_SSZ-13 samples.

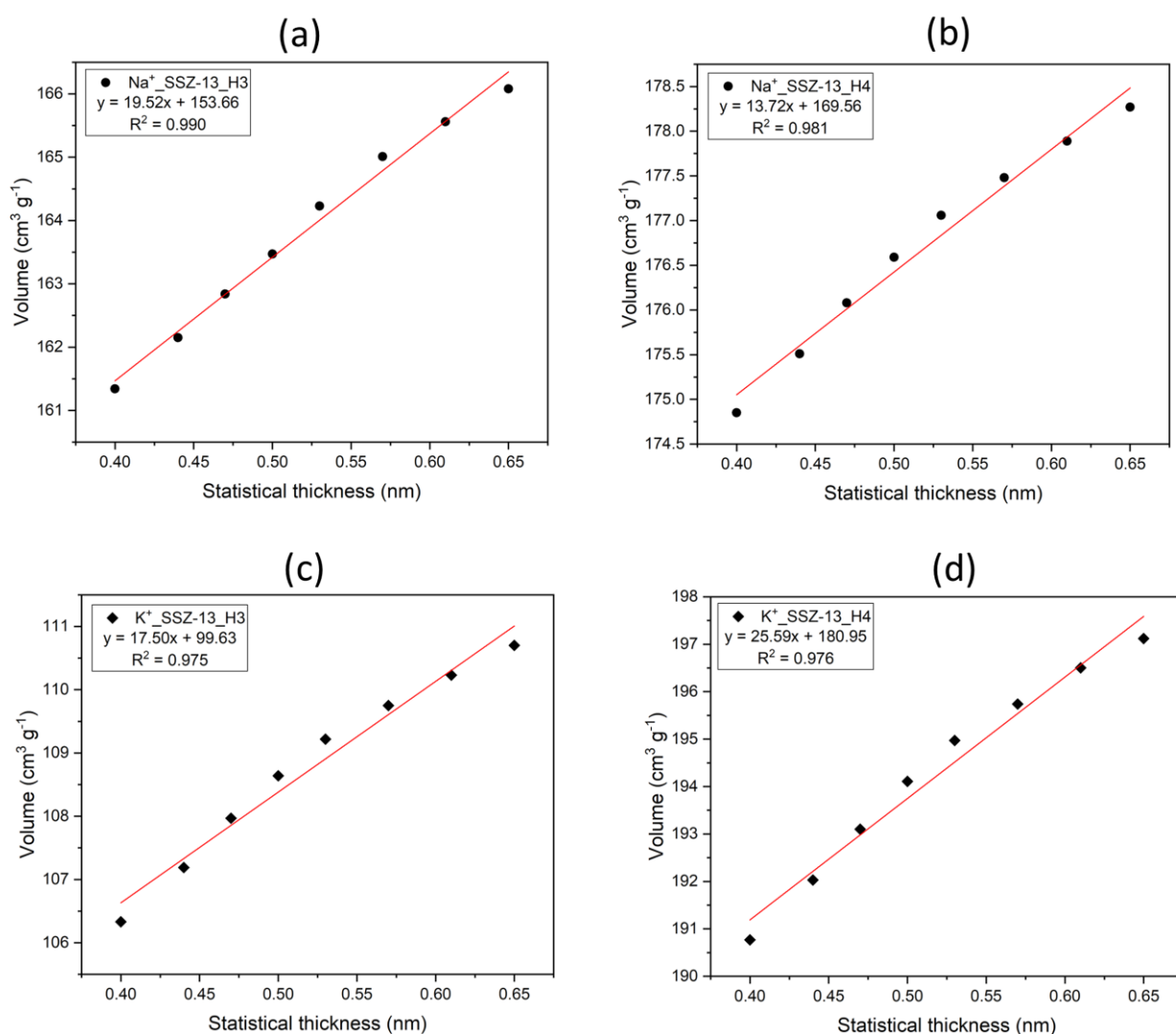


Figure A5. *t*-Plot graph of the samples (a) Na⁺_SSZ-13_H3, (b) Na⁺_SSZ-13_H4, (c) K⁺_SSZ-13_H3 and (d) K⁺_SSZ-13_H4.

