



Universidade de Brasília
Instituto de Química



PPGQ – PROGRAMA DE PÓS-GRADUAÇÃO EM QUÍMICA
Laboratório de Materiais Cerâmicos e Nanoestruturados

Saulo Lucas Pereira da Silva

DEVELOPMENT OF SAPO-34 ZEOLITE MEMBRANES
SUPPORTED ON α -Al₂O₃ FOR GAS SEPARATION

Doctoral Thesis

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Brasília – DF

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Doctoral Thesis presented to the Postgraduate Program in Chemistry (PPGQ), IQ-UnB, as one of the requirements for obtaining the title of Doctor in Chemistry, under the supervision of Professor Dr. Alysson Martins Almeida Silva.

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“The simplest things and the most sophisticated often merge; at times, true sophistication lies in pure simplicity.”

ACKNOWLEDGEMENTS

First and foremost, I would like to express my gratitude to God, whose presence accompanied me throughout every moment of this doctoral journey. His guidance, strength, and the health bestowed upon me were vital during the most challenging periods of this endeavor.

I am also deeply grateful to my family—Rita, Edgar, and Samara—for their unwavering support, for providing me with a home and comfort throughout the development of this work. Your presence, willingness to help, and even the occasional stern advice was instrumental in fostering the resilience I needed to complete this dissertation.

To my advisor, Professor Alysson Martins, I extend my sincere appreciation for his remarkable patience and support throughout the research process, even in the face of costly experimental setbacks. His insightful guidance, thoughtful reflections, and unwavering dedication to our collaborative projects have been essential in cultivating a healthy and motivating laboratory environment. I consider myself truly fortunate in the selection of advisors throughout my postgraduate studies.

I would also like to thank all colleagues and friends from the Laboratory of Ceramic and Nanostructured Materials (LMCNano) and the research group based at the Federal University of Minas Gerais who contributed to this project. I am certain that each of you has contributed to a profoundly positive impact on every student-researcher who has had the privilege of working with you.

My heartfelt thanks go to my partner, Thais Christine, who entered my life at the beginning of this doctoral journey. I dedicate this brief paragraph to you, whose presence illuminated this path in such a meaningful way. Words cannot fully express how important your support has been. We shared frustrations, joys, motivational messages, and even some tough love, all of which helped me persevere.

I am grateful to the Institute of Chemistry and the Analytical Center for providing part of the infrastructure necessary for the execution of this work. I also thank the Federal University of Minas Gerais for granting access to microscopy and mechanical testing equipment. My appreciation extends to the Faculty of Technology, the Laboratory of Geodynamic and Environmental Studies, and the Institute of Biology at the University of Brasília (UnB) for providing access to scanning electron microscopy analyses.

RESUMO

Título da Tese: DESENVOLVIMENTO DE MEMBRANAS DE ZEÓLITA SAPO-34 SUPORTADAS EM α -Al₂O₃ PARA SEPARAÇÃO DE GASES

Dentro dos processos industriais de tratamento do gás natural, a remoção dos gases CO₂ e N₂ é fundamental para garantir a pureza do produto final e maximizar sua eficiência como combustível. Neste contexto, este estudo propõe a produção de membranas seletivas comportadas por substratos macroporosos comerciais e de produção própria para separação gasosa de misturas importantes no contexto do tratamento do gás natural. A produção de suportes cerâmicos envolveu a investigação da influência composicional da mistura de solventes naftaleno-cânfora e das condições de densificação na formação da estrutura macroporosa de monólitos de α -alumina utilizando o processo de freeze-casting com controle de temperatura de congelamento. A técnica de freeze-casting permitiu a produção controlada de monólitos com alta porosidade (65-70%) e morfologias de poros distintas com base no ajuste da composição do solvente e tempo de sinterização. O uso da composição hipereutética com tempo de sinterização de 2 h promoveu um melhor equilíbrio entre porosidade aberta (~ 53%) e resistência à compressão (~ 16 MPa). A produção de tubos monocanais de mesma composição promoveu a formação de estrutura porosa semelhante ao observado para os monólitos correspondentes, entretanto, houve queda no percentual de porosidade aberta do material (~ 40%). Posteriormente, investigou-se a influência da proporção de precursores e da aplicação de direcionador orgânico de estrutura único ou duplo na produção de SAPO-34 via método hidrotérmico, uma peneira molecular promissora por apresentar janelas de poros com diâmetros de 3,8 Å. Utilizando um único direcionador, hidróxido de tetraetilamônio (TEAOH), observou-se que o aumento da concentração dos precursores de Si, P e template proporcionou a formação de material mais cristalino (~ 85%) e com menor tamanho médio de partícula (~ 2,3 µm). O uso de duplo template - TEOH/morfolina ou TEOH/dipropilamina - levou à formação de matérias com média-alta cristalinidade e tamanhos de partículas menores ou similares ao observado anteriormente. Estudos utilizando aquecimento por micro-ondas permitiram a obtenção de materiais com alta cristalinidade (até 92%), tamanhos de partículas menores para tempo de tratamento térmico 4 vezes menor do que via rota hidrotérmica. Zeólitas produzidas via micro-ondas foram utilizadas como sementes para produção de membranas em tubos comerciais e produzidos via *freeze-casting*. Amostras com 12 h de tratamento hidrotérmico e 3 deposições de semente apresentaram bom recobrimento da superfície, apresentando espessura máxima de 15,1 µm. Além disso, seletividades de adsorção medidas para as misturas 50:50 mol%. de CO₂/CH₄ e CH₄/N₂ apresentaram valores de 16 e 3, respectivamente.

Palavras-chaves: gás natural; *freeze-casting*; naftaleno-cânfora; peneiramento molecular; síntese por micro-ondas; crescimento secundário; IAST.

ABSTRACT

In industrial natural gas treatment processes, the removal of CO₂ and N₂ is essential to ensure the purity of the final product and to maximize its efficiency as a fuel. In this context, the present study reports the development of selective membranes supported on both commercial and in-house-produced macroporous substrates, designed for the separation of gas mixtures relevant to natural gas purification. The fabrication of ceramic supports involved investigating the compositional influence of the naphthalene–camphor solvent mixture and the densification conditions on the formation of macroporous α -alumina monoliths produced via a freeze-casting process under controlled freezing temperature. This technique enabled the tailored fabrication of monoliths with high porosity (65–70%) and distinct pore morphologies, depending on the solvent composition and sintering duration. The use of a hypereutectic solvent composition combined with a 2 h sintering step provided an optimal balance between open porosity (~ 53%) and compressive strength (~ 16 MPa). Single-channel tubes prepared with the same composition exhibited porous structures similar to those of the corresponding monoliths; however, a reduction in open porosity (~ 40%) was observed. Subsequently, the influence of precursor ratios and the use of single or dual organic structure-directing agents were examined in the hydrothermal synthesis of SAPO-34 zeolite, a promising molecular sieve owing to its 3.8 Å pore openings. When employing a single structure-directing agent, tetraethylammonium hydroxide (TEAOH), increasing the concentrations of Si, P, and template precursors led to the formation of highly crystalline (~ 85%) materials with smaller average particle sizes (~ 2.3 μ m). The use of dual templates, TEAOH/morpholine or TEAOH/dipropylamine, also yielded well-crystallized materials with comparable or reduced particle sizes. Microwave-assisted synthesis further demonstrated the feasibility of obtaining highly crystalline materials (up to 92%) with reduced particle sizes and narrow size distributions, while requiring a thermal treatment time four times shorter than that of the conventional hydrothermal method. Zeolites synthesized via microwave heating were subsequently employed as seeds for secondary-growth membrane fabrication on both commercial and freeze-cast tubes. Samples prepared with 12 h of hydrothermal treatment and three consecutive seed depositions exhibited excellent surface coverage, achieving a maximum film thickness of 15.1 μ m. Additionally, adsorption selectivities estimated by Ideal Adsorbed Solution Theory (IAST) for 50:50 mol% CO₂/CH₄ and CH₄/N₂ mixtures reached 16 and 3, respectively.

Keywords: natural gas; freeze-casting; camphor-naphthalene; molecular sieving, microwave synthesis; secondary growth; IAST.

ABBREVIATIONS AND SYMBOLS

Abbreviation / Symbol	Meaning
A_C	Integrated area of the crystalline peaks
AEI	Framework type
AFI	Framework type
$Alip$	Aluminum isopropoxide
$AlPO_4-n$	Aluminophosphate with various framework types
ANP	Brazilian National Agency of Petroleum
A_T	Total XRD area including crystalline and amorphous regions
b	Langmuir affinity constant (equilibrium constant)
BET	Brunauer–Emmett–Teller theory
C	BET constant
CHA	Chabazite framework type
CIS	Commonwealth of Independent States
D	Grain size
d	Liquid film thickness
$D6R$	Double six-membered rings
d_c	Kinetic diameter
DDR	Framework type
DEA	Diethylamine
DPA	Dipropylamine
EDS	Energy-dispersive X-ray spectroscopy
Eu	Samples produced in a eutectic-composition solvent
F	Driving force
F_A	Attractive force
FAU	Faujasite framework type

F_E	Extrinsic force
F_R	Repulsive force
$FTIR$	Fourier-transform infrared spectroscopy
$FWHM$	Full width at half maximum
G	Symmetric conductance matrix of dimension $N * N$
g_{ij}	Conductance of the throat between pore i and pore j
GPU	Gas permeance unit (Barrer)
<i>Hyper</i>	Samples produced in a hypereutectic-composition solvent
<i>Hypo</i>	Samples produced in a hypoeutectic-composition solvent
HT	Hydrothermal treatment
$HT_{1.6D_1T_X}$	Samples synthesized by hydrothermal treatment using DPA/TEAOH for X hours
$HT_{1.5M_0.5T_X}$	Samples synthesized by hydrothermal treatment using MOR/TEAOH for X hours
$HT_{3M_1T_X}$	Samples synthesized by hydrothermal treatment using MOR/TEAOH for X hours
HT_{T1_X}	Samples synthesized by hydrothermal treatment with reaction ratio T1 for X hours
$0.8 P$	Samples synthesized via the T1 method with a phosphorus molar ratio of 0.8
$1.5 P$	Samples synthesized via the T1 method with a phosphorus molar ratio of 1.5
$0.3 Si$	Samples synthesized via the T1 method with a silicon molar ratio of 0.3
$1.2 Si$	Samples synthesized via the T1 method with a silicon molar ratio of 1.2
$2.8 T$	Samples synthesized via the T1 method with a tetraethylamonium hydroxide molar ratio of 2.8
$3.5 T$	Samples synthesized via the T1 method with a tetraethylamonium hydroxide molar ratio of 3.5
HT_{T2_X}	Samples synthesized by hydrothermal treatment with reaction ratio T2 for X hours
$IAST$	Ideal Adsorbed Solution Theory
$ICSD$	Inorganic Crystal Structure Database
IEO	International Energy Outlook
$IUPAC$	International Union of Pure and Applied Chemistry

J	Histogram' bin width
J_i	Flux of component “i” through the membrane
K	Scherrer constant
k	Permeability
K_H	Henry's constant
L	Length of the porous network in the flow direction
l_{ij}	Length of modeled cylindrical throats
<i>LMCNano</i>	Laboratório de Materiais Cerâmicos e Nanoestruturados
<i>LNG</i>	Liquefied Natural Gas
<i>LPG</i>	Liquefied petroleum gas
<i>LUDOX AS-40</i>	Colloidal Silica
L_β	Full width at half maximum
M_m	Molar mass
<i>MMSCFD</i>	Million standard cubic feet per day
<i>MSCF</i>	Thousand standard cubic feet
<i>MOF</i>	Metal-organic framework
<i>MOR</i>	Morpholine
<i>MW</i>	Microwave heating
<i>MW_3M_1T_X</i>	Samples synthesized by microwave heating using MOR/TEAOH for X hours
<i>MW_T1_X</i>	Samples synthesized by microwave heating with reaction ratio T1 for X hours
n_0	Diameters of the smallest particle
n_f	Diameters of the largest particle
N_A	Avogadro's number
<i>NC</i>	Naphthalene-camphor
<i>NG</i>	Natural gas
<i>NMR-MAS</i>	Nuclear Magnetic Resonance with Magic Angle Spinning

<i>OSDAs</i>	Organic structure-directing agents
P	Vector of size N corresponding to the pressure at each pore
$P_{f,i}$	Partial pressures of component “i” in the feed
P_i	Partial pressure of componente i
P_i^0	Hypothetical pressure of pure component i
$\Delta P_{ln,i}$	Logaritmic mean pressure difference for component “i”
<i>PNM</i>	Pore network model
$P_{p,i}$	Partial pressures of component “i” in the permeate
$P_{r,i}$	Partial pressures of component “i” in the retentate
<i>PSA</i>	Pressure-swing adsorption
<i>PVA</i>	Polyvinyl alcohol
q_i	Partially adsorbed amount of component “i”
q_{ij}	Flow rate between pore “i” and pore “j”
q_{max}	Maximum adsorption capacity (Langmuir isotherm)
q_T	Total adsorbed amount
R	Universal gas constant
r_{ij}	Radius of cylindrical throats
<i>SAPO-5</i>	Silicoaluminophosphate with AFI framework type
<i>SAPO-18</i>	Silicoaluminophosphate with AEI framework type
<i>SAPO-34</i>	Silicoaluminophosphate with CHA framework type
S_{ads}	Adsorption selectivity
S_{BET}	Total specific surface area
S_C	Avarage crystallite size
S_{ext}	External surface area
S_{micro}	Micropore surface area
S_T	Total surface area

<i>SEM</i>	Scanning Electron Microscopy
<i>T</i>	Temperature
<i>T_b</i>	Boiling point
<i>T_g</i>	Polymer's glass transition temperature
<i>T_h</i>	Hydraulic tortuosity
<i>TEAOH</i>	Tetraethylammonium Hydroxide
<i>TEOS</i>	Tetraethyl orthosilicate
<i>TSA</i>	Temperature-swing adsorption
<i>V_a</i>	Apparent volume
<i>V_{meso}</i>	Mesopore volume
<i>V_{micro}</i>	Micropore volume
<i>V_{op}</i>	Open pore volume
<i>V_s</i>	Solid volume
<i>X_C</i>	Relative crystallinity
<i>x_i</i>	Mole fraction of component i in the vapor phase
<i>XRD</i>	X-ray diffraction
<i>W</i>	Amount of adsorbed mass (BET method)
<i>w_d</i>	Dry mass (Archimedes' method)
<i>w_i</i>	Immersed mass (Archimedes' method)
<i>W_m</i>	Mass adsorbed in a complete monolayer (BET method)
<i>w_w</i>	Wet mass (Archimedes' method)
<i>y_i</i>	Mole fraction of component i in the adsorbed phase
<i>α_p</i>	Polarizability
<i>α_i</i>	Selectivity
<i>α_{A/B}</i>	Selectivity in binary gas mixture
<i>δ</i>	Specific surface energy

A	Cross-sectional area
ρ_{H2O}	Density of water
ρ_s	Density of the solid
σ_{sp}	Interfacial energies of the particle and the frozen solid phase
σ_{lp}	Interfacial energies of the particle and the unfrozen liquid phase
σ_{sl}	Interfacial energies of the solid and the liquid phase
Θ	Quadrupole moment
μ	Dipole moment
μCT	Microtomography
θ	Bragg angle
λ	Wavelength of the radiation source
v	Velocity of the solidification front
v_c	Critical velocity

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CHAPTER 1

1.1. INTRODUCTION

According to the International Energy Outlook 2021 (IEO 2021), natural gas (NG) is projected to experience the most pronounced growth among the fuels used for primary energy supply, since it has a lower environmental impact compared to other fossil fuels. The IEO 2021 expects natural-gas production to increase by 50% between 2010 and 2050.¹

Natural gas (NG) is a fossil fuel that can be extracted from natural reservoirs, whether associated with oil or not. It consists of a mixture of light hydrocarbons, primarily alkanes. Its composition is dominated by methane (CH_4), which makes up roughly 85% of natural gas, with smaller fractions of other alkanes such as ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}). However, contaminant gases often present include nitrogen (N_2), carbon dioxide (CO_2), and sulfur-derived compounds.^{2,3}

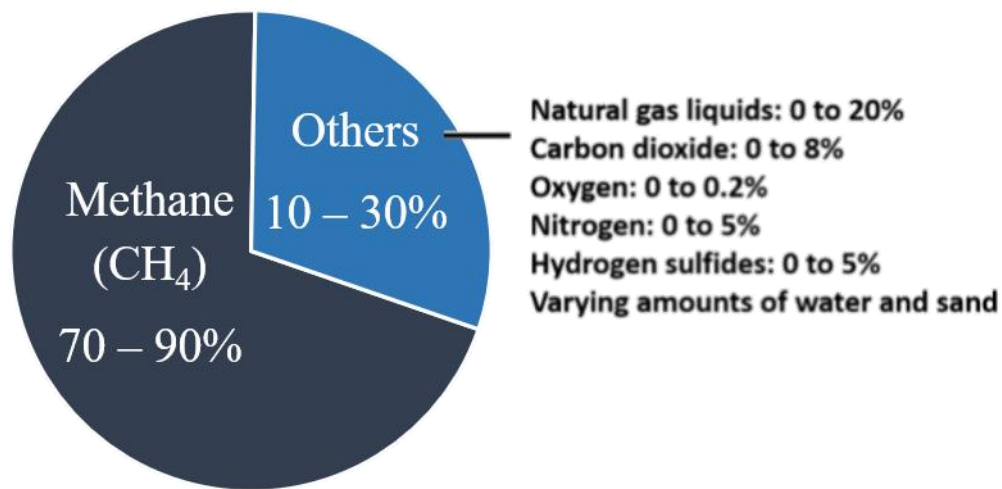


Figure 1. Natural Gas Composition (Adapted from Shiverly *et al.* 2017).⁴

Nitrogen gas is known to be an inert gas and, thereby, its presence in natural gas has a negative impact on the fuel's heating value. Moreover, a high nitrogen content complicates the liquefaction and transportation of natural gas and contributes to the formation of nitrogen oxides (NO_x), which are, for example, partly responsible for acid rain. To mitigate these problems, it is therefore essential to develop efficient processes for removing such contaminants from natural gas.^{5,6}

In the mid-1980s, commercial-scale production of polymeric membranes was implemented, making membrane-based gas-separation a highly competitive technology. Unlike conventional unit operations such as cryogenic distillation and adsorption, gas-separation membranes do not require phase changes of the natural gas to function. They also offer low manufacturing costs, high energy efficiency, and reduced environmental impact. The absence of moving parts makes these membranes particularly suitable for deployment in remote locations, for example offshore gas-processing platforms.^{7,8}

Currently, ceramic and polymeric membranes (glassy or elastomeric) are being used for these purposes thanks to their excellent mechanical properties.⁹ Polymeric membranes are known to exhibit an inverse relationship between permeability and selectivity.⁹ Elastomeric membranes are soft and flexible; able to operate above their glass-transition temperature; and, generally, display low selectivity and high permeability. For this reason, they are often unsuitable for industrial-scale applications. Glassy membranes, on the other hand, are hard and rigid, exhibiting high selectivity but lower gas permeability. An alternative method to enhance the gas-separation performance of such materials is to use inorganic or mixed-matrix membranes. Mixed-matrix membranes are produced by modifying conventional membranes through the incorporation of porous materials such as zeolites, carbon nanotubes, and silica-type particles.⁹

In inorganic membranes, it is common to deposit a thin selective-material layer (film) onto a ceramic or metal support, which enhances the material's mechanical strength. In this context, the freeze-casting technique has emerged as an effective approach for the fabrication of ceramic substrates. This method enables precise control over key properties, including mechanical strength, porosity, and pore geometry of the resulting support. Furthermore, ceramic materials offer advantages such as reduced weight, relative simplicity of fabrication, and high porosity, the latter being particularly beneficial for minimizing mass transport resistance during separation processes.

Zeolites are particularly promising for composing the selective film, as their ultramicropore sizes can be tuned to control membrane selectivity for simple or complex gas mixtures based on molecular size. Their properties make them suitable for high-complexity applications such as the separation of gas pairs (CO_2/N_2 , CO_2/CH_4 , N_2/CH_4 , etc.).^{10–12}

Among known zeolites, SAPO-34 has emerged as a particularly promising material for gas-separation membranes, showing superior CO₂/CH₄ separation performance compared with polymers, metal-organic frameworks (MOFs), and zeolites such as T, Y, and MFI. The outstanding performance of SAPO-34 is attributed to its strong affinity for polar molecules and its small pore aperture (~0.38 nm). Although most studies focus on CO₂/CH₄ separations, SAPO-34 has also delivered favorable results for N₂/CH₄ separation, typically exhibiting higher N₂ permeance than other zeolite frameworks such as SSZ-13.^{13,14}

Starting from these challenges, this research project aims to identify an efficient and economically viable approach to improve methane purification — a problem faced by major oil and natural-gas industries worldwide. To this end, it proposes the fabrication of ceramic-supported membranes using SAPO-34 zeolite as the selective phase. An innovative methodology is presented for the production of ceramic tubes with refined control over their final properties, together with a systematic investigation of different compositions and reaction pathways for the synthesis of the active phase. Finally, this work inaugurates a new research line within the Laboratório de Materiais Cerâmicos e Nanoestruturados (LMCNano), covering SAPO-34 synthesis, fabrication of macroporous supports via freeze-casting with a scarcely explored solvent, and the development of membranes selective for binary gas mixtures.

1.2. OBJECTIVES

1.2.1. GENERAL OBJECTIVES

This research project aims to synthesize SAPO-34, perform comprehensive characterization, and evaluate SAPO-34 membranes deposited on commercial and lab-made α -Al₂O₃ supports for application in mixed-gas separation specifically N₂/CH₄ and CO₂/CH₄.

1.2.2. SPECIFIC OBJECTIVES

- Production of ceramic supports via the freeze-casting technique, employing strategies to control pore morphology, porosity, and mechanical strength, including variation of sintering time and solvent composition. Characterization of the produced supports by X-ray

Diffraction (XRD), porosity analysis by Archimedes' method, Scanning Electron Microscopy (SEM), Microtomography (μ CT) and compression testing;

- Investigation of SAPO-34 synthesis by secondary growth employing hydrothermal and microwave-heating routes, with emphasis on the use of different reaction compositions and organic structure-directing agents. Characterize zeolitic materials by XRD, Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy SEM, physisorption (adsorption/desorption), and nuclear magnetic resonance (NMR) spectroscopy;
- Synthesis of SAPO-34 membranes on commercial and freeze-cast α - Al_2O_3 supports via the secondary-growth method, with controlled crystal orientation and film thickness. Characterize membranes in terms of texture, morphology and physicochemical properties;
- Quantification of the separation performance of SAPO-34 zeolite for N_2/CH_4 and CO_2/CH_4 binary mixtures through adsorption selectivity studies;
- Identify the dominant separation mechanisms for CO_2/CH_4 and N_2/CH_4 in the synthesized molecular sieves.

CHAPTER 2 – LITERATURE REVIEW

2.1. CHALLENGES OF NATURAL GAS PURIFICATION IN INDUSTRY

Natural gas originates beneath the Earth's surface and serves as an important source of fossil energy. It is formed when buried plants, gases, and animals are subjected to high temperatures and pressures over thousands of years. Comprised of a variety of substances, its principal component is methane (CH₄), which consists of one carbon atom bonded to four hydrogen atoms. It also includes smaller quantities of hydrocarbon gas liquids and non-hydrocarbon gases such as water vapor and nitrogen (N₂). Widely used in numerous countries, natural gas is employed for both heating and food preparation, as well as for electricity generation and as a vehicle fuel.

According to the Statistical Review of World Energy 2023, natural gas ranks second among primary energy sources by global consumption. In certain regions - such as the Commonwealth of Independent States (*CIS*, comprising the eleven countries of the former Soviet Union) and the Middle East - methane stands out as the principal fuel in use (Figure 2).¹⁵

Regional consumption pattern 2022

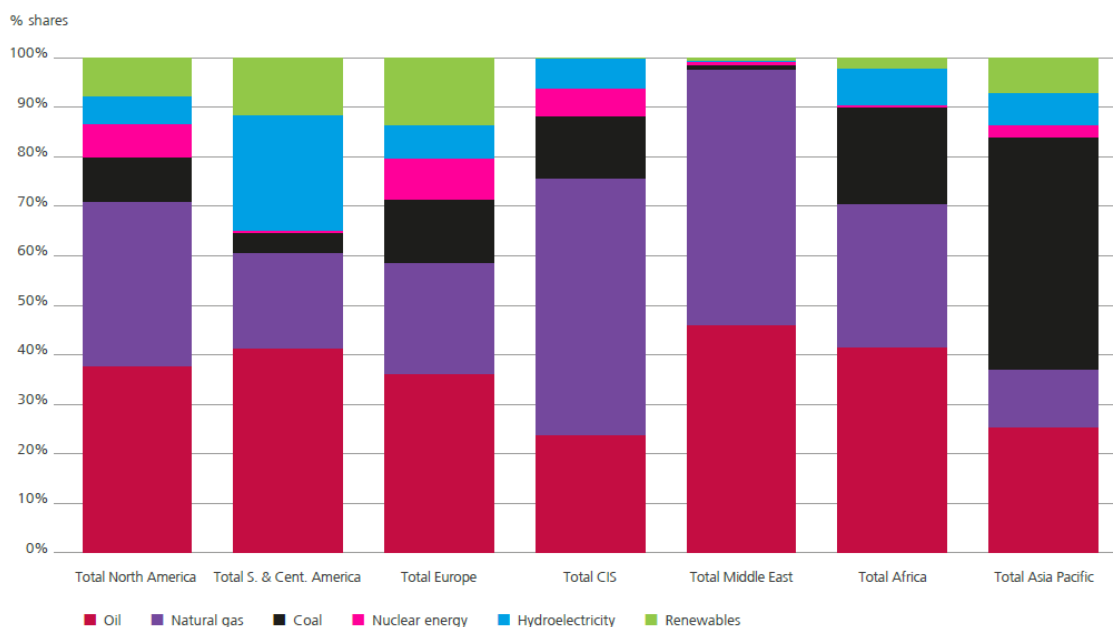


Figure 2. Analysis of global energy consumption produced by the Statistical Review of World Energy 2023.¹⁵

The rising demand for natural gas over the past two decades has prompted renewed interest in developing and exploiting previously untapped or remote unconventional reserves that contain higher concentrations of contaminants and were formerly considered uneconomical. Many gas fields are also located far from major markets, requiring producers and exporters to transport large volumes over long distances via extensive pipeline networks or by sea as liquefied natural gas (LNG).⁵

Estimates of worldwide subquality natural-gas reserves—including acid-gas deposits with high hydrogen sulfide (H₂S) content—are significant, accounting for approximately 16% of the planet's natural-gas resources. These reserves are commonly defined as fields containing > 2 vol% CO₂, > 4 vol% N₂, or > 4 ppm H₂S.⁵ In certain natural gas sources, nitrogen levels can reach up to 15 vol %. In Brazil, the Urucu Basin, for example, features natural gas with inert gas contents on the order of 14.5 vol % (CO₂ + N₂).¹⁶ The specification for commercial natural gas, in accordance with the parameters established by the Brazilian National Petroleum Agency (*ANP – Agência Nacional do Petróleo*), sets limits of up to 6 mol % for inert gases (CO₂ + N₂) and 10 mg/m³ of H₂S for the Central-West region (Table 1).¹⁶

Table 1. Specifications established by the ANP for Brazilian natural gas production.¹⁶

Characteristics	Unit	Limit		
		NORTH	NORTH EAST	OTHERS
Calorific value	kJ/m ³	34000 - 38400	35000 - 43000	
	kWh/m ³	9.47 - 10.67	9.72 - 11.94	
Methane (Minimum)	% mol	68.0	85.0	
Ethane (Máximo)	% mol	12.0	12.0	
Propane (Maximum)	% mol	3.0	6.0	
Butane and heavier (Maximum)	% mol	1.5	3.0	
Oxygen (Maximum)	% mol	0.8	0.5	
Inerts (Maximum)	% mol	18.0	8.0	6.0
H ₂ S (Maximum)	mg/m ³	10.0	13.0	10.0
CO ₂ (Maximum)	% mol	3.0		

Carbon dioxide and hydrogen sulfide (H₂S), together with other acid-forming gases, must be removed from natural gas because they promote corrosion of pipelines and

equipment in the presence of moisture and pose risks to public health and the environment..^{13,14,17,18}

Inert gases, such as N_2 and CO_2 , must be removed from the natural-gas mixture for several reasons. First, they do not contribute to the gas's calorific value and are therefore classified as inert gases. Second, The liquefaction of natural gas is a process that requires a substantial amount of energy that becomes even more onerous in the presence of these components. Consequently, their separation is crucial and requires processes designed to minimise their concentrations in the final product.

Cryogenic process are commonly employed to remove inert gases such as N_2 and are particularly suitable for large natural-gas wells producing between 50 and 500 million standard cubic feet per day (MMSCFD) over a 10-20 year period. The high production capacity of these wells enables the amortization of the initial investment in cryogenic plants over time.¹⁹

The cost intensity of the cryogenic method is significant and varies with the scale of the facility. For a unit with a capacity of 20 MMSCFD - and assuming a gas price of \$4 per MSCF and an inlet composition of 15 vol % N_2 - the operating cost for separation is approximately \$0.80 per MSCF. By contrast, for a smaller 1 MMSCFD unit the operating cost may rise to about \$2.40 per MSCF, a threefold increase that can render the cryogenic route uneconomical at small scale.¹⁹

In this context, the pursuit of alternative separation technologies that offer a favorable cost-efficiency balance has become critically important in recent years, since enabling the viable exploitation of small wells is essential to meeting the growing demand for natural gas. Given the importance of natural-gas processing for commercialization, the technologies used for this purpose are briefly reviewed in Section 3.2.

2.1.1. Challenges in separating nitrogen gas from methane gas

Effective separation of a binary mixture requires that the two components possess sufficiently distinct properties; larger differences increase the attainable separation efficiency.²⁰ However, the challenges in promoting the separation of N_2/CH_4 arise from the similarities these gases exhibit in their physicochemical properties. On the other hand this problem is less imminent in the separation of CO_2/CH_4 . The table below highlights some of these properties, where T_b is the boiling point, d_c is the kinetic diameter, α_p is the polarizability, μ is the dipole moment (D, Debye unit), and Θ is the quadrupole moment.¹²

Table 2. Physicochemical properties of nitrogen, carbon dioxide and methane gases.¹²

Components	T _b (K)	d _c (Å)	α _p (Å ³)	μ (D)	Θ (D. Å)
N ₂	77.3	0.364	1.710	0	1.54
CO ₂	194.6	0.330	2.507	0	4.30
CH ₄	111.7	0.380	2.448	0	0.02

The differences in normal boiling points among N₂, CO₂, and CH₄ are sufficiently large to permit efficient separation of N₂/CH₄ or CO₂/CH₄ mixtures by distillation. Such separations require cryogenic conditions, however, which entail very high energy demands. Economic viability therefore depends on large, continuous feed flows, making cryogenic distillation best suited to large-scale gas reservoirs. Despite its cost and scale requirements, cryogenic distillation remains the prevailing technology for removing nitrogen from methane.^{12,20}

The dipole moments of N₂ and CH₄ are negligible, so both gases are essentially nonpolar and exhibit very low solubility in common polar solvents such as water and ethanol. No solvent has been reported that dissolves N₂ more readily than CH₄. Methane, however, dissolves appreciably in certain organic solvents, particularly in oil-like mixtures containing short hydrocarbon chains (C₅-C₉). These solubility differences can be exploited to design separation processes based on selective dissolution.^{12,20}

Polarizability, dipole moment, and quadrupole moment govern gas–solid interactions and are fundamental to adsorption and membrane-based separations. Polarizability contributes to both *van der Waals* (non-electrostatic) forces and induced electrostatic interactions. Both N₂ and CH₄ have negligible permanent dipole moment and thus no dipolar contribution. The quadrupole moment generates electrostatic interactions in the presence of an electric-field gradient near solid surfaces. Because N₂ has a larger quadrupole moment while CH₄ is more polarizable, their differential interaction with typical solid adsorbents or zeolitic frameworks is usually modest. By contrast, CO₂ combines a relatively small kinetic diameter with a substantially larger quadrupole moment, which strengthens its interaction with many solid adsorbents and improves separation performance in CO₂/CH₄ and CO₂/N₂ mixtures.^{12,20}

The kinetic diameter of a molecule refers to its probability of colliding with another species or with the wall of a pore.²¹ Thus, separation methods can be applied to gas mixtures by exploiting differences in the kinetic diameters of their components.

Devices that utilize this principle are known as molecular sieves (e.g., membranes). However, methane and nitrogen gases have very similar kinetic diameters, making the development of technologies for separating N_2/CH_4 mixtures via molecular sieving particularly challenging. In this context, to achieve such separation, the sieves must possess pore sizes in the range of 3.64 to 3.8 Å.^{12,20}

2.2. PROCESSING OF RAW NATURAL GAS

The conversion of raw natural gas into pipeline-quality fuel for for transportation to commercial or consumption centers often requires a complex, sequential treatment chain whose stages and unit operations depend on the feed composition at the wellhead. A typical processing plant commonly includes the following units: (i) gas-oil separator; (ii) condensate separator; (iii) dehydrator; (iv) acid-gas removal unit; (v) nitrogen removal or nitrogen rejection unit (NRU); (vi) de-methanizer; and (vii) fractionator.^{19,22}

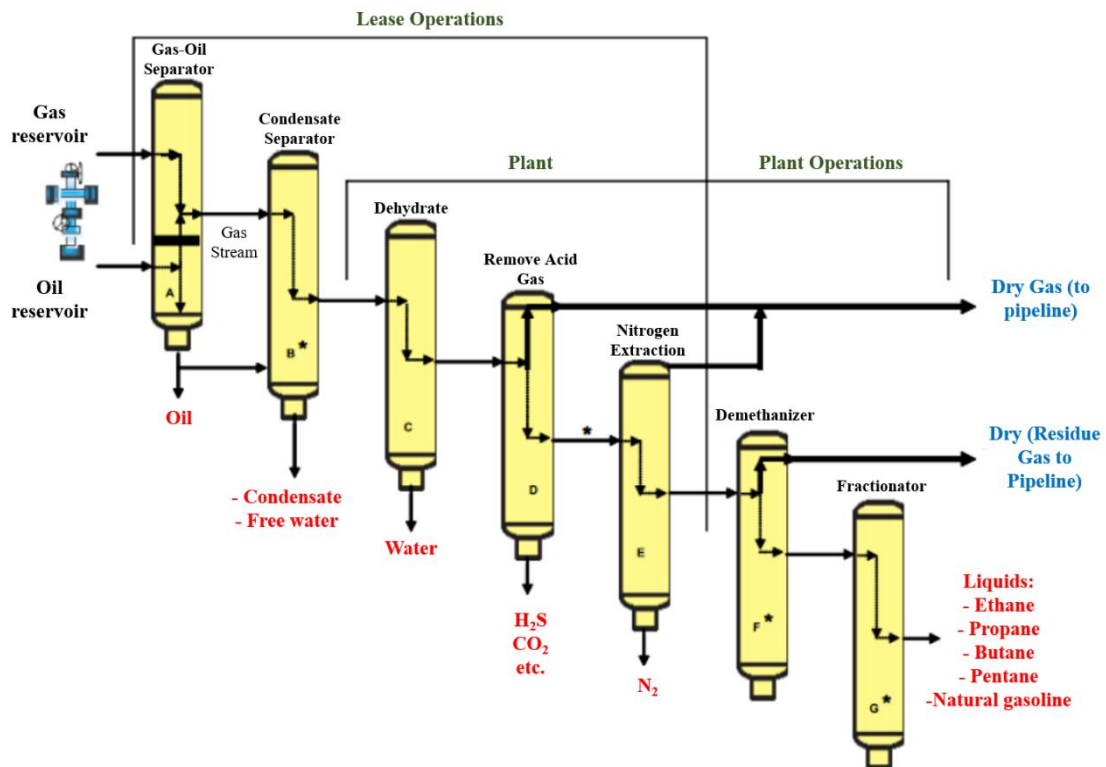


Figure 3. Natural gas processing plant in a simplified schematic model (Adapted).¹⁹

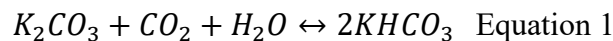
Gas-oil separators are employed to promote the separation of the gas stream and crude oil in the upper and lower sections of the cylindrical unit, respectively, due to the

pressure exerted by the well. Gravity acts as the separating force between the hydrocarbons in the gas and the heavier oils.^{19,22}

Condensate separators, in turn, remove condensates from the gas stream using mechanical devices. In the condensate treatment section, two main operations are carried out: water washing and condensate stabilization. In this process, the condensate may require washing with a water stream to remove salts and additives, depending on the quality of the feed gas.^{19,22}

Dehydration units are used to remove water vapor through a dehydrating agent, ensuring that the natural gas is free from hydrate formation, corrosion issues, and dew point concerns. The most commonly employed method is the absorption process using triethylene glycol (C₆H₁₄O₄), which is capable of removing water and other particles from the feed stream. Typically, high-pressure saturated gas contains approximately 1000 ppm of water. The purpose of absorption-based gas dryers is to reduce this concentration to approximately 100 ppm. This measure is effective in preventing the occurrence of undesirable phenomena during the process. An alternative option for water removal is adsorption, which employs dehydration towers with dry bed systems.^{19,22}

Acid gas removal towers are used to eliminate contaminants in dry gas, such as CO₂, H₂S, residual water vapor, and inert gases such as helium and oxygen. Alkanolamines are commonly employed to absorb CO₂ and H₂S from the feed gas. An alternative method is the Benfield process, which consists of two stages: gas absorption and carbonate regeneration. Potassium carbonate (K₂CO₃) is the alkaline compound used in the absorption solvent. In this process, K₂CO₃ reacts with CO₂ and H₂S in an absorber tower, forming potassium bicarbonate (KHCO₃). This reaction enables the solvent to dissolve more CO₂ and H₂S than would be possible with pure water alone. The solvent is then stripped of the absorbed CO₂ and H₂S through a distillation process carried out in a regeneration tower. Subsequently, the regenerated solvent is recycled for reuse. The reactions involved in this process are shown in the following chemical equations.^{19,23}



The nitrogen rejection unit is used to remove nitrogen gas from the gas stream. Two methods are widely employed: in the first, nitrogen is cryogenically separated from the gas stream based on the differences in boiling points of the components; in the second,

the separation of the CH₄/N₂ binary mixture is carried out through a physical absorption process. Absorption-based separation is not widely adopted, with only five registered patents mentioning this technique. Among the five identified, four utilize the same solvent-liquids composed of transition metal complexes. If traces of inert gases such as helium are present, a pressure swing adsorption (PSA) unit may be included as a complementary procedure to extract them from the gas stream.^{19,22,23}

The demethanization unit is employed to separate methane from liquefied petroleum gases (LPG) via either cryogenic processing or absorption techniques. Compared with absorption methods, cryogenic separation is more effective for isolating lighter hydrocarbons such as ethane. Finally, fractionation towers are utilized to separate the LPG components present in the gas stream by exploiting differences in the volatility of the constituent hydrocarbons. In this stage, the feed passes through a series of towers and is incrementally heated to raise the gas stream's temperature. The process enhances vapor-liquid contact, thereby facilitating the vaporization and condensation of individual components and enabling their efficient separation.^{19,22}

Once the processes that raw natural gas undergoes prior to commercialization have been briefly outlined, and given that this work seeks to develop an alternative method for gas separation, the following sections will provide a more detailed examination of the most widely employed techniques aimed at separating N₂, CO₂ and CH₄ components. It is worth reiterating that, with respect to the separation of methane and nitrogen gases, the processes most commonly used fall into three categories: cryogenic distillation, adsorption, and absorption.

2.2.1. Cryogenic Distillation

Cryogenic distillation is one of the most well-established separation technologies in the oil and natural gas industry. Its driving force lies in the difference in volatility between different gas molecules. Nitrogen's normal boiling point is -195.8 °C, whereas methane and carbon dioxide boils at -161.5 °C and -78.5 °C, respectively. This disparity is sufficient to ensure a high degree of separation efficiency. The component with the lower boiling point is collected at the top of the column, while the component with the higher boiling point accumulates as a liquid at the bottom. Typically, the distillation column operates within a two-phase region, where vapor-liquid contact plays a fundamental role in mass transfer. Liquid flows downward from the top of the column to

its base, while vapor ascends in the opposite direction. It is within this vapor-liquid interaction zone that mass is transferred, effecting the separation.^{24–26}

It is reported in the literature that this technology can achieve very high gas purities, yielding compositions of approximately 98 vol % methane with less than 1 vol % nitrogen in the natural-gas feed, and fewer than 1 vol % methane in the nitrogen-rich stream. However, the process requires operation under cryogenic conditions, which mandates that the feed gas undergo pre-treatment to remove carbon dioxide. Furthermore, as noted previously, the technique entails high operating costs for cryogenic plants, becoming even more expensive if liquefaction of the nitrogen present in the mixture is required.^{24–26}

Currently, nitrogen-rejection units are situated at the final stage of the liquefied natural gas production process. According to Tagliabue *et al.* (2009), cryogenic nitrogen rejection becomes economically viable at gas feed rates exceeding 15 MMSCFD; however, feed rates on the order of 50 MMSCFD are more commonly recommended.¹²

2.2.2. Adsorption

Adsorption processes can be classified, according to the method employed for adsorbent regeneration, into two types: temperature-swing adsorption (TSA) and pressure-swing adsorption (PSA).