Figure A6 refers to the particle size distribution of the K⁺_SSZ-13_375 samples synthesized over 3 and 4 days.

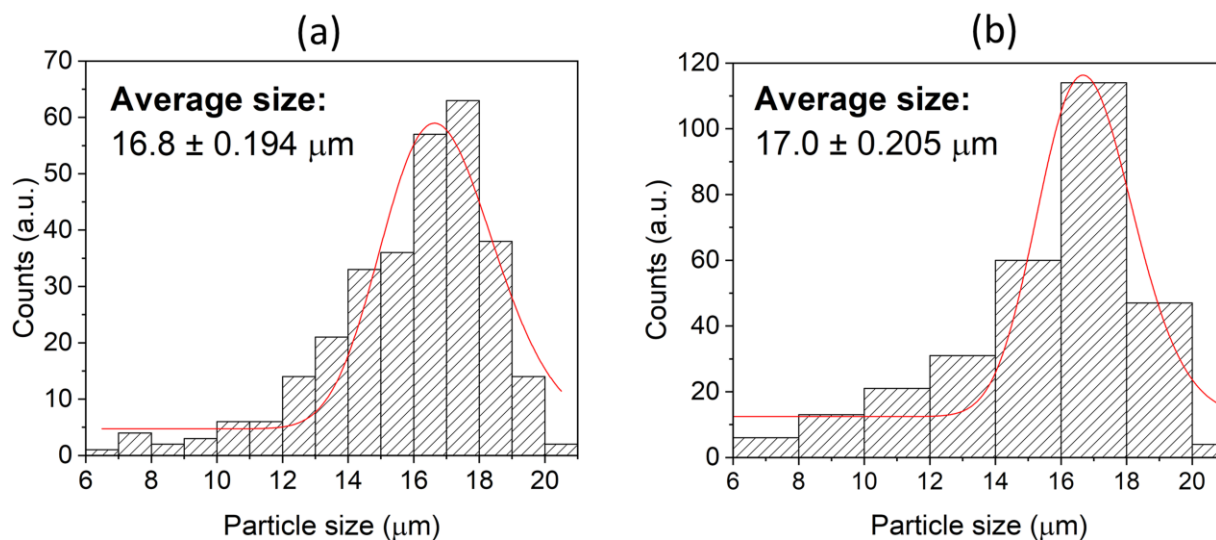


Figure A 6. Particle size distribution of the samples (a) K⁺_SSZ-13_H3_375 and (b) K⁺_SSZ-13_H4_375.

Figure A7 refers to the *t*-plot graph obtained from the N₂ isotherm analysis of the K⁺_SSZ-13_H3_375 and K⁺_SSZ-13_H4_375.

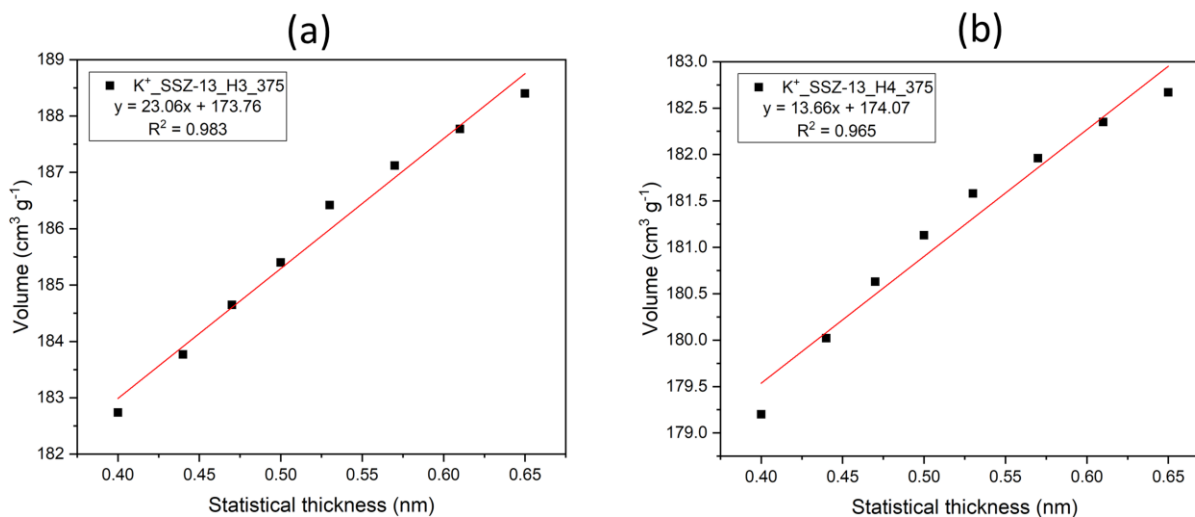


Figure A 7. *t*-plot graph of the samples (a) K⁺_SSZ-13_H3 and (b) K⁺_SSZ-13_H4.

Figure A8 refers to the particle size distribution of the SSZ-13_MW samples.