Temperature-swing adsorption is predominantly applied to dehydration processes, in which the adsorbents most commonly used are zeolitic molecular sieves and silica gel. A complete TSA cycle, accounting for both heating and cooling of the system, may span anywhere from several hours to multiple days. This technique is not suitable for nitrogen removal, since the concentration of N₂ in the gas mixture is typically much higher than that of water, and the adsorbents employed exhibit greater selectivity for water than for other components in the stream.^{19,20,27}

Pressure-swing adsorption operates by adsorbing at elevated pressures (≈ 300 psi) and desorbing at reduced pressures (≈ 50 psi). In this configuration, the adsorption beds can be pressurized and depressurized rapidly, yielding cycle times on the order of minutes. Consequently, the required quantity of adsorbent is lower than that needed for temperature-swing adsorption. The materials most commonly employed for N₂/CH₄ separation include zeolitic molecular sieves and carbon-based adsorbents. Numerous studies have investigated zeolites such as mordenite, ZSM-5, and NaY; overall, these

materials exhibit selectivities in the range of 3.5 - 5.0, with the highest values observed when pore diameters closely match the kinetic diameters of nitrogen and methane, although such selectivities remain insufficient for many industrial applications. Carbon adsorbents, such as the activated carbon examined by Zhang et al. (2023), demonstrate comparable or inferior performance to these zeolites, with selectivities typically ≤ 4 .²⁸

Although promising, the method remains uncommon in industry because suitable adsorbent materials that combine acceptable cost and performance are difficult to find.^{19,20,27}

2.2.3. Absorption

One of the processes most used by industry in the removal of CO₂, the absorption technique relies on a liquid solvent to separate a gaseous mixture within an absorption column. In the column, the liquid flows countercurrently, from the base to the top, while the gas mixture is introduced at the lower section. Components exhibiting high solubility in the chosen solvent are absorbed into the liquid phase, whereas the remaining gases exit at the column's apex. The enriched solvent is then pumped to a subsequent regeneration column, where it is stripped of absorbed gases via temperature or pressure swings; the liberated gases are collected for further processing. The overall cost of this process is governed by three principal factors: the circulating rate of the absorbent liquid, the energy required for solvent regeneration, and the compression energy needed to condition the methane stream for commercial delivery. Moreover, two primary absorption schemes have been investigated for N₂/CH₄ separation: selective methane absorption in lean oil and selective nitrogen absorption in ammonia.²⁰

Selective methane absorption in lean oil operates via a physical absorption mechanism, in which the affinity between the oil and methane exceeds that for nitrogen; consequently, the majority of methane is retained within the liquid phase. The performance of this process is enhanced under low temperature and high-pressure operating conditions. However, the substantial operating costs associated with circulating the solvent and repressurizing the methane stream render the technique economically prohibitive for applications such as liquefied natural gas production.²⁰

Selective nitrogen absorption in ammonia, by contrast, offers the advantage of requiring a smaller solvent inventory, since nitrogen is present at lower concentrations than methane in natural gas. Research on this technology commenced in the mid-20th

century, culminating in the issuance of a U.S. patent in the 1950s.^{20,29–31} Although it offers higher efficiency than selective CH₄ absorption in lean oil, the process operates under hazardous conditions, since ammonia is handled at elevated pressures (≈ 725 psi) and very low temperatures (≈ -100 °C to -30 °C). Moreover, both the system's refrigeration cycle and the recovery of ammonia rely on costly operations, rendering the process economically unviable at certain levels of daily natural gas throughput. Finally, the low selectivity of nitrogen over methane necessitates additional stages to recover the methane stream.^{30,31}

Thus, given that suitable N₂/CH₄ separation processes must exhibit low to moderate energy consumption, minimal environmental impact, scalability, regenerability, safety, and high separation efficiency, absorption methods prove unattractive for industrial - scale implementation. Consequently, the pursuit of new technologies that fulfill these criteria has stimulated research into the development and application of novel materials, such as membranes, for this purpose.

2.3. MEMBRANE SEPARATION

A membrane is a thin physical barrier which, upon contact with a liquid and/or gaseous mixture, enables the selective transport of mass from one phase to another while restricting the passage of other chemical species according to a specific mechanism. Membranes may be homogeneous or heterogeneous, symmetric or asymmetric, and neutral, charged, or both. Their thickness can range from the nanometer scale up to several centimeters.^{32,33}

The driving force for mass transport across a membrane may arise from the gradients of chemical potential, pressure, or temperature. Depending on the driving force and the size of the species to be separated, membrane processes can be classified as gas separation, pervaporation, electrodialysis, dialysis, reverse osmosis, nanofiltration, ultrafiltration, and microfiltration.³⁴

The liquid and/or gaseous stream retained by a membrane is termed the concentrate or retentate, whereas the fraction capable of passing through the membrane is referred to as the permeate. In membrane separation experiments, the primary parameters of interest are flux, permeance, permeability, and selectivity.³⁵

Permeance (P) quantifies the productivity of a separation membrane and may be defined as the amount of permeate passing through a given membrane area per unit time

under a specified pressure gradient. Permeance values are commonly reported in GPU ($1 \text{ GPU} = 10^{-6} \text{ cm}^3 \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$).^{14,34,35} This parameter can be calculated using the following equations:

$$P_i = \frac{J_i}{\Delta P_{\ln,i}} \quad \text{Equation 3}$$

$$\Delta P_{\ln,i} = \frac{(P_{f,i} - P_{r,i})}{\ln \left[\frac{P_{f,i} - P_{p,i}}{P_{r,i} - P_{p,i}} \right]} \quad \text{Equation 4}$$

in which J_i is the flux of component “i” through the membrane, $\Delta P_{\ln,i}$ is the logarithmic mean pressure difference for component “i”, and $P_{f,i}$, $P_{r,i}$ e $P_{p,i}$ are, respectively, the partial pressures of component “i” in the feed, the retentate and the permeate.^{14,35}

Permeability — also termed the permeability coefficient — is defined as the product of permeance and membrane thickness. This parameter characterizes the intrinsic transport properties of the membrane material and, for an ideal homogeneous membrane, should be independent of thickness; in practice, however, measured permeabilities may vary with both membrane thickness and its fabrication or operational history. Permeability values are typically reported in Barrer ($1 \text{ Barrer} = 10^{-10} \text{ cm}^3 \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1} = 3.35 \times 10^{-16} \text{ mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$).³⁵

Selectivity (α_i) refers to the membrane's ability to separate the target components within a mixture. In a binary gas system composed of components A and B, selectivity is typically defined as the ratio of their respective permeabilities ($\alpha_{A/B}$). Multicomponent selectivity depends on the thermodynamic and mass transfer properties of the membrane, the composition of the fluid, the configuration of the permeation module, and the flow conditions. As a general rule, membranes with high permeance or permeability tend to exhibit low selectivity, and vice-versa.^{14,34,35}

In commercial terms, the industrial-scale application of membranes for gas separation began with the pioneering work of Loeb and Sourirajan in 1962. They developed a high-flux asymmetric cellulose acetate membrane initially intended for reverse osmosis, which, over time, was also employed for gas separation. This work significantly stimulated the pursuit of high-performance, low-cost membrane technologies. Although gas separation membranes have been known for over a century, it is only within the past four decades that they have been recognized as a competitive and efficient technology, gaining widespread adoption in industrial separation processes.

Gas separation through membranes has experienced exponential growth since the introduction of polysulfone hollow fiber membranes (PRISM[®]) by Permea (Monsanto), which were first used to separate hydrogen from gas streams containing ammonia. The commercial use of synthetic membranes by major gas industries, oil producers, chemical companies, and refineries began in the early 1980s. However, even today, polymeric membranes dominate the market. In the second half of the 1980s, studies began exploring the use of inorganic membranes, such as those based on zeolites and MOFs, for gas separation. Key historical milestones in the development and application of membranes for gas separation up until 2010 are depicted in Figure 4.³⁵

A notable example of membrane application in the natural gas industry is the largest CO₂/CH₄ separation membrane plant installed in Pakistan in 1995.³⁵ Currently, membranes are widely used in four major gas separation applications, which account for nearly 90% of the market: nitrogen production (O₂/N₂), natural gas treatment (CO₂/CH₄, H₂S/CH₄, He/CH₄), hydrogen recovery (H₂/N₂, H₂/CH₄, H₂/CO), and vapor recovery (C₃H₆/N₂, C₂H₄/N₂, C₂H₄/Ar, CH₄/N₂). For example, membrane-based natural gas treatment generated approximately 300 million dollars in 2018, with projections for significant growth in the coming years. Although only polymeric membranes have been significantly used in gas separation plants, recent studies have reported significant advances in the development of inorganic membranes, making them promising as alternative and competitive materials for the market.

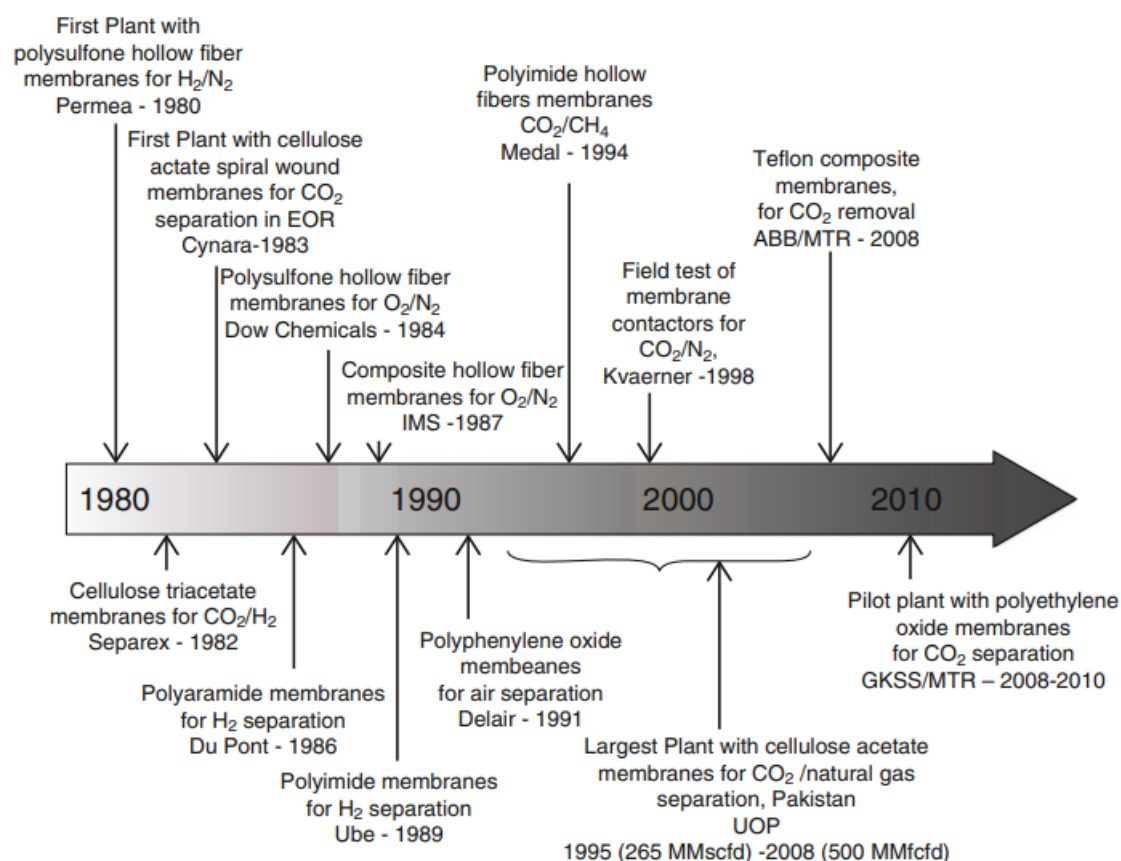


Figure 4. A brief history of industrial applications of membrane technology in gas separation.³⁵

The membrane separation process, recognized for its high energy efficiency, operational simplicity, and low capital investment, still cannot directly compete with cryogenic N_2/CH_4 separation methods, mainly due to its limited permselectivity performance. Two types of membranes are commonly employed in this context: CH_4 -selective and N_2 -selective membranes. In CH_4 -selective membranes (CH_4/N_2 systems), methane is enriched on the permeate (low-pressure) side, requiring recompression before being introduced into the subsequent processing unit. Conversely, in N_2 -selective membranes (N_2/CH_4 systems), CH_4 remains on the high-pressure (retentate) side, leading to substantial energy savings associated with recompression. From an economic and energy-efficiency standpoint, the development of N_2 -selective membranes is therefore highly desirable.³⁶

2.3.1. Polimeric Membranes

Polymeric membranes can be classified as elastomeric or glassy. Their main differences arise from the principle that the first one operates above the polymer's glass transition temperature (T_g), while the latter operates below T_g .³⁷

In elastomeric polymers, where the material is above the glass transition temperature (T_g), the polymer chains possess sufficient energy to allow greater segmental mobility of the amorphous phase, which in turn results in higher permeability of the material. This is because their properties favor rapid diffusion of gas species through the mobile polymer chains. However, the transient distribution of molecular-sized vacancies created by segmental movements during gas passage makes elastomeric polymers less efficient in gas separation when based on differences in molecular sizes (molecular sieving).^{37,38} In elastomeric polymer membranes, selectivity based on solubility dominates over selectivity based on diffusivity. As a result, mass transport is favored with an increase in the permeate's dimensions and the ease of gas condensation. Polymers such as polydimethylsiloxane, polyether, polyurethane, and polybutadiene are commonly used commercially for such purposes.³⁸

In glassy polymers, where the material is below the T_g , the chains are more rigid, restricting their movement and resulting in a smaller free volume of the material. In this case, selectivity based on diffusivity is dominant, and the effect of the penetrant's molecular size is crucial in determining the overall selectivity of the process. The diffusion coefficient of the permeating molecule in glassy polymers is small and tends to decrease with the increase in particle size. Based on the size differences of the molecules that make up the gas, the glassy polymer allows for achieving high selectivity in the process, at the expense of low gas permeability, creating a *trade-off* in choosing a candidate material for a particular application.^{32,35,38} For example, by 2018, cellulose acetate membranes represented nearly 80% of the total membrane market used in the oil and natural gas industry.^{38,39}

Although polymeric membranes are widely used in the market due to their generally good efficiency and low manufacturing, operating, and maintenance costs, this class of materials also presents some disadvantages and challenges for their development. The main issues faced by polymeric membranes are the potential for swelling and plasticization during the separation process. Under high feed pressure conditions, commonly used in the oil and natural gas industry, polarizable gases such as CO_2 and

light hydrocarbons tend to swell and plasticize the membranes, causing a sharp decline in the material's permselectivity. Additionally, polymeric membranes have a limited efficiency in gas separation due to the upper bound of Robeson, which demonstrates the trade-off between permeability and selectivity.^{38,40,41}

In 1991, Robeson conducted a study that sheds light on the gas separation performance of various polymeric membranes by constructing permeability vs. selectivity graphs for binary mixtures, including CO₂/CH₄, H₂/N₂, O₂/N₂, He/N₂ and others. He observed that there were limits beyond which no polymeric membrane studied could achieve. Robeson's study highlights a major challenge in the development of high-permeability and high-selectivity polymeric membranes, as the concurrent improvement of both selectivity and permeability is limited by the material's inherent nature. The following figure illustrates the limits observed by Robeson for the separation of the CO₂/CH₄ and N₂/CH₄ binary mixture using different polymeric.

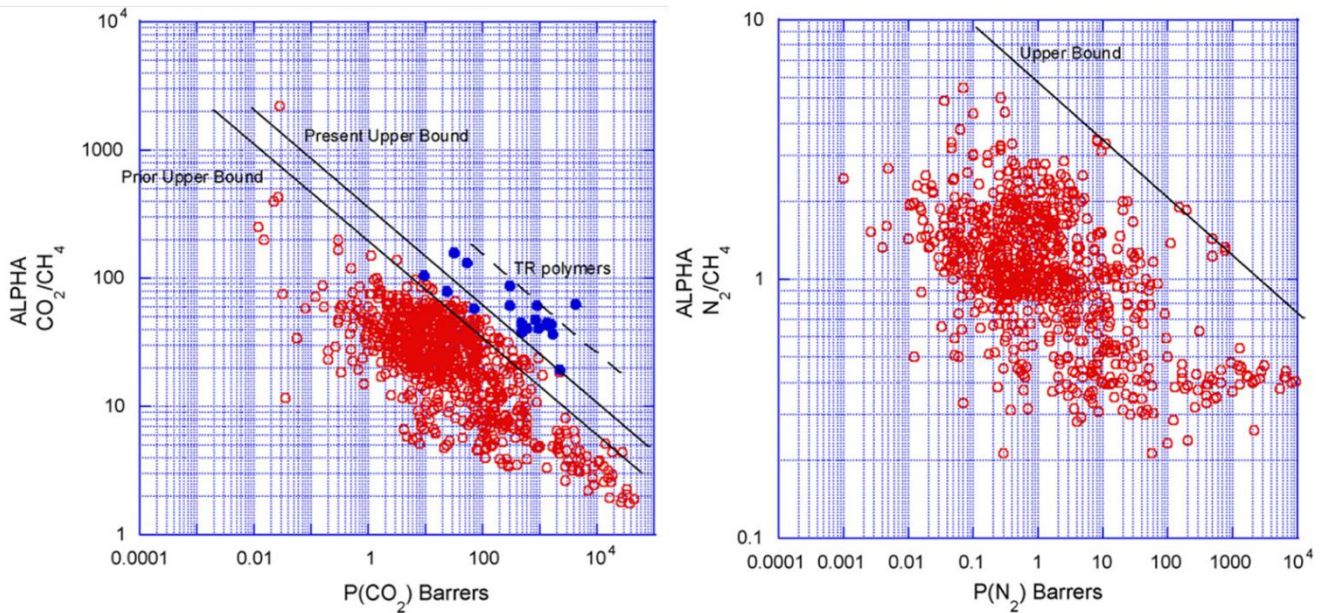


Figure 5. Robeson's superior limit for different polymeric membranes applied in CO₂/CH₄ and N₂/CH₄ separation.⁴⁰

As an alternative, and considering the barriers faced by the nature of polymeric materials, the next section will present inorganic membranes. These have gained significant attention in the literature in recent years due to their higher durability, resistance to more extreme temperature and pressure conditions, and lower environmental impact.

2.3.2. Inorganic Membranes

Currently, there is a growing trend in the production and application of inorganic membranes for processes where conditions such as high temperature, pressure, and harsh chemical environments are prohibitive for the use of polymeric membranes.³⁴ For comparative purposes, polymeric membranes typically operate at temperatures up to 120 °C, whereas inorganic membranes can withstand operating conditions as high as 900 °C.^{34,38} Although they exhibit higher costs, the thermal and chemical stability of these materials make them promising candidates for gas separation plants.

In terms of microstructure, inorganic membranes can be classified as either dense or porous. Dense membranes are free of discrete or well-defined pores and can be fabricated from various materials. For instance, dense membranes based on palladium are selective for hydrogen, whereas metal oxide membranes are selective for oxygen. Permeation in this type of membrane depends on the interaction between the gas and the membrane material and occurs through mechanisms such as solution-diffusion or solid-state ionic conduction. Dense systems exhibit high selectivity, albeit at the expense of lower permeability. Moreover, these membranes require high capital investment due to the use of noble metals and the complexity of both synthesis and operation.^{35,39,42} On the other hand, porous inorganic membranes consist of a thin selective layer deposited onto a porous ceramic or metallic support, which may be configured in the form of disks, tubes, or hollow fibers. The primary materials used for the fabrication of porous inorganic membranes include alumina, carbon, silicon carbide, and zeolites. These materials can be supported on a variety of substrates, such as α -alumina, γ -alumina, and zirconia. Porous inorganic membranes are also classified based on their pore size (d) into three categories: microporous ($d < 2$ nm), mesoporous (2 nm $< d < 50$ nm), and macroporous ($d > 50$ nm).^{38,42–45}

Under conditions in which the separation layer and the substrate are indistinguishable and exhibit a homogeneous structure and composition, the membrane is classified as symmetric or isotropic. Given that the permeation flux through a membrane is inversely proportional to its thickness, it is advantageous to make the homogeneous, selective layer as thin as possible. However, membranes with very small and unsupported thicknesses tend to suffer from compromised mechanical strength. A practical solution to this issue is the fabrication of an asymmetric or composite membrane, in which a thin selective layer is deposited onto a macroporous substrate with a high open

porosity. In this anisotropic configuration, both the selective separation of the gas stream components and most of the resistance to flow (also known as the pressure drop) primarily occur in the thin top layer. The support, therefore, must be mechanically robust and sufficiently porous so as not to contribute significantly to mass transfer resistance during the process.⁴² Figure 6 presents schematic illustrations of the main possible membrane configurations.

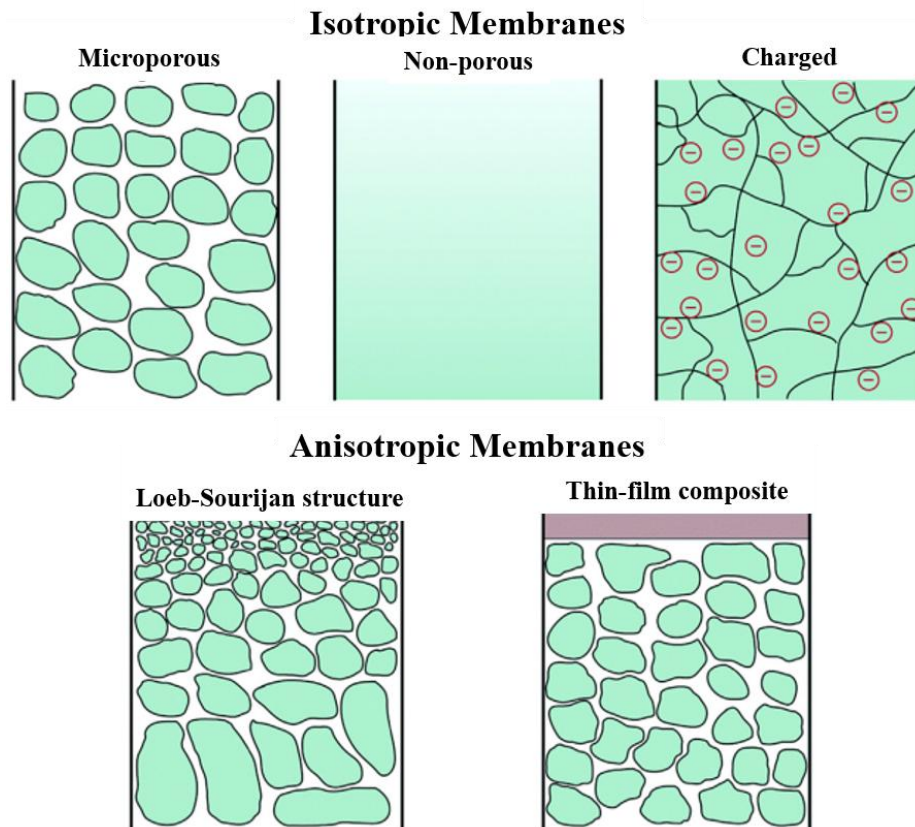


Figure 6. Schematic illustration of the main configurations of commercial membranes (Adapted).⁴⁶

Given that separation processes depend on the properties of the gas mixture to be separated, the characteristics of the selective barrier, and the separation conditions (temperature and pressure), different mass transfer mechanisms may occur depending on these variables. These mechanisms are described and Illustrated (Figure 7) below:

- **Molecular Diffusion (*Poiseuille* Flow):** *Poiseuille* flow refers to a non-selective, laminar mass transfer driven by a pressure gradient between the two ends of the membrane. In this mechanism, the mean free path of gas

molecules is smaller than the pore diameter, and diffusion occurs primarily through intermolecular collisions,^{34,35,42}

- **Knudsen Diffusion:** Knudsen diffusion occurs in long pores with small diameters (2–50 nm) due to frequent collisions between gas molecules and the pore walls. This mass transport mechanism becomes significant when the mean free path of the gas molecules is greater than the pore diameter. In such cases, molecule-wall collisions dominate over intermolecular collisions. Separation selectivities under this mechanism are generally low and are proportional to the inverse square root of the molar mass of the species. Knudsen diffusion is typically predominant in macroporous and mesoporous membranes;^{34,35}
- **Surface Diffusion:** It occurs when at least one of the species in the mixture that permeates the membrane has a strong affinity for the membrane's surface, adsorbing along the pore walls. Here, separation is based on the differences in the amount of adsorption of the permeating species. This mechanism typically occurs at temperatures below 300°C and often in parallel with other mass transport mechanisms, such as Knudsen diffusion;^{34,35}
- **Capillary Condensation:** It occurs when a partially condensed phase fills the pores of the membrane. If the pores are completely filled, only the species soluble in the condensed phase can permeate through the membrane. The selectivity is generally high, as well as the operating flux. The mechanism depends on the gas composition, pore size, and the uniformity of pore sizes;³⁵
- **Molecular Sieving:** It occurs when the pore sizes are small enough (3.0 - 5.2 Å), promoting the separation of molecules based on the difference in their kinetic diameters. Molecules larger than the pore opening are blocked, while smaller molecules permeate through the membrane.³⁵

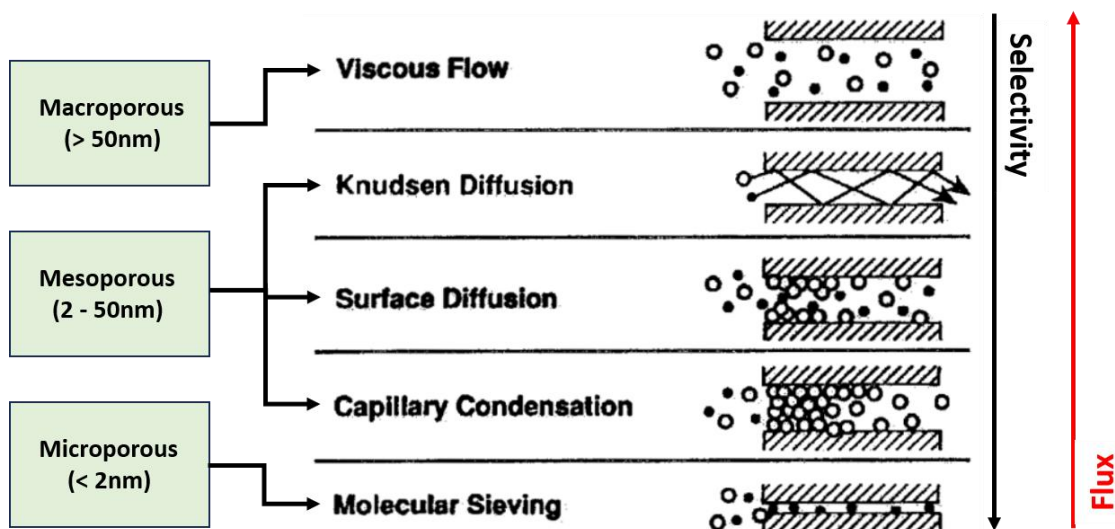


Figure 7. Schematic image of the possible mass transfer mechanisms in porous inorganic membranes.

Microporous inorganic membranes, more suitable for gas separation, are composed of amorphous materials (such as silica and carbon) and/or crystalline materials (such as zeolites). These microporous inorganic membranes separate gas or liquid molecules through a solution-diffusion mechanism for molecules smaller than the pore size of the membranes, or through a molecular sieving mechanism for mixtures containing molecules larger than the pores of the membranes. Silica microporous membranes have shown promise for molecular sieving applications. However, synthesis mechanisms that allow for precise control of pore size (0.3 - 0.4 nm in diameter) to enable sieving separation have not yet been developed for amorphous inorganic membranes. Furthermore, these materials are chemically, mechanically, and thermally less resistant than membranes formed by zeolites.^{35,45}

Microporous zeolites with uniform subnanometric porosity are capable of separating small gas molecule mixtures based on the principle of molecular sieving. One of the advantages of zeolites over polymeric membranes is their thermal stability, which can exceed 500°C, and their chemical stability under acidic and/or alkaline conditions. This enables the material to form membranes suitable for applications that require such harsh conditions. Zeolitic membranes are typically supported on stainless steels or porous α -alumina using in situ or secondary growth methodologies. The literature reports numerous examples of membranes made from various zeolites, including chabazite (CHA), DDR, and faujasite (FAU), which exhibit promising separation performance for different gas compositions.^{25,38,47,48} Zong *et al.* (2017) reported in their study using

SAPO-34 (CHA) zeolite as the selective material for N₂/CH₄ separation, membranes that achieved selectivity and permeability values for N₂ of 9.2 and 1160 GPU, respectively.⁴⁹ Zhang *et al.* (2024) presented in their study the application of SSZ-13 (CHA) zeolite, showing selectivity and permeability values for N₂/CH₄ separation on the order of 13.3 and 407 GPU.⁵⁰ Vaezi *et al.* (2018) demonstrated that DDR-type zeolites exhibited selectivity and permeability values for N₂/CH₄ separation of 8 and 30 GPU, respectively.⁵¹ FAU-type zeolites are not commonly studied for such separations, as their pore diameters exceed the kinetic diameters of CO₂, N₂, and CH₄.⁵²

This work addresses the fabrication of macroporous supports via freeze-casting and the synthesis of a SAPO-34 zeolite-based selective layer for membranes designed for natural gas separation. The following sections detail the methods for producing both the support and the crystalline and selective microporous material.

2.4. PRODUCTION OF POROUS SUBSTRATES VIA FREEZE-CASTING

The freeze-casting technique, also known as ice templating, has been the subject of numerous studies since the early 2000s due to its ability to form materials with various geometries (such as tubes, monoliths, etc.) and to be capable to control the formation of hierarchically structured porosity. Due to its simplicity and low operational cost, the method has proven to be efficient in producing porous materials with high surface area for biomedical, separation, and energy applications. One of the advantages of the process is its versatility in operational conditions and material selection for the final product, allowing the fabrication of systems based on ceramics, metals, polymers, and biomaterials.^{53,54}

The manufacturing of ceramics can be planned to combine various natural properties of their structure: they are lightweight; can exhibit open or closed porosity (allowing the construction of insulators or filters); are resistant to high temperatures; and can possess high mechanical strength, particularly in compression. The traditional ceramic manufacturing methods include Replication, Direct Foaming, Extrusion, and Sacrificial Material techniques.^{53–55} When compared to traditional processes, the freeze-casting method offers several advantages, including control over porosity and material morphology. Furthermore, it enables the production of materials with connected pores and anisotropic properties. Deville *et al.* (2008) mentioned an extensive list of ceramic materials obtained via freeze-casting, highlighting oxides (alumina, magnesium, silica,

titanium, zirconia, mullite, and silica-alumina), biomaterials (hydroxyapatite, tricalcium phosphate), and non-oxides (silicon nitride and carbide).^{54,55} Liu *et al.* (2018) reported the fabrication of α -alumina via freeze-casting with dendritic porosity capable of performing ultrafiltration of anionic dyes.⁵⁶ Ojuva *et al.* (2015) produced, from a mixture of zeolite 4A, bentonite ($\text{Al}_2\text{O}_3 \cdot 4(\text{SiO}_2) \cdot \text{H}_2\text{O}$), polyethylene glycol, and water, a material with lamellar porosity that showed good CO_2 capture capacity in a 1:9 CO_2/N_2 mixture.⁵⁷

The maximum potential of ceramics will only be achievable when a method that allows precise control over size, shape, and porosity is available. Although control over the structure and functional properties of ceramics is continuously evolving, all known processing mechanisms suffer from inherent limitations of the method, as each manufacturing technique is naturally limited to a narrow range of pore characteristics.⁵⁵ Knowing that, freeze-casting begins with the freezing of a liquid suspension (aqueous or non-aqueous), followed by the sublimation of the solidified solvent from the solid state to the gaseous state in a low-pressure environment, and subsequent thermal treatment (sintering) to consolidate and densify the material walls.^{54,55} For unidirectional freezing, a pore structure aligned with the freezing direction is obtained, where, according to Deville, the pores will be a replica of the solvent crystals that were sublimated.^{54,55} The schematized process can be seen in the following figure.

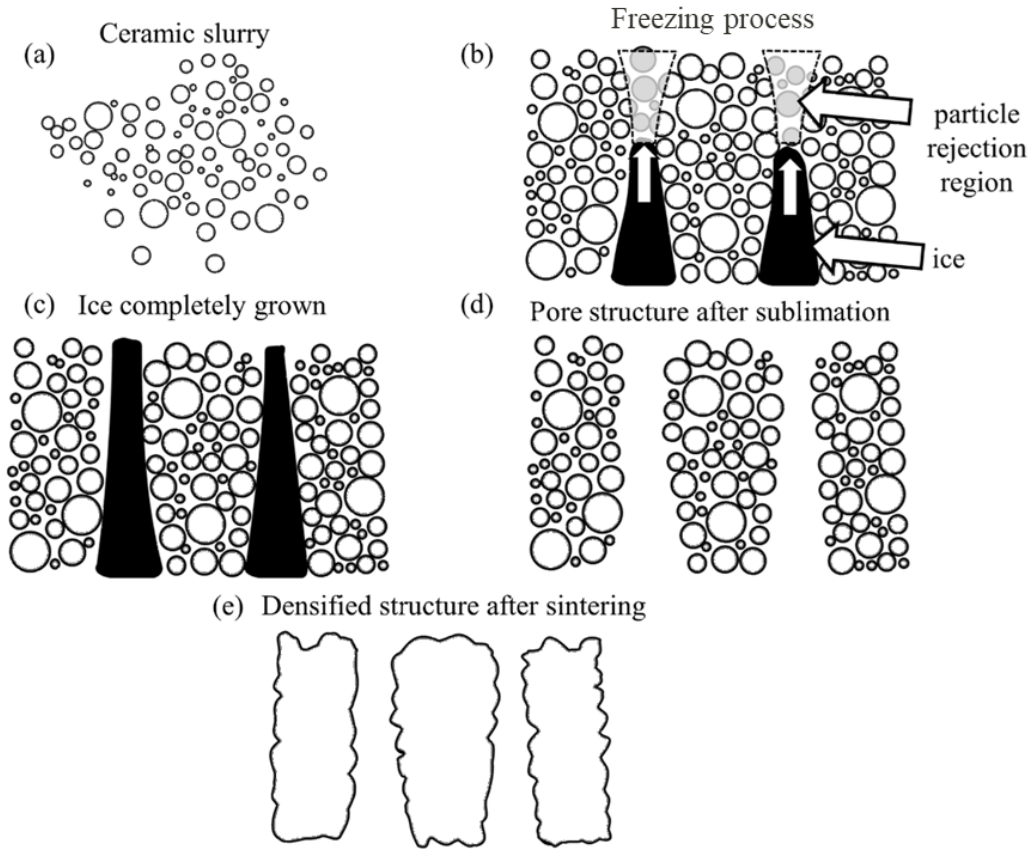


Figure 8. Schematic diagram of the processes involved in ceramic manufacturing via freeze-casting (Adapted from Athayde *et al.* 2019).⁵⁸

As previously mentioned and shown in Figure 8, this manufacturing method goes through four stages. These stages will be further elaborated in the following topics.

2.4.1. Suspension Formation

The preparation of the suspension has many similarities with traditional ceramic manufacturing methods, such as slip-casting. Increasing the solid fraction and reducing the particle size can compromise the dispersion and stabilization of the suspensions, potentially leading to defects and heterogeneities in the microstructure of the final product.⁵⁹ The physicochemical properties of the solvent (nature, viscosity, dielectric constant, etc.), the particle (density, size, surface area, etc.), and the dispersing agent (polarity, molar mass, etc.) are crucial when aiming to obtain suspensions suitable for the freeze casting process. They can also function as modulators of the final porosity desired for a specific application.^{54,55}

To ensure proper dispersion of the ceramic powder, dispersing agents and binders are commonly used in the method.^{53,55} The dispersion temperature must be within the

range in which the solvent is liquid. For water, for example, room temperature can be used, but different temperatures are required for suspensions based on camphene (60 °C), camphor-naphthalene (70 °C), and tert-butyl alcohol (25 °C). In general, the solid load used varies between 10 to 40% by suspension volume, depending on the desired total porosity. Control of the suspension stability is crucial to avoid segregation phenomena that may occur in the second stage, resulting in variations in density and porosity in the final product. Finally, the presence of a binder is necessary to provide strength to the green body (the material produced between the sublimation and sintering stages). Although the solvent plays the roles of structuring agent, binder, and pore-forming agent, its removal during the sublimation stage causes the green body to collapse in the absence of an organic binder.⁵⁵

2.4.2. Suspension Solidification

In this stage, the particles that make up the ceramic powder in suspension must be rejected by the advancing freezing front and trapped between the growing ice crystals. This aspect can be understood by considering the interaction between the solvent's solidification front and the suspended particles. A simplified thermodynamic criterion can be used for an initial understanding. The thermodynamic condition for a spherical particle to be rejected by the solidification front (pushed away from the freezing front rather than being trapped inside it – see Figure 9) is that there should be a general increase in surface energy if the particle is engulfed by the solid, that is:

$$\Delta\sigma = \sigma_{sp} - (\sigma_{lp} + \sigma_{sl}) > 0 \quad \text{Equation 5}$$

in which $\Delta\sigma$ depends on the interfacial energies of the particle and the frozen solid phase (σ_{sp}), the particle and the unfrozen liquid phase (σ_{lp}), the solid with the liquid phase (σ_{sl}). For a particle to be trapped, the interfacial free energy created during the process between the particle and the solid solvent, σ_{sp} . For a particle to be trapped, the interfacial free energy created during the process between the particle and the solid solvent, σ_{sp} , must be greater than the sum of the energies lost to the system during trapping ($\sigma_{lp} + \sigma_{sl}$), resulting in a lower energy state. The free energy described here is a critical element for the equilibrium of this simplified system, where the particle will experience both repulsive (F_R) and attractive (F_A) forces towards the freezing front due to *van der Waals* interactions at the liquid-solid interface and viscous drag, respectively.^{53,59}

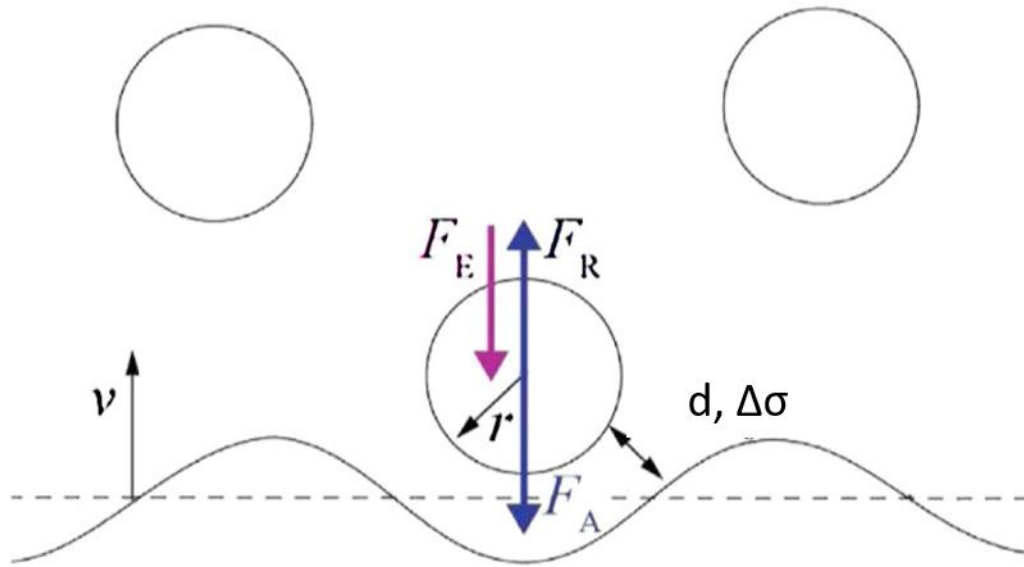


Figure 9. Dependency of the energy equilibrium between the freezing front and solid loading particles of radius "r," according to the classical freeze-casting theory. F_E represents an extrinsic or external force that can be applied experimentally to control the properties of the resulting material.⁵³

When the criterion is met and the particles are rejected by the front, a thin liquid film (d) must exist between the solidification front and the particle to promote the adequate transport of molecules toward the growing crystal. The thickness of this film decreases as the velocity of the solidification front (v) increases. Above the so-called critical velocity (v_c), this film ceases to exist.^{54,55} A significant amount of theoretical and experimental work has addressed this issue, and several expressions have been derived for the critical velocity. The main physical parameters to be considered include the viscosity of the liquid, the particle size, the film thickness, and the variation in free energy defined in Eq. 5.^{55,59}

It is important to emphasize that this simplified model only considers the interactions between a single particle and the solidification front. However, the reality is much more complex, as numerous particles interact with each other within the suspension. Peppin *et al.* (2006) and Saint-Michel *et al.* (2017) conducted studies attempting to describe more complex systems, where an additional force is exerted on a particle interacting with the solidification front within the liquid suspension.^{60,61} Although the complexity of the phenomenon generates discussion regarding the relevance of the various existing models, they are useful for an initial understanding of the influence of

physical parameters on the behavior of systems and the morphology of the materials resulting from these interactions.