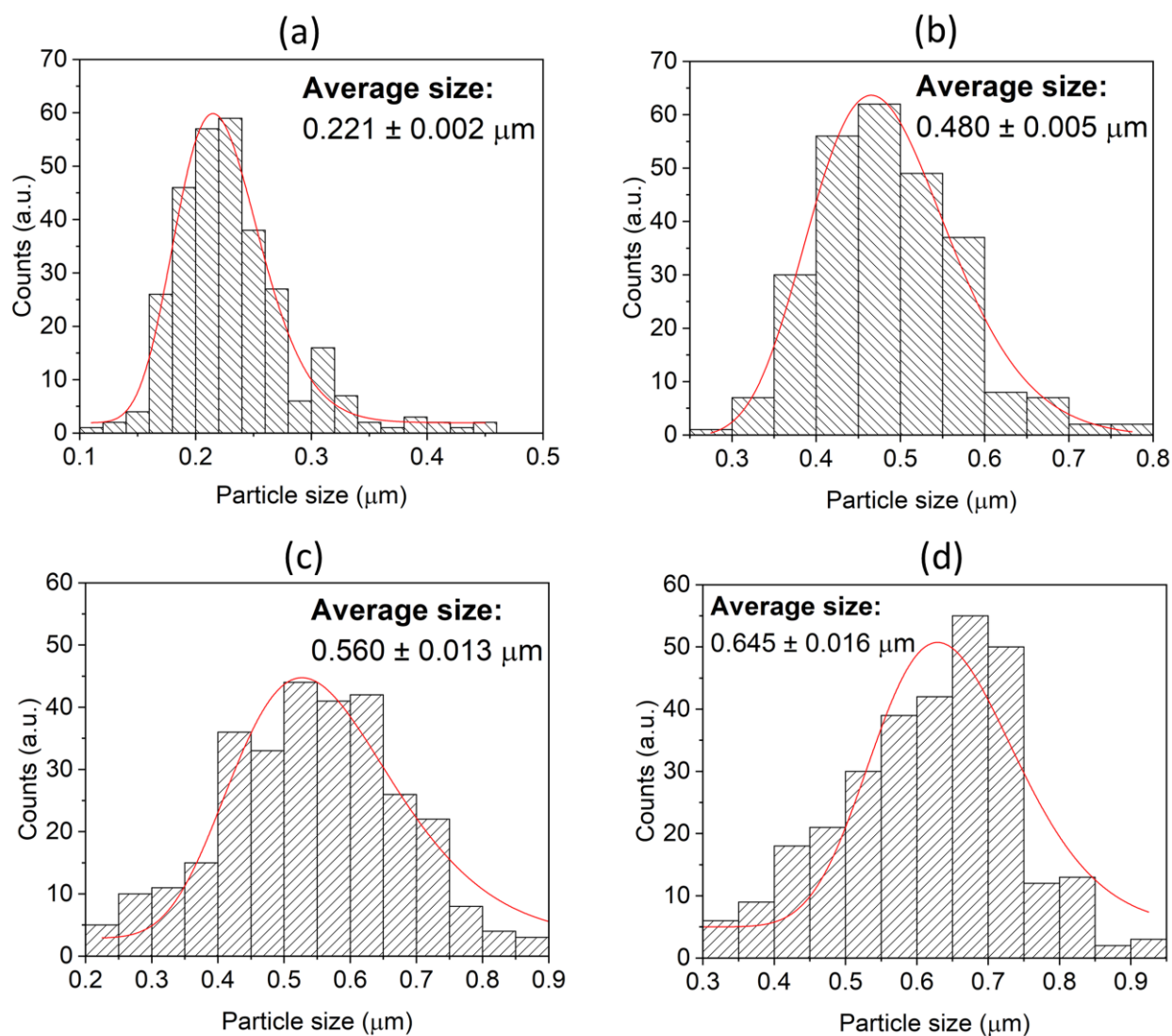


Figure A 8. Particle size distribution of the samples (a) SSZ-13_MW15, (b) SSZ-13_MW30, (c) SSZ-13_MW45 and (d) SSZ-13_MW60.

Figure A9 refers to the *t*-plot graph obtained from the N₂ isotherm analysis of the SSZ-13_MW samples.