2.4.3. Sublimation

After the complete solidification of the sample is transferred to a low temperature and pressure environment, with parameters determined by the physical properties of the solvent. The solidified solvent is converted to the gas phase, and porosity is created in the locations where the crystals of the liquid phase were, resulting in a porous structure in the green body. Deville *et al.* (2008) describes the porosity as a direct mimicry of the structure of the solidified solvent. When using water, a conventional lyophilizer can be employed. In the case of camphene and camphor-naphthalene, the vapor pressure of approximately 1.3 kPa is high enough to allow sublimation at ambient temperature.^{54,55}

2.4.4. Densification (Sintering)

After the complete removal of the liquid phase, the material can be sintered. In order to induce an increase in the mechanical strength of the green body, it must undergo a sequence of thermal treatments that can be divided into three stages: pre-sintering, sintering, and cooling.⁵⁴

The first stage involves heating the material to the maximum temperature where sintering will occur. In this stage, residues of the liquid phase and chemically bound water on the surface of the particles will be removed. Additionally, organic additives (dispersing agent and binder) will undergo decomposition and pyrolysis. Phase changes, allotropism transformations, and solid-state reactions may also occur. To minimize the formation of defects (such as cracks and deformations), special control of the heating rates during pre-sintering is required.⁵⁴

The sintering process is driven by the reduction of the free surface energy of the particle set. This reduction can occur through the decrease in the total surface area due to the increase in grain size, known as *coarsening*, or by replacing the solid/vapor interfaces with solid/solid interfaces, leading to the formation of grain boundaries. When mechanisms that promote densification, such as grain boundary diffusion, lattice diffusion, viscous flow, or plastic flow are predominant, pores tend to decrease and disappear. However, if the *coarsening* mechanism is dominant, pores and particles will

increase in size as sintering time progresses. The following figure illustrates the difference between densification and coarsening.^{54,62,63}

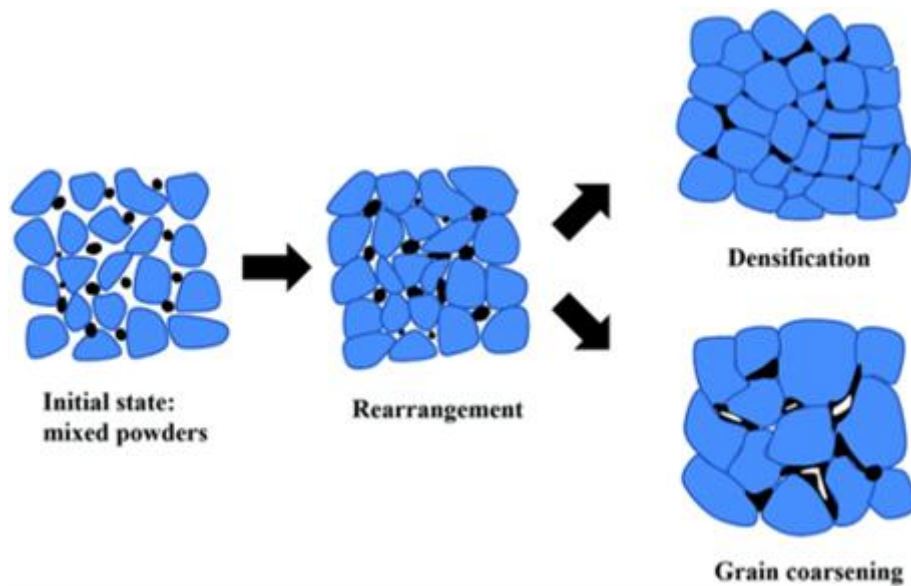


Figure 10. Schematic illustration of densification and coarsening process.⁶³

The microstructural evolution of the green body during the sintering stage progresses through several phases. Initially, primary bonds form between particles in contact, leading to the development of necks and a likely reduction in surface roughness. At this stage, the pores still exhibit a three-dimensional interconnected structure, and the volumetric shrinkage is relatively minor compared to the changes observed in the subsequent stage. At this point, the relative density increases by approximately 5%.⁵⁴

In the subsequent stage, the necks between particles grow and, typically, both porosity and the distances between particle centers decrease (densification). This stage concludes when the interconnected cylindrical pores are transformed into spherical and closed pores.^{54,55,63} In the final stage, closed porosity is eliminated through vacancy diffusion along the grain boundaries. The elimination of these pores and the vacancy diffusion process can be facilitated by grain boundary movement and controlled grain growth. However, if grain growth occurs too rapidly, the grain boundary advances faster than the pores, effectively isolating them within the grain. Since the grain continues to grow, the pores become increasingly distant from the boundary, making their removal more difficult. Therefore, grain growth must be carefully controlled to ensure that the majority of the closed porosity is eliminated.⁵⁴ Finally, cooling must also be controlled to

prevent the development of internal stresses that could lead to the formation of cracks or other structural defects.

It is important to highlight that, when considering the use of these ceramic materials as supports for membranes, it is not desirable for the sintering process to be prolonged to the point of eliminating the interconnected porosity present in the earlier stages. Such a loss would lead to increased resistance to mass transport in gas separation processes. In the case of membranes, this step is designed to enhance the mechanical strength of the material, enabling its application under conditions typically encountered in industrial and commercial settings.

2.4.5. Camphor-Naphthalene as a dispersion medium in the *freeze-casting* technique

A wide variety of freezing vehicles have been investigated in the freeze-casting process. Examples include water, camphene, tert-butyl alcohol, urea, and naphthalene-camphor (NC). Water is an attractive solvent due to its low cost, versatility, and minimal hazards to both operators and the environment. However, its solidification occurs at temperatures below 0 °C, and its sublimation must be carried out under reduced pressure, thereby increasing process complexity owing to the requirement for specialized equipment and precautions between freezing and sublimation. Camphene is widely reported in the literature as a solvent for the fabrication of macroporous materials because of its low toxicity and ease of sublimation at ambient temperature. Nevertheless, since camphene exhibits dendritic growth during solidification, the porous structures obtained with this solvent can, in some instances, contain closed pores, which may detrimentally affect the material's performance in certain applications.

The binary naphthalene-camphor solvent (Figure 11) is a freezing vehicle that has demonstrated considerable promise for the manufacture of macroporous structures. This mixture exhibits low viscosity, facilitating the preparation of highly concentrated suspensions and the production of more densely structured materials. It possesses a relatively high melting point (approximately 70 °C) and elevated vapor pressure, thereby enabling the solidification and sublimation of ceramic suspensions under milder conditions. Araki *et al.* (2004) fabricated macroporous architectures using various NC compositions and observed that the pore morphology could be tailored by adjusting the solvent ratio. Nonetheless, this finding applied only to samples with low overall porosity

because of the high solid loading used, and was based solely on a single freezing temperature ($-196\text{ }^{\circ}\text{C}$).⁶⁴ Lacerda *et al.* (2018) reported the fabrication of α -alumina components using various NC compositions and different freezing temperatures. It was observed that lower temperatures led to a reduction in the dimensions of the resulting pores. However, the study did not employ a precise control mechanism for the freezing temperature during the freeze-casting process.⁶⁵

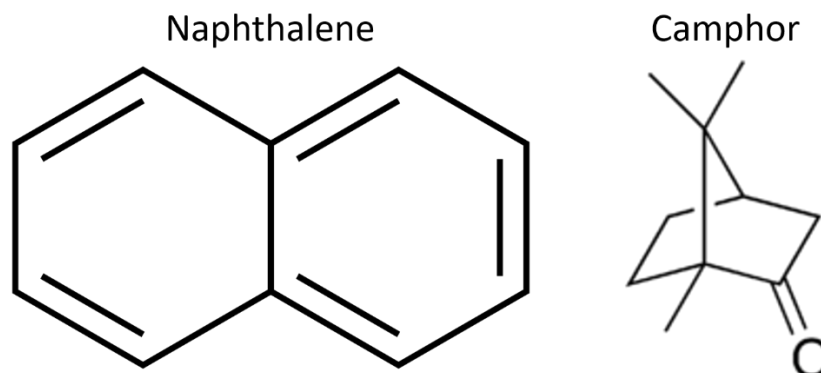


Figure 11. Chemical structure of naphthalene and camphor.

In general, this binary solvent remains scarcely explored in the literature, particularly with respect to α -alumina components fabricated via freeze-casting. Accordingly, the present work proposes the use of this solvent as a dispersing medium in the production of porous supports. Its potential in this application is mainly related to the ability to achieve fine control over porosity, both in terms of pore morphology and pore size, through planned modifications of the mixture composition and the freezing conditions.

2.5. SAPO-34 ZEOLITE AND ITS POTENCIAL FOR THE PRODUCTION OF SELECTIVE MEMBRANES

2.5.1. SAPO-34 structure and properties

Zeolites (from the Greek *zeo* = “to boil”; *lithos* = “stone”) are regarded as an important class of crystalline inorganic materials that have attracted considerable interest for applications in the petrochemical and fine-chemical industries, as well as in catalysis, adsorption, and ion exchange. Owing to the high crystallinity of their frameworks, zeolites exhibit an ordered distribution of micropores, which generally possess diameters below 2 nm. In contrast to other microporous materials, the three-dimensional structure

of a zeolite is constructed exclusively from TO_4 tetrahedra (where T denotes tetrahedrally coordinated elements such as Al and Si).⁶⁶ The TO_4 tetrahedra connect to four neighboring units by sharing their oxygen atoms. When Si^{4+} is substituted by Al^{3+} , a charge imbalance is introduced, which is neutralized by compensating cations (e.g., Na^+ , K^+). Although all zeolites are constructed from TO_4 tetrahedra, variations in the tetrahedral arrangement and in the constituent elements give rise to the diversity of zeolite frameworks.⁶⁶

The incorporation of phosphorus atoms into zeolites was first reported in 1971.⁶⁷ The class designated as aluminophosphate ($\text{AlPO}_4\text{-n}$, where n varies with the framework type) was synthesized from an aluminosilicate gel to which phosphate groups were introduced. Consequently, as the phosphorus/phosphate content increased, the material's ion-exchange capacity diminished. Since the aluminum tetrahedron carries a negative charge (AlO_4^-) and the phosphorus tetrahedron a positive charge (PO_4^+), the net effect is framework neutralization. Hence, the use of compensating cations, required in conventional zeolites, is rendered unnecessary.⁶⁸

Although conventional zeolites and aluminophosphates share many similarities, the chemical pathways for their formation differ markedly. Zeolites are typically synthesized under alkaline conditions, in which silanol groups can be deprotonated, whereas acid-media gels often yield dense aluminosilicate phases. By contrast, acidic or neutral pH environments are ideal for aluminophosphate synthesis. However, pH values below 3 promote the emergence of dense phases, and pH values above 10 lead to diminished yields due to solubilization and re-solubilization of aluminophosphate species and aluminum sources, thereby reducing the degree of crystallinity.⁶⁸

Lok *et al.* (1984) proposed the incorporation of silicon atoms into the aluminophosphate framework, leading to the formation of silicoaluminophosphates (SAPO-n) and the generation of Brønsted acid sites, which are particularly pertinent to acid-catalyzed reactions. The material was synthesized via a hydrothermal method from a synthesis gel containing pseudoboehmite, phosphoric acid, silica sol, and organic structure-directing agents based on amines or quaternary ammonium compounds.⁶⁹

Three distinct mechanisms have been proposed for the incorporation of Si into the framework. In mechanism SM1, a silicon atom occupies a site originally occupied by aluminum, yielding a net positive framework charge. However, the Si–O–P linkage formed in SM1 is energetically disfavoured and is rarely observed experimentally. In

mechanism SM2, silicon substitutes for a hypothetical phosphorus site, resulting in a Si(4Al) coordination and introducing a net negative charge that is balanced by protonation of Si–O–Al bridges. A third possibility, SM3, involves the simultaneous substitution of adjacent Al and P atoms by two Si atoms. This double-substitution mechanism gives rise to Si(3Al), Si(2Al), Si(1Al), and Si(OAl) coordinations. The extent of SM3 substitution increases with the silicon content of the synthesis gel, leading to the formation of silicon-rich islands. Furthermore, the Si(OAl)₄ coordination produced via SM2 can generate medium Brønsted acid centres. All three mechanisms are illustrated in Figure 12.^{68,70,71}

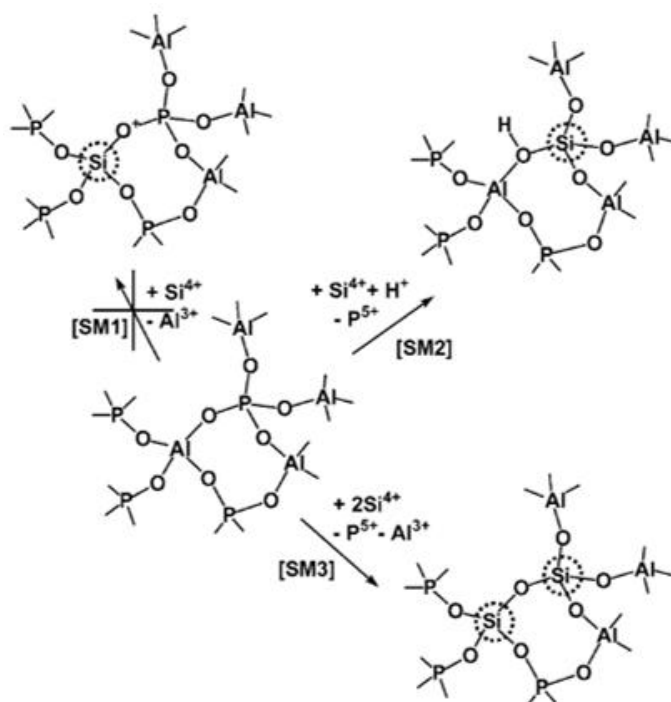


Figure 12. Substitution mechanism for the formation of SAPOs.⁶⁸

Based on previous context, the SAPO-34 zeolite belongs to the silicoaluminophosphate (SAPO) family. Its composition may be expressed as $\text{Si}_x\text{Al}_y\text{P}_z\text{O}_2$, in which $x + y + z = 1$ and $x + z = y$. Structurally, SAPO-34 has the chabazite (CHA) framework, crystallizing as typically rhombohedral, pseudocubic crystals. The CHA lattice is built from double six-membered rings (D6R) interconnected by four-membered rings, and each cage is attached to its neighbors via six eight-membered rings. Intracrystalline pore volumes range from 0.18 to 0.48 cm³.g⁻¹, with pore diameters between 0.3 and 0.8 nm. Its eight-membered rings enclose cavities of 9.4 Å, with pore apertures measuring 3.8 Å × 3.8 Å.^{41,72–74} The structure of SAPO-34 can be seen in Figure 13.

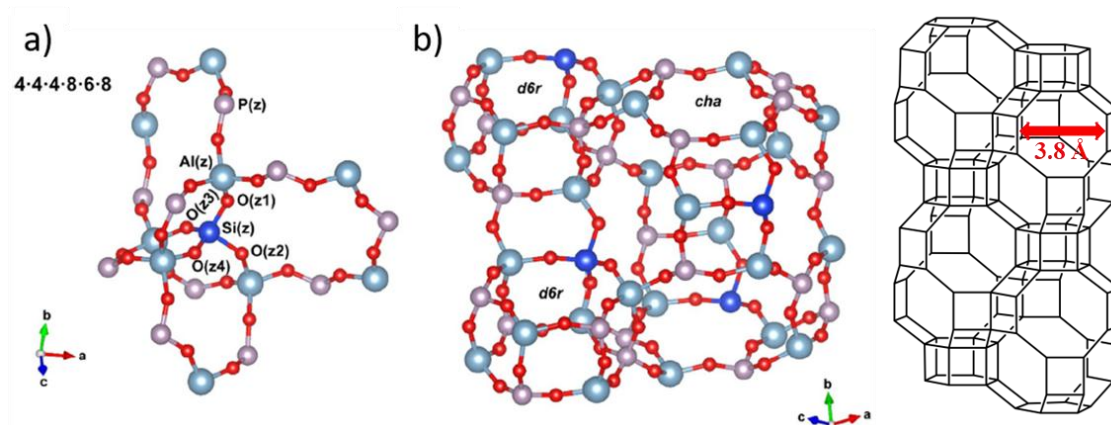


Figure 13. Structure of SAPO-34. (a) Illustration of the six rings that constitute the framework, with Si(z) denoted by “4.4.4.8.6.8.” Each value indicates the number of framework cations forming each ring, accordingly, the structure is formed by three four-membered rings, one six-membered ring, and two eight-membered rings. (b) SAPO-34 framework showing the chabazite (CHA) cages, the double six-membered rings (D6R), and their interconnections (Adapted).⁷⁵

2.5.2. Precursors for SAPO-34 synthesis

The synthesis of SAPO-34 requires five essential components: a silicon source, an aluminum source, a phosphorus source, organic structure-directing agents (OSDAs or templates), and deionized water. Common aluminum precursors are pseudoboehmite and aluminum isopropoxide, while silica is typically supplied as colloidal silica or tetraethyl orthosilicate (TEOS). Phosphoric acid is the usual phosphorus reagent. Frequently used organic templates include morpholine, tetraethylammonium hydroxide (TEAOH), triethylamine (TEA), and diethylamine (DEA). Each precursor plays a decisive role in determining the physicochemical properties and overall quality of the final product. The most common synthesis methods are hydrothermal crystallization, two-step (seeded) crystallization, and microwave-assisted synthesis.^{13,76}

2.5.2.1. Silicon source

The silica source and its concentration influence both the crystallinity of the final product and the formation of acidic sites. Silicon is one of the key elements responsible for the acidity of SAPO-34, and its selection is considered one of the most critical aspects when defining a methodology for molecular sieve synthesis. A major current research

focus is the optimization of the spatial distribution of silicon atoms within the SAPO-34 framework to enhance the catalytic lifetime of the molecular sieve.⁷⁶

Silica sources commonly used in SAPO-34 synthesis include TEOS, fumed silica, colloidal silica, and silicic acid. Askari *et al.* (2016) demonstrated that the silica source strongly affects the crystallinity, crystal size, and morphology of the zeolite due to their different solubilities in the alkaline medium. Moreover, the distinct surface areas of the various silica sources considerably influence the crystallization rate.⁷⁷

The effect of using TEOS and fumed silica was evaluated by Askari's group. In their studies, neither silicon source affected the purity of the produced crystals, but both influenced crystal size, shape, and morphology. When TEOS was used, smaller crystals with a narrower size distribution were obtained. The authors attribute these effects to the different solubilities and reactivity rates of the silica sources. Si species originating from TEOS contribute more to nucleation due to their faster dissolution in the alkaline medium, thereby accelerating nucleation and promoting a wider distribution of species among the numerous available nuclei.⁷⁷

Salmasi *et al.* (2012) synthesized two SAPO-34 samples under identical conditions using colloidal silica and silicic acid. Crystallinity decreased when silicic acid was used, whereas colloidal silica produced smaller crystals. However, both silica sources resulted in cubic morphology. These findings confirm previous observations regarding the differing reactivity and solubility of various silica sources, which lead to distinct product characteristics. In this case, the high surface area of colloidal silica facilitates its dissolution in the basic medium more readily compared to silicic acid.⁷⁸

2.5.2.2. Aluminum source

Overall, the aluminum source exerts a lesser influence on SAPO-34 synthesis compared to other precursors. Álvaro-Muñoz *et al.* (2014) synthesized a SAPO-34 catalyst using AlCl_3 as the aluminum precursor. It was observed that employing a highly diluted precursor solution led to a reduction in crystal size, yielding rhombohedral crystals with dimensions of 200 - 300 nm.⁷⁹ Askari *et al.* (2016) reported that using pseudo-boehmite as the aluminum source allows the production of molecular sieves with small particle size, higher specific surface area, and moderate acid site density. The catalytic performance of SAPO-34 molecular sieves synthesized using aluminum hydroxide or aluminum isopropoxide as the aluminum source does not differ from that of

the SAPO-34 sieves obtained with the latter.⁷⁷ However, the study by Li *et al.* (2010) demonstrates that the use of aluminum hydroxide tends to promote the formation of larger zeolitic particles compared with syntheses employing aluminum isopropoxide. The rapid hydrolysis of aluminum isopropoxide in water favors the generation of monomeric and oligomeric soluble Al species that are more uniformly distributed. This behavior increases the nucleation rate, leading to the formation of smaller crystals.^{80,81}

2.5.2.3. Phosphorous and water

Phosphorus content and water amount can significantly influence the formed phase, crystallinity, and particle size. Variation in water content affects the crystallinity of the products by altering the pH and ion concentration in the synthesis gel.

Sedighi *et al.* (2014) investigated the effect of both parameters in SAPO-34 synthesis using two different molar compositions: 1 Al₂O₃ : 0.4 SiO₂ : 0.6–1.4 P₂O₅ : 0.5 TEAOH : 1.5 MOR : 60 H₂O; and 1 Al₂O₃ : 0.4 SiO₂ : 1 P₂O₅ : 0.5 TEAOH : 1.5 MOR : 60–100 H₂O. The results indicate that increasing the phosphorus content from 0.6 to 1 enhances both crystallinity and surface area; however, further addition of phosphorus to 1.2 may reduce crystallinity, and a P₂O₅/Al₂O₃ molar ratio near 1.4 leads to the formation of a minor SAPO-41 phase. These observations suggest that high incorporation of phosphorus into the crystal framework results in decreased crystallinity and phase transformation.⁸²

Regarding the effect of water content, a high-water concentration (100 H₂O in the molar composition, compared to 75 and 60) results in lower crystallinity due to the dilution of precursors and ions in the gel, which reduces the driving force of the synthesis. Furthermore, higher water content yields smaller crystals without distinct morphology, indicating that water content can be used as an optimization tool to obtain small crystals with high crystallinity.⁸²

2.5.2.4. Template effect

Organic structure-directing agents (OSDAs, or templates) play two primary roles in the synthesis process: structural organization through space-filling and charge compensation. Moreover, as the main alkaline component in the composition, OSDAs significantly influence the pH of the reaction gel. To date, more than 100 templates have been identified as effective for zeolite synthesis. These molecules mainly belong to the

quaternary ammonium group and various organic amines, including primary, secondary, and tertiary alkylamines, cyclic amines, and alkanolamines.⁷⁷

Uncharged templates, such as tetraalkylammonium hydroxide or non-protonated amines, interact with the framework through *van der Waals* forces, occupying the cavities and enhancing the thermodynamic stability of the structure. In contrast, organic ammonium cations or protonated amines neutralize the charge of AlPO_4 frameworks, which become negatively charged due to anionic ligands (hydroxides, fluorides, and phosphates). In such cases, a stoichiometric relationship generally exists between the template molecules and the structural elements.^{77,83}

The most used directing agent in SAPO-34 synthesis is tetraethylammonium hydroxide (TEAOH). This directing agent is capable of delivering structures with high crystallinity, purity, and reduced particle sizes. However, due to its high toxicity, potential corrosiveness, and high cost, researchers have explored the use of other amines as organic structure-directing agents (OSDAs). Several amines have been investigated in the synthesis of SAPO-34, each leading to the production of crystals with different phases, crystallinities, and physicochemical properties.⁸³

Overall, the dimensions of the structure-directing molecules must be compatible with the size of the zeolite cavities. However, this relationship is not always straightforward. Smaller OSDAs allow multiple molecules to occupy the same intracrystalline cavity, increasing the time and temperature required for crystallization and potentially leading to the formation of secondary phases. The presence of two directing molecules, as occurs with morpholine, within a single cavity can influence the silicon distribution in the framework and, consequently, the density and acid strength of SAPO-34.^{83,84} The formation of silicon islands reduces the density of acid sites while enhancing the acid strength at the edges of these islands.

However, size is not the only determining factor. In addition to exerting an electronic role in directing a specific framework, the OSDA must exhibit a suitable energetic interaction with the crystal lattice, as well as geometric compatibility. For example, n-hexylamine and n-butylamine have dimensions comparable to the SAPO-11 framework; nevertheless, they are not effective templates for its formation.⁸³

The use of secondary amines, such as dipropylamine (DPA – $125.4 \text{ \AA}^3$) and morpholine (MOR – $90.4 \text{ \AA}^3$), has been extensively studied in recent years. The small size of the MOR molecules can allow two of them to occupy a single CHA-type cavity,

promoting higher silicon incorporation and an increased presence of Si(4Al) species. Crystals formed using MOR generally exhibit larger particle sizes than those obtained with other alkylamines. The oxygen atom in the framework establishes hydrogen bonds with Brønsted acid groups in the structure, accelerating crystal growth. SAPO-34 with high phase purity directed solely by DPA is obtained only under more aggressive hydrothermal conditions (200 °C, 120 h) and requires a higher template concentration to prevent the formation of SAPO-31 and SAPO-11 phases.⁸³ However, the application of systems employing multiple templates in a single synthesis can mitigate this effect.

Some templates, such as TEOAH, are very expensive and have harmful effects on the user and the environment. The use of mixed organic directing agents can contribute to the reduction of the final product cost and to the minimization of the toxicity of some OSDAs. In addition, the combination of templates can favor the production of smaller crystals and the increase of the product crystallinity.^{77,84}

Doan *et al.* (2019), through hydrothermal synthesis, produced SAPO-34 using combinations of the templates MOR/Triethylamine (TEA)/TEAOH. Using a single directing agent, the work showed that TEA was more suitable for synthesizing SAPO-5, while TEOAH and MOR favored the formation of SAPO-34. However, when combining the three templates in the proportion 3 MOR : 3 TEA : 1 TEOAH, there was a decrease in the particle size of the samples. Thus, their material showed an increase in surface area, reduction in crystal size, improvement in crystallinity, and an increase in acidity content.⁸⁴

In the context of SAPO-34 membrane production, tetraethylammonium hydroxide (TEAOH) is the most commonly employed organic structure-directing agent, although it is often used in combination with an additional OSDA, such as dipropylamine (DPA) or, less frequently, morpholine (MOR). According to Xu *et al.* (2021), the use of DPA can increase the alkalinity and, consequently, the nucleation rate, which favors the formation of even smaller crystals. This favorable growth characteristic leads to thinner membranes with more effective intercrystalline growth, reducing potential defects. TEOAH and TEOAH/DPA are the most commonly used organic structure-directing agents for SAPO-34 membrane synthesis reported in the literature.⁴¹

2.5.2.5. Synthesis methods of the SAPO-34 molecular sieve

The synthesis of SAPO-34 zeolite can be conducted by different methodologies, each one influencing in a distinct way the structural, morphological, and textural

properties of the final material. The choice of the synthesis method, as well as the experimental conditions employed, plays a crucial role in obtaining phase purity, in controlling the crystal size, and the distribution of its pores. The control of synthetic routes is fundamental to adapt SAPO-34 to specific applications, such as heterogeneous catalysis, selective adsorption, and gas separation in membranes. The main synthesis methodologies employed in the production of this molecular sieve are presented and discussed below.

In the hydrothermal method, synthesis begins by combining specified amounts of the silicon source, aluminum source, phosphorus source, structure-directing agent, and deionized water according to the prescribed molar ratios. The resulting mixture is then aged, stirred or not, at ambient temperature. After aging, the suspension is transferred into a Teflon-lined vessel, sealed within an autoclave, and placed in an oven, where crystallization proceeds at 165 – 200 °C for up to eight days. Then, the solid product is recovered by centrifugation, washed, dried, and calcined at 450 - 600 °C. Nafaji *et al.* (2014) synthesized different SAPO-34s using the hydrothermal method, with crystal sizes ranging from 100 to 2000 nm, by mixing or not different OSDAs in the suspension.^{76,85}

In the two-step crystallization process, the aged solution is first transferred to a Teflon-lined vessel and subjected to crystallization at a low temperature for a specified period. Following this initial stage, the material is removed and diluted with distilled water. The diluted solution is then placed back into the Teflon liner and crystallized at a higher temperature for an additional period. This approach is theoretically responsible to the formation of SAPO-34 crystals with more uniform and smaller particle sizes. The initial low-temperature crystallization stage promotes the formation of a greater number of crystal nuclei. The addition of distilled water aids in dispersing the formed nuclei and prevents their agglomeration. The second, high-temperature crystallization step primarily facilitates the growth and maturation of the zeolitic crystals. Furthermore, the dilution of the solution reduces the ionic concentration, thereby inhibiting the development of large crystal grains and ultimately leading to smaller SAPO-34 molecular sieve particles.⁷⁶ Wang *et al.* 2013 synthesized SAPO-34 via a two-step crystallization process, obtaining particle sizes ranging from 160 to 550 nm and a specific surface area of 648 m²/g.⁸⁶

Microwave-assisted crystallization can rapidly supply the thermal energy required for the formation of molecular sieves. Microwave irradiation enhances particle collisions, promoting uniform dispersion of the synthesis gel and leading to the formation of dense

crystal nuclei. Simultaneously, the gel is heated quickly and homogeneously, which not only accelerates the crystallization rate and improves phase purity, but also reduces the zeolite particle size and promotes a more uniform grain size distribution. Moreover, microwave heating mitigates the occurrence of undesirable temperature gradients during crystallization. Alam *et al.* (2021) synthesized SAPO-34 zeolites via microwave-assisted crystallization, employing irradiation times of up to 24 hours and varying the Si/Al ratio in the precursor gel. They observed that this ratio significantly influences the density of acid sites, thereby affecting the catalytic performance of the material.⁸⁷

2.5.3. Applications of SAPO-34 in membrane technology

For the fabrication of membranes using SAPO-34 zeolite, two main methods (Figure 14) are commonly employed: *in situ* (direct) crystallization and secondary (seeded) growth. In the direct method, the synthesis solution and the macroporous support are placed together in a Teflon-lined vessel, promoting direct contact between them. As previously discussed, the synthesis solution typically consists of a mixture containing an aluminum source, a silica source, a phosphoric acid (H_3PO_4), an organic structure-directing agent, and deionized water. The system is then sealed in an autoclave and subjected to hydrothermal conditions (temperatures of up to 200 °C and autogenous pressure).¹³

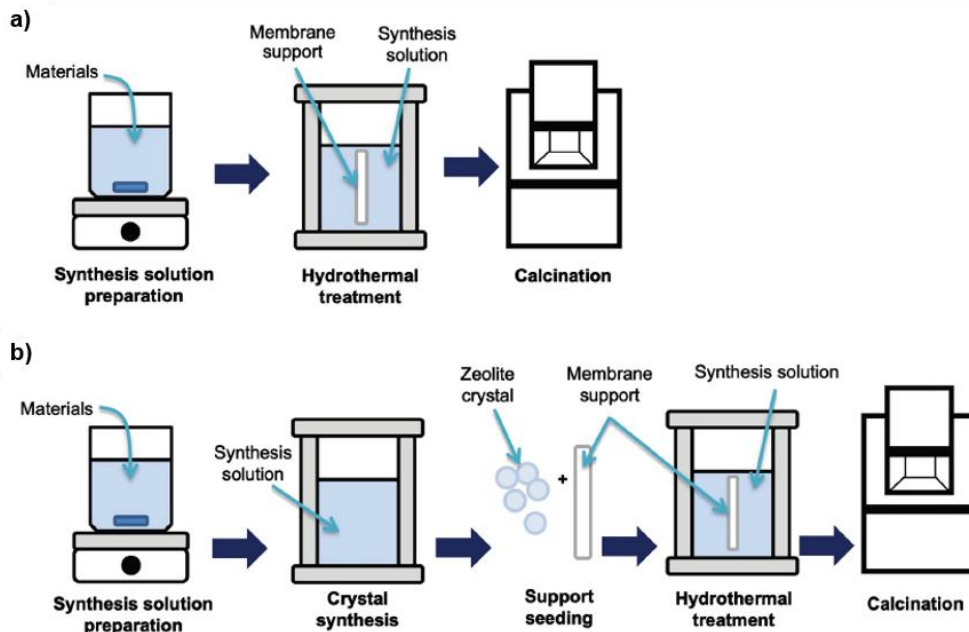


Figure 14. Conventional methods for SAPO-34 membranes production. (a) Direct crystallization and (b) secondary growth.

Two critical stages must be carefully considered during the formation of the zeolitic membrane: nucleation and crystal growth. In the *in situ* method, the nucleation process plays a crucial role in zeolite membrane formation. The size, orientation, and subsequent growth of the crystals are governed by the number and nature of nuclei formed on the support. Zeolitic nuclei may form directly on the support via heterogeneous nucleation or may be deposited as embryonic seed crystals from solution through homogeneous nucleation. The nucleation process is highly sensitive to synthesis composition and temperature, to the physicochemical properties of the support material, and to the presence of impurities. These factors make the nucleation stage during direct crystallization difficult to control, often leading to poor reproducibility of the membrane microstructure.¹³ Porshusta *et al.* (2000) observed that SAPO-34 membranes exhibiting higher permeances were obtained by extending the support's immersion time in the synthesis solution from 2 to 24 h.⁸⁸ However, subsequent studies by the same group revealed that SAPO-34 membranes prepared via the *in situ* crystallization method suffer from the formation of amorphous phases, which leads to a decrease in separation performance.

In the secondary growth method, nucleation becomes largely independent of zeolite growth through the introduction of a thin seed layer of zeolitic crystals pre-deposited onto the support surface. The formation of this seed layer is critically important for ensuring the quality and integrity of the resulting zeolitic membrane. Seed deposition can be performed using various methods, including dip-coating (immersion), rub-coating (manual or mechanical abrasion), spin-coating (rotation), and spray-coating. Among these techniques, rub-coating and dip-coating are the most widely employed in the literature for the fabrication of SAPO-34 membranes.^{13,14,41,49,88–90}

The friction (rub-coating) method is a simple, low-cost technique that involves the manual or mechanical spreading of a paste containing zeolitic seeds onto the porous substrate, and can be implemented without the need for sophisticated equipment. Moreover, it is well suited to deposition on substrates with irregular or highly rough surfaces. However, owing to its heavy reliance on the operator's technical skill and its non-automated nature, this method suffers from poor reproducibility, considerable difficulty in producing uniform coatings, and limited scalability.^{91–93}

The dip-coating deposition technique, in turn, entails the formation of a liquid film by the controlled withdrawal of a substrate immersed in a solution. The process typically

comprises four stages: immersion of the substrate into the liquid; dwell time for a predetermined duration; controlled withdrawal of the substrate; and drying. During the withdrawal stage, the dip-coating process can be characterized by the interplay of two sets of forces: drainage forces and drag forces. Drainage forces act to remove liquid from the substrate and return it to the bath, whereas drag forces act to retain fluid on the substrate. The balance between these forces determines the thickness of the film that coats the substrate. Owing to its precise control over critical parameters, such as immersion and withdrawal speeds and dwell time, the method enables the fabrication of homogeneous films on smooth substrates with high reproducibility. However, the technique requires stringent control over solution viscosity, ambient conditions during operation, and the protection of areas not intended for coating.⁹⁴

The seeded surface is brought into contact with a suspension under the seed-crystal growth conditions to form a continuous film. The primary advantage of this method is that, by applying a seed-coat, typically composed of zeolitic crystals, the continuous membrane develops via secondary growth of the deposited crystals. This approach drastically reduces the influence of the support, eliminates the nucleation stage owing to the presence of seed crystals on the support surface, and affords enhanced control over both the microstructure of the formed film and its reproducibility.^{13,95}

Until now, the literature shows a pronounced predominance of SAPO-34 membranes produced primarily on disc-shaped, hollow-fiber, or tubular supports via the secondary-growth method. The application of SAPO-34 zeolite membranes as selective media for the gas-phase separation of mixtures containing N₂ (kinetic diameter = 0.36 nm), CO₂ (0.33 nm), and CH₄ (0.38 nm) is especially promising, owing to their affinity for polar molecules and their small pore aperture (0.38 nm). However, as discussed in Section 3.1.1, N₂/CH₄ separation remains significantly more challenging than CO₂/CH₄ separation, due to the closer proximity of the components' kinetic diameters and physicochemical properties.¹⁴

Hernández-Palomares *et al.* (2024) reported a study on the separation of CO₂/CH₄ using SAPO-34 membranes deposited via secondary growth on various macroporous supports. By employing seeds obtained through the alkaline digestion of alumina waste, the group successfully fabricated α -Al₂O₃-supported membranes exhibiting a CO₂/CH₄ selectivity of 130 and a CO₂ permeability of 7.1×10^{-7} mol.m⁻².s⁻¹.⁹⁶ Mirfendereski *et al.* (2024) fabricated various membranes by modifying both the SAPO-34 seed surfaces and

the substrate. By applying a masking agent and a cationic polymer to the substrate surface, the group successfully produced SAPO-34 membranes exhibiting a CO₂/CH₄ selectivity of 146.⁹⁷

Li *et al.* (2015) conducted a study on N₂/CH₄ separation by fabricating various SAPO-34 membranes while systematically varying key parameters, as: the duration of the hydrothermal treatment, the dilution of the synthesis suspension, and the type of commercial support possessing different pore diameters. Membranes exhibiting N₂ permeances as high as 500 GPU and an N₂/CH₄ selectivity of 8 were obtained when tested with an equimolar gas mixture. An accompanying techno-economic assessment indicated that such SAPO-34 membranes could potentially compete with cryogenic distillation for N₂ rejection, particularly in the context of applications in small scale wells.¹⁴

Zong e Carreon (2017) synthesized SAPO-34 membranes for N₂/CH₄ separation in stainless-steel autoclaves, systematically varying the post-hydrothermal treatment cooling method, as: immersion in a water bath, an ice bath, or running water. They were able to achieve membranes exhibiting an N₂/CH₄ selectivity of 8.6 and an N₂ permeance of 2,150 GPU when cooled in an ice bath.⁴⁹

Huang *et al.* (2015) employed thin plate-like SAPO-34 seed crystals to synthesize, via secondary growth, high-quality thin SAPO-34 membranes for N₂/CH₄ separation. These finely structured seeds yielded some of the thinnest SAPO-34 crystals reported at the time, approximately ten unit-cell layers in thickness, and enabled the growth of membranes as thin as 2.3 μm. Remarkably, the authors found that the seeds' aspect ratio (height-to-width) not only influenced membrane thickness but also played a crucial role in defect control: high-aspect-ratio crystals packed more uniformly, forming a thinner, denser seed layer than did regular cubic crystals. Testing with an equimolar N₂/CH₄ mixture demonstrated selectivities up to 11.2 alongside N₂ permeances of approximately 860 GPU.⁹⁸

Although a large number of studies have reported the use of SAPO-34 as the active phase for gas mixture separation, relatively little attention has been devoted to reducing synthesis costs and improving reproducibility. In this context, the use of mixed organic structure-directing agents (OSDAs) may significantly lower the production cost of the molecular sieve, given that tetraethylammonium hydroxide — widely regarded as the optimal OSDA for SAPO-34 synthesis — is both costly and highly toxic. Furthermore,

replacing techniques such as rubbing coating with dip-coating may enhance the reproducibility of zeolite membrane fabrication.

Considering the potential of SAPO-34 for membrane applications, the following chapter will describe the methodological procedure for fabricating the macroporous support and the microporous-selective crystalline framework.

CHAPTER 3 - MATERIALS & METHODS

3.1. Materials

The main materials and reagents used to carry out this work will be presented in the following table.

Table 3. Starting reagents for carrying out the research.

Section	Materials
Freeze-Casting	α -Al ₂ O ₃ : CT-3000 LS SG (α -Al ₂ O ₃ - Almatís Brasil, 99.8 wt%, D50 0.5 μ m)
	Camphor (C ₁₀ H ₁₆ O - 152.2 g.mol ⁻¹ - Sigma-Aldrich, 95 wt%)
	Commercial alumina tubes (Tecnicer Cerâmica inner diameter = 8 mm outer diameter = 12 mm)
	EFKA [®] FA 4663 (Cognis, Southampton Hampshire, Reino Unido)
	Ethanol – EtOH (C ₂ H ₅ OH - 46.1 g.mol ⁻¹ - Dinâmica, 95 wt%)
	Naphthalene (C ₁₀ H ₈ - 128,1 g.mol ⁻¹ - Sigma-Aldrich, 99 wt%)
	Polyvinyl Alcohol – PVA ((C ₂ H ₄) _n - Sigma-Aldrich, 90 wt%)
SAPO-34 zeolite	Ultrapure Water (resistivity: 18 M Ω cm)
	Phosphoric Acid (H ₃ PO ₄ - 97.9 g.mol ⁻¹ - Sigma-Aldrich, 85 wt%)
	Dipropylamine – DPA ((C ₃ H ₇) ₂ NH - 101.2 g.mol ⁻¹ - Sigma-Aldrich, 99 wt%)
	Tetraethylammonium Hydroxide – TEAOH ((CH ₃) ₄ N(OH) - 147.3 g.mol ⁻¹ - Sigma-Aldrich, 35 wt%)
	Aluminum Isopropoxide – Alip (C ₉ H ₂₁ O ₃ Al – 204.2 g.mol ⁻¹ - Sigma-Aldrich, 98% m/m)
	Morpholine – MOR (C ₄ H ₉ NO - 81.1 g.mol ⁻¹ – ACS, 99 wt%)
	Colloidal Silica - LUDOX AS-40 (SiO ₂ - 60.1 g.mol ⁻¹ - Sigma-Aldrich, 40 wt%)

3.2. Experimental methodology: Freeze-Casting

The production of ceramic monoliths was carried out using CT-3000 LS SG alumina powder as the source of α -Al₂O₃. In a typical preparation of the α -alumina suspension, the dispersing agent EFKA[®] FA 4663 and the binary solvent, consisting of a

mixture of camphor and naphthalene, were added to a sealed container. The composition of EFKA[®] FA 4663 is proprietary and thus not publicly disclosed; however, its technical specifications describe it as a 50% solution of an electroneutral salt derived from a polycarboxylic acid and amine derivatives, dissolved in higher aromatics. The solvent, with a well-defined composition, was subjected to magnetic stirring and heating at 80 °C until complete transition from the solid to the liquid state. Subsequently, the alumina source was slowly added. After one minute of stirring, the binder, polyvinyl alcohol (PVA), was introduced into the mixture.

The sealed flask was then transferred to a mechanical stirrer (IKA T25 ULTRATURRAX). To minimize solvent loss during the process, a lid adapted to the stirring shaft was used. The suspension was stirred at 80 °C and 8000 rpm for five minutes. For the composition of the liquid solvent, three mass ratios commonly reported in the literature⁶⁴ were investigated:

- **Naphthalene-rich or hypoeutectic phase:** 60 wt%. camphor and 40 wt%. naphthalene;
- **Eutectic composition:** 65 wt%. camphor and 35 wt%. naphthalene;
- **Camphor-rich or hypereutectic phase:** 70 wt%. camphor and 30 wt%. naphthalene.

The solid loading was fixed at 20 vol%. of α -Al₂O₃. The dispersant and binder contents were set at 2% and 1% by mass, respectively, relative to the mass of α -Al₂O₃. The phase diagram of the binary solvent is presented in Figure 15.

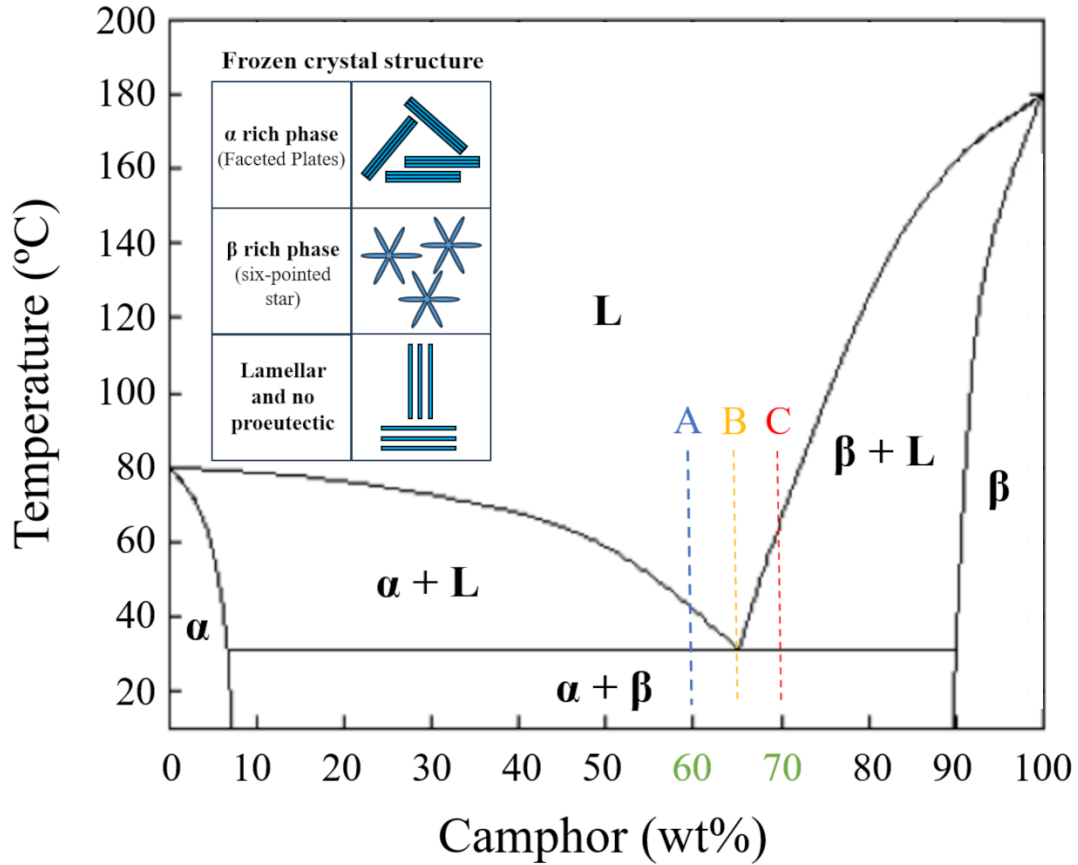


Figure 15. Phase diagram for the naphthalene-camphor mixture. According to the phase diagram, the structure consisting of faceted plates predominates in the hypoeutectic composition (A), whereas the structure consisting of six-pointed stars predominates in the hypereutectic composition (C). Accordingly, these are described as the naphthalene-rich proeutectic phase (α) and the camphor-rich proeutectic phase (β), respectively. B represents the eutectic composition (Adapted from Araki *et al.* 2004).⁶⁴

After the dispersion step under mechanical stirring, the suspension was poured into a Technyl[®] mold (Nylon 6 PA polyamide, 13 mm in height and 22 mm in outer diameter) supported on a copper rod partially immersed in liquid nitrogen. Temperature control was achieved using an electronic device equipped with a thermocouple fixed to the copper rod. The freezing temperature investigated was -130 °C. Prior to use, the Technyl[®] molds were preheated to 80 °C and lubricated with silicone. During cooling, the upper part of each mold was kept open under ambient temperature and pressure conditions. The average freezing time for the suspensions was 4.5 minutes. The apparatus used to promote controlled freezing of the suspensions is shown in Figure 16.

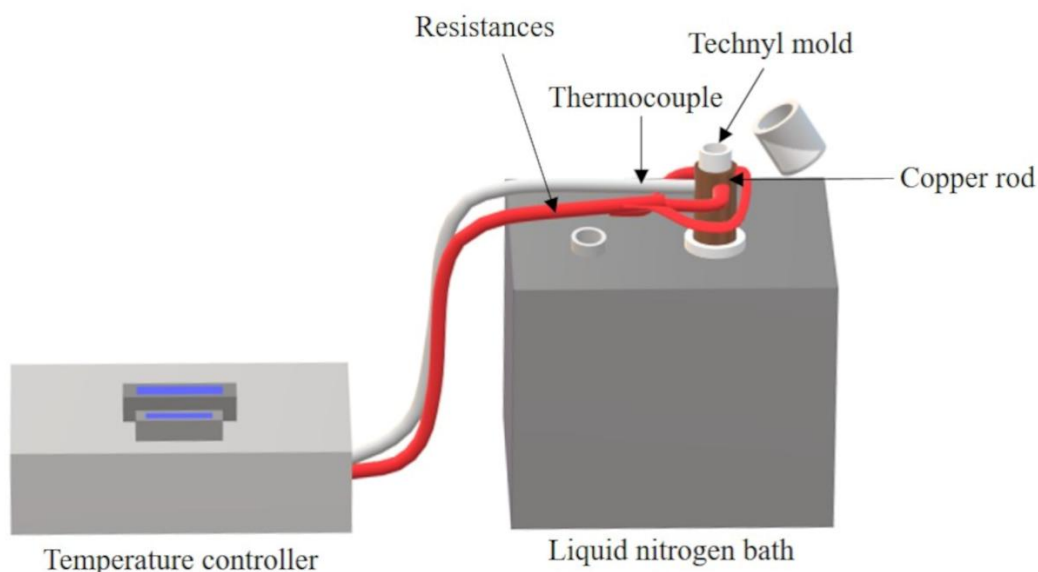


Figure 16. Apparatus for performing the freeze-casting technique.

The frozen samples were placed in a fume hood for five days to allow partial sublimation of the solvent. After this period, the monoliths were transferred to a tray cooled with liquid nitrogen. The tray was then placed inside a freeze-dryer (TERRONI LS3000, condenser temperature of $-110\text{ }^{\circ}\text{C}$ and pressure of $50\text{ }\mu\text{mHg}$), where complete sublimation of the solvent was carried out over 72 hours to obtain the green body. Finally, the green body was sintered in a muffle furnace (Nabertherm 3000) at a heating rate of $2\text{ }^{\circ}\text{C}/\text{min}$ and held at a temperature of $1500\text{ }^{\circ}\text{C}$. The sintering time was varied to 1, 2, and 3 hours. The produced samples were designated as NC_Eu_X, NC_Hypo_X, and NC_Hyper_X, where NC stands for naphthalene-camphor; Eu, Hypo, and Hyper refer to the eutectic, hypoeutectic, and hypereutectic compositions, respectively; and X corresponds to the sintering time in hours. The process, along with the composition of the suspensions, is shown in Figure 17 and Table 4.

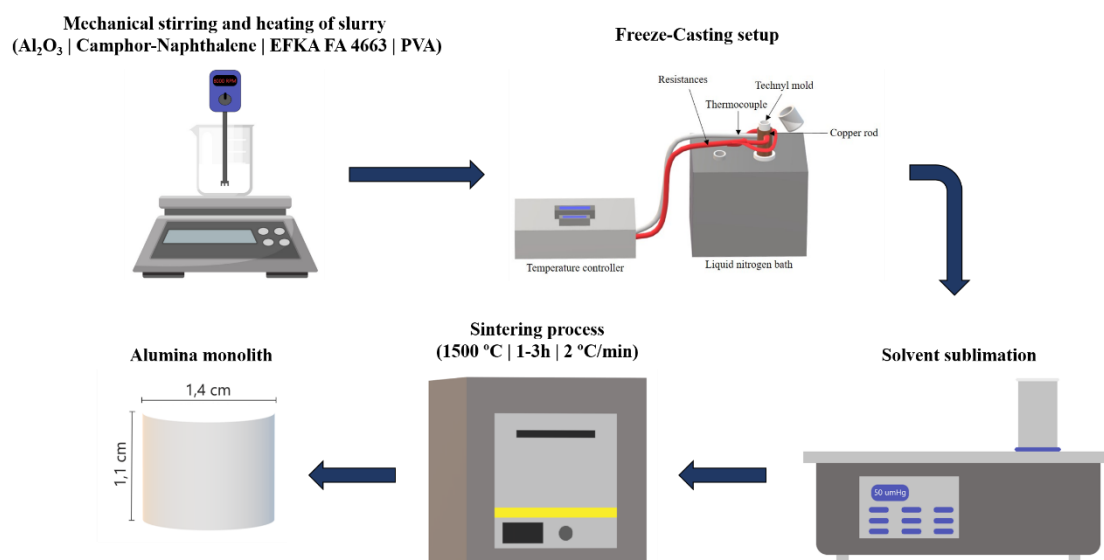


Figure 17. Experimental scheme for the production of monoliths via freeze-casting.

Table 4. Typical composition of a 60 mL suspension for freeze-casting.

COMPOSITION	REAGENTS				
	α -Al ₂ O ₃ (g)	Naphthalene (mL)	Camphor (mL)	EFKA FA 4663 (g)	PVA (g)
Hypoeutectic	46.8	20.1	30.1	0.936	0.468
Eutectic	46.8	17.5	32.4	0.936	0.468
Hypereutectic	46.8	14.9	34.7	0.936	0.468

3.2.1. Production of Porous Tubes via Freeze-Casting

The study conducted for the production of α -alumina monoliths provided the basis for selecting the most suitable composition for the fabrication of porous tubes. The manufacturing of α -Al₂O₃ tubes was carried out using a freeze-casting system similar to that shown in Figure 17. The cooling base was replaced with a copper rod containing a central cavity (depth = 10 cm). A Technyl[®] rod was inserted into the center of this cavity to act as a demolding core for the tubes.

The production conditions established for the monoliths were replicated for the fabrication of the tubes. However, since the external surface of the tube was in complete contact with the internal surface of the copper rod, the freezing rate was reduced, resulting in freezing times of approximately 15 seconds at the same cooling temperature (-130 °C).

3.2.2. Characterization of the Ceramic Materials

3.2.2.1. X-Ray Diffraction

X-ray diffraction (XRD) analyses of selected samples were performed at the Faculty of Technology (UnB) using a Lab XRD-6000 (Shimadzu) diffractometer with CuK α radiation ($\lambda = 0.15409$ nm), a scan rate of 1°/min, a step size of 0.02°, a voltage of 40 kV, a 2θ range from 10° to 80°, and a current of 30 mA. The diffractograms were processed using OriginPro® 2018 software. For further analyses, the X'Pert HighScore® software was employed.

3.2.2.2. Scanning Electron Microscopy

The morphology of the grains and pores was analyzed using a JEOL JSM 7100F scanning electron microscope (SEM) at the Scanning Electron and Confocal Laser Microscopy Laboratory of the Faculty of Technology, University of Brasília, equipped with an EDS detector. For the analyses, the samples were cut in half along the freezing direction to evaluate the cross-section of each selected monolith. Additionally, a carbon coating was applied to their surfaces prior to image acquisition.

3.2.2.3. Porosity Analysis

The characterization of the porosity of the produced materials was carried out using two methodologies. The first involved the Archimedes' method, following the ASTM B962-13 standard. According to Archimedes' principle, an object immersed in a fluid experiences a force equal to the weight of the fluid displaced by the object. This principle allows for the determination of the material's open, closed, and total porosity.

For this purpose, the sintered ceramic monoliths were weighed to obtain the dry mass (w_d). Subsequently, the immersed mass (w_i) of the monoliths in distilled water was measured using an Archimedes balance. The samples were then removed from the apparatus, gently blotted with moistened cotton, and weighed again to obtain the wet mass (w_w). The procedure was performed in triplicate for each system.

The obtained masses were used to calculate the apparent volume of the samples (V_a), the open pore volume (V_{op}), and the solid volume (V_s) using the following equations:

$$V_a = \frac{w_w - w_i}{\rho_{H_2O}} \quad \text{Equation 6}$$

$$V_{op} = \frac{w_w - w_d}{\rho_{H_2O}} \text{ Equation 7}$$

$$V_s = \frac{w_w - w_i}{\rho_s} \text{ Equation 8}$$

where ρ_{H_2O} is the density of water (0.998 g/cm³) and ρ_s is the density of the solid. Subsequently, the open and total porosities were determined using Equations (9) and (10).

$$\text{Open Porosity (\%)} = \frac{V_{op}}{V_a} \text{ Equation 9}$$

$$\text{Total Porosity (\%)} = \frac{V_a - V_s}{V_a} \text{ Equation 10}$$

The second methodology was carried out using microtomography (μ CT – microCT HeliScan, FEI) on one sample of each composition, whereby X-ray microtomography images were acquired to evaluate the three-dimensional morphology and properties of the fabricated monoliths. Image acquisition was performed using Qrumba 1.1.2.231 software under the following conditions: voltage of 100 kV, current of 70 μ A, 1×1 binning, and minimum and maximum voxel sizes (representing a value on a regular grid in three-dimensional space) of 6.5 and 6.8 μ m, respectively. The Pymango software was used for data processing and 3D reconstruction of the monolith images. The reconstructed images were further analyzed using Avizo[®] 3D software to determine total porosity, pore sizes, pore structure models, and tortuosity.

3.2.2.4. Mechanical Strength Tests

Compression tests were performed on selected monoliths using an Instron 5882 testing machine, equipped with 5 and 10 kN load cells, at the Center for Nuclear Technology Development of Minas Gerais. The tests were conducted at a speed of 0.5 mm/min. To ensure uniform data acquisition, the top and bottom surfaces of the samples were previously polished with sandpaper. For each composition, 8 to 10 monoliths were tested.

3.3. Experimental Methodology: SAPO-34

The selective material (SAPO-34) proposed for this study was synthesized using two different growth methodologies: hydrothermal heating and microwave-assisted heating (Figure 18). Further details are provided in the following sections.

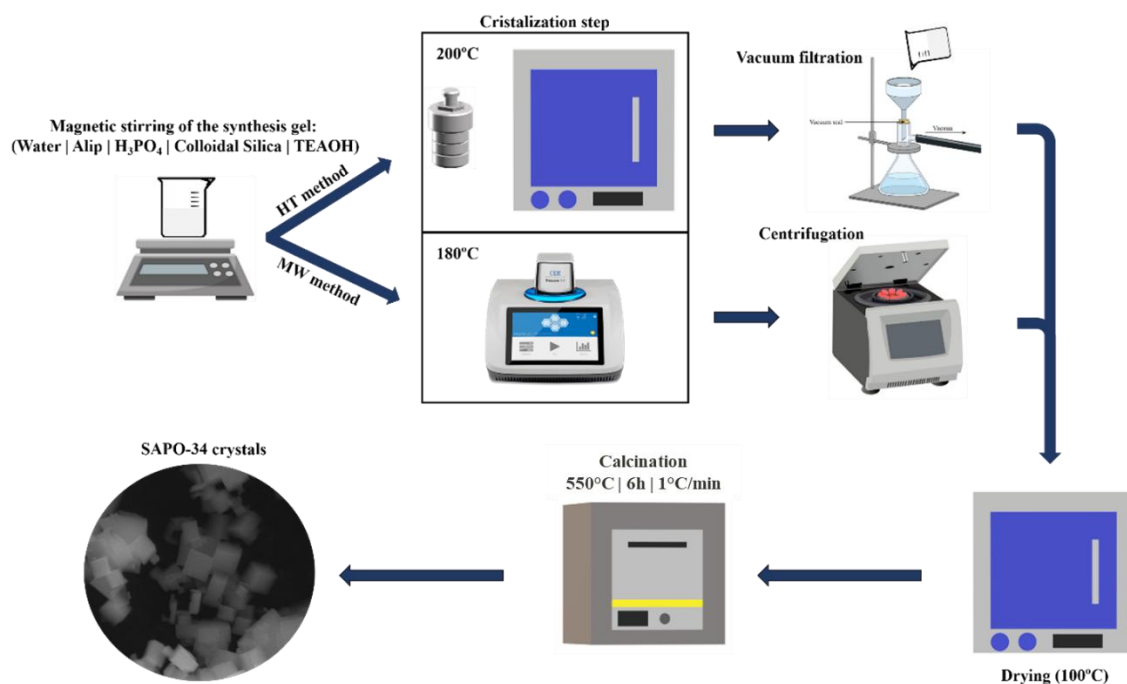


Figure 18. Schematic image illustrating the SAPO-34 synthesis methodologies adopted in this study.

3.3.1. Hydrothermal Synthesis: Application of a Single Organic Structure-Directing Agent

The hydrothermal syntheses carried out for SAPO-34 (methodologies T1 and T2) were based on the works of Li *et al.* (2015), Zheng *et al.* (2022) and Zong *et al.* (2016; 2017).^{14,49,99,100} Initially, two synthesis ratios were proposed for the first attempts at producing the zeolitic crystals.

In the first approach, designated as HT_T1_X (X = hydrothermal treatment time), syntheses were carried out using the following reaction ratio: 1 Al₂O₃ : 2 P₂O₅ : 0.6 SiO₂ : 4 TEOAH : 150 H₂O (T1). In this methodology, 13.4 mL of deionized water and 3.76 g of aluminum isopropoxide (Alip) were added to a 50 mL beaker and subjected to magnetic stirring for 1 hour at 40 °C. Subsequently, 2.47 mL of H₃PO₄ was added, and the mixture was stirred for an additional 2 hours. After this period, 0.625 mL of LUDOX AS-40 was introduced, and the mixture was stirred for another 3 hours. Finally, 14.9 mL of the organic structure-directing agent (OSDA), TEOAH, was added, and the system was maintained under stirring overnight.

Once 35 mL of the suspension was formed, the white-colored suspension was transferred to a 50 mL Teflon container with a lid. The Teflon vessel was sealed in a stainless-steel autoclave and placed in an oven at 200 °C. Different thermal treatment

times for zeolitic crystal growth were tested, ranging from 24 to 96 hours. After the hydrothermal process, the material was vacuum-filtered and washed with 500 mL of deionized water until a neutral pH was reached to remove residual reagents. The wet powder was subsequently dried in an oven at 100 °C, transferred to a ceramic crucible, and calcined in a muffle furnace at 550 °C for 6 hours with a heating rate of 1 °C/min. Finally, the zeolitic crystals were obtained.

In the second methodology, designated HT_T2_X, syntheses were carried out using the following reaction ratio: 1 Al₂O₃ : 0.8 P₂O₅ : 0.3 SiO₂ : 2.8 TEAOH : 150 H₂O. In this methodology, 17.9 mL of deionized water and 1.04 mL of H₃PO₄ were added to a 50 mL beaker and stirred for 5 minutes at 40 °C. Subsequently, 3.98 g of aluminum isopropoxide (Alip) was added, and the mixture was stirred for an additional 2 hours. After this period, 0.431 mL of LUDOX AS-40 was introduced, and the mixture was stirred for another 2 hours. Finally, 11 mL of the organic structure-directing agent, TEAOH, was added, and the system was maintained under stirring until the following day.

Once 35 mL of the mixture was formed, the white-opaque suspension was transferred to a 50 mL Teflon container with a lid, which was then sealed in a stainless-steel autoclave and placed in an oven at 200 °C. The subsequent steps (filtration, washing, drying, and calcination) were carried out in the same manner as described for methodology HT_T1_X.

Specific variations in the composition were also carried out to investigate the influence of the amount of each precursor on the characteristics and properties of the final product. The syntheses performed, along with a methodological summary, are presented in Table 5 and Figure 18.

Table 5. Samples produced via the hydrothermal route applying a single OSDA.

Sample	Molar ratio	Time (h)
HT_T1_24H	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.6 SiO ₂ : 4 TEAOH : 150 H ₂ O	24
HT_T1_48H	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.6 SiO ₂ : 4 TEAOH : 150 H ₂ O	48
HT_T1_72H	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.6 SiO ₂ : 4 TEAOH : 150 H ₂ O	72
HT_T1_96H	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.6 SiO ₂ : 4 TEAOH : 150 H ₂ O	96
HT_T2_24H	1 Al ₂ O ₃ : 0.8 P ₂ O ₅ : 0.3 SiO ₂ : 2.8 TEAOH : 150 H ₂ O	24

HT_T2_48H	1 Al ₂ O ₃ : 0.8 P ₂ O ₅ : 0.3 SiO ₂ : 2.8 TEAOH : 150 H ₂ O	48
HT_T2_72H	1 Al ₂ O ₃ : 0.8 P ₂ O ₅ : 0.3 SiO ₂ : 2.8 TEAOH : 150 H ₂ O	72
HT_T2_96H	1 Al ₂ O ₃ : 0.8 P ₂ O ₅ : 0.3 SiO ₂ : 2.8 TEAOH : 150 H ₂ O	96
0.8 P	1 Al ₂ O ₃ : 0.8 P ₂ O ₅ : 0.6 SiO ₂ : 4 TEAOH : 150 H ₂ O	96
1.5 P	1 Al ₂ O ₃ : 1.5 P ₂ O ₅ : 0.6 SiO ₂ : 4 TEAOH : 150 H ₂ O	96
0.3 Si	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.3 SiO ₂ : 4 TEAOH : 150 H ₂ O	96
1.2 Si	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 1.2 SiO ₂ : 4 TEAOH : 150 H ₂ O	96
2.8 T	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.6 SiO ₂ : 2.8 TEAOH : 150 H ₂ O	96
3.5 T	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.6 SiO ₂ : 3.5 TEAOH : 150 H ₂ O	96

3.3.2. Hydrothermal Synthesis: Application of a Dual Structure-Directing Agent

SAPO-34 syntheses using a dual structure-directing agent were based on the works of Doan *et al.* (2019), Lee *et al.* (2009), Nishiyama *et al.* (2009), Iwase *et al.* (2009), Vomscheid *et al.* (1994) and Salmasi *et al.* (2012).^{78,84,101–104} In this study, two combinations of structure-directing agents were proposed: TEAOH–MOR (TEAOH–morpholine) and TEAOH–DPA (TEAOH–dipropylamine).

In the first approach, designated HT_yM/D_zT_X (y: molar ratio of morpholine or dipropylamine; z: molar ratio of tetraethylammonium hydroxide, X = hydrothermal treatment time), syntheses were carried out using the following reaction ratios:



In this methodology, deionized water and aluminum isopropoxide were added to a 50 mL beaker and subjected to magnetic stirring for 1 hour at 40 °C. Subsequently, H₃PO₄ was added, and the mixture was stirred for an additional 2 hours. After this period, LUDOX AS-40 was introduced, and the mixture was stirred for another 3 hours. Finally, the OSDAs, TEAOH and DPA/MOR, were added sequentially, with a 1-hour interval of stirring between each addition. The system was then allowed to age overnight.

Once the suspension was formed, the white-colored mixture was transferred to a Teflon container with a lid, which was then sealed in a stainless-steel autoclave and placed in an oven at 200 °C. The syntheses were conducted with a hydrothermal treatment time of 96 hours. After the process, the material was vacuum-filtered and washed with 500 mL of deionized water until a neutral pH was reached to remove residual reagents. The wet powder was then dried in an oven at 100 °C, transferred to a ceramic crucible, and calcined in a muffle furnace at 550 °C for 6 hours with a heating rate of 1 °C/min, ultimately yielding the zeolitic crystals.

Table 6. Samples produced via the hydrothermal route using a dual structure-directing agent.

Sample	Molar ratio	Time (h)
HT_1.5M_0.5T_96H	1 Al ₂ O ₃ : 1 P ₂ O ₅ : 0.6 SiO ₂ : 1.5 MOR: 0.5 TEAOH : 75 H ₂ O	96
HT_3M_1T_96H	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.6 SiO ₂ : 3 MOR: 1 TEAOH : 75 H ₂ O	96
HT_1.6D_1T_96H	1 Al ₂ O ₃ : 1 P ₂ O ₅ : 0.6 SiO ₂ : 1.6 DPA: 1 TEAOH : 75 H ₂ O	96

3.3.3. Microwave-Assisted Synthesis: Approach Using Single and Dual Structure-Directing Agents

Based on the most promising results obtained through the methodologies described in Sections 4.3.1 and 4.3.2, the synthesis of SAPO-34 using single and dual structure-directing agents via microwave-assisted heating was proposed. The production of the zeolitic crystals was carried out using the following compositions:

1 Al₂O₃ : 2 P₂O₅ : 0.6 SiO₂ : 4 TEAOH : 150 H₂O (T1)

1 Al₂O₃ : 2 P₂O₅ : 0.6 SiO₂ : 3 MOR: 1 TEAOH : 75 H₂O (3M_1T)

The suspension preparation methodologies were carried out in a similar way to those described in Sections 4.3.1 and 4.3.2. The resulting aqueous suspensions were transferred to Pyrex reaction vessels, which feature a lid and an inner wall coated with a thin layer of Teflon. This approach, however, allowed precise control over the heating power (300 W) and internal pressure (200 psi) during thermal treatment. The syntheses were conducted at 180 °C for growth times ranging from 30 minutes to 24 hours.

After the process, the material underwent repeated centrifugation cycles until the washing residue reached a neutral pH. The wet powder was then transferred to an oven and dried at 100 °C. Finally, the powder was calcined in a muffle furnace at 550 °C for 6 hours with a heating rate of 1 °C/min.

Table 7. Samples produced via microwave-assisted synthesis.

Sample	Molar ratio	Time (h)
MW_T1_24H	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.6 SiO ₂ : 4 TEAOH : 150 H ₂ O	24
MW_T1_12H	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.6 SiO ₂ : 4 TEAOH : 150 H ₂ O	12
MW_T1_6H	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.6 SiO ₂ : 4 TEAOH : 150 H ₂ O	6
MW_T1_4H	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.6 SiO ₂ : 4 TEAOH : 150 H ₂ O	4
MW_T1_2H	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.6 SiO ₂ : 4 TEAOH : 150 H ₂ O	2
MW_T1_1H	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.6 SiO ₂ : 4 TEAOH : 150 H ₂ O	1
MW_T1_30min	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.6 SiO ₂ : 4 TEAOH : 150 H ₂ O	0.5
MW_3M_1T_24H	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.6 SiO ₂ : 3 MOR: 1 TEAOH : 75 H ₂ O	24
MW_3M_1T_12H	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.6 SiO ₂ : 3 MOR: 1 TEAOH : 75 H ₂ O	12
MW_3M_1T_6H	1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.6 SiO ₂ : 3 MOR: 1 TEAOH : 75 H ₂ O	6

3.3.4. Characterization of SAPO-34 Zeolites

3.3.4.1. XRD characterization

X-ray diffraction (XRD) analyses were performed on selected samples at the Faculty of Technology (UnB) using a Lab XRD-6000 (Shimadzu) diffractometer. The experiments were conducted with CuK α radiation ($\lambda = 0.15409$ nm), a scan rate of 0.5°/min, a step size of 0.02°, a voltage of 40 kV, a 2 θ range from 5° to 50°, and a current of 30 mA. The diffractograms were processed using OriginPro[®] 2018 software, and further analyses were carried out with X'Pert HighScore[®].

3.3.4.2. FTIR analysis

Fourier-transform infrared (FT-IR) spectroscopy analyses were conducted using a Nicolet iS50 spectrometer (Thermo Fisher Scientific) employing the Attenuated Total Reflectance (ATR) mode. In this method, a high-refractive-index crystal is used, which allows total internal reflection of the infrared beam as it passes from the crystal into the sample. The beam penetrates slightly into the less dense material, forming an evanescent wave. The sample then absorbs part of this evanescent radiation, causing attenuation of the beam intensity at specific absorption wavelengths. The spectra of the zeolitic powders were recorded over a spectral range of 400–4000 cm^{-1} , which includes characteristic bands corresponding to the molecular vibrations of the materials under study. The spectra were acquired with a resolution of 4 cm^{-1} and 32 scans.

3.3.4.3. SEM analysis

The morphology of SAPO-34 crystals was analyzed using the following scanning electron microscopes: JEOL JSM 7100F at the Scanning and Confocal Laser Microscopy Laboratory of the Faculty of Technology, University of Brasília, and FEI Quanta 200 FEG at the Microscopy Center of the University of Minas Gerais. Both instruments are equipped with Energy-Dispersive X-ray Spectroscopy (EDS). For the analyses, the samples were deposited on carbon tapes mounted on copper stubs, and a carbon coating was applied to their surfaces prior to imaging. Images were acquired under operating conditions of 10–15 kV and 7–10 mA.

3.3.4.4. Textural Analysis by N₂ Adsorption

Nitrogen adsorption analysis was performed to evaluate the total surface area (BET method – Brunauer-Emmett-Teller theory); micropore area, micropore volume, and external surface area (t-plot method); as well as the total pore volume.

The BET equation is widely used for the determination of surface area, as once the amount of adsorbed mass (W) and the amount of mass adsorbed in a complete monolayer (W_m) are known, the total specific surface area of the material (S_{BET}) can be determined.^{105,106} To facilitate the determination of W_m , the BET equation can be rearranged into its linear form, given by:

$$\frac{P}{W[(P_0/P)-1]} = \frac{1}{W_m C} + \left(\frac{C-1}{W_m C} \right) \frac{P}{P_0} \quad \text{Equation 11}$$

in which P and P_0 are the equilibrium and saturation pressures of the adsorbate at the adsorption temperature, and C is a constant. The determination of W_m is performed by manipulating the slope and intercept of the linear plot. Knowing Avogadro's number ($N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$), the cross-sectional area (Λ), and the molar mass (M_m), it is possible to calculate the total surface area (S_T , Equation 12). The specific surface area (S_{BET}) is then determined by dividing S_T by the sample mass.^{105,106}

$$S_T = \frac{W_m N_A \Lambda}{M_m} \quad \text{Equation 12}$$

The t-plot method developed by de Boer involves measuring the amount of nitrogen adsorbed by the sample at various P/P_0 values.¹⁰⁶ The procedure is similar to that used for determining the BET surface area but extends to higher pressure ranges, allowing the calculation of the matrix surface area and external surface area, that is, the non-microporous portion of the material. A t-curve is plotted as the volume of gas adsorbed versus “t”, which represents the statistical thickness of the adsorbed film. The statistical thickness can be determined using de Boer's empirical equation (Equation 13).¹⁰⁶

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

When micropores are present in the sample, the t-plot will exhibit a positive y-axis intercept. This intercept (i), when converted to liquid volume, provides the micropore volume (V_{micro}). The slope (η), on the other hand, when appropriately converted, yields the approximate external surface area (S_{ext}) of the sample.¹⁰⁶

$$V_{\text{micro}}(\text{cm}^3/\text{g}) = i * 0.001547 \quad \text{Equation 14}$$

$$S_{\text{ext}}(\text{m}^2/\text{g}) = \eta * 0.001547 * 10^4 \quad \text{Equation 15}$$

The BET linear region for microporous materials generally appears at relative pressures below 0.1. The linear range of the t-plot occurs at higher relative pressures and depends on the micropore size distribution. The micropore surface area (S_{micro}) is then determined as the difference between the BET surface area (S_{BET}) and the external surface area from the t-plot (S_{ext}).^{105,106}

$$S_{\text{micro}}(\text{m}^2/\text{g}) = (S_{\text{BET}} - S_{\text{ext}}) * 10^4 \quad \text{Equation 16}$$

In this context, the analyses were carried out through N₂ adsorption at liquid nitrogen temperature (77 K). The experiments for the calcined SAPO-34 samples were performed using an Autosorb iQ XR-XR Model 7 (Quantachrome®) instrument. Approximately 50 mg of each sample were pretreated using a heating protocol consisting of: heating to 80 °C for 30 minutes at a rate of 2 °C/min, heating to 120 °C for 2 hours at a rate of 2 °C/min, and finally heating to 350 °C for 5 hours at a rate of 5 °C/min. After this pretreatment, the materials were subjected to nitrogen adsorption analysis.

The adsorption isotherms were obtained over a P/P₀ range from 7.5 × 10⁻⁶ to 0.95. The data were collected and processed using Quantachrome® ASiQwin™ 5.2x software. To determine the points used for the calculation of the total surface area via the BET method, the “Micropore BET Assistant” tool available in the software was employed. For the t-plot model, data points within the P/P₀ range of 0.15 to 0.50 were selected. Finally, the total pore volume was obtained by selecting the penultimate adsorption point of the isotherms.

The collected data were processed using OriginPro® 2018 software in order to maintain the standard formatting adopted in this study.

3.3.4.5. Solid-State Nuclear Magnetic Resonance Spectroscopy (NMR-MAS)

The nuclear magnetic resonance (NMR) technique was employed to characterize the synthesized materials. The acquisitions were performed using magic angle spinning (MAS), and the chemical environments of the ²⁷Al, ²⁹Si, and ³¹P nuclei were analyzed separately. The spectra were obtained using a Magneto Ascend 600 spectrometer equipped with an Avance III HD console, operating at a magnetic field strength of approximately 14 T, corresponding to 600 MHz for the ¹H nucleus. A 4 mm CP/MAS solid-state probe was used, with the samples packed into a zirconia rotor, under specific conditions defined for each nucleus:

- ²⁷Al NMR-MAS was performed at 156.39 MHz with a spinning frequency of 10 kHz, a 90° pulse angle, and a pulse delay of 2s, employing heteronuclear decoupling and acquiring 512 scans per spectrum. The external reference standard used was a 0.1 M aluminum chloride (AlCl₃) solution in deuterated water;

- ^{29}Si NMR-MAS was performed at 119.24 MHz with a spinning frequency of 10 kHz, a 45° pulse angle, and heteronuclear decoupling, acquiring between 1268 and 2048 scans per spectrum. Tetramethylsilane (TMS) was used as the external reference standard;
- ^{31}P NMR-MAS was performed at 242.95 MHz with a spinning frequency of 10 kHz, a 45° pulse angle, and heteronuclear decoupling, acquiring 64 scans per spectrum. The external reference standard used was a 0.1 M phosphoric acid (H_3PO_4) solution in deuterated water;

The acquired spectra were processed using SpecManager 10.8 and OPUS 3.1 software. Spectral deconvolutions were performed using OMNIC 8.0.342, applying the *Voigt* mathematical function for peak modeling. Final data processing and formatting of the spectra were carried out using OriginPro[®] 2018.

3.4. Experimental Methodology: Membrane Production

3.4.1. Production of SAPO-34 Membranes

Considering the studies previously detailed regarding the synthesis of SAPO-34 (Sections 4.2 and 4.3) and the discussion presented in the literature review, the most promising compositions were selected for the deposition of zeolitic membranes on commercial single-channel tubes (Tecnicer Ceramica) and on tubes fabricated via freeze-casting process (based on the experimental conditions described in section 4.2) employing the secondary growth method.

Initially, both commercial and freeze-cast α -alumina substrates were sectioned using an IsoMet 1000 Precision Saw equipped with a diamond blade. The tube surfaces were then polished using silicon carbide abrasive papers with grit sizes of 800, 1200 and 2500. Subsequently, the substrates underwent a three-step ultrasonic cleaning process in acetone (20 min), isopropanol (20 min), and deionized water (20 min). Finally, the cleaned tubes were dried in an oven at 100 °C. The dimensions of the tubular substrates are listed in the table below.

Table 8. Dimensions of the substrates used in this study.

Parameters	Commercial	Freeze-cast
Length (mm)	45	45
Internal Diameter (mm)	7.6	6.5
External Diameter (mm)	11.6	9.7

Following the tube treatment, some zeolite crystals synthesized in this study were selected as seeds for the secondary growth process aimed at membrane formation on α -alumina tubular supports.

Initially, suspensions of SAPO-34 (1 wt%.) were prepared in beakers using the selected seeds. Ethanol (Dinâmica, 95%) was used as the dispersion medium. The suspensions were magnetically stirred for 15 minutes at 400 r.p.m. and subsequently subjected to an ultrasonic bath for an additional 15 minutes.

After the seed suspension process, the material was subjected to deposition via the dip-coating technique (KSV NIMA Dip Coater). Commercial alumina tubes (Tecnicer Ceramica | inner diameter = ~ 8 mm | outer diameter = ~ 12 mm) and those fabricated via freeze-casting were fixed on the instrument holder, with their ends sealed using Teflon tape, as illustrated in Figure 19. Deposition was then initiated with equal immersion and withdrawal speeds of the tubes (90 mm/min). The dwell time of the tubes within the suspensions was 60 seconds. Additionally, the effect of multiple seed layer depositions was studied, considering 1, 2, and 3 layers. Between each layer deposition, the tubes underwent a two-step drying process: first at room temperature for 20 minutes, and then in an oven at 70 °C for 2 hours.

After completing the depositions, the tubes were subjected to the hydrothermal growth process in an autoclave. With both ends sealed to prevent membrane growth in the inner region, the tubes were placed inside Teflon vessel. The synthesis gel, covering the entire tube, was then added, with a composition corresponding to: 1 Al_2O_3 : 1 P_2O_5 : 0.6 SiO_2 : 1.6 DPA: 1 TEAOH : 75 H_2O . The Teflon compartments were then placed inside the autoclave, and the system was subjected to hydrothermal treatment in an oven at 200 °C. The hydrothermal growth times investigated in this study were 6, 12, and 24 hours for each seed applied.

Finally, the tubes were washed with 500 mL of ultrapure water and dried in an oven at 100 °C overnight. After drying, the materials were calcined in a tubular furnace at 550 °C for 10 hours, with heating and cooling rates of 0.5 °C.min⁻¹.