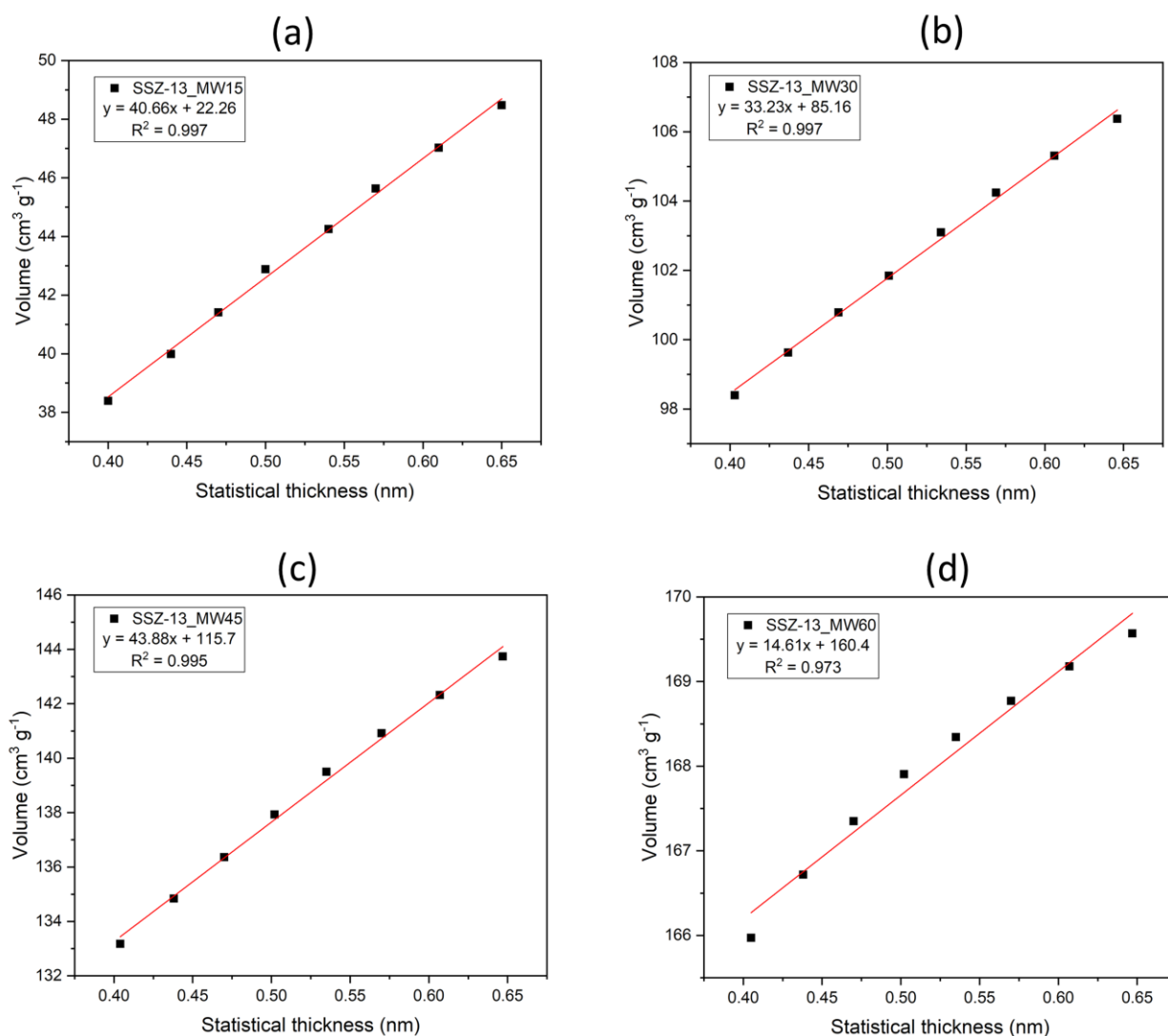


Figure A 9. *t*-Plot graph of the samples (a) SSZ-13_MW15, (b) SSZ-13_MW30, (c) SSZ-13_MW45 and (d) SSZ-13_MW60.

Figure A10 shows the thickness distribution of the silica layer on commercial α -Al₂O₃ and freeze-cast samples.

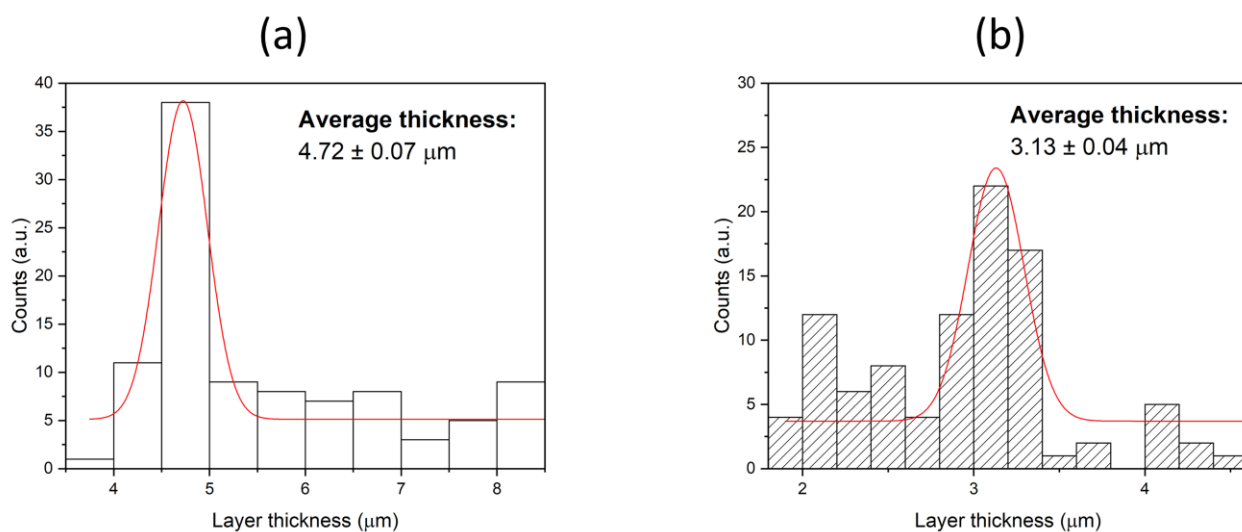


Figure A 10. SEM images of the thickness distribution of the silica layer on: (a) commercial α -Al₂O₃ and (b) freeze-cast α -Al₂O₃ samples.

Figure A11 refers to the thickness distribution of the HM samples.