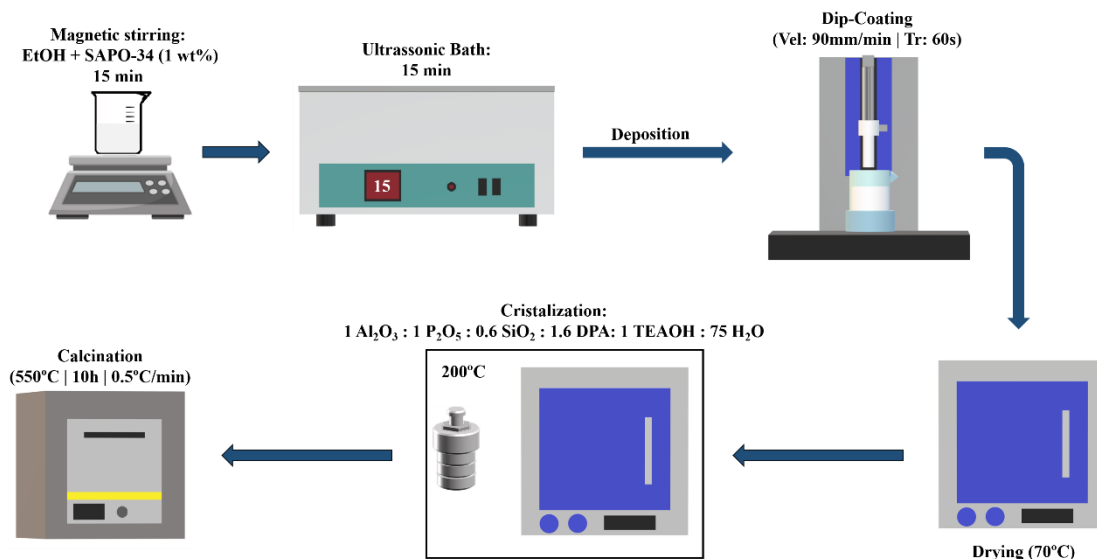


Figure 19. Schematic representation of the membrane deposition process on α -alumina tubular supports.

3.4.2. Characterization of the SAPO-34 membranes

3.4.2.1. Surface and cross-sectional characterization by Scanning Electron Microscopy

The surface analysis of SAPO-34 membranes was developed using the scanning electron microscope JEOL JSM 7100F at the Scanning and Confocal Laser Microscopy Laboratory of the Faculty of Technology, University of Brasília. For the analyses, the samples were deposited on carbon tapes mounted on copper stubs, and a gold coating was applied to their surfaces prior to imaging. For surface analysis of the tubular substrates, the samples were sputter-coated with gold. To visualize the thickness of the deposited films, the coated tubular supports were sectioned into ring-shaped samples using an IsoMet 1000 Precision Saw equipped with a diamond blade. The cross-sectional surfaces were then polished using silicon carbide abrasive papers with grit sizes of 1500 and 2500 for 1 min each. SEM images were acquired under operating conditions of 10-15 kV and 7-10 mA.

3.4.2.2. Adsorption selectivity analysis using the Ideal Adsorbed Solution Theory (IAST) method

Gas adsorption measurements were performed on SAPO-34 seed samples using N₂, CO₂, and CH₄ as adsorbates, employing an Autosorb iQ XR-XR Model 7 instrument. The experiments were conducted at 298.15 K (25 °C) over a relative pressure (P/P₀) range from 1.0×10^{-4} to 0.97. The Quantachrome® AsiQwin™ software was used for the partial collection and processing of the data.

Based on the collected absolute isotherms, the adsorption data were fitted using the Langmuir model with OriginPro® 2018 software. The expression representing the Langmuir adsorption model is shown in the following equation:

$$q = q_{\max} * \frac{bP}{1+bP} \quad \text{Equation 17}$$

where $q_{\max}$ is the maximum adsorption capacity, b is the Langmuir affinity constant (equilibrium constant), and P is the partial pressure or concentration in the gas or liquid phase. Despite the limitations of the model — such as assuming adsorption occurs exclusively in a monolayer, considering the solid surface as homogeneous, and neglecting adsorbate–adsorbate interactions — the Langmuir model proves useful for modeling the isotherm of microporous materials and estimating $q_{\max}$. In this case, the Brunauer–Emmett–Teller (BET) isotherm model was not used, as it is valid only over a limited relative pressure range (0.05–0.35 P/P₀), which would compromise the IAST analysis that requires an accurate model for pure gas adsorption over a wide pressure range.¹⁰⁷

The adsorption selectivity, defined as the ratio between the adsorbed mole fractions of two components and the corresponding ratio of their mole fractions in the bulk phase, can be applied to evaluate the performance of competitive adsorption between these components. A higher adsorption selectivity indicates that more strongly adsorbed molecules can replace those that previously occupied the adsorption sites. The low-pressure limit of the Langmuir isotherm ($P/P_0 \cong 0$) is given by $q_{\max} \cdot b$, which corresponds to the Henry's constant (K_H). Therefore, the ratio between the initial slopes of the adsorption isotherms of two components, $K_{H,1}/K_{H,2}$, represents the Henry's selectivity.^{107,108}

In gas separation processes, the adsorptive factor can have a significant influence on the separation mechanism between the components of interest. Assessing the

multicomponent adsorption selectivity of the active material is crucial for both the study and the development of separation technologies. Therefore, this work proposes the use of the Ideal Adsorbed Solution Theory (IAST) to predict the adsorption of gas mixtures based on the pure-component isotherms. IAST is founded on a Raoult-type relationship between the fluid phase and the adsorbed phase:

$$P_i = P \cdot y_i = P_i^0 \cdot x_i \quad \text{Equation 18}$$

$$\sum_{i=1}^n x_i = \sum_{i=1}^n \frac{P_i}{P_i^0} = 1 \quad \text{Equation 19}$$

where P_i is the partial pressure of component i , P is the total pressure, P_i^0 is the hypothetical pressure of pure component i , y_i and x_i represent the mole fractions of component i in the vapor phase and in the adsorbed phase, respectively.¹⁰⁸

The IAST method assumes that the spreading pressures — a thermodynamic quantity representing the force per unit length exerted by an adsorbed layer on the solid surface — are equal for all components in equilibrium with the spreading pressure of the mixture. The $\pi_i^0 = \pi \cdot P_i^0$ is defined from the Gibbs adsorption isotherm:

$$\frac{\pi A}{RT} = \int_0^{P_i^0} \frac{q_i(P_i)}{P_i} dP_i = \Pi(\text{constant}) \quad \text{Equation 20}$$

where π is the spreading pressure, A is the specific surface area of the adsorbent ($\text{m}^2 \cdot \text{g}^{-1}$), R is the universal gas constant, T is the temperature (K), and $q_i(P_i)$ is the adsorption equilibrium of the pure component obtained from the isotherm ($\text{mmol} \cdot \text{g}^{-1}$).¹⁰⁸

SAPO-34, a zeolite with a complex chemical and three-dimensional structure, possesses multiple adsorption sites (e.g., cations and distinct cavities) with different interaction energies. For this reason, the dual-site Langmuir (DSL – Equation 21) isotherm model was employed. The DSL model can partially represent the heterogeneity of adsorptive sites on the zeolitic surface by describing adsorption on two types of independent sites, unlike the simple Langmuir model.¹⁰⁷ Therefore, the DSL fitting was adopted for the IAST selectivity prediction in order to achieve higher accuracy. For this isotherm, the analytical expression of the integral can be described as follows:

$$q = q_{\max,1} * \frac{b_1 P}{1+b_1 P} + q_{\max,2} * \frac{b_2 P}{1+b_2 P} \quad \text{Equation 21}$$

Equation 22:

$$\frac{\pi A}{RT} = \int_0^{P_i^0} \frac{q_i(P_i)}{P_i} dP_i = q_{m,1} \ln \left(1 + b_{1,i}(P_i^0) \right) + q_{m,2} \ln \left(1 + b_{2,i}(P_i^0) \right)$$

In a binary system (e.g. N₂/CH₄), P_i^0 can be obtained by the simultaneous solution of Equations 18 and 20. Thus, the amount adsorbed of each component in a mixture is given by:

$$q_i = x_i q_T \quad \text{Equation 23}$$

$$\frac{1}{q_T} = \sum_{i=1}^n \frac{x_i}{q_i(P_i^0)} \quad \text{Equation 24}$$

where q_i is the partially adsorbed amount of component i (mmol·g⁻¹) and q_T is the total adsorbed amount (mmol·g⁻¹).¹⁰⁸

To reach a solution, an iterative trial-and-error procedure is performed until all values of π and P_i^0 converge. Once these values are obtained, the mole fractions in the adsorbed phase (x_i) and the total adsorbed amount (q_T) are determined from Equations 18 and 24, respectively. Finally, the adsorption selectivity (S_{ads}) is calculated using the following equation:

$$S_{ads} = \frac{x_1/y_1}{x_2/y_2} = \frac{x_1/x_2}{y_1/y_2} = \frac{q_1/q_2}{y_1/y_2} \quad \text{Equation 25}$$

Considering the theoretical background of the model, the IAST was applied in this work to investigate the adsorption selectivity of SAPO-34 seeds for binary gas mixtures of CO₂/CH₄, CH₄/CO₂, N₂/CH₄, CH₄/N₂, N₂/CO₂, and CO₂/N₂ at 298.15 K and pressures up to 0.97 bar. The calculations were performed by varying the mole fraction of component x and y from 0.1 to 0.9. The calculations were performed using the GraphIAST software, freely available from Wageningen University & Research.

CHAPTER 4 – RESULTS AND DISCUSSION: FREEZE-CASTING

4.1. Results Analysis: Freeze-Casting

The results discussed in this section refer to material derived from this study, which was published in the *Journal of the American Ceramic Society* and entitled as “*Role of solvent composition and sintering time on the porosity of α -alumina monoliths produced by freeze casting*”.¹⁰⁹

4.1.1. Microstructure and Densification

The X-ray diffraction patterns of the α -Al₂O₃ standard (ICSD 25778) and of the materials synthesized in this study with different solvent compositions are shown in Figure 20. The samples exhibit the characteristic peaks, in agreement with the ICSD database standard, corresponding to the corundum-like crystalline structure of α -Al₂O₃ at 25.6° (0 1 2), 35.2° (1 0 4), 37.8° (1 1 0), 43.4° (1 1 3), 52.6° (0 2 4), 57.5° (1 1 6), 66.5° (2 1 4), 68.3° (3 0 0), and 76.9° (1 0 10), which are consistent with the α -alumina crystallographic phase without the presence of secondary phases. In the corundum phase, oxygen atoms form a hexagonal structure, with aluminum cations occupying two-thirds of the octahedral interstices. This phase is characterized by high mechanical and thermal resistance.⁵⁴

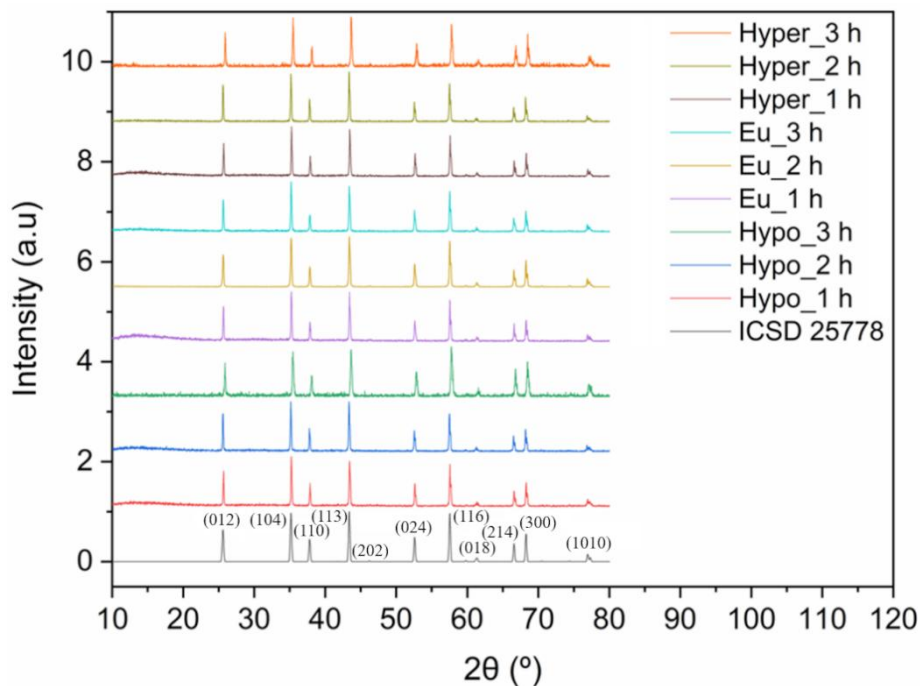


Figure 20. X-ray diffraction patterns of α -Al₂O₃ monoliths produced in this research.

From the above diffraction patterns, it was possible to calculate the average crystallite size (S_c) using the Scherrer equation^{110,111}, that is:

$$S_c = \frac{K\lambda}{L_\beta \cos(\theta)} \quad \text{Equation 26}$$

where K is the Scherrer constant ($K = 0.9$), λ is the wavelength of the radiation source, L_β is the full width at half maximum (FWHM) of the diffraction peak, and θ is the Bragg angle.^{110,111} The values obtained for all samples did not show significant variation with increasing sintering time, indicating that the proposed thermal treatment conditions did not exert a considerable impact on this parameter. The calculated values ranged from 49.1 to 54.8 nm for hypoeutectic samples, 44.9 to 54.9 nm for eutectic samples, and 50.8 to 54.9 nm for hypereutectic samples, in agreement with values reported in the literature.^{112,113} A clear trend in crystallite size variation was observed with increasing sintering time for the different solvent compositions. Therefore, such small variations in crystallite size may be attributed to differences in mass diffusion from the outer layers of neighboring grains in each sample.^{114,115} Furthermore, these results are directly related to the α - Al_2O_3 precursor. According to Alves *et al.* (2018), the precursor has a significant influence on the formation of the crystalline domain structure after monolith sintering.¹¹⁶ The data used for the crystallite size calculations are presented in the following table:

Table 9. Parameters used to use the Scherrer Equation.

Sample	2 θ (°)	FWHM (°)	S_c (nm)
Hypo_1H	35.2	0.160	52.1
Hypo_2H	35.1	0.152	54.8
Hypo_3H	35.4	0.212	49.1
Eu_1H	35.2	0.152	54.9
Eu_2H	35.2	0.186	44.9
Eu_3H	35.2	0.153	54.4
Hyper_1H	35.2	0.152	54.9
Hyper_2H	35.2	0.164	54.8
Hyper_3H	35.5	0.157	53.0

Figure 21 shows the average relative density calculated for the α -Al₂O₃ monoliths, determined in triplicate, using different monoliths for each system, by the Archimedes' principle, as a function of thermal treatment time and for the different naphthalene–camphor compositions proposed in this study. This parameter depends on several factors, including particle size distribution, particle shape, interparticle friction, agglomeration tendency, structural defects, composition, temperature, and sintering time.^{55,117}

The samples exhibited low standard deviations, ranging from ± 0.12 to 1.87 in relative density percentage, with the lowest and highest values corresponding to the Eu_3H and Hyper_2H compositions, respectively. Overall, a clear trend was observed toward increasing material density in the hypoeutectic (for sintering times up to 2 h), eutectic, and hypereutectic compositions as the sintering time increased. Furthermore, the samples produced in hypoeutectic solvents (up to 2 h of sintering) and in hypereutectic solvents displayed a higher relative density compared to the eutectic monoliths.

The results obtained are consistent with those reported by Araki *et al.* (2004) for monoliths produced in a naphthalene–camphor solvent with 20 vol% solid loading, which exhibited a relative density ranging from 37% to 42% with respect to the theoretical density of α -Al₂O₃ (3980 kg·m⁻³).⁶⁴ Moreover, since the sintering process induces different mass transfer mechanisms that generally involve a reduction of surface area and densification of the material, an increase in monolith density was expected for longer sintering times. This phenomenon was indeed observed for the eutectic and hypereutectic systems.¹¹⁸ It was found that after 2 hours of sintering, there was a decrease in the densification rate, more pronounced in the hypereutectic composition, most likely caused by the elimination of smaller grains, which leads to a reduction in the average driving force and an increase in the average diffusion distance.¹¹⁹ However, this trend was not observed for monoliths produced using the hypoeutectic composition at a sintering time of 3 hours, in which density decreased sharply compared to the other proposed sintering times.

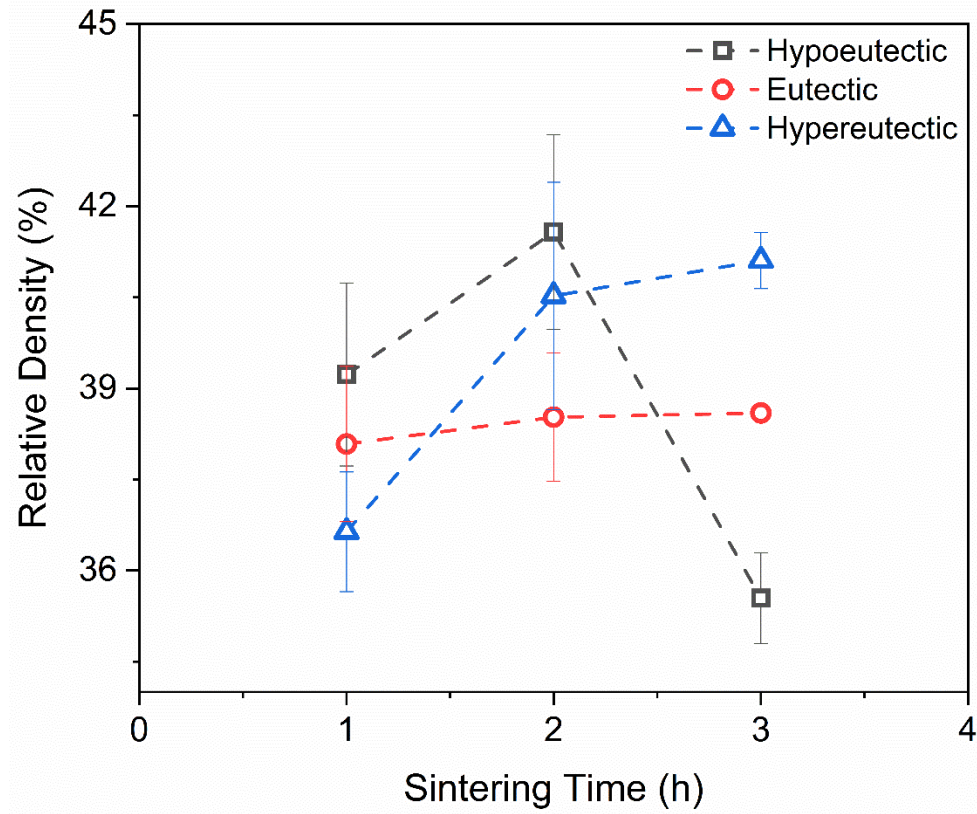


Figure 21. Average relative density as a function of sintering time of α -alumina monoliths produced in different naphthalene-camphor proportions.

A more in-depth investigation into the causes of the density differences observed in Figure 22 was carried out. For this purpose, microstructural analyses were performed using images obtained by X-ray Microtomography (μ CT) and Scanning Electron Microscopy (SEM). Figure 22 presents μ CT images, processed with Avizo[®] 3D software, of the samples in their respective cross-sections.

In the cross-sections of the monoliths, the formation of only a few agglomerates was observed in all cases. This indicates that the conditions for suspension formation by mechanical stirring were appropriate and effective in achieving good dispersion of the α - Al_2O_3 particles. Furthermore, a decrease in material density was observed from the lower regions (in contact with the cold surface during freezing) toward the corresponding upper regions (in contact with the atmospheric air during freezing).

In the fabrication process of porous ceramic materials by freeze-casting, it is expected that, as the distance from the freezing surface (copper rod) increases, the pore dimensions in the upper regions of the monoliths will be larger than those in the regions close to or in direct contact with the cooling surface (copper rod). This phenomenon is explained by the heat transfer process between the copper surface and the suspension.

With a very high temperature gradient (copper rod = $-130\text{ }^{\circ}\text{C}$; suspension and Technyl[®] mold = $80\text{ }^{\circ}\text{C}$), the initial freezing rate becomes sufficiently fast to instantaneously freeze the suspension in contact with, or very close to, the copper surface. Consequently, a denser layer with smaller and randomly oriented pores is formed in the lower regions. This denser layer affects the heat transfer process between the metallic plate and the suspension, leading to a decrease in the freezing rate throughout the material. Subsequently, along the freezing direction, the solvent crystals tend to grow, inducing an increase in pore size in the final ceramic material.^{55,59,120,121}

In Figures 22 (a), (c), (d), and (f), some linear cracks can be observed, more pronounced in (c) and (f), as well as bubble-like regions in the structures of the monoliths. These features were likely caused by the rapid sublimation of the binary solvent during the proposed procedure and by the entrapment of air bubbles during the freezing process, originating from the vigorous stirring of the suspension. When comparing the images of the hypoeutectic system, Figures 22 (a), (b), and (c), it is evident that the sample sintered for 3 hours exhibits cracks in the left and lower regions, extending throughout the material (highlighted in yellow). This phenomenon may have resulted in the decrease in the material's relative density observed in the Figure 21. This is believed to have been caused by the rapid sublimation of residual solvent during sintering, which also corroborates the formation of defects and, consequently, the anomalous density behavior calculated for the Hypo_3h monolith.

The orthogonal slices also reveal that the alumina monoliths prepared with the eutectic composition (Figures 22 (d), (e), and (f)) exhibit a highly porous structure, which is clearly observed in the upper half of the samples and is similar to that of the hypoeutectic composition. Some defects are noticeable, highlighted in the images, for the Eu_1H and Eu_3H samples. However, these defects did not extend throughout the entire sample. In contrast, Figures 22 (g), (h), and (i) show that the hypereutectic alumina monoliths present a denser region with a low presence of structural defects, entrapped air bubbles within the structure, and agglomerates.

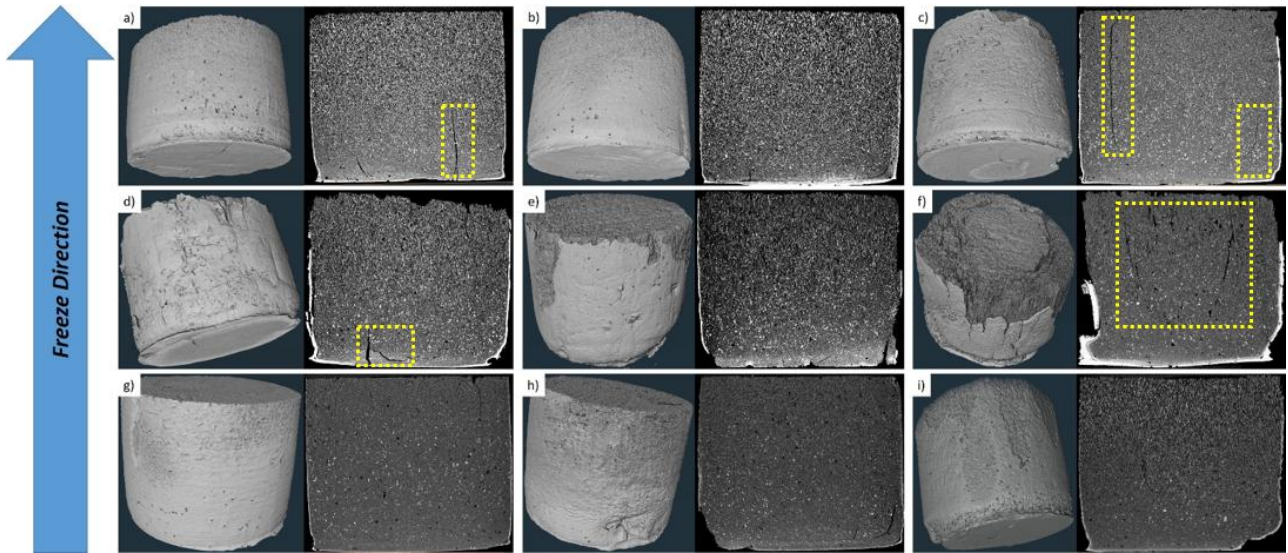
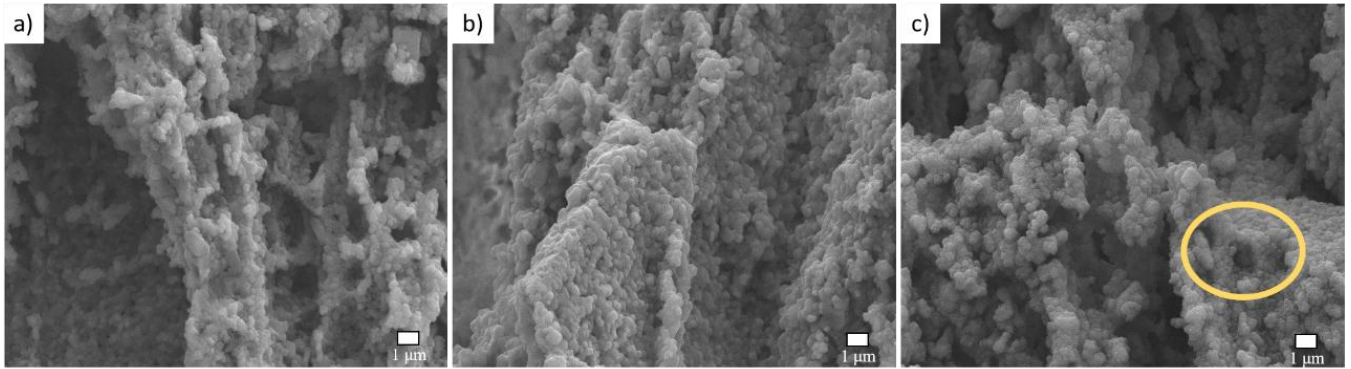


Figure 22. μ CT images processed using Avizo[®] 3D software based on microtomography analysis. (a), (b) and (c) represent the samples produced in hypoeutectic composition for sintering times of 1, 2 and 3h, respectively; (d), (e) and (f) eutectic composition for sintering times of 1, 2 and 3h, respectively; (g), (h) and (i) present the hypereutectic composition for sintering times of 1, 2 and 3h, respectively. The yellow highlights indicate the presence of defects.

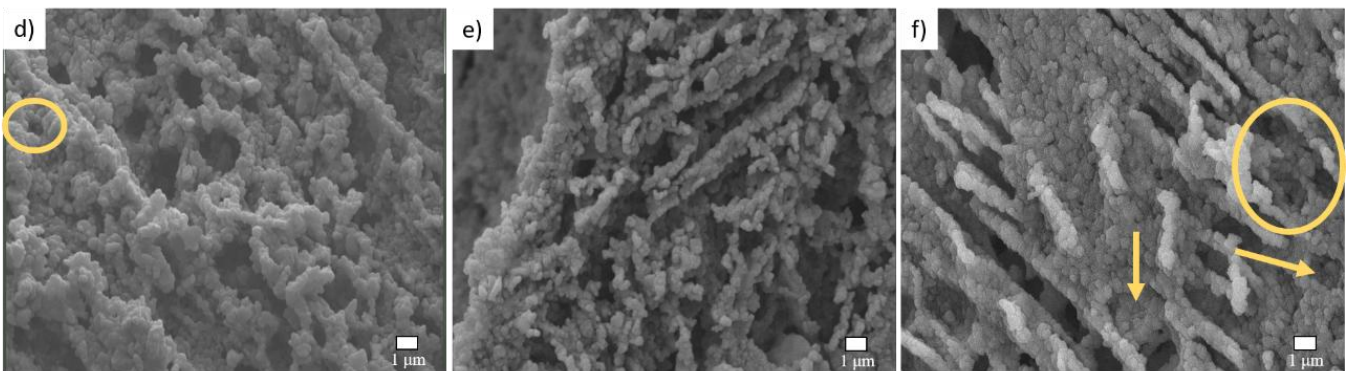
The overall increase in material density follows the evolution of the grains throughout the sintering process. Figures 23 and 24 show high-magnification SEM images of the samples produced under the different proposed conditions. Intergranular pores were larger in the samples sintered for 1 hour. Samples prepared with the hypoeutectic composition (Figures 23 (a), (b), and (c)) did not show a clear pattern with increasing sintering time. However, when comparing Figures 23 (a) and (b), the formation of denser regions, with intergranular neck formation (highlighted in Figure 24) and some isolated pores in Hypo_2H, was observed, indicating a possible reduction in the sample porosity.

Similarly, for the eutectic and hypereutectic samples, the transformation of some large intergranular pores into smaller, more isolated pores dispersed within a dense region of the material is clearly observed. These appear to form closed pores (highlighted in yellow), along with the growth of larger grains as sintering time increases, which constitute the structure. This is caused by the dominance of diffusion processes at the grain boundaries and within the bulk during the thermal treatment applied in sintering. Therefore, with increasing sintering time, a decrease in interconnected porosity and an increase in isolated porosity are expected, due to the isolation of open pores through neck formation and the progression of densification.^{113,122}

Hypoeutectic (Naphthalene-rich phase)



Eutectic



Hypereutectic (Camphor-rich phase)

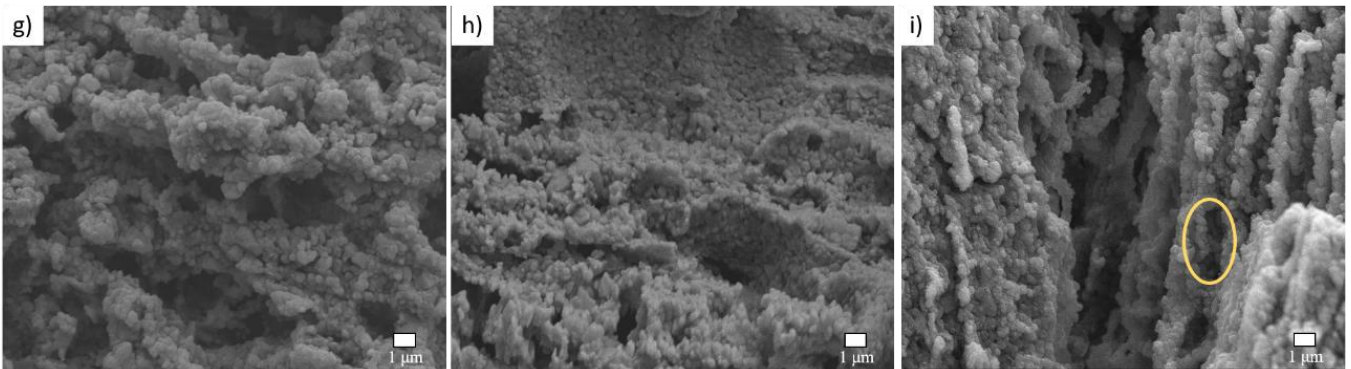
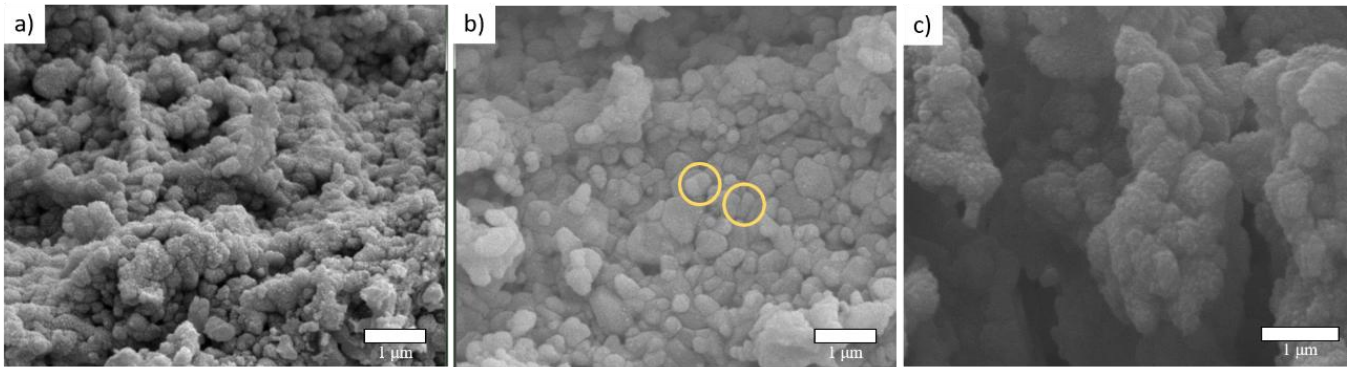
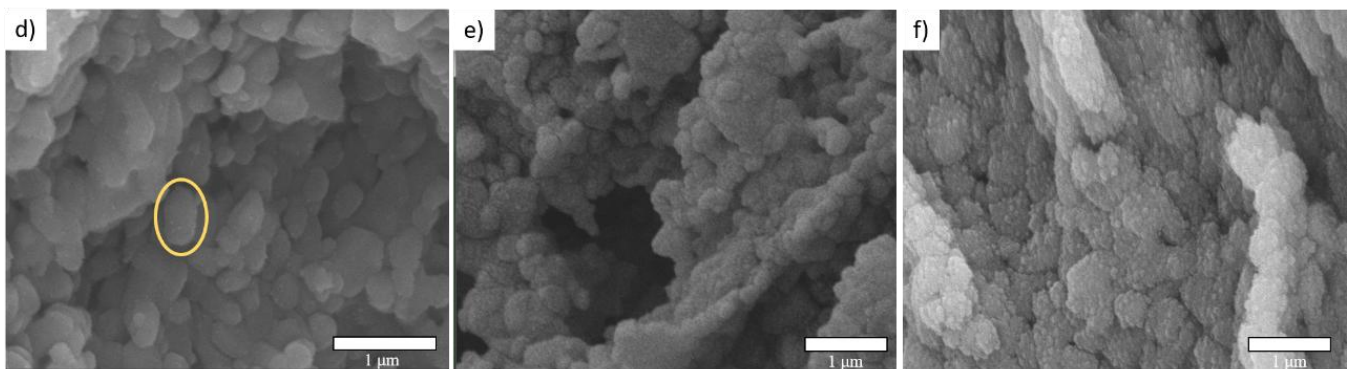


Figure 23. Micrographs for analysis of grains of monoliths produced under: (a), (b) and (c) composition of the naphthalene-rich phase for sintering times of 1, 2 and 3h, respectively; (d), (e) and (f) eutectic composition for sintering times of 1, 2 and 3h, respectively; (g), (h) and (i) composition of the camphor-rich phase for sintering times of 1, 2 and 3h, respectively. All images were produced at 5000x magnifications. Yellow highlights indicate the presence of closed pores.

Hypoeutectic (Naphthalene-rich phase)



Eutectic



Hypereutectic (Camphor-rich phase)

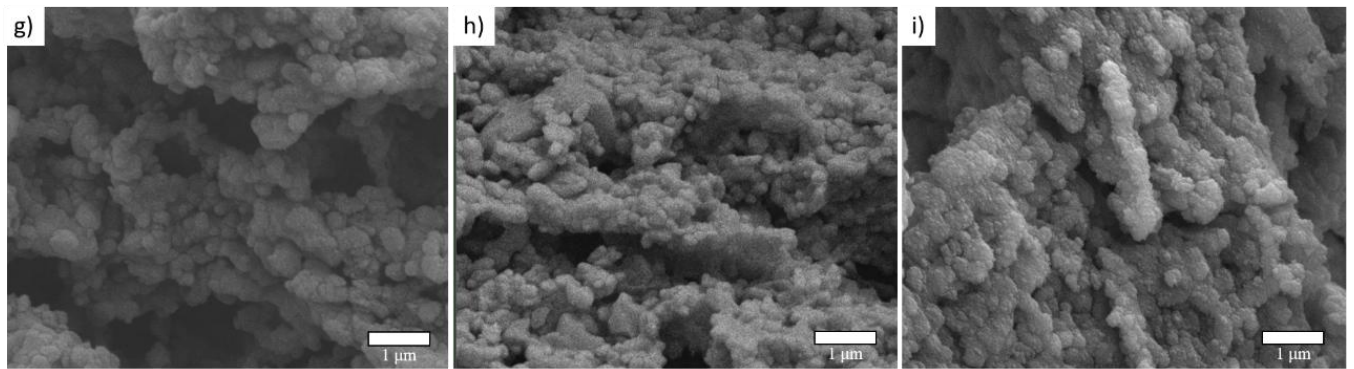


Figure 24. Micrographs for densification analysis of monoliths produced under: (a), (b) and (c) composition of the naphthalene-rich phase for sintering times of 1, 2 and 3h, respectively; (d), (e) and (f) eutectic composition for sintering times of 1, 2 and 3h, respectively; (g), (h) and (i) composition of the camphor-rich phase for sintering times of 1, 2 and 3h, respectively. All images were produced at 8000x magnification. Yellow highlights indicate the presence of necks.

Following the acquisition of SEM images of the grains (Figure 23), a grain size study was conducted for the monoliths produced with different binary solvent compositions and sintering temperatures. For this analysis, ImageJ® software was used to

measure the grain sizes. A standard average count of 300 grains per sample was performed. To generate histograms and determine their bin widths (j), Sturges' rule was applied.¹²³ That is:

$$j = \frac{n_f - n_0}{1 + 3.222 \log n} \quad \text{Equation 27}$$

where n_f and n_0 are, respectively, the diameters of the largest and smallest particles, and n is the number of terms. To construct the histograms from the collected data, the LogNormal function available in Origin[®] 2018 software was applied to determine the average grain sizes. The graphs and data are shown in Figure 25.

Figure 25 shows that increasing the sintering time resulted, for all compositions, in an increase in the mean grain size of the microstructures. This effect was more pronounced for the hypoeutectic samples, in which grain growth may have been favored by the higher density achieved during the initial stages of the sintering step. In this case, the Hypo_3H sample exhibited the largest overall average grain size, with a value of 596 nm.

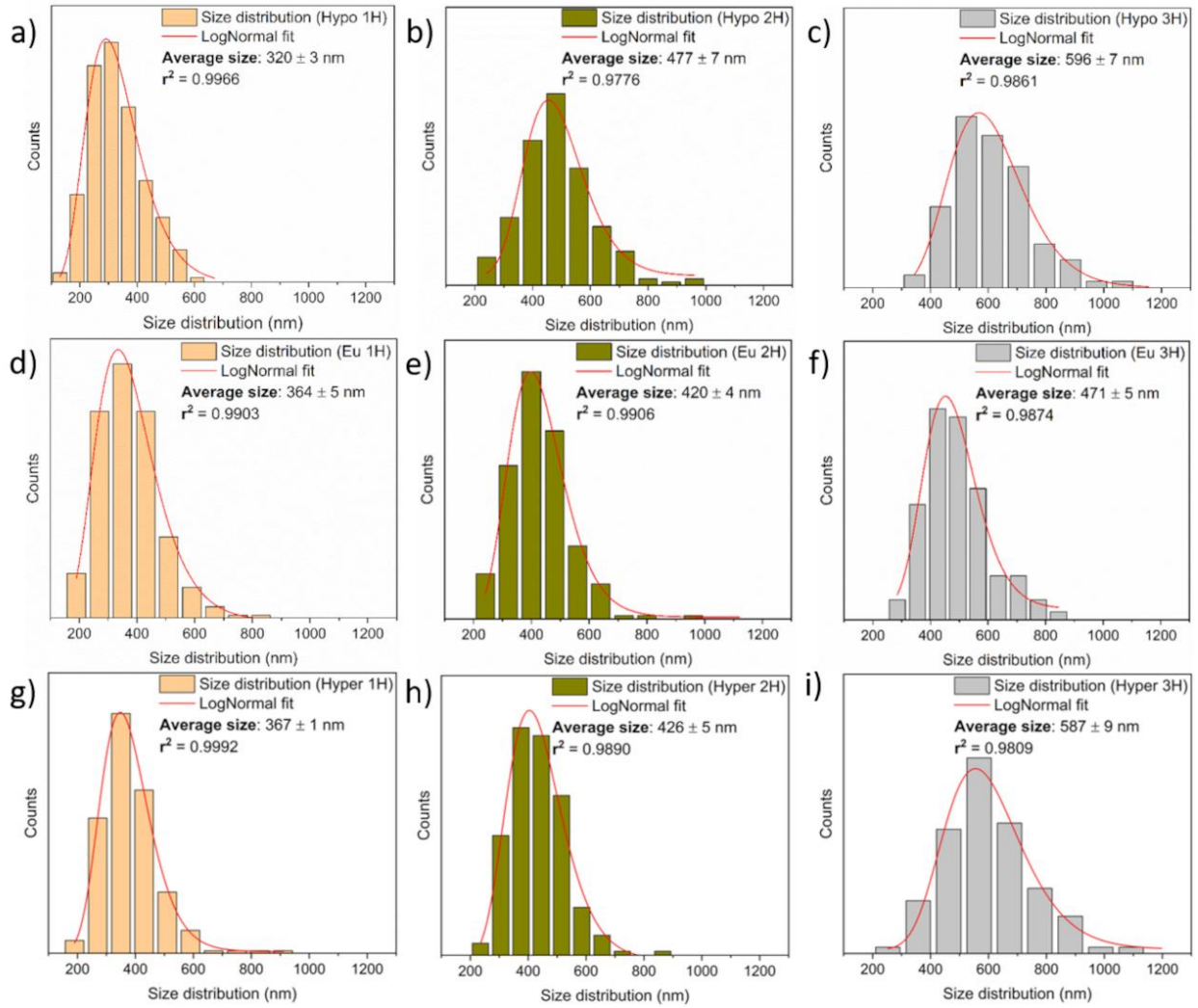


Figure 25. Grain size study of the synthesized monoliths. (a), (b) and (c) represent hypoeutectics for sintering times of 1, 2 and 3h, respectively; (d), (e) and (f) represent eutectics for sintering times of 1, 2 and 3h, respectively; (g), (h) and (i) represent hypereutectics for sintering times of 1, 2 and 3h, respectively.

According to grain growth dynamics, the solid-state diffusion process is dependent on the thermal treatment time in conventional sintering techniques.¹²⁴ Based on grain growth dynamics, the driving force (F) of the process can be described by Equation 28:

$$F = \frac{2\delta}{D} \quad \text{Equation 28}$$

where δ is the specific surface energy and D is the grain size.¹²⁴ It can be observed in Eq. 28 that as grain size decreases, the surface energy increases, and consequently, the driving force for grain growth also increases. The surfaces of larger crystalline grains possess

lower surface energy compared to the adjacent smaller grains. Therefore, increasing the sintering time causes the interfaces of the larger grains to be driven by interfacial energy toward the centers of grains with smaller curvature radii. In this way, the α -Al₂O₃ particles grow, and the smaller grains gradually diminish as the thermal treatment progresses. This behavior results in an increase in the average grain size of the alumina structures.^{113,124}

The results observed in Figure 25 are consistent with the prediction of Equation 28, which indicates an increase in the average grain size as the thermal treatment time progresses. The higher free energy at the surfaces of smaller grains results in thermodynamically favorable growth in order to minimize the total energy of the structures. However, longer sintering times can cause abnormal grain growth, which may lead to a decrease in the degree of densification and, consequently, deformation of the sintered body.¹²⁴ This phenomenon may have occurred in the Hypo_3h sample, although it is believed that the solvent sublimation process had a greater impact on the formation of structural defects in this sample.

4.1.2. The Influence of Solvent Composition and Sintering Time on the Final Porosity of α -Al₂O₃ Monoliths

Figures 26, 27, and 28 present scanning electron microscopy (SEM) images, computed microtomography images of the sample cross-sections, and the corresponding estimated porosity values, respectively. These analyses enabled an investigation of the effects of solvent composition and the densification process on the final pore structure of the ceramic materials.

Figures 26 and 27 show that the pore morphologies formed in the materials are consistent with the crystallization mechanisms of the naphthalene-camphor compositions studied. This pore network formation phenomenon occurs during freezing, in which the particles dispersed in the suspension are rejected by the advancing freezing front and trapped between the solid solvent crystals. According to Deville *et al.* (2007), the structure formed by the freezing front, dictated by the nature of the solvent, is the main factor determining the pore morphology of the sample. However, when comparing the results obtained in this study with those reported by Araki *et al.* (2004) and Lacerda *et al.* (2018), it becomes evident that the controlled freezing temperature of -130 °C and the lower applied solid loading (20 vol%) can also influence the final pore structure.^{64,65,125}

Figures 26 (a)–(c), corresponding to the samples produced under hypoeutectic conditions, show the formation of large, isolated voids with rod-like geometry (highlighted in yellow) aligned with the freezing direction, reproducing the faceted plate-like morphology characteristic of the naphthalene-rich proeutectic phase. In the study by Araki *et al.* (2004), it was observed that samples produced under hypoeutectic conditions, with a solid loading of 48 vol% and solidified at room temperature, generated denser structures with elongated pores of random orientation. Lacerda *et al.* (2018), in turn, reported the formation of structures similar to those obtained in this work for the hypoeutectic system with a 20 vol% solid loading, frozen without temperature control at -196 °C.^{64,65} The presence of large spherical voids (highlighted in red), which do not follow the organized geometry of freeze-casting pores, can be observed in samples produced under hypoeutectic conditions. This is possibly due to the presence of air bubbles in the suspension that became trapped in the structure during freezing. As the temperature decreases, the dissolved air is expelled from the crystal networks in the form of microbubbles and subsequently captured by the advancing freezing front. Another possible explanation for the appearance of these structures is the formation of defects during the sample cutting process.

The solvent crystallization process for the eutectic system, shown in Figures 26 (d)–(f), led to the formation of lamellar porosity, resulting from the growth of continuous thin, plate-like crystals. These lamellae are aligned along the freezing front direction but are misaligned in the region perpendicular to the front.

In the samples fabricated with the hypereutectic composition, shown in Figures 26 (g)–(i), the formation of small pores resembling distorted dendrites can be observed, replicating the morphology of the camphor-rich proeutectic frozen crystals (highlighted in yellow). Well-distributed dendritic structures were observed throughout the material, albeit with random orientations. Furthermore, elongated voids are absent in the solid body, and the structure is more porous than those reported in the previously mentioned studies. These results demonstrate that different freezing conditions, thermal treatment, and solid loading can influence the final pore structure of the material and, consequently, its properties.

Podolinski *et al.* (1979; 1986) showed in their studies that camphor crystals exhibit spherical growth morphologies when precipitated from a binary solution (such as naphthalene–camphor). The increase in crystal size under constant supercooling

conditions leads to a transition in the frozen crystal structure toward a symmetrically distorted spherical geometry, characterized by the growth of four or six symmetric tips within the same plane, which serve as precursors for the development of future dendrimers. Consequently, this process results in the formation of dendritic structures.^{126,127}

Lacerda *et al.* (2018) carried out a unidirectional solidification process of different naphthalene–camphor mixtures using the vapor deposition technique. In this study, it was observed that the morphology of the frozen solvent crystals was directly influenced by the ratio of naphthalene to camphor in the solution. According to the group, the hypoeutectic composition resulted in randomly oriented rod-like solvent crystals when solidified at slower cooling rates. Solidification under eutectic conditions led to the formation of thin plates aligned with the freezing direction. The hypereutectic composition, however, produced spherical and fine rod-shaped crystals.⁶⁵

Araki *et al.* (2004) reported that under hypereutectic conditions, freezing favored the formation of six-pointed star-shaped crystals. According to the group, and based on the phase diagram presented in Figure 15 (Section 3.2), it is known that the proeutectic naphthalene–camphor crystals (the point at a given temperature where the composition transitions to a mixture of two solids) obtained from the hypoeutectic composition are characterized by a naphthalene-rich phase (α), which accounts for 8.5 wt% of the solidified solvent, while the eutectic fraction represents 91.5 wt%. In the hypereutectic mixture, the proeutectic naphthalene–camphor crystals correspond to a camphor-rich phase (β), which represents 20 wt% of the solidified crystal, whereas the eutectic phase accounts for the remaining 80 wt%.⁶⁴

Thus, since the pore structure of materials produced by freeze casting is strongly influenced by the structure of the solidified binary solvent crystals, it is expected that distinct pore architectures will be formed for each composition studied.

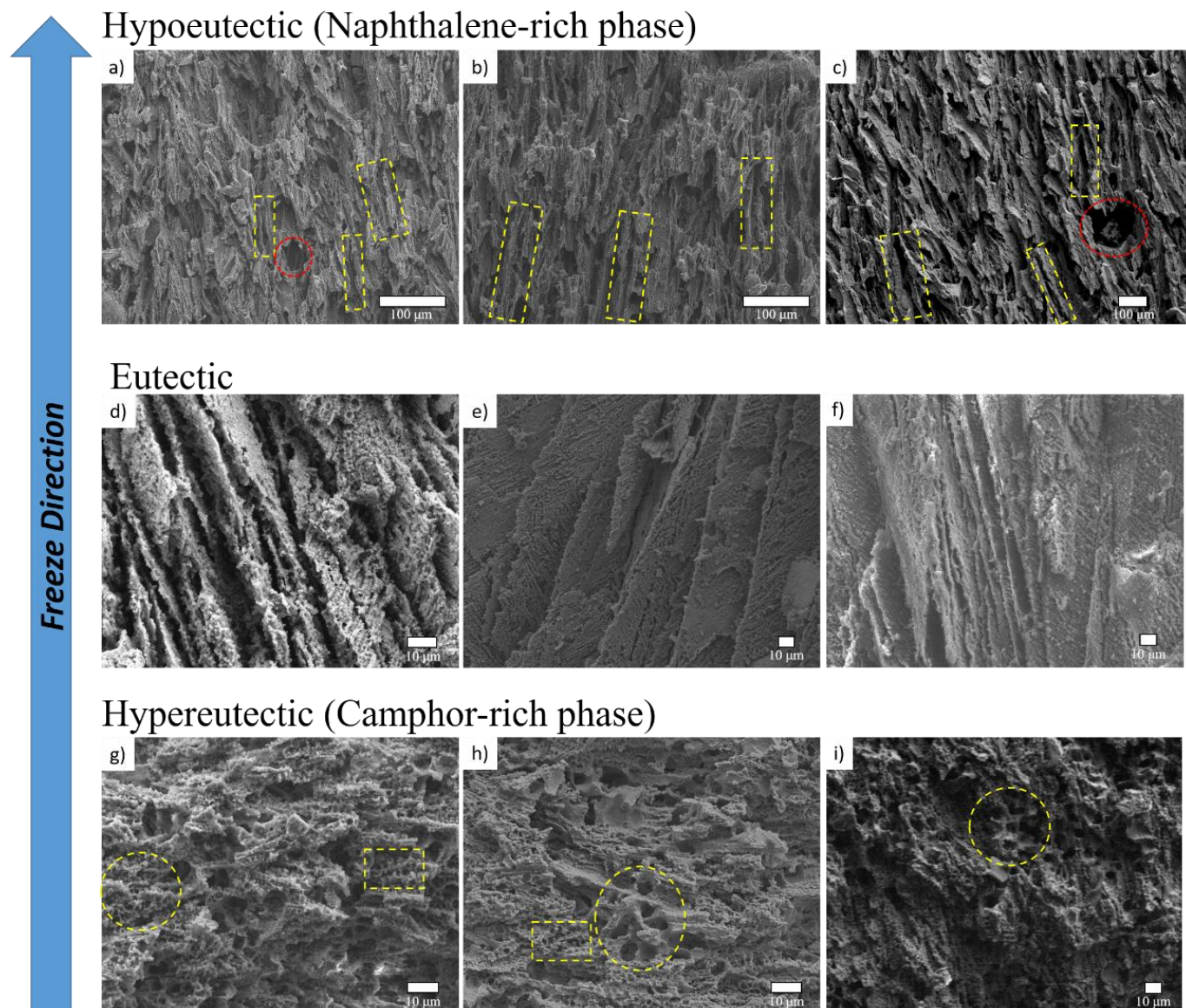


Figure 26. SEM images showing the pore structures of the monoliths produced in: (a), (b) and (c) hypoeutectic system for sintering times of 1, 2 and 3h, respectively; (d), (e) and (f) eutectic composition for sintering times of 1, 2 and 3h, respectively; (g), (h) and (i) hypereutectic system for sintering times of 1, 2 and 3h, respectively. Highlights in yellow and red show specific morphological characteristics detected in the samples.

Figure 27 presents 2D microtomography images with greater detail of the samples sintered for 2 hours, clearly demonstrating the feasibility of producing different pore morphologies by altering the composition of the freezing vehicle. It is evident that the components fabricated with hypoeutectic and eutectic compositions exhibited greater pore alignment compared to those produced in the hypereutectic system. These results

are consistent with the observations from the SEM images. Images of the remaining samples can be found in the appendix (Figure A1).

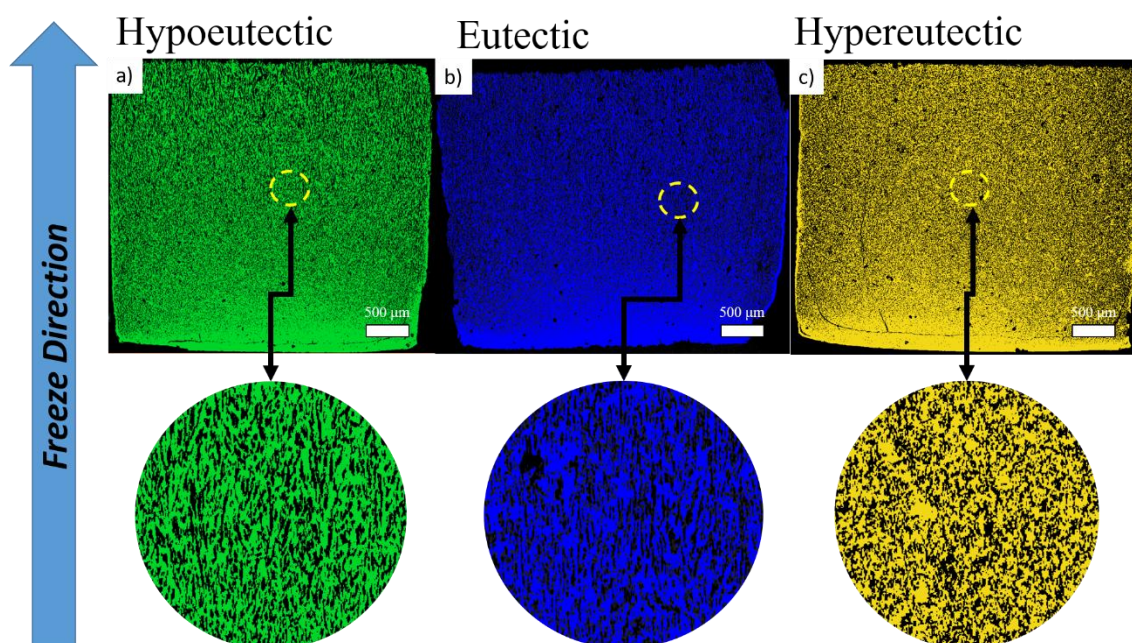


Figure 27. Representation of pore morphology from 2D sections approximated by microtomography images of the monoliths sintered for 2 hours. Images for the other samples can be seen in the appendix.

Figure 28 illustrates the behavior of porosity according to the variables studied in this work. Considering the eutectic and hypereutectic systems, it is observed that the longer the sintering time, the lower the open porosity and the higher the closed porosity of the final products. As shown in the grain size study, the increase in sintering time promoted greater grain growth in the hypereutectic system than in the eutectic system. In general, as sintering time increases, open pores become isolated due to grain growth and the significant formation of grain junctions, a factor that favors the development of closed porosity in the samples. Therefore, knowing that grain growth is directly proportional to the percentage of closed porosity in the material, this increase was more pronounced for the hypereutectic composition. This result is consistent with expectations reported by Lacerda *et al.* (2018), as the pore structure of materials produced via freeze casting is formed after the sublimation of the naphthalene–camphor solvent and consolidated during sintering.⁶⁵ However, a high percentage of open pores is observed in the samples prepared in this work, a crucial factor for enabling the application of these materials as supports in membrane separation processes.

Bringing into focus the discussion presented earlier with Equation 28, it is evident that as the sintering time increases, the free energy of the surface particles tends to decrease, resulting from a reduction in the solid–gas interfacial area and an increase in the solid–solid interfacial area. In this process, the particles spread and bind to one another, reducing their curvature or filling the internal pores of the material, thereby decreasing open porosity. However, the reduction in the system’s surface free energy can also occur through grain growth via the coalescence mechanism, in which both the pores and the particles increase in size.^{128–130}

Regarding longer sintering times, as appears to have occurred with the Hypo_3H sample, sintering results in significant growth of the α -Al₂O₃ grains and a reduction in open pores. Consequently, according to Chu *et al.* (2017), the grains form a three-dimensional network with large void spaces within the material.¹²⁴ The result is an additional increase in the material’s porosity, as shown in Figure 28.

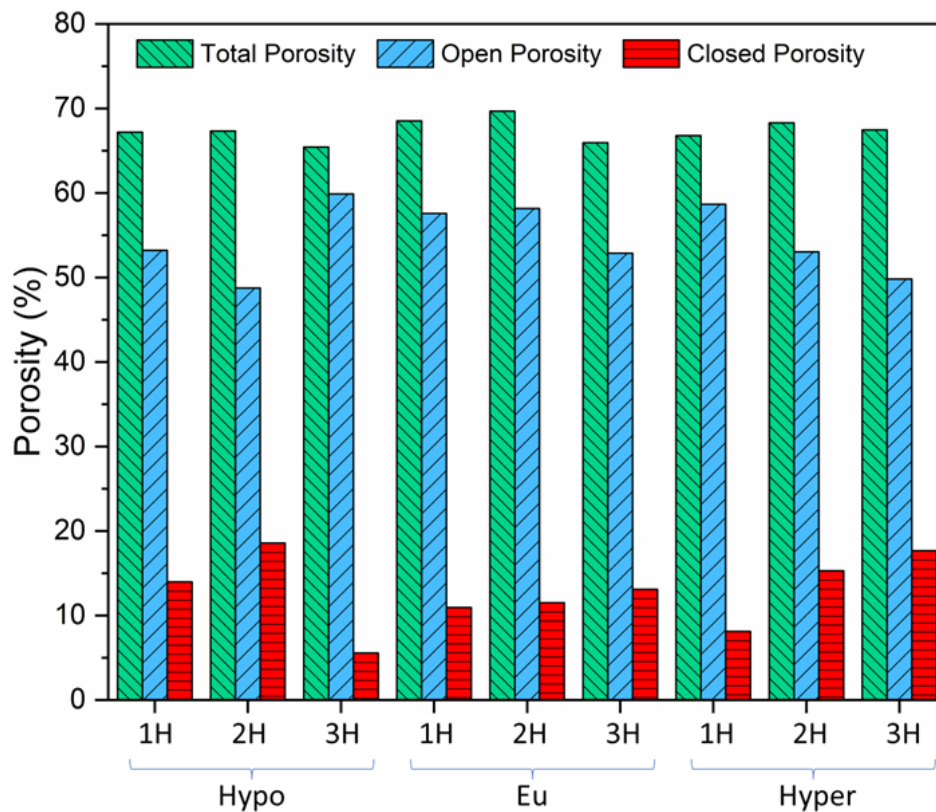


Figure 28. Total, open and closed porosities acquired by the Archimedes’ methodology of samples synthesized at different compositions and sintering time.

The numerical porosity values measured using the Archimedes’ principle and microtomography are presented in Table 10. During sintering, a gradual transition is

generally expected from a structure with higher open porosity to one with greater closed porosity. Open porosity is accessible to the external environment and can allow fluid permeation through the structure. In contrast, closed porosity is isolated and does not communicate with the external environment.¹²² It is observed that the solvent composition and sintering time did not significantly affect the total porosity of the monolith, which remained within the range of 65–70%. However, different sintering times were found to cause significant changes in the open and closed porosity of the samples.

According to the anomaly observed and predicted in the analyses discussed thus far, the hypoeutectic system exhibited higher open porosity in the samples sintered for 3 hours compared to other sintering times, while closed porosity experienced a drastic reduction. Conversely, samples produced from binary solvents with eutectic and hypereutectic compositions tended to show an increase in closed porosity and a decrease in open porosity as the sintering time progressed, a phenomenon that aligns with the expected behavior discussed earlier.

However, although the total porosities measured by the Archimedes' principle did not show significant variation over the sintering time range considered in this work, microtomography revealed a clear trend of decreasing total porosity with increasing sintering time for samples produced from eutectic and hypereutectic solvent compositions. Furthermore, the total porosities measured by μ CT were generally lower, yet close to the values obtained via the Archimedes' method, due to the equipment's resolution. The difference between total porosity values measured by μ CT and the Archimedes' principle was approximately 10%. It is common for micro and mesopores to be excluded by the pore volume selection tool, leading to a reduction in the calculated total porosity. At the same time, microtomography is more sensitive to the presence of structural defects in the material and can account for them in porosity calculations, which may also influence the measured porosity values.

Table 10. Porosity data obtained using Archimedes and microtomography techniques.

Composition	Sintering time (h)	Closed pores (%)	Open pores (%)	Total porosity (%)	μ CT – Total porosity (%)
Hypoeutectic	1	13.98	53.21	67.19	57.02
	2	18.57	48.75	67.32	56.85
	3	5.56	59.88	65.44	68.15
Eutectic	1	10.94	57.57	68.52	71.09
	2	11.52	58.17	69.69	69.15
	3	13.09	52.87	65.96	62.28
Hypereutectic	1	8.12	58.67	66.79	69.62
	2	15.29	53.03	68.31	61.63
	3	17.66	49.81	67.46	57.75

Figure 29 and Table 11 highlight the pore diameter distribution and the average pore size of the monoliths prepared in this work, as measured using the Avizo[®] 3D software. The algorithm implemented in Avizo[®] 3D is based on a hybrid approach proposed by Youssef *et al.* (2007), which integrates techniques that enable a statistically representative reconstruction of the pore networks. This network represents the pores through simplified units based on the ball & stick model, preserving the topological characteristics of the pore structure.

Although the representation does not accurately reflect the actual pore morphologies, the topological properties (e.g., pore coordination number and pore coordination spectrum) provide data that enable precise estimation of relevant characteristics such as connectivity, tortuosity, and network permeability. Furthermore, the assessment of pore dimensions is carried out by segmenting the pore space into individual pores using a voxel growth algorithm, which allows for the automatic separation of the reconstructed labeled pores. The pore dimensions are then estimated based on voxel sizes, modeled as pore diameters. It is important to note that, given the pore geometries observed in the previous SEM and μ CT results, the pore diameters identified by the model should be interpreted as pore widths, which is the terminology adopted hereafter. Further details regarding the models and algorithms used in the Avizo[®] 3D software can be found in the literature.^{131–134}

Given that sequences of spherically connected pores arranged in alignment can represent pores of various topologies (dendritic, lamellar, etc.), and considering the resolution limitations imposed by the voxel size ($\sim 6.5 \mu\text{m}$) and the ball-and-stick model,

it was decided to conduct the pore dimension analysis of the samples using the microtomography technique.

Overall, it can be stated that all monoliths exhibited pore sizes in the range of 7-12 μm (except for the Hyper_3H sample), with average pore diameter values between 8-10 μm (Table 11). Furthermore, as the sintering time increased, a higher percentage of larger pores above 12 μm was observed, similar to the findings reported by Souza *et al.* (2014).¹³⁵ As previously discussed, the densification mechanism promotes an increase in the average grain size of some samples. Consequently, larger grains can form a three-dimensional network structure with void spaces (of larger sizes), which can lead not only to a reduction in total porosity by consuming smaller pores but also to an increase in the frequency of larger pores throughout the structure.^{124,135} With a broad particle size distribution, pore growth can easily occur during the densification process. During sintering, the volumetric shrinkage of the sample is hindered by the presence of large particles with low surface energy. As the smaller particles densify, void spaces form in the interstices between the larger particles, leading to an increase in the average pore size without significantly altering the total porosity of the material.^{124,136}

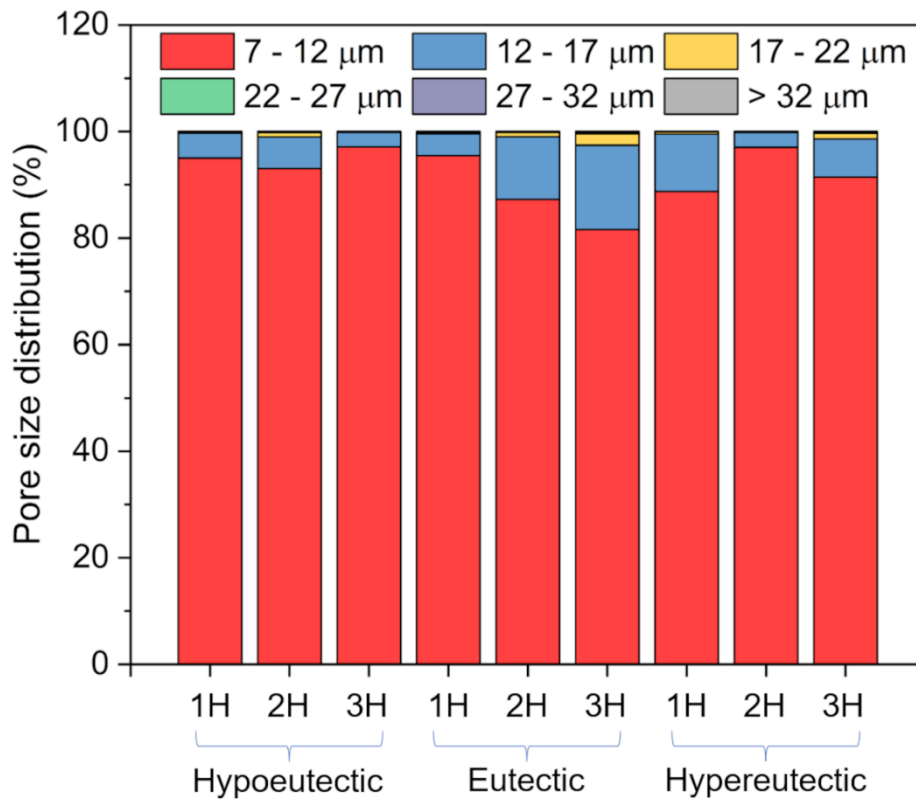


Figure 29. Pore width distribution of monoliths produced at different solvent compositions and sintering time.

Table 11. Average pore width for the α -alumina monoliths. The distribution curves associated with these values can be seen in the appendix section (Figure A2).

Composition	Sintering time (h)	Pore width (μm)
Hypoeutectic	1	8.5 ± 1.6
	2	9.3 ± 2.0
	3	8.3 ± 1.3
Eutectic	1	8.9 ± 1.6
	2	9.5 ± 2.1
	3	9.9 ± 2.6
Hypereutectic	1	9.4 ± 1.8
	2	8.7 ± 1.4
	3	9.2 ± 2.3

The pore interconnectivity of selected samples was evaluated using reconstructed microtomography images, which were processed with the *Pore Network Modeling* (PNM) tool available in the Avizo[®] 3D software (Figure 30). In pore network models, an idealized network consisting of pores and throats with simplified geometrical shapes is constructed based on the actual pore space, represented by three-dimensional images of the porous materials. The PNM approach uses as input a labeled image representing the segmented pore space, where each individual pore is identified by a unique color. This allows for the visualization and representation of pores (depicted as spheres) and throats (the connecting channels between pores) through a ball & stick model, as well as the evaluation of the pore coordination number (the average number of throats connected to a given pore). This method of pore network acquisition has the advantage of preserving the topology of the void space. Moreover, the tool enables the assessment of key properties such as absolute permeability, total flow rate, and hydraulic tortuosity. In this way, the program simulates the interaction between the sample and a laminar flow fluid (Poiseuille flow), assuming that the network is completely saturated with a single fluid phase.^{131,132,135,136}

The operating mechanism of the hybrid algorithm used in the pore network model is described in detail in the work of Youssef *et al.* (2007).¹³² Initially, the algorithm identifies the channels based on the pore skeleton. Simultaneously, it calculates the connectivity number for each channel and measures their lengths, from which the hydraulic tortuosity is determined. The next phase involves segmenting both the skeleton and the channels according to the various pores present in the sample. In the final step, the pore space is divided into distinct pores using a voxel growth algorithm, enabling the

automatic separation of reconstructed and labeled pores. These computational calculations assume that, under steady-state flow of an incompressible fluid permeating through the sample, mass conservation for each porous body is described as:

$$\sum_{i \rightarrow j} q_{ij} = 0 \quad \text{Equation 29}$$

in which the summation is performed over all pores “j” connected to pore “i”, and q_{ij} represents the flow rate between pore “i” and pore “j”. Under laminar flow conditions, the relationship between the pressure drop and the flow rate is linear and can be expressed as:

$$q_{ij} = g_{ij}(P_i - P_j) \quad \text{Equation 30}$$

in which g_{ij} represents the throat conductance between pore “i” and pore “j”. Since the conducting throats are modeled as cylindrical tubes with radius r_{ij} and length l_{ij} , the hydraulic conductance is given by Poiseuille’s law, where μ is the fluid viscosity.

$$g_{ij} = \frac{\pi r_{ij}^4}{8\mu l_{ij}} \quad \text{Equation 31}$$

Thus, when a pressure difference is applied across the pore network, a linear system of equations is obtained, which can be solved numerically. Equations 29 and 30 lead to the construction of the following matrix: $G * P = S$, where G is a symmetric conductance matrix of dimension $N * N$, with N being the number of pores in the network; P is a vector of size N corresponding to the pressure at each pore (the unknowns of the problem); S is a vector of size N , constrained by the pressure boundary conditions at the inlet and outlet of the system. Therefore, the total flow rate can then be calculated as $Q = \sum g_{ij}(P_i - P_j)$ for each pair of pores “i, j” sharing an arbitrary surface area “A”. The permeability “k” of the network can then be determined using Darcy’s law:

$$k = \frac{Q}{\Delta P} \frac{\mu L}{A} \quad \text{Equation 32}$$

in which ΔP is the applied pressure difference (inlet and outlet pressure) and L is the length of the porous network in the flow direction. Based on the velocities obtained from the absolute permeability calculations described above, it is possible to determine the hydraulic tortuosity (T_h) of the material. By knowing the velocities in each throat,

tortuosity is deduced by summing the lengths of all velocity paths and dividing by the sum of their projections along the flow direction:

$$T_h = \frac{\sum_{i=0}^n |v_i|}{\sum_{i=0}^n |v_{xi}|} \quad \text{Equation 33}$$

where "n" is the number of throats, v_i is the fluid velocity through throat "i" and v_{xi} is the projection of the velocity along the fluid flow direction through throat "i".^{132–134}

As input values for simulating flow through the samples, an inlet pressure of 1.3×10^5 Pa, an outlet pressure of 1.0×10^5 Pa, and a fluid viscosity of 0.001 Pa.s were defined. The hydraulic tortuosity was calculated based on the velocities obtained from the absolute permeability computation for each pore throat. The results can be seen in Figure 30 and Table 12.

It is observed in Figure 30 that the samples exhibited a tendency for pore size to increase along the freezing front direction. However, the pore network of the sample produced with a hypoeutectic solvent composition showed greater pore alignment compared to the others, consistent with the tortuosity results presented in Table 12. Furthermore, the images indicate a seemingly high pore interconnectivity, with an average coordination number of 12, 13, and 14 for Hypo_2H, Eu_2H, and Hyper_2H, respectively.

Tortuosity values increased for the samples produced with a higher percentage of camphor in the binary solvent. This phenomenon may be related to the freezing mechanism in the freeze-casting technique. As the freezing front advances, the crystals tend to grow perpendicular to the copper surface (along the freezing thermal gradient). However, as discussed in Figure 22, the suspension experiences non-linear freezing rates that decelerate along the temperature gradient, and due to the crystalline anisotropy of the solvent, the preferred growth direction may differ, with anisotropic interface kinetics playing a significant role in the freezing process. Macroscopically, this effect can produce a slight inclination in the growth of the solvent crystals (affecting the tilt of the ceramic lamellae), as the directions of the thermal gradient and anisotropic effect are not aligned. This phenomenon depends on the magnitude of the anisotropic interface kinetics. Furthermore, as previously observed, the crystals exhibit unique structures for each solvent composition used in this study, which can also influence the anisotropic effect and, consequently, the tortuosity of the pores.^{55,125,137}

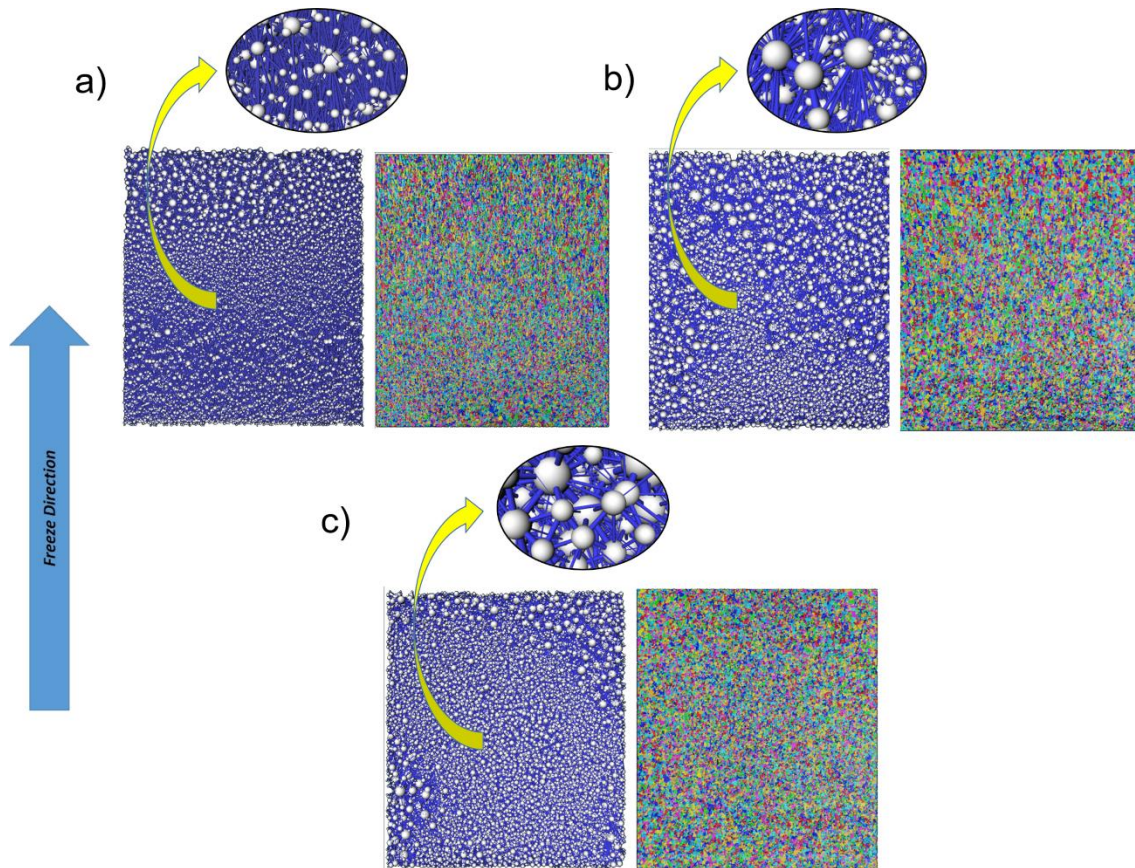


Figure 30. Modeling of the pore network (left image) and segmented and labeled pores (right image) of (a) Hypo_2H, (b) Eu_2H, and (c) Hyper_2H. Each segmented pore has its own identifier represented by a specific color.

Table 12. Properties of monoliths measured by Avizo[®] 3D software when applying the PNM tool.

Composition	Sintering time (h)	Total flow rate (cm ³ /s)	Absolute permeability (P _A)	Hydraulic tortuosity factor
Hypoeutectic	2	26.53	454.74	1.30
Eutectic	2	73.59	1049.15	1.46
Hypereutectic	2	36.33	479.79	1.53

When comparing the results presented in Tables 11 and 12 with those in Figure 28, a well-established relationship can be observed between open porosity and total porosity with the values of absolute permeability and total flow rate. The eutectic sample sintered for 2 hours exhibited the highest total porosity (69.69%) and open porosity (58.17%) among the three samples, as well as one of the largest average pore sizes (9.5

μm). The proportion of open pores can significantly influence the mass transfer capacity through the ceramic material, as can the average pore size, since smaller pores tend to increase the flow resistance to fluids.

Furthermore, studies by Dong *et al.* (2017) and Arai *et al.* (2019) demonstrate that lamellar structures naturally tend to exhibit lower flow resistance than dendritic, faceted, or prismatic structures, for example. This resulted in an increase of approximately 230% in absolute permeability compared to the lowest value (observed in the hypoeutectic sample). The same trend is observed for the estimated total flow rate. These results are consistent with what has been reported in the literature for a Darcy permeability regime.^{133,134}

4.1.3. Impact of Microstructural Properties on Compressive Strength

Figure 31 and Table 13 present the compressive strength results of α -Al₂O₃ samples obtained via freeze-casting, for a load applied parallel to the freezing direction. As previously discussed, it is expected that the higher the total porosity, the lower the compressive strength of ceramic materials. However, this behavior was not observed for all monoliths produced with different naphthalene-camphor compositions in this study.

In the previous results presented in Table 10 (Section 4.1.2), it was observed that the eutectic samples generally exhibited higher total porosity compared to the other compositions. Concurrently, a pronounced reduction in the mechanical strength of this composition was observed relative to the hypoeutectic and hypereutectic systems, presenting maximum strengths of, respectively, $4,8 \pm 1,1$ MPa, $23,6 \pm 5,2$ MPa and $23,5 \pm 4,6$ MPa.

The low mechanical strength of the eutectic system can be explained by the geometry of its pores. Tang *et al.* (2016) demonstrated that, in structures produced via freeze-casting from alumina compounds containing varying proportions of water and tert-butyl alcohol, the formation of lamellar porous configurations led to a significant decrease in mechanical strength compared to other pore structures such as hexagonal or dendritic. Furthermore, differences in the volume fraction of frozen camphor and naphthalene crystals can lead to the formation of cracks or microcracks and the development of irregular wall density within the pores, which are further exacerbated during the sintering stage. This process can result in a reduction of the compressive strength of the porous ceramic produced under eutectic conditions.¹³⁸ It is also observed that, for the eutectic

composition, monoliths sintered for 1 h exhibited lower compressive strength compared to those sintered for longer periods. This outcome may be attributed to the higher total porosity in their structure, which adversely affects the manifestation of this mechanical property.

A clear trend can also be observed for the monoliths produced using the binary solvent with a hypereutectic composition. As previously discussed, increasing the sintering time led to a higher fraction of closed pores and a decrease in open porosity in the ceramics. This behavior had a direct impact on the compressive strength of this system. The increase in sintering time and its effects on porosity resulted in a gradual improvement in the compressive mechanical strength of the monoliths, due to the progressive densification of the material. Densification, evidenced by the formation of necks and growth of α -Al₂O₃ particles, facilitated a more uniform distribution of the applied load throughout the ceramic structure, enhancing the material's strength. However, as previously noted in this study, Hypo_3H exhibited anomalous behavior compared to the other compositions. Defects observed via microtomography may have contributed to structural embrittlement, leading to an unexpected decrease in the strength of these monoliths.

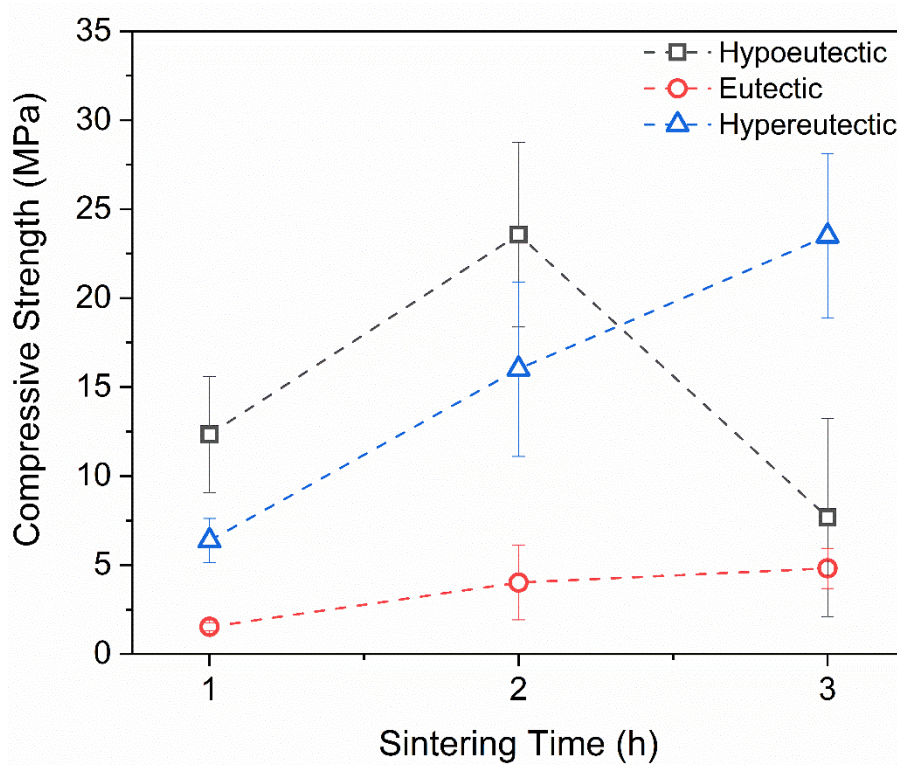


Figure 31. Compressive strength test results for samples produced via freeze-casting.

Table 13. Compressive strength values for samples produced via freeze-casting.

Composition	Sintering time (h)	Compressive strength (MPa)
Hypoeutectic	1	12.3 ± 3.3
	2	23.6 ± 5.2
	3	7.7 ± 5.6
Eutectic	1	1.5 ± 0.2
	2	4.0 ± 2.1
	3	4.8 ± 1.1
Hypereutectic	1	6.4 ± 1.2
	2	16.0 ± 4.9
	3	23.5 ± 4.6

The results reported in this study demonstrate that the properties of α -Al₂O₃ monoliths can be tailored based on the composition of the naphthalene-camphor solvent and the sintering time, allowing for a high versatility of applications of this material according to the required specifications. This outcome is further supported by the low toxicity of the binary solvent, enabling applications in diverse contexts and rendering this solvent highly promising.

Furthermore, it was observed that the solvent removal process can be accelerated by combining sublimation under ambient conditions with freeze-drying, whereas longer durations for the removal of the binary solvent (12 days), as proposed by Lacerda *et al.* (2018), could be avoided (in this study: 8 days).

However, it is important that the freeze-drying parameters are properly controlled to prevent potential damage to the green body structure caused by rapid solvent sublimation, which could be further exacerbated during the sintering stage.