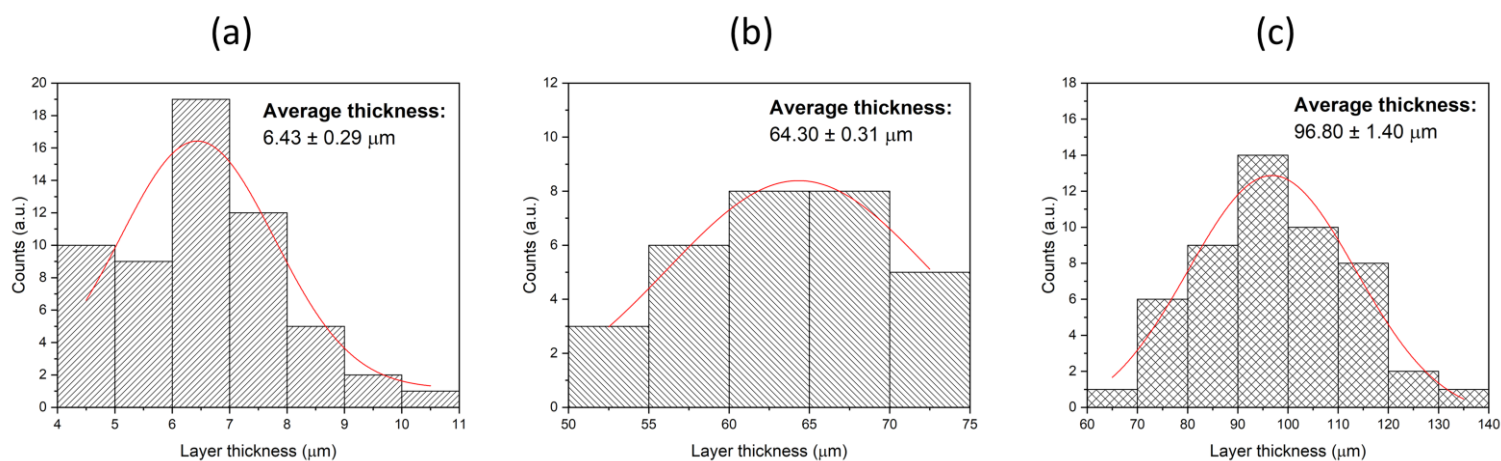


Figure A 11. SEM images of the thickness distribution obtained for the SSZ-13 membranes (HM): (a) 6 hours - 3 seed layer depositions, (b) 12 hours - 1 seed layer deposition, and (c) 24 hours - 1 seed layer deposition.

Figure A12 refers to the thickness distribution of the MWM samples.

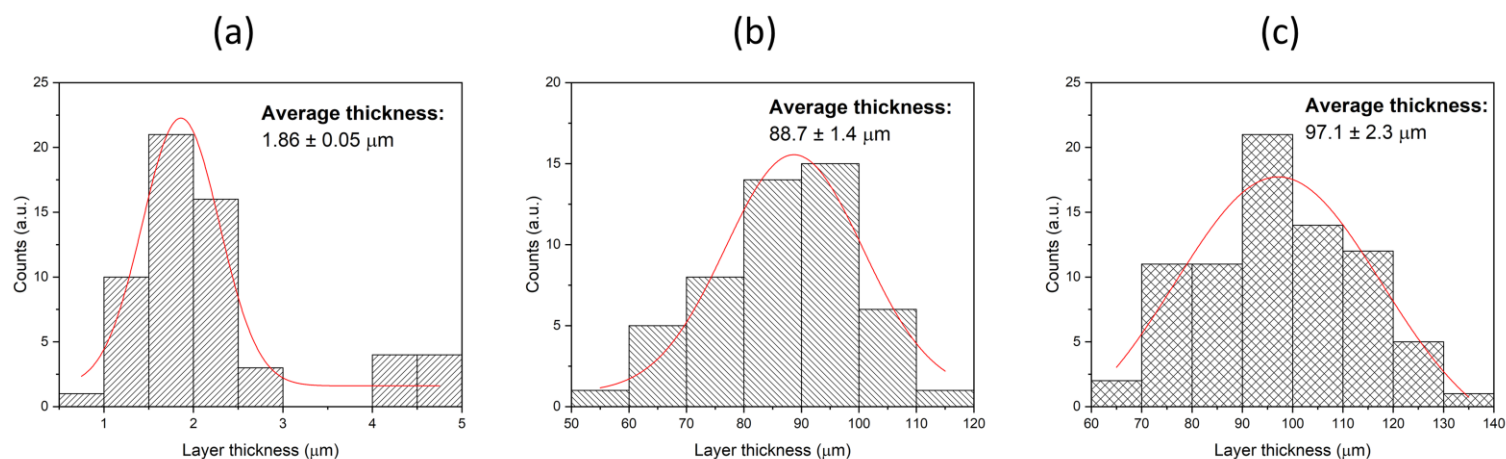


Figure A 12. SEM images of the thickness distribution obtained for the SSZ-13 membranes (MWM): (a) 6 hours - 3 seed layer depositions, (b) 12 hours - 1 seed layer deposition, and (c) 24 hours - 1 seed layer deposition.