Finally, a direct relationship between sintering time, solvent composition, and porosity is evident in this study, impacting the properties of the pores. As observed, longer sintering times generally resulted in grain growth, increased closed porosity, the formation of more isolated intergranular pores, and affected the tortuosity and permeability of the fabricated ceramic materials. Furthermore, the mechanical properties of the samples exhibit a clear trend, with the exception of Hypo_3H.

4.1.4. Surface Morphology and Porosity of α -Al₂O₃ Tubes

Considering the final goals of this study — which involve the production of gas separation membranes — the use of macroporous tubular supports is more advantageous

than that of planar (disc-shaped) ones.⁵⁸ The tubular geometry offers a higher surface area-to-volume ratio, enabling higher permeation rates for similar membrane modules.^{58,139,140} Furthermore, its fabrication through the freeze-casting process allows the formation of radially aligned pores in a concentric arrangement, which is particularly favorable for fluid permeation.^{58,139} From a mechanical standpoint, the cylindrical configuration ensures a uniform distribution of mechanical stresses, providing enhanced resistance to the pressure differential between the inner and outer tube surfaces.^{139,140} In contrast, planar supports are more susceptible to bending and fracture, especially under high pressures or thermal gradients. Additionally, the tubular design promotes laminar and well-controlled flow, reducing stagnation zones and facilitating membrane cleaning and regeneration. Therefore, based on the previous discussions concerning the optimization of monolith production through the freeze-casting process, one of the compositions was selected for use in the fabrication of single-channel α -alumina tubes.^{139,140}

The production of tubular supports via the freeze-casting process remains largely unexplored in the literature, and, to date, no studies have employed camphor-naphthalene as a solvent. Another critical aspect concerns the limited discussion on the deposition of microporous films onto the surface of tubular supports produced by freeze-casting. The formation of a uniform and active layer can be particularly challenging due to differences in the chemical nature of the substrate and selective layer materials, as well as the disparity in pore sizes between the substrate (> 50 nm) and the selective layer (< 2 nm). This often necessitates the deposition of multiple layers to obtain a homogeneous film with minimal defects.⁵⁸

The Hyper_2H composition exhibited noteworthy results, including a well-defined pore structure, high total (68.3%) and open (53.0%) porosity, low flow resistance, and the second-highest compressive strength among the samples investigated (16 MPa). These properties suggest that the Hyper_2H composition is a promising candidate for the fabrication of single-channel tubes via the freeze-casting process (Figure 32).

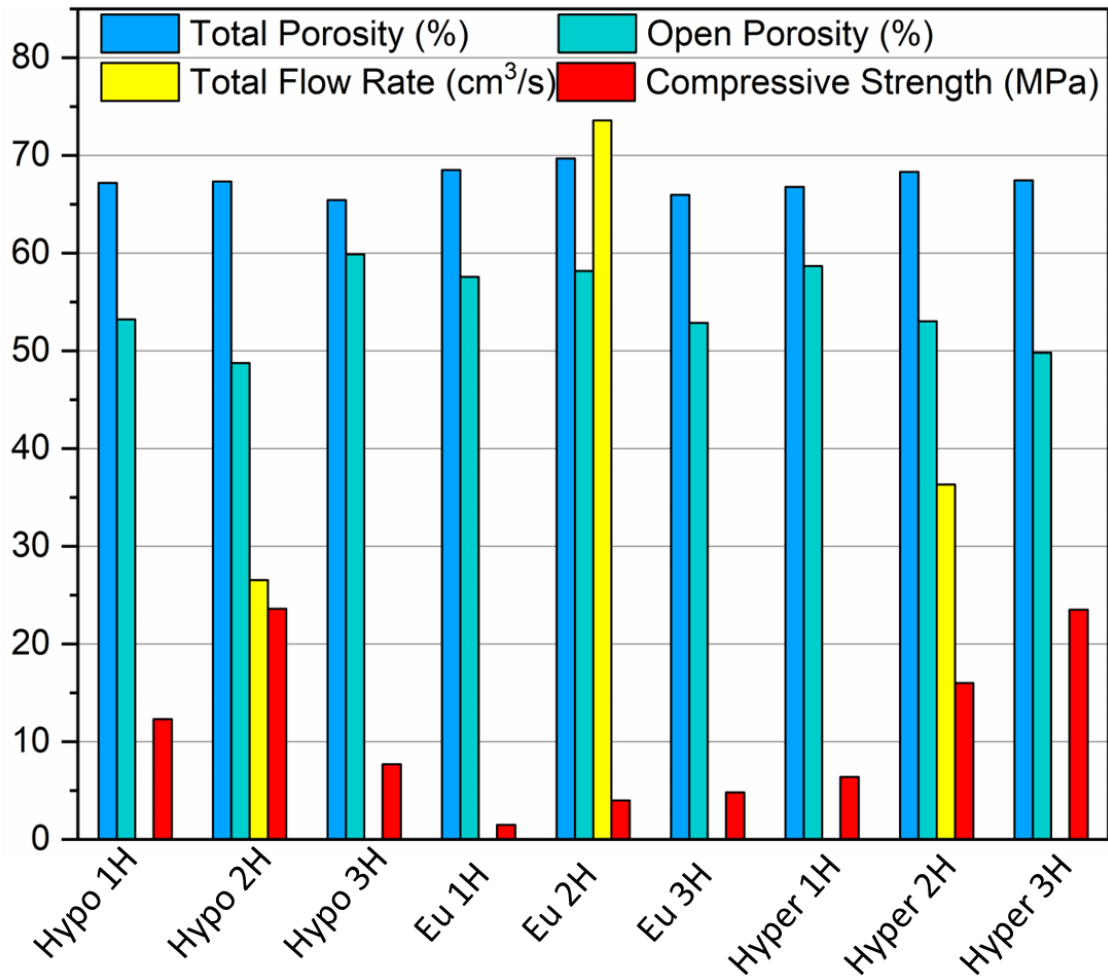


Figure 32. Graph of the overall properties of the compositions investigated for the production of ceramic monoliths.

Figure 33 shows images of the internal (a-b) and external (c-d) surfaces of the tubes produced using the Hyper_2H composition. The internal region, which comes into contact with the Technyl[®] mold release, exhibited high porosity compared to the external region, which is in contact with the copper surface. As in the monolith production process, the temperature gradient between the copper (-130 °C) and the Technyl[®] (25 °C) is high and, in this case, leads to a freezing front that moves from the external region to the internal region.^{55,125,141}

In this configuration, with a tube wall thinner than the monolith height and the copper support fully immersed in liquid nitrogen, the freezing time is drastically reduced to approximately 15 seconds. Consequently, the external surface freezes almost instantaneously, resulting in a denser layer characterized by randomly distributed porosity and smaller pores (Figure 33 c-d). This dense layer influences heat transfer between the metal cylinder, the suspension, and the Technyl[®], thereby reducing the freezing rate

throughout the material. As a result, solvent crystals tend to grow along the freezing direction, leading to increased porosity and larger pore sizes in the internal region.^{55,125,141}

From the standpoint of employing this type of tube as a membrane support, it is important to highlight that the pore formation mechanism facilitates the deposition of active films on its surface, particularly in the external region of the tube. The presence of smaller pores and controlled porosity in this region minimizes issues related to incrustation and incomplete coating. Since the pores are substantially larger than the kinetic diameters of the gases investigated in this study, this characteristic ensures that mass transfer along the support is not significantly impeded. Moreover, the gradient in pore size along the support favors the permeation process.

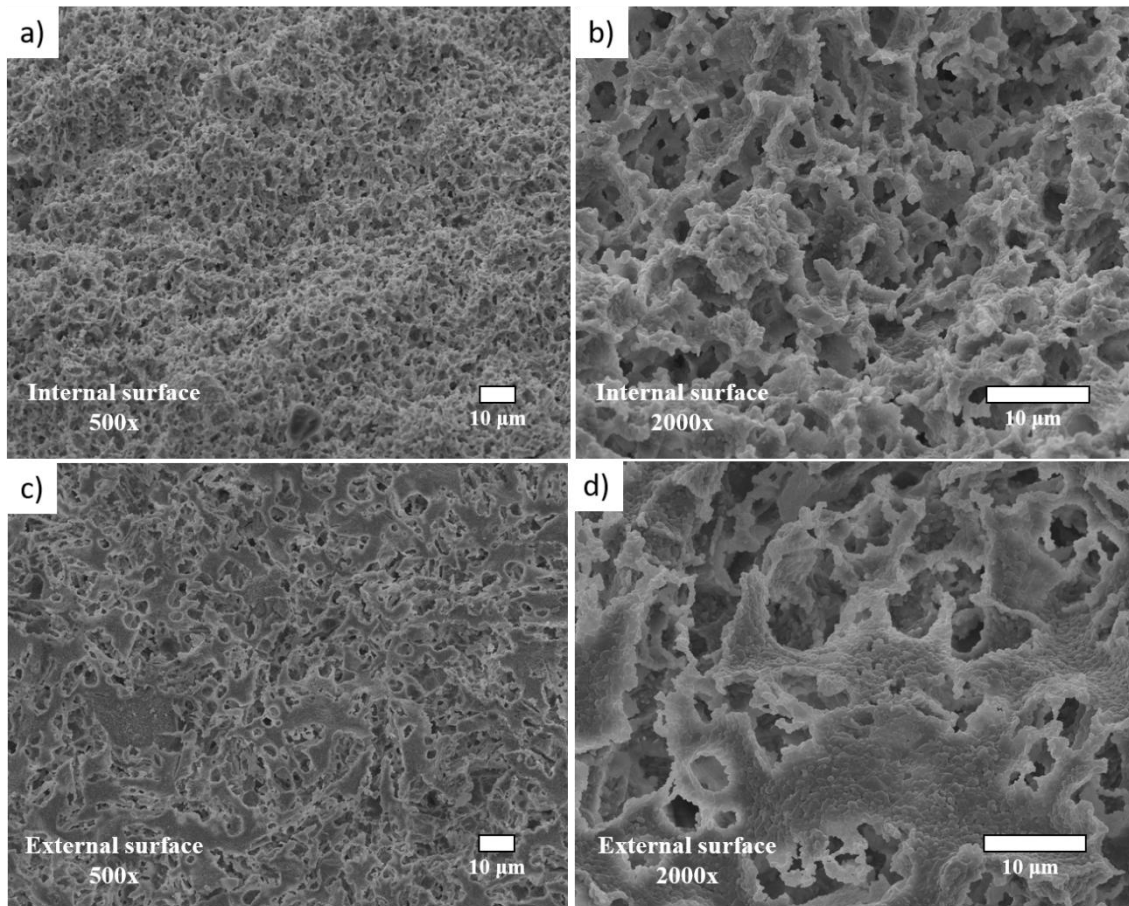


Figure 33. SEM micrographs of the internal (a–b) and external (c–d) surfaces of the tube fabricated using the Hyper_2H composition.

Figure 34 presents the grain size distribution (a) and a comparison of porosity values determined by the Archimedes' method for monoliths and tubes fabricated using the Hyper_2H composition. As shown in Figure 34(a), the average grain size of the tube was slightly larger than that of the monolith produced with the same composition,

increasing from 426 to 431 μm . Moreover, Figure 34(b) indicates that the tubes, analyzed in triplicate, exhibited an average decrease in total ($\downarrow 10.7\%$) and open ($\downarrow 25.5\%$) porosities, accompanied by a substantial increase in closed porosity ($\uparrow 29.1\%$).

The observed reduction in total and open porosities, accompanied by an increase in closed porosity and average grain size, can be attributed to the smaller wall thickness of the tube (~ 3.2 mm) compared with the height of the monolith (~ 11 mm). In this configuration, the freezing front travels a shorter distance, leading to the development of a denser three-dimensional microstructure. This occurs because the region in direct contact with the cooled metal surface exerts a stronger influence on the solidification dynamics than in the case of the thicker monolith. As previously discussed, this region marks the onset of nucleation and the directional propagation of the solidification front. At the initial stage, the solidification rate is very high, and suspended particles are rapidly engulfed by the advancing front. The limited time available for particle rejection and the strong local thermal gradient promote particle entrapment near the solid–liquid interface, resulting in the formation of a denser zone with reduced pore interconnectivity. Consequently, deviations from the ideal pore morphology expected in freeze-cast structures may occur.¹²¹

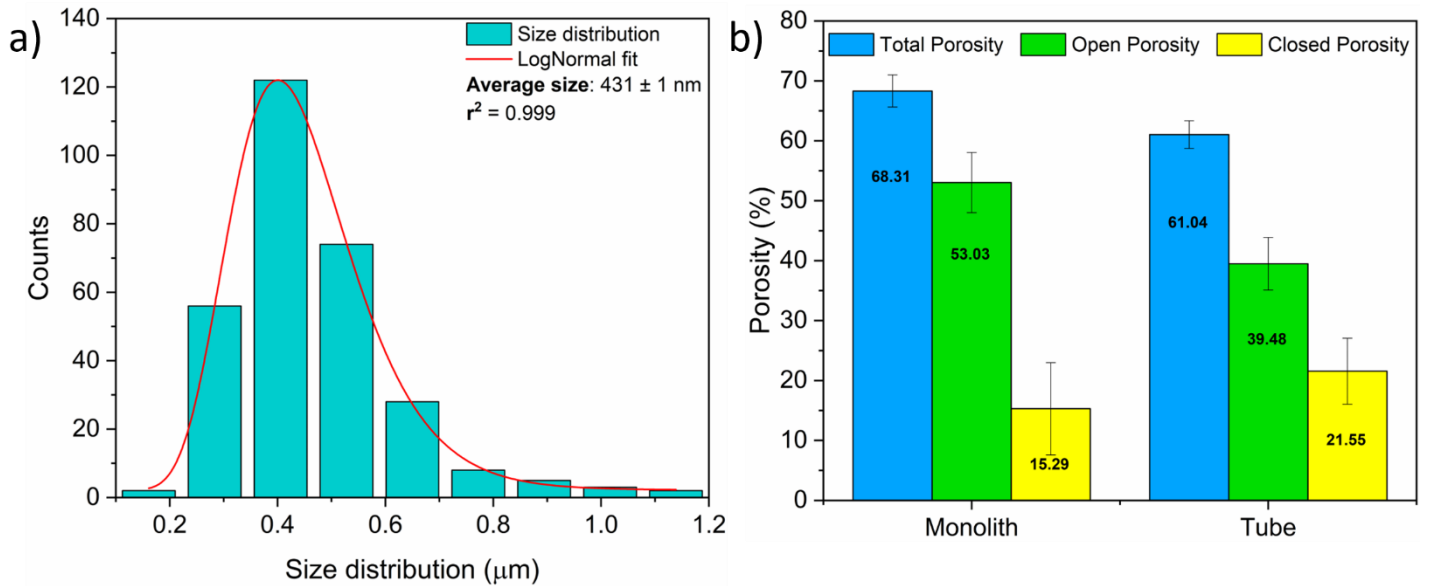


Figure 34. (a) Grain size distribution and (b) comparison of total, open, and closed porosities determined by the Archimedes' method for monoliths and tubes fabricated using the Hyper-2H composition.

It is important to emphasize that, during the tube formation process by the freeze-casting method using the proposed setup, the freezing front develops in two directions:

radially-concentrically and from the copper base upward. Consequently, the solidification proceeds bidirectionally. This may lead to the formation of cracks or defects at the tube ends; therefore, these regions are typically removed prior to the material's final application.

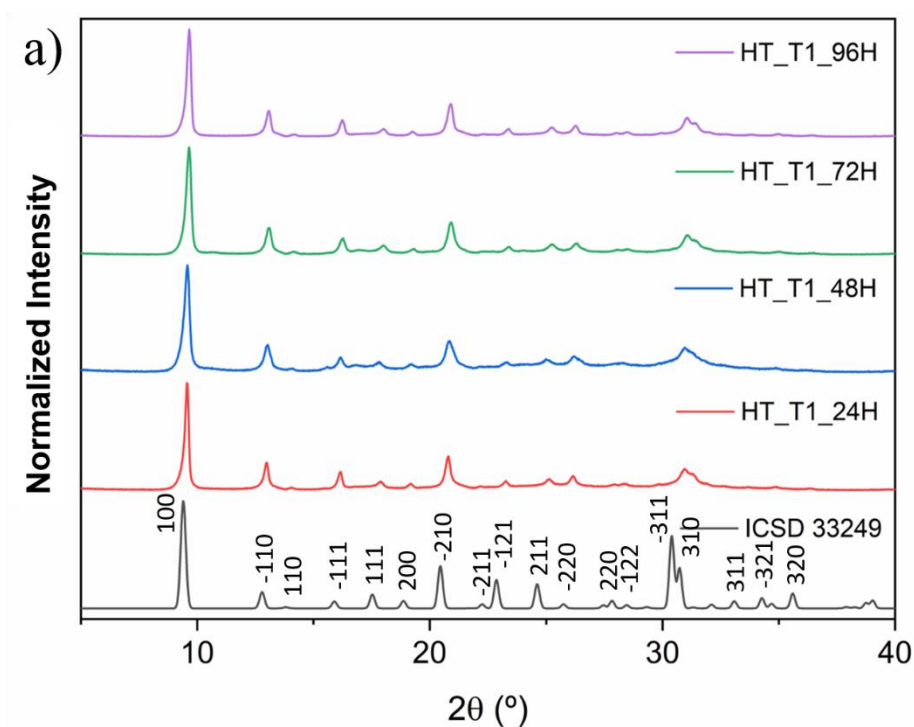
CHAPTER 5 - RESULTS ANALYSIS: SAPO-34

5.1. Hydrothermal Synthesis: Application of a Single Structure-Directing Agent

5.1.1. Microstructural Analysis

The X-ray diffraction patterns of the samples produced in this study are shown in Figure 35. For all crystalline samples, the main peaks are observed in the 2θ regions with the following approximate hkl indices: 9.6° (100); 13° (-110); 16.2° (-111); 17.9° (111); 19.2° (200); 20.8° (210); 23.3° (-121); 25.1° (211); 26.2° (-220); 31° (-311); and 31.3° (310). According to the signal profiles observed in Figures 35(a) and 35(b), it can be confirmed that both molar ratios adopted in this study were able to induce the formation of the chabazite (CHA) structure, characteristic of SAPO-34 zeolite, when compared to the ICSD 33249 chabazite structure standard.

All observed peaks can be attributed to the SAPO-34 zeolite structure, confirming that the syntheses were successful for most of the samples. Furthermore, X-ray diffraction did not reveal any impurities after the hydrothermal treatment and calcination steps.



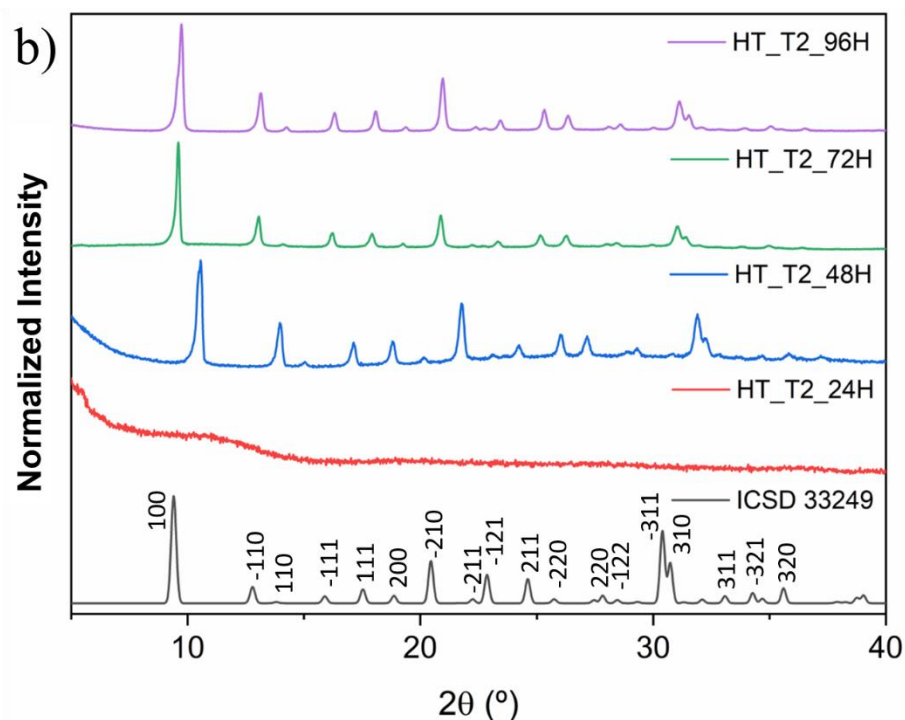


Figure 35. X-ray diffraction patterns (XRD) for samples synthesized via hydrothermal route at different times and with reaction molar ratios (a) T1 and (b) T2.

Figure 35 also illustrates that variations in the reactant ratio (T1 and T2) did not produce significant effects on the crystalline structure of the samples. Even with this change, it is evident that the growth direction or preferred orientation of the crystal structures occurred along the (100) plane. Furthermore, better peak definition and separation are observed at $2\theta = 31^\circ$ (-311) and 31.3° (310) for crystals produced via the T2 route. However, the peak intensities for samples with the T1 ratio were higher than those observed for T2, indicating a higher degree of crystallinity for T1 method. For instance, the T1 reactant ratio was able to form crystalline structures within the first 24 h of hydrothermal synthesis. In contrast, under T2 conditions, the presence of an amorphous fraction (silica) persisted up to the first 48 h of reaction, as evidenced by the significant baseline shift and peak position displacement typical of SAPO-34 (a 1° shift for HT_T2_48H). This indicates that increasing the proportion of Si and P sources, as well as the structure-directing agent, promoted a faster formation of the chabazite structure.

The observed difference can be attributed to a few factors. Firstly, the OSDA acts as a template for the formation of the cavities and channels of the SAPO-34 structure and also contributes as a mineralizing agent. The OH^- ion increases the pH of the medium, promoting favorable conditions for the dissolution of silica and alumina, thus providing an environment suitable for the polymerization and crystallization of the structure. The

higher presence of TEOH in T1 contributes to the formation of an environment capable of dissolving SiO₂ and Al₂O₃ precursors more rapidly, generating more building units (silicate, aluminate, phosphate) in solution or nucleation sites. Furthermore, the proportional increase in the silicon source to replace phosphorus atoms in the framework facilitates the substitution processes of aluminum and phosphorus, thereby also favoring the formation of the desired SAPO-34 structure. The low amount of silica in T2 may lead to a longer crystallization induction period.

Based on the diffractograms, the crystallite size (S_c) was calculated using the Scherrer equation (Equation 34), and the percentage of crystallinity was determined. The relative crystallinity (X_c) was evaluated using OriginPro® 2018 software for signal processing. The calculation was performed using the following equation:

$$X_c(\%) = \frac{\sum A_c}{A_T} \times 100 \% \quad \text{Equation 34}$$

in which A_c is the area of the crystalline diffraction peaks and A_T is the total area, including both the crystalline and amorphous regions of the samples. The results are presented in Table 14.¹⁴²

The crystallite size values for all samples ranged from 30 to 50 nm. These values are within the range commonly reported in the literature for syntheses via the hydrothermal route.¹⁴³ Overall, the crystallite sizes observed exhibits a tendency to increase with the enhancement of material crystallinity. The crystallinity percentage represents the fraction or degree of long-range crystalline order within the sample. The crystallite size, in turn, corresponds to the dimension of the smallest coherent domain that constitutes a particle, thereby reflecting the degree of structural ordering. Hence, higher crystallinity values promoted the formation of crystallites with more extended long-range order.¹⁴⁴

The crystallinity values, in general, show a clear trend of increasing with the progression of the crystallization process. Only the HT_T1_24H sample did not follow this trend, exhibiting crystallinity levels lower than those of HT_T1_96H, HT_T1_72H, and HT_T2_96H. Furthermore, as previously discussed and expected, the crystallinity values for samples produced via the T1 method (46.5–85.2%) were higher than those for samples produced via the T2 route (0-76.2%).

The increase in the material's degree of crystallinity is important, as it promotes the formation of better-structured and uniformly distributed pores throughout the crystal.

This advantage can enhance the diffusion rate and the separation efficiency of gas mixtures, such as N_2/CH_4 . In products with lower crystallinity, local defects may form due to alterations in the coordination number of tetrahedral sites, resulting in lower coordinations such as T-OH (free hydroxyls) or even higher coordinations (octahedral Al atoms). Local disturbances in the pore structure of the material can induce an increase in the size of the channels or cages surrounding the displaced sites, thereby reducing the free space in neighboring channels or cages.¹⁴⁵

Table 14. Crystallite sizes and crystalline fraction of SAPO-34 samples.

Sample	2 θ (°)	FWHM (°)	S _c (nm)	X _c (%)
HT_T1_24H	9.56	0.199	40.1	57.3
HT_T1_48H	9.58	0.278	28.7	48.9
HT_T1_72H	9.64	0.257	31.1	71.9
HT_T1_96H	9.66	0.224	35.7	85.2
HT_T2_24H	--	--	--	--
HT_T2_48H	10.56	0.265	30.1	39.5
HT_T2_72H	9.57	0.167	47.8	64.9
HT_T2_96H	9.56	0.161	49.6	76.2

In order to investigate the impact of each component varied between the T1 and T2 reactant ratios, six syntheses were performed by independently varying the molar ratio of the phosphorus and silicon sources, as well as the structure-directing agent. The diffractograms and crystallite property results for these products are shown in Figure 35 and Table 14.

Figure 36 shows that the excessive reduction in the amount of phosphorus source (1 Al₂O₃ : 0.8 P₂O₅ : 0.6 SiO₂ : 4 TEAOH : 150 H₂O) was not sufficient to induce the formation of SAPO-34, even after prolonged hydrothermal treatment (96 h). The diffraction pattern in this case was similar to that observed for sample HT_T2_24H. In contrast, the sample designated as 1.5 P exhibited a typical SAPO-34 pattern with good crystallinity (75.1%). However, in this latter case, a slight splitting of the peak located at 9.6° was observed. The phosphorus deficiency in the structure may be associated with the formation of stresses in the crystalline lattice, which can generate microdomains with distinct lattice parameters.

By only reducing the proportion of Si in the synthesis mixture (1 Al₂O₃ : 2 P₂O₅ : 0.3 SiO₂ : 4 TEAOH : 150 H₂O), a crystalline pattern compatible with that observed for the samples synthesized under the T2 condition was obtained. In this sense, the reduction

of the silicon source was sufficient to produce the chabazite phase, characteristic of the SAPO-34 zeolite. The crystalline fraction in this case was 63.7%, lower than those found for HT_T1_72H and HT_T2_72H under the same reaction times. The sample designated as 1.2 Si, in turn, exhibited broader peaks, indicating that the excess of Si may have caused strong lattice distortions and the formation of silicon-rich domains.

Although the 0.3 Si sample exhibited a satisfactory result, it is important to emphasize that decreasing the Si/Al ratio in the crystalline structure is not particularly desirable for applications aimed at gas separation. Higher Si/Al ratios tend to yield membranes with fewer defects and greater hydrothermal and chemical stability. Synthesis gels with low Si/Al ratios are more susceptible to the formation of impurities such as SAPO-5 (AFI-type) and SAPO-18 (AEI-type), which reduce the selectivity of SAPO-34 membranes by allowing the passage of gases with larger kinetic diameters.⁴¹ Furthermore, lower Si/Al ratios tend to make the zeolitic framework more hydrophilic. Consequently, the blockage of channels by water adsorption hinders the efficiency of the molecular sieving mechanism, which is crucial for N₂/CH₄ separation.^{13,146} Given the negligible quadrupole moment of CH₄ compared to N₂, variations in silicon content in SAPO-34 can differentially affect their adsorption behavior. While methane adsorption is only weakly influenced by framework composition, nitrogen adsorption is highly sensitive to the local electrostatic environment and the distribution of acidic sites, meaning that changes in Si incorporation do not necessarily lead to a decrease in N₂ adsorption enthalpy. Consequently, the impact of Si content on N₂/CH₄ separation in SAPO-34 depends on the balance between adsorption strength and diffusion kinetics.^{14,36}

The exclusive reduction in the amount of organic structure-directing agent (1 Al₂O₃ : 2 P₂O₅ : 0,6 SiO₂ : 2,8 TEAOH : 150 H₂O) led to an interesting crystallization behavior. Its diffraction pattern revealed the formation, in addition to the chabazite structure, of two new phases attributed to the AFI (SAPO-5) and AEI (SAPO-18) frameworks. However, the sample designated as 3.5 T exhibited a higher predominance of the SAPO-34 phase, although discrete peaks corresponding to the AEI phase were still observed.

SAPO-5 is formed by the incorporation of Si into the aluminophosphate AlPO₄-5 framework. Its structure consists of cylindrical channels composed of 12-membered rings with diameters of approximately 0.74 nm.⁹⁰ The evidence of its formation is primarily indicated by the appearance of a diffraction peak near 7.5°. ^{147,148}

SAPO-18, in turn, corresponds to the AEI-type phase, and its crystalline structure is closely related to that of the CHA framework, exhibiting the same framework density and similar three-dimensional pore systems. However, the cages present in the AEI and CHA structures differ in shape: the AEI cage has a basket-like form with a wider base compared to the CHA cage.¹⁴⁹ Its presence is primarily evidenced by the appearance of a diffraction peak near 10.5°, another at 16.5°, and three additional peaks in the region between 19° and 22°.¹⁵⁰

Thus, only the isolated variation of the Si source proved to be promising for the synthesis of the SAPO-34 zeolite, exhibiting a peak pattern similar to that observed in the syntheses carried out via the T2 route.

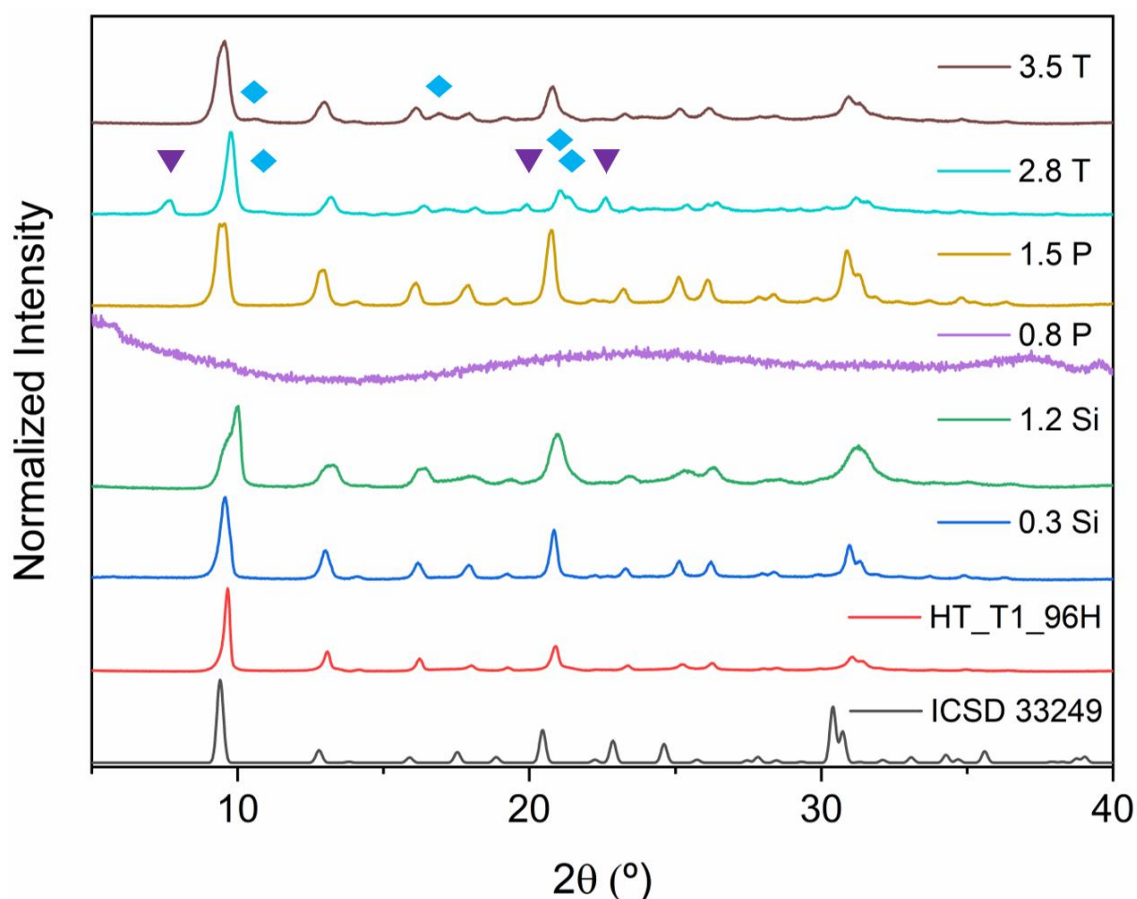


Figure 36. X-ray diffraction pattern for the single-component variation tests based on the T1 reaction ratio. The purple triangles indicate the main signals observed and attributed to the AFI phase (SAPO-5). The blue diamonds indicate the main signals observed and attributed to the AEI phase (SAPO-18).

Table 15. Crystallite sizes and crystalline fraction of modified SAPO-34 samples.

Sample	2 θ (°)	FWHM (°)	S _c (nm)	X _c (%)
3.5 T	9.49	0.315	25.3	56.6
2.8 T	MULTIPHASE	MULTIPHASE	MULTIPHASE	MULTIPHASE
1.5 P	9.48	0.315	25.3	75.1
0.8 P	AMORPHOUS	AMORPHOUS	AMORPHOUS	AMORPHOUS
1.2 Si	9.75	0.492	16.2	63.5
0.3 Si	9.58	0.216	36.8	69.9
HT_T1_96H	9.66	0.224	35.7	85.2

5.1.2. Analysis of SAPO-34 Zeolites by Fourier Transform Infrared Spectroscopy (FT-IR)

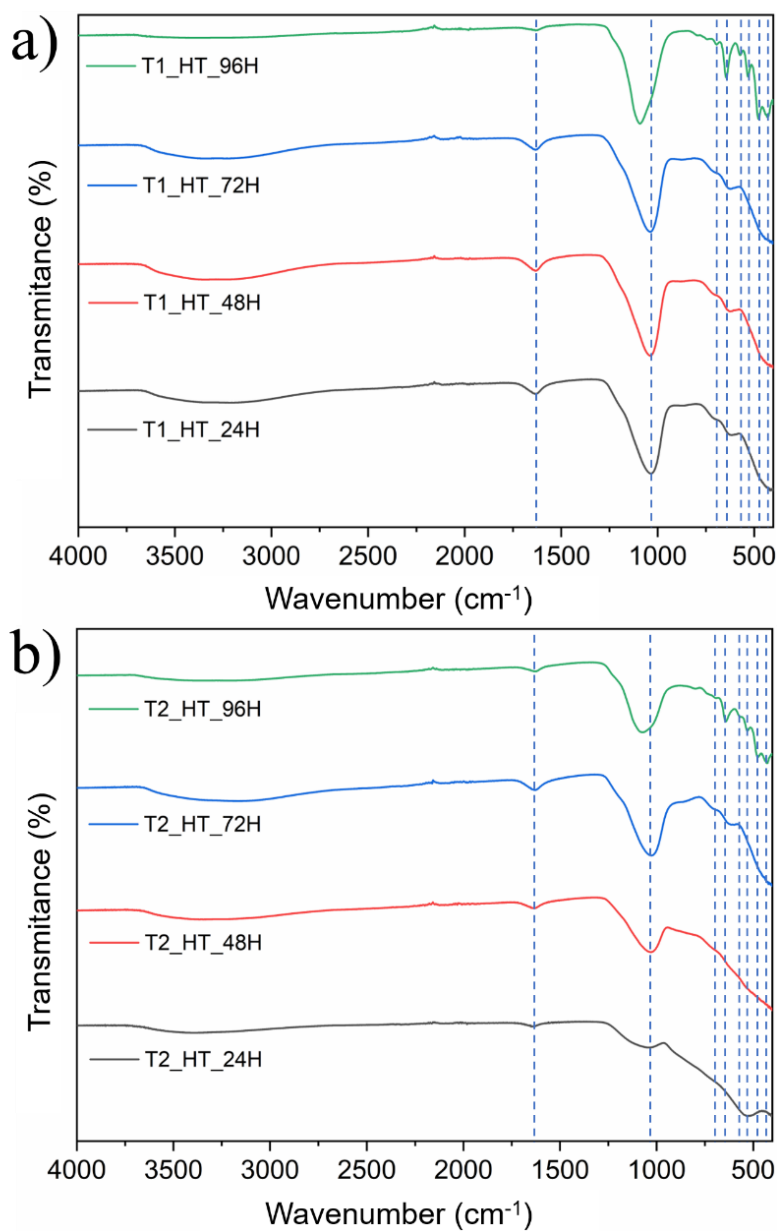
The FT-IR spectroscopy data of the synthesized samples are presented in Figure 37 and Table 16. In general, the crystalline samples exhibited spectra displaying the characteristic bands of SAPO-34, which are consistent with those reported in the literature.^{151,152}

All characteristic bands of the samples, shown in Figures 37(a) and (b), exhibit good correspondence with those reported in the literature. In the fingerprint region (400-1300 cm⁻¹), the bands observed at 490-574 cm⁻¹ and 638 cm⁻¹ are assigned, respectively, to the T-O bending vibrations of the AlO₄ | SiO₄ | PO₄ rings and to the bending of the D6R rings.¹⁵¹⁻¹⁵³ The latter one is of fundamental importance, as its presence provides strong evidence confirming the formation of the chabazite structure. Therefore, based on both X-ray diffraction and FT-IR results, all crystalline samples analyzed can be confirmed as forming the SAPO-34 phase.

The vibrational bands observed near 740 cm⁻¹ and 1280-980 cm⁻¹ are assigned, respectively, to the symmetric stretching of Si-O | P-O | Al-O and the asymmetric stretching of Si-O | Al-O | P-O. The band around 1640 cm⁻¹ corresponds to the bending vibration of water physically adsorbed on the surface of SAPO-34.¹⁵² In the 3000-4000 cm⁻¹ region, a broad stretching vibration band is observed, attributed to the bridging hydroxyl groups, Si-OH-Al, which are responsible for the Brønsted acidity of the SAPO-34 zeolite, and to the Al-OH, which confer Lewis acidity to the material.¹⁵¹⁻¹⁵³ Thus, the spectroscopic results once again confirm the formation of SAPO-34.

Moreover, it was observed that the samples with higher crystallinity exhibited better resolution of the characteristic bands of the material, particularly those in the 450-1300 cm⁻¹ range, even for the 1.5 P, 0.3 Si, and 3.5 T samples. According to Tan *et al.*

(2002) this is expected, as a higher presence of amorphous phase in the material leads to broadening of these bands.¹⁵⁴ Another important feature is the appearance of the band corresponding to the D6R rings (638 cm^{-1}), which was already observed within the first 24 hours for T1 and after 72 hours of synthesis for T2. As also seen in the XRD results, this further demonstrates that the T1 proportion promotes a faster formation rate of the desired zeolite. Additionally, slight shifts of the main band in the $1280\text{--}980\text{ cm}^{-1}$ range, corresponding to the asymmetric stretching of Si-O | Al-O | P-O, were observed toward higher frequencies in the HT_T1_96H and HT_T2_96H samples.



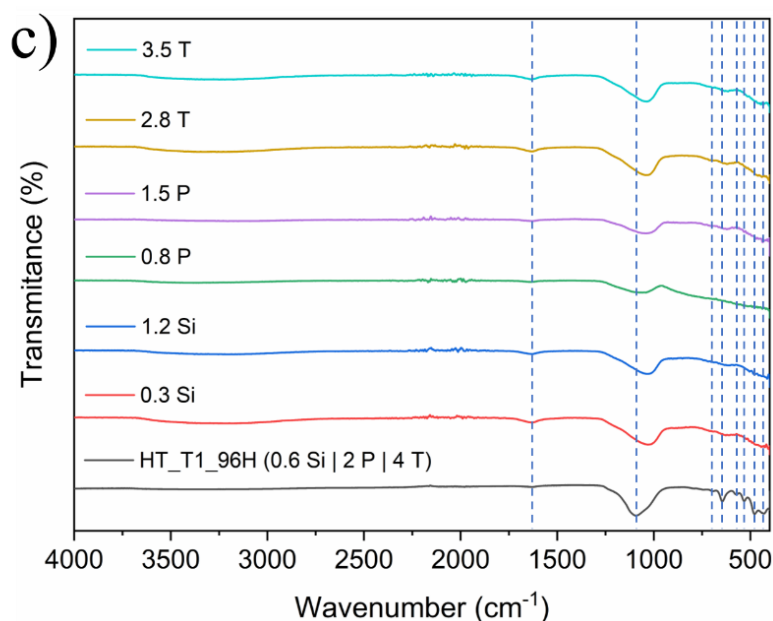


Figure 37. FT-IR spectra for samples synthesized via route (a) T1; (b) T2; and (c) varying P, Si and TEAOH.

Table 16. Vibrational modes observed via FT-IR spectroscopy.