Figure A13 refers to the thickness distribution of the FCM sample.

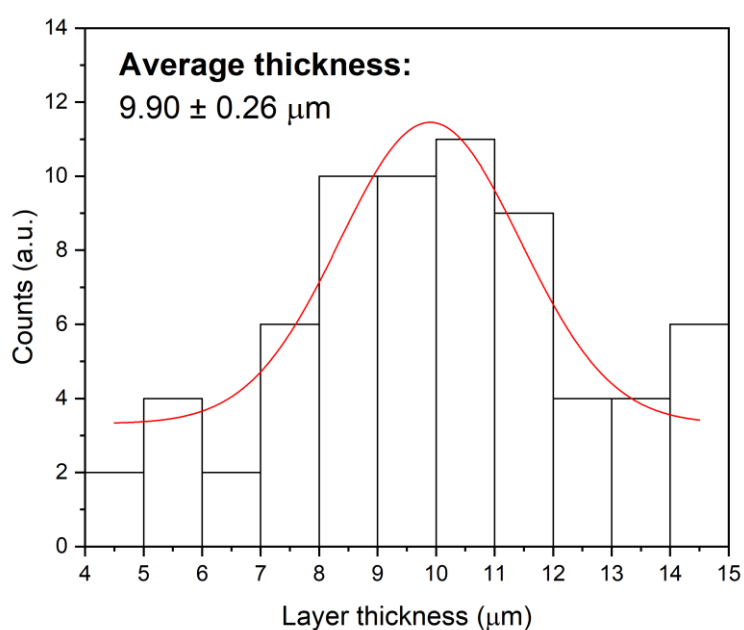


Figure A 13. SEM image of the thickness distribution obtained for the SSZ-13 membrane (FCM).

Table A1 presents the fitting parameters of the *Dual Side Langmuir* function used for the IAST calculations.

Table A 1. Fitting parameters of the *Dual Side Langmuir* function used for the IAST calculations.

Gas:	M1:	K1:	M2:	K2:	RMSE:
CH ₄	0.277470	0.443680	1.674936	0.437702	0.000454
CO ₂	3.358045	1.379653	0.797136	32.554636	0.006070
N ₂	-0.166871	-0.146147	1.038975	0.189272	0.000267

Appendix B: Article

The front page of the article published in the Journal of Materials Science on April 16, 2024. Product of the thesis, related to the topic of ceramic support production by the freeze-casting process (DOI: <https://doi.org/10.1007/s10853-024-09589-2>).

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Influence of citric acid and EFKA as dispersants on the properties of alumina monoliths produced by *tert*-butyl alcohol-based freeze-casting

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ABSTRACT

In this paper, EFKA FA 4663 (EFKA) dispersant was used for the first time in the alumina slurries *tert*-butyl alcohol-based freeze-casting and compared to the commonly used anionic dispersant citric acid (CA). The comparison of both dispersants was analyzed at the beginning of the process at different ultra-low freezing temperatures (− 170 to − 130 °C). The monoliths obtained with EFKA presented promising properties due to its stabilization of alumina particles by both electrostatic interactions and steric impediment, a considerable improvement when compared to the CA that promotes the stabilization of alumina particles only by electrostatic interaction. The use of different dispersants, as well as the control of freezing temperature, significantly influenced the microstructural properties of the monoliths. The monoliths exhibited prismatic pore geometry with high connectivity, forming a complex pore channel with total porosity up to 64.7%, and open porosity up to 48.5%. Results confirmed that the modification of the type of dispersant led to a difference in the grain size (up to 23.1%) and pore size (up to 30.5%) obtained in the materials. The monoliths produced with EFKA dispersant presented a considerable compressive strength resistance up to 11.7 MPa due to its dispersion mechanism that provided the thickening of the walls, confirming that the type of dispersion has a strong influence on the final properties of the materials. Therefore, the type of dispersant proved to be another parameter that allows the refinement of alumina monoliths properties, highlighting the use of EFKA as a promising alternative in the system studied.

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