Wavenumber (cm ⁻¹)	Vibrational Modes
475, 530 e 574	T-O bending (SiO ₄ AlO ₄ PO ₄ rings)
638	Bending of D-6 rings
740	Symmetric stretching of P-O Al-O Si-O
1280-980	Asymmetric stretching of P-O Al-O Si-O
1640	Bending of physically adsorbed water
3000-4000	Stretching of bridged hydroxyl groups (Si-OH-Al and T-OH)

5.1.3. Evaluation of Zeolitic Crystal Morphology by Scanning Electron Microscopy (SEM)

The scanning electron microscopy images of the samples produced via hydrothermal treatment with the T1 and T2 reaction proportions are shown in Figures 38 and 39, respectively.

In Figure 38, it can be observed that, for the 24-hour synthesis (Figure 38(a)), cubic structures typical of the SAPO-34 zeolite were formed.^{155,156} However, the image also shows the presence of circular and irregular structures surrounding some zeolitic crystals, indicating the presence of an amorphous phase. Another important feature is the clear visualization of crystals in the process of formation, as seen at the center of the image. The crystals appear to exhibit a medium to high size distribution.

Figures 38(b) and (c) show the materials formed after 48 h and 72 h of synthesis, respectively. Structures different from those observed at 24 h are evident, with smaller rhombohedral crystals predominating and exhibiting a thin, sheet-like appearance. Crystal growth is noticeable as the hydrothermal treatment time increases when comparing the results for 48 h and 72 h. Figure 38(c), in turn, shows that after 96 h of hydrothermal treatment, the crystals reached a more mature stage of growth, tending toward the formation of slightly larger, cubic structures. As observed, it is likely that longer synthesis times would lead to the formation of the cubic-structured crystals expected for SAPO-34.

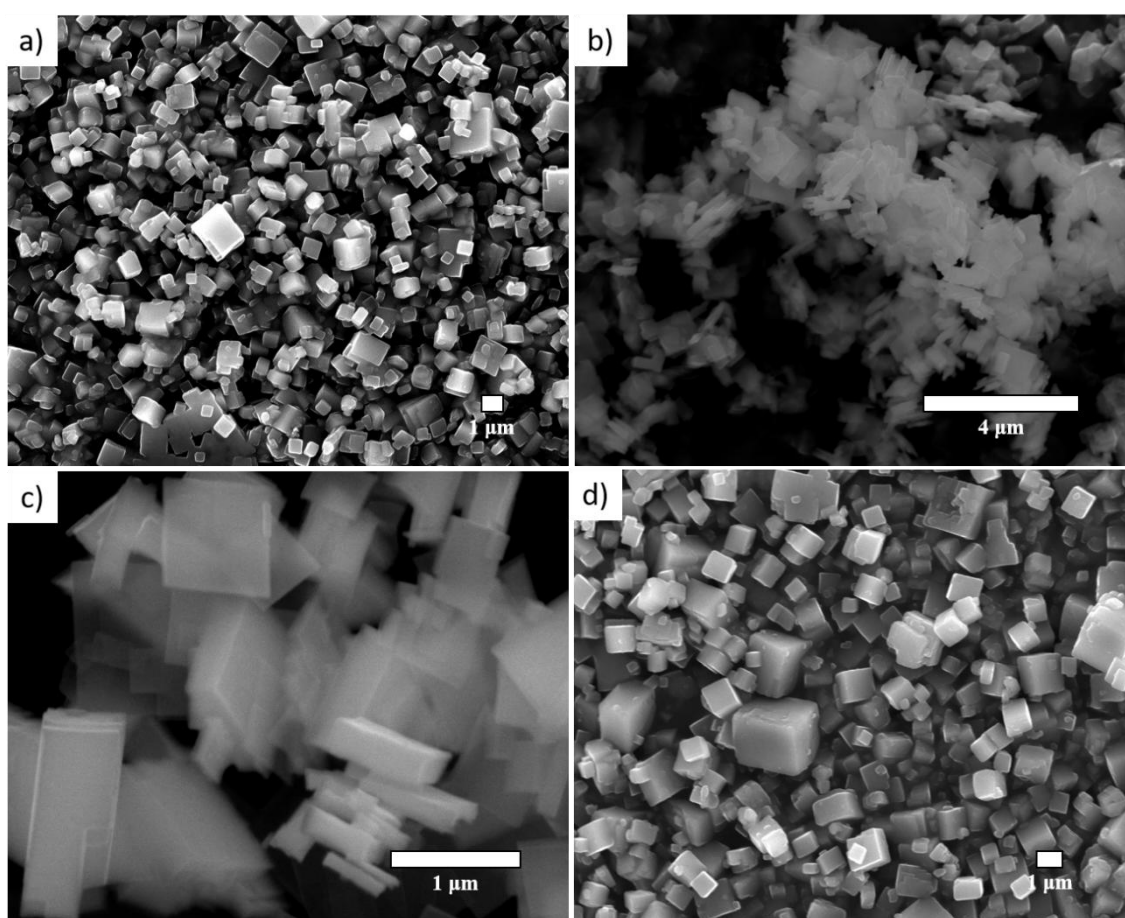


Figure 38. SEM images of samples produced from composition T1 and hydrothermal treatment of (a) 24h, (b) 48h, (c) 72h and (d) 96h.

In Figure 39(a), it can be observed that, for the 24-hour synthesis under the T2 composition, no structures typical of the SAPO-34 zeolite were formed, which is consistent with the results of previous characterizations. Only amorphous structures were present throughout the material. However, as the synthesis time increased to 48 h (Figure 39(b)), the initial formation of SAPO-34 zeolitic crystals was observed. In this case,

although amorphous regions still predominated around the few formed crystals, the expected rhombohedral structures of the material were already visible. From 72 h of synthesis onward, the zeolitic crystals became predominant over the amorphous material; however, as in the previous composition, a considerable dispersion in crystal size was observed for both 72 h and 96 h of synthesis. Additionally, it is noteworthy that, for HT_T2_96H, crystals growing on top of each other can be seen at the center and upper left of the image. Overall, when comparing T1 and T2, the latter favored the formation of larger zeolitic crystals than those observed for T1.

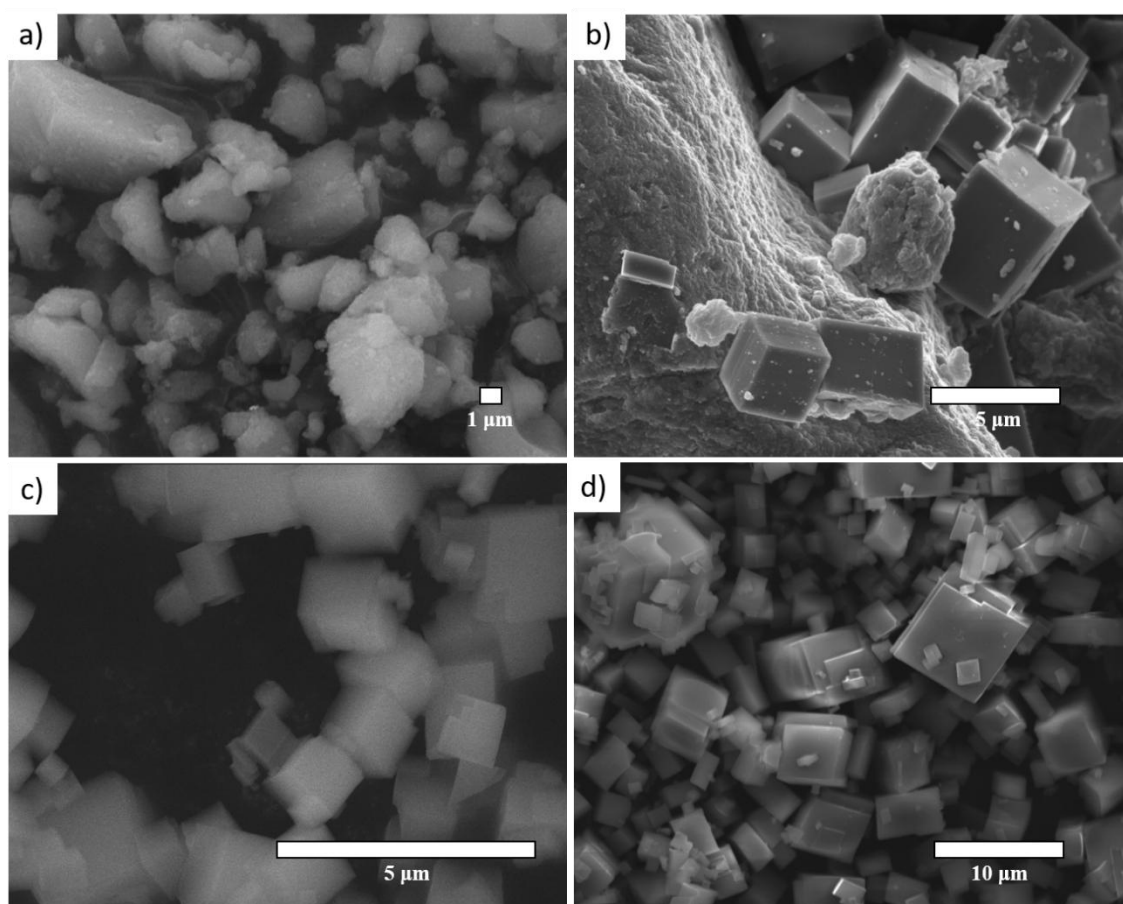


Figure 39. SEM images of samples produced from composition T2 and hydrothermal treatment of (a) 24h, (b) 48h, (c) 72h and (d) 96h.

Figures 40(a-d) show the crystals formed in the 0.3 Si, 2.8 T, 1.5 P, and 3.5 T syntheses. Considering that the samples with variations in phosphorus (0.8 P) and silicon (1.2 Si) resulted in the formation of more amorphous materials, their characterization by this technique was not performed.

Figure 40(a) shows the appearance of some rhombohedral structures throughout the formed material. However, as expected from the XRD analysis, even after 96 hours

of synthesis, the material still exhibits spherical structures, indicating a probable excess of silica or insufficient time for its consumption in this composition for SAPO-34 formation. Therefore, although the XRD pattern is consistent with the formation of SAPO-34, it is evident that a reduction in the SiO_2 proportion or longer synthesis times would be necessary to achieve optimal crystallization of the structures. Thus, this reaction composition was once again less efficient than those initially proposed (T1 and T2).

Figure 40(b), in turn, highlights the presence of a mixture of morphologies/phases throughout the sample, as expected from the XRD analyses. The AEI phase (SAPO-18) can be identified by the presence of small elongated structures in the material, while the AFI phase (SAPO-5) is indicated by the presence of irregular hexagonal structures.^{90,148,157}

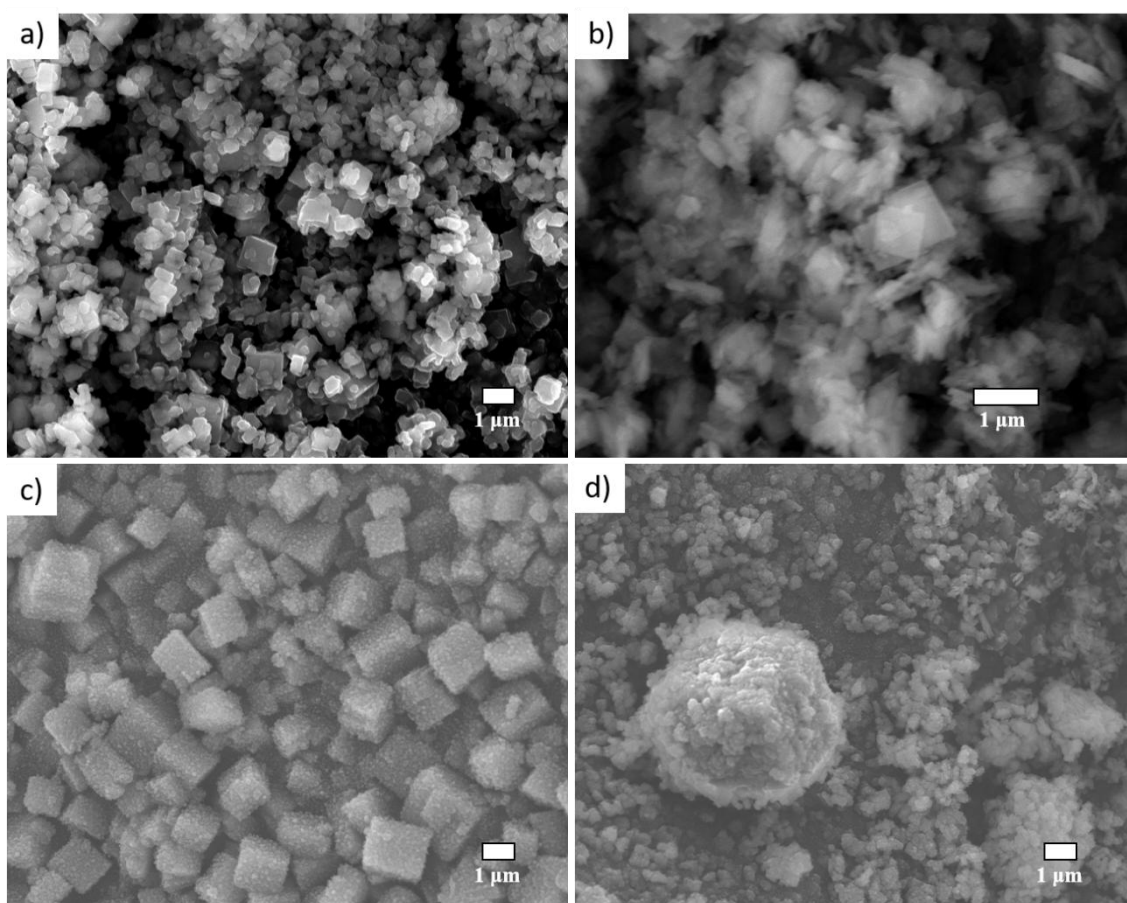


Figure 40. Images of samples (a) 0.3 Si, (b) 2.8 T, (c) 1.5 P and (d) 3.5 R.

In order to investigate the variation in crystal sizes for the HT_T1 and HT_T2 samples, size distribution curves were constructed using Sturges' rule, based on the SEM images collected, with the support of ImageJ[®] and OriginPro[®] 2018 software. A total of

400 particles were counted for each sample as the standard. The results are presented in Figure 41 and Table 17.

For the T1 composition, it was observed that, in general, the formation of smaller crystals was favored, with a clear tendency for their growth from 48 hours of hydrothermal treatment onward. The crystal sizes ranged from $0.81 \pm 0.03 \mu\text{m}$ (HT_T1_48H) to $2.29 \pm 0.02 \mu\text{m}$ (HT_T1_96H). The size distribution was relatively broad for all samples, being widest for the sample produced at 72 h and narrowest for the one produced at 96 h.

The T2 composition, in turn, exhibited a tendency for crystal growth starting from 72 hours of synthesis. Although HT_T2_48H showed larger values than the 72-hour sample, it is important to note that this sample contained a high proportion of amorphous regions, allowing the counting of only 105 particles. From 72 hours onward, the crystalline structure predominated in the samples, enabling the production of more reliable data. Overall, the T2 composition favored the formation of larger crystals compared to those observed in T1. This could be a disadvantage for membrane applications, as larger crystals can lead to thicker membranes, thereby compromising the material's permeability.

These results are consistent with the findings from the X-ray diffraction analysis. As observed, increasing the molar ratio of OSDA and silica enhances the dissolution of precursor species and accelerates the nucleation stage. The formation of a larger number of nuclei causes the available precursors in the solution to be distributed among them, limiting the amount of material available for individual crystal growth. Consequently, the crystals have less opportunity to grow before the nutrient supply is depleted. Conversely, the reaction conditions in T2 promote the formation of fewer nuclei, which allows for more extensive crystal growth.

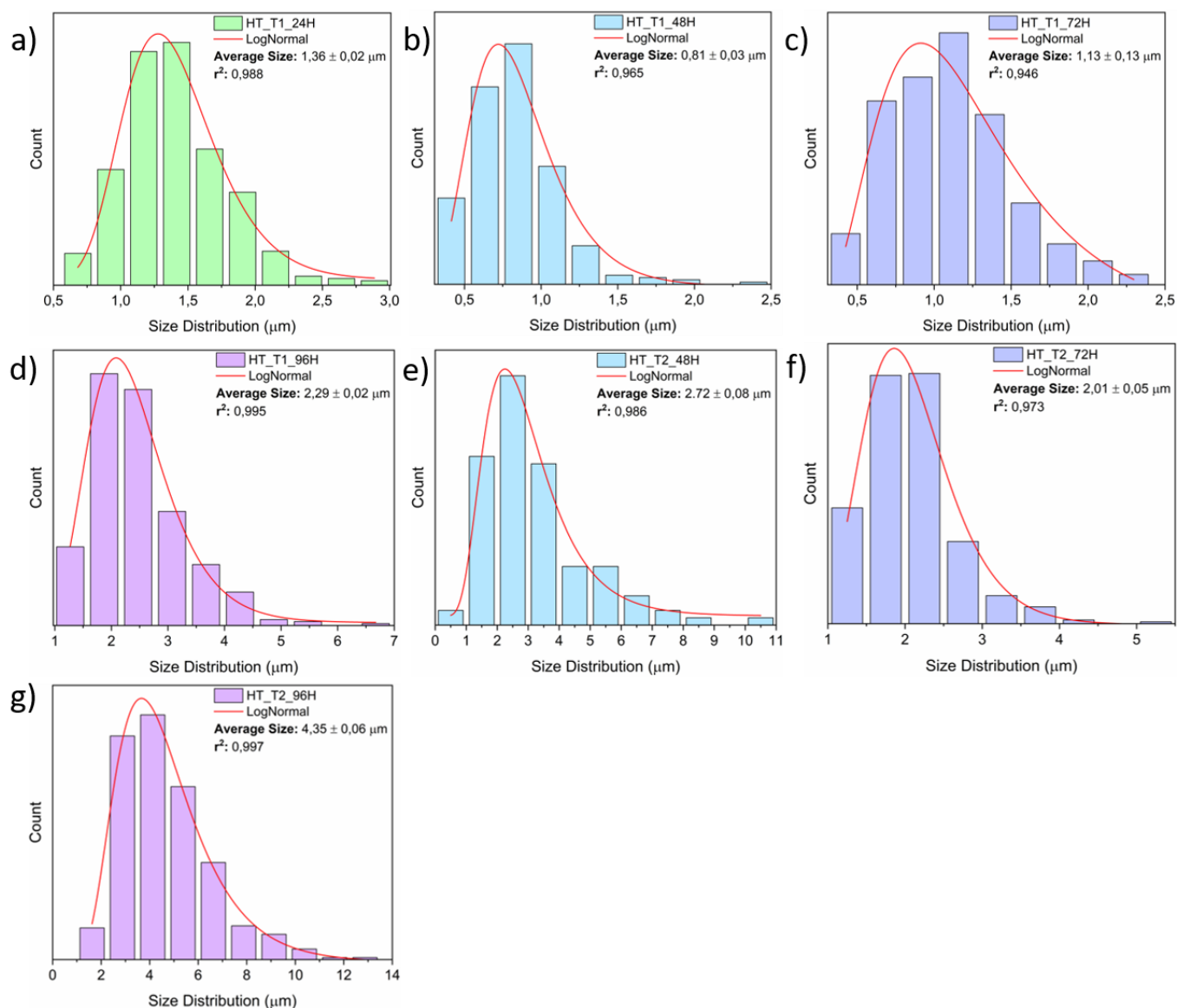


Figure 41. Crystal size distribution for samples synthesized by T1 (a-d) and T2 (e-f) methodologies.

Table 17. Size distribution for the samples HT_T1 and HT_T2.

Sample	Average size (μm)	r^2
HT_T1_24H	1.36 ± 0.02	0.988
HT_T1_48H	0.81 ± 0.03	0.965
HT_T1_72H	1.13 ± 0.13	0.946
HT_T1_96H	2.29 ± 0.02	0.995
HT_T2_24H	AMORPHOUS	AMORPHOUS
HT_T2_48H	2.72 ± 0.08	0.986
HT_T2_72H	2.01 ± 0.05	0.973
HT_T2_96H	4.35 ± 0.06	0.997

5.1.4. Elemental Mapping Analysis by Energy-Dispersive X-ray Spectroscopy (EDS)

Elemental analysis of the HT_T1 and HT_T2 samples was performed using the EDS technique. Although this method is sensitive only to the surface regions of the sample, it is capable of providing preliminary compositional information. The results are compiled in Table 18.

The processed EDS results indicate a clear trend of increasing Si incorporation into the SAPO-34 crystals as the crystallization time progresses. In the HT_T1 composition, for example, the observed Si/Al and Si/(Al+P+Si) ratios tend to reach their limits within the first 48 hours of reaction. Lower values were observed for the sample synthesized at 24 hours.

The HT_T2 composition, in turn, naturally exhibits lower theoretical values for these ratios, given the smaller fraction of silicon in the molar reaction proportion. Nevertheless, the trend of increasing Si/Al_{obs} and Si/(Al+P+Si)_{obs} ratios with longer crystallization times remains, showing higher values after 96 hours of synthesis.

Finally, the EDS results demonstrate that more Si is incorporated into the structure during the later stages of the crystallization process. Since the Brønsted acidity in SAPO-34 zeolite originates from the substitution of a P atom by a Si atom, a higher Si concentration may result in increased levels of Brønsted acidity. Additionally, the observed ratios exceeding the theoretically expected values could be attributed to instrumental errors inherent to the EDS technique.^{158,159}

Table 18. Compilation of data collected via EDS.

Sample	Si/Al _{gel}	Si/Al _{obs}	Si/(Al+P+Si) _{gel}	Si/(Al+P+Si) _{obs}
HT_T1_24H	0.30	0.18	0.090	0.08
HT_T1_48H	0.30	0.28	0.090	0.13
HT_T1_72H	0.30	0.26	0.090	0.12
HT_T1_96H	0.30	0.28	0.090	0.13
HT_T2_24H	0.15	---	0.075	---
HT_T2_48H	0.15	0.11	0.075	0.075
HT_T2_72H	0.15	0.14	0.075	0.068
HT_T2_96H	0.15	0.25	0.075	0.120

*obs = observed value in SAPO-34 crystals.

*gel = theoretical value expected in the composition of the synthesis gel.

5.1.5. Analysis by Solid-State NMR Spectroscopy

As previously discussed, this study has, to date, focused on the synthesis of SAPO-34 zeolite using two different primary molar compositions of the reaction gel. In this context, solid-state NMR spectroscopy was applied to investigate the effects of each composition on the chemical environments of Al, P, and Si in the synthesized samples. The results of the ^{27}Al , ^{29}Si , and ^{31}P analyses for the calcined HT_T1_96H and HT_T2_96H samples are shown in Figure 42.

The NMR spectra show that different compositions generated distinct chemical environments within the structures. In the HT_T1_96H sample, the solid-state ^{27}Al NMR signals (Figure 42(a)) are observed at 71.7, 39.3, 8.6, and -8.4 ppm. The small signal at -8.4 ppm corresponds to the presence of octahedral aluminum species (Al^{VI}), likely resulting from the coordination of two water molecules within the structure. This suggests that the octahedral Al may be a framework-associated species, related to tetrahedral Al coordinated with two water molecules. The peak at 8.6 ppm can be attributed to pentacoordinated aluminum (Al^{V}) arising from incomplete hydration. The signal at 39.3 ppm indicates a predominant presence of tetrahedrally coordinated aluminum (Al^{IV}), corresponding to that in the zeolitic framework — $[\text{Al}(\text{OP})_4]$.^{160–162} According to Zhang *et al.* (2015), the most downfield peak at 71.7 ppm may be assigned to the formation of a variant Al^{IV} in aluminosilicate domains, where Si is the nearest neighbor.¹⁶² These results indicate that a significant portion of aluminum was incorporated into the SAPO-34 structure under these conditions.

In the HT_T2_96H sample, the solid-state ^{27}Al NMR signals (Figure 42(d)) are observed at 75.4, 43.9, 15.6, -9.5, and -44.0 ppm. The small signal at -9.5 ppm corresponds to the presence of Al^{VI} species. The peak at 15.6 ppm can be attributed to pentacoordinated aluminum interacting with a water molecule. The signal at 43.9 ppm indicates tetrahedrally coordinated aluminum (Al^{IV}) within the zeolitic framework.^{160–162} In this case, the Al^{IV} and Al^{VI} peaks exhibit similar intensities. The unexpected bands at 75.4 and -44.0 ppm again reveal the presence of distinct species in the material. These, combined with the high presence of Al^{VI} , may suggest that aluminum incorporation into the zeolitic framework was lower than that observed in the HT_T1_96H sample. The resonance signals between 16 and -10 ppm weaken with increasing Si content in the structure ($\text{T2} = 0.3 \text{ SiO}_2$; $\text{T1} = 0.6 \text{ SiO}_2$), indicating that interactions between tetrahedral Al species and water molecules are weakened.

The ^{31}P NMR spectra (Figures 42(b) and (e)) exhibit different behaviors for the two samples, revealing distinct chemical environments. For HT_T1_96H (Figure 42(b)), the signals at -9.2 and -51.1 ppm are attributed to spinning sidebands (artifacts). The central peak at -30.1 ppm is assigned to the $\text{P}(\text{OAl})_4$ species.¹⁶¹

The HT_T2_96H sample, in turn, exhibited a more complex ^{31}P NMR spectrum. Peaks are observed at 3.7, -6.6, -17.3, -24.5, -28.3, and -48.3 ppm. The central peaks at -28.3, -24.5, and -17.3 ppm are assigned, respectively, to $\text{P}(\text{OAl})_4$ species; distorted $\text{P}(\text{OAl})_4$ species (positions where bond angles deviate from the ideal 109.5°); and $\text{P}(\text{OAl})_x(\text{H}_2\text{O})_y$ species, with $x = 4 - y$, corresponding to phosphorus atoms in the framework coordinated with water.^{162–164} The peaks at 3.7, -6.6, and -48.3 ppm are considered spectral artifacts.

The ^{29}Si NMR spectra (Figures 42(c) and (f)) exhibit slightly different behaviors for the two samples. The ^{29}Si spectrum for the HT_T1_96H sample shows multiple signals, indicating highly complex silicon environments. The signals are located at -83.3, -90.8, -94.3, -99.5, -104.8, -109.5, -113.8, and -120.2 ppm. According to Wang *et al.* (2016), the low-intensity peak at -83.3 ppm, observed through deconvolution, likely arises from $\text{Si}(\text{OAl})_3(\text{OH})$ or $\text{Si}(\text{OAl})(\text{OSi})(\text{OH})_2$ species, resulting from the breaking of some Si-OH-Al bonds, disordered $\text{Si}(4\text{Al})$ linkages, or partially hydrated Si species located at Si domain boundaries. The peaks at -90.8, -94.3, -99.5, -104.8, and -109.5 ppm are assigned to $\text{Si}(4\text{Al})$, $\text{Si}(3\text{Al})$, $\text{Si}(2\text{Al})$, $\text{Si}(1\text{Al})$, and Si islands, $\text{Si}(0\text{Al})$, respectively. The signals at -113.8 and -120.2 ppm can be attributed to $\text{Si}(0\text{Al})$ species that are crystallographically distinct for the NMR equipment, although not necessarily structurally different (distorted).^{161,165}

The ^{29}Si NMR spectrum for the HT_T2_96H sample shows signals similar to those of the previous sample. The peak at -86.2 ppm is attributed to $\text{Si}(\text{OAl})_3(\text{OH})$ or $\text{Si}(\text{OAl})(\text{OSi})(\text{OH})_2$ species, resulting from the breaking of some Si-OH-Al bonds, disordered $\text{Si}(4\text{Al})$ linkages, or partially hydrated Si species located at Si domain boundaries. The peaks at -90.7, -95.1, -98.5, -104.6, and -110.1 ppm are assigned to $\text{Si}(4\text{Al})$, $\text{Si}(3\text{Al})$, $\text{Si}(2\text{Al})$, $\text{Si}(1\text{Al})$, and Si islands, $\text{Si}(0\text{Al})$, respectively. The signals at -115.8 and -123.8 ppm can be attributed to distorted $\text{Si}(0\text{Al})$ species.^{161,165}

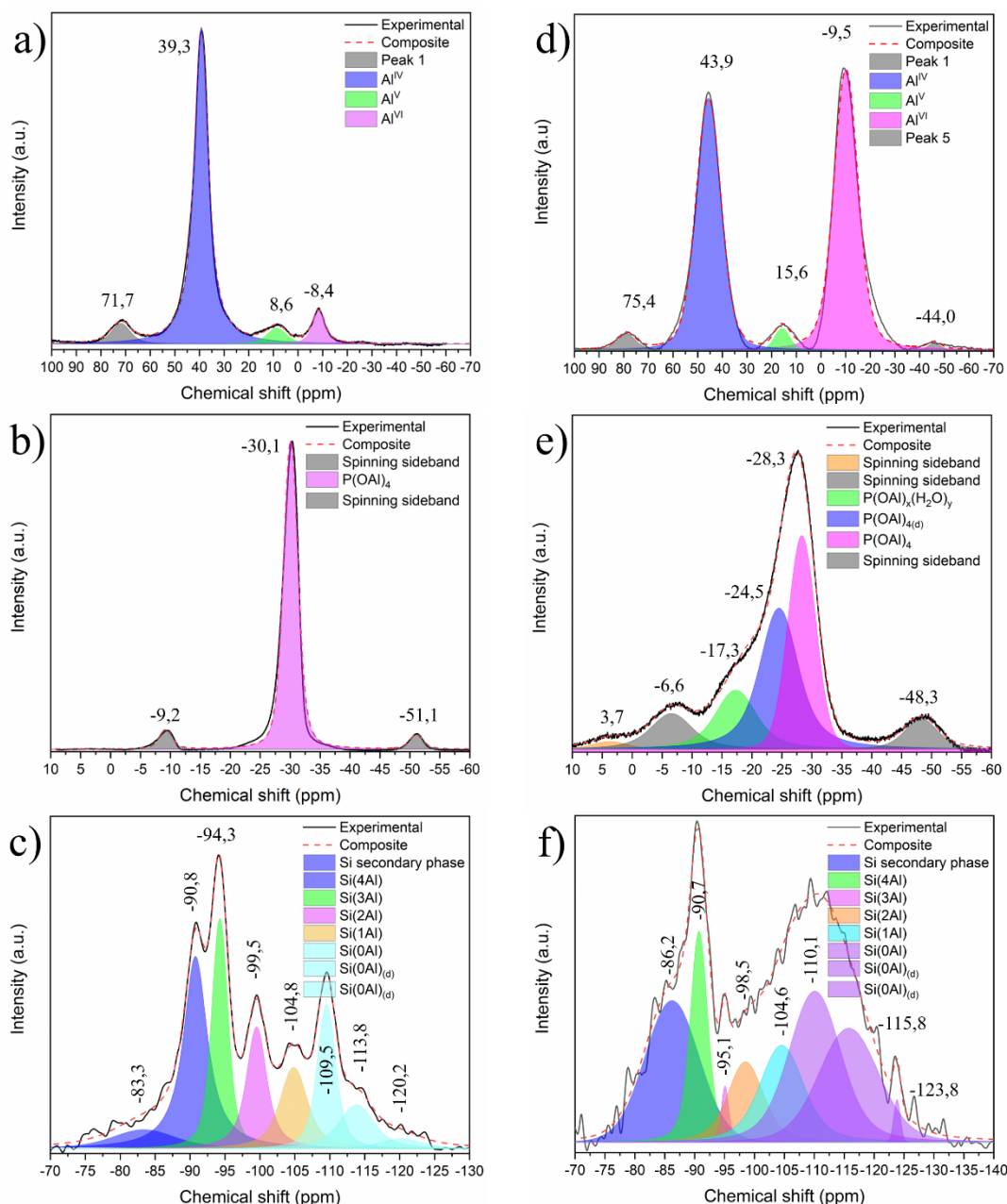


Figure 42. MAS-NMR spectra of ^{27}Al , ^{31}P and ^{29}Si for samples HT_T1_96H (a, b, c) and HT_T2_96H (d, e, f).

Based on the spectra shown in Figure 42, a quantitative analysis was performed to determine the percentage of the species identified in the samples. For this purpose, the following equation was used:

$$\% \text{ Species} = 100 * \frac{\text{Specie Area}}{\sum \text{Identified Species Area}} \quad \text{Equation 35}$$

The results can be seen in Figure 43 and Table 19. For the HT_T1_96H sample, the predominant species for ^{27}Al and ^{31}P are the expected Al^{IV} (87.7%) and $\text{P}(\text{OAl})_4$

(100%), indicating that their incorporation into the SAPO-34 framework was successful. The ^{29}Si analysis shows a high presence of Si(4Al) at 27.1%. Additionally, the other signals corresponding to Si(3Al), Si(2Al), Si(1Al), and Si(0Al) display similar percentages, ranging from 11.7 to 22%. This indicates that the SM2 and SM3 substitution mechanisms occur simultaneously during the formation of the SAPO-34 structure. However, the higher proportion of Si(4Al) species favors the presence of Brønsted acid sites.

In HT_T2_96H, it is observed that, for ^{27}Al , the expected groups Al^{IV} (40%) and Al^{VI} (47%) are present. This indicates a greater interaction of the material with water and, possibly, a higher degree of disorder in the zeolitic structure. This result can be associated with the lower Si/Al ratio used in this sample's composition. In the ^{31}P analysis, despite the appearance of new species, the distorted (35.1%) and undistorted (31.6%) $\text{P}(\text{OAl})_4$ species remain predominant. The ^{29}Si analysis again shows that the SM2 and SM3 substitution mechanisms occur simultaneously during the formation of the SAPO-34 structure. However, it is notable that Si islands exhibit a higher percentage compared to the other species.

Considering these results, it can be concluded that after 4 days of synthesis, the T1 composition exhibited better utilization of the aluminum (Alip), phosphorus (H_3PO_4), and silicon (SiO_2) sources. In this composition, the presence of undesired species in the ^{27}Al , ^{31}P , and ^{29}Si NMR analyses was significantly lower. In contrast, T2 showed substantial presence of new species for both ^{27}Al and ^{31}P . As previously discussed, this may indicate the formation of phases such as $\text{AlPO}_4\text{-n}$ alongside the SAPO-34 zeolite. Therefore, achieving optimal SAPO-34 formation under T2 conditions would likely require longer hydrothermal treatment to eliminate or significantly reduce these undesired phases. This process is important, as the presence of multiple phases can compromise the selectivity of membranes subsequently produced from this material.

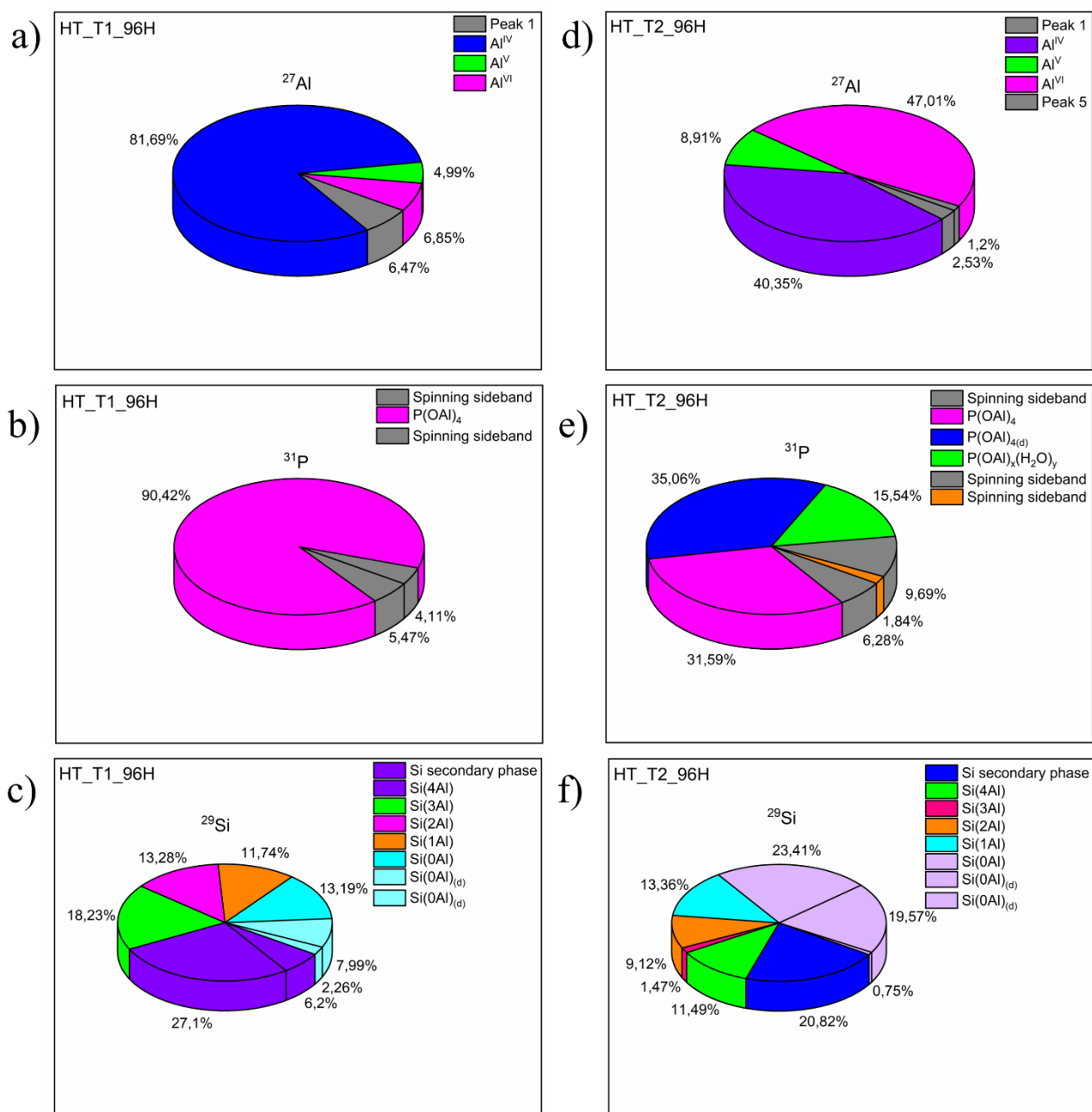


Figure 43. Percentages of species identified via MAS-NMR spectroscopy for the samples HT_T1_96H and HT_T2_96H.

Table 19. Quantitative analysis of the RAM-NMR spectra of ^{27}Al , ^{31}P and ^{29}Si for samples HT_T1_96H and HT_T2_96H. Side bands are highlighted in red.

HT_T1_96H				HT_T2_96H			
<i>Element</i>	δ (ppm)	<i>Peak Area (a.u)</i>	<i>Specie percentage (%)</i>	<i>Element</i>	δ (ppm)	<i>Peak Area (a.u)</i>	<i>Specie percentage (%)</i>
^{27}Al	71.7	1.13E+08	6.95	^{27}Al	75.4	5.45E+07	2.53
	39.3	1.43E+09	87.69		43.9	8.68E+08	40.35
	8.6	8.72E+07	5.36		15.6	1.92E+08	8.91
	-8.4	1.20E+08	7.35		-9.5	1.01E+09	47.01
	-	-	-		-44.0	2.58E+07	1.20
^{31}P	-	-	-	^{31}P	3.7	4.54E+06	0.75
	-9.2	2.95E+07	5.47		-6.6	2.38E+07	9.69
	-	-	-		-17.3	3.82E+07	15.54
	-30.1	4.88E+08	90.42		-24.5	8.63E+07	35.06
	-51.1	2.22E+07	4.11		-28.3	7.78E+07	31.59
	-	-	-		-48.2	1.55E+07	6.28
^{29}Si	-83.3	5.87E+06	6.20	^{29}Si	-86.2	1.20E+07	20.82
	-90.8	2.57E+07	27.10		-90.7	6.64E+06	11.49
	-94.3	1.73E+07	18.23		-95.1	8.49E+05	1.47
	-99.5	1.26E+07	13.28		-98.5	5.27E+06	9.12
	-104.8	1.11E+07	11.74		-104.6	7.72E+06	13.36
	-109.5	1.25E+07	13.19		-110.1	1.35E+07	23.41
	-113.8	7.57E+06	7.99		-115.8	1.13E+07	19.57
	-120.2	2.15E+06	2.26		-123.8	4.33E+05	0.75

5.1.6. Textural Analysis of SAPO-34 Zeolite

The nitrogen adsorption-desorption isotherms for the SAPO-34 samples synthesized via the HT_T1 methodology are shown in Figure 39. Overall, according to IUPAC classification, the obtained isotherms are Type I, characterized by a plateau that begins at low P/P_0 values, indicating complete filling of the micropores. This plateau is governed by the accessible micropore volume. When it occurs at significant volumes and very low P/P_0 levels, it indicates that adsorbate–adsorbent interactions take place within micropores of molecular dimensions. Thus, it is evident that the adsorption mechanisms occur in microporous solids, as expected for these samples.^{166,167} Furthermore, the absence of hysteresis in all samples produced with the T1 molar ratio indicates good homogeneity in pore size distribution.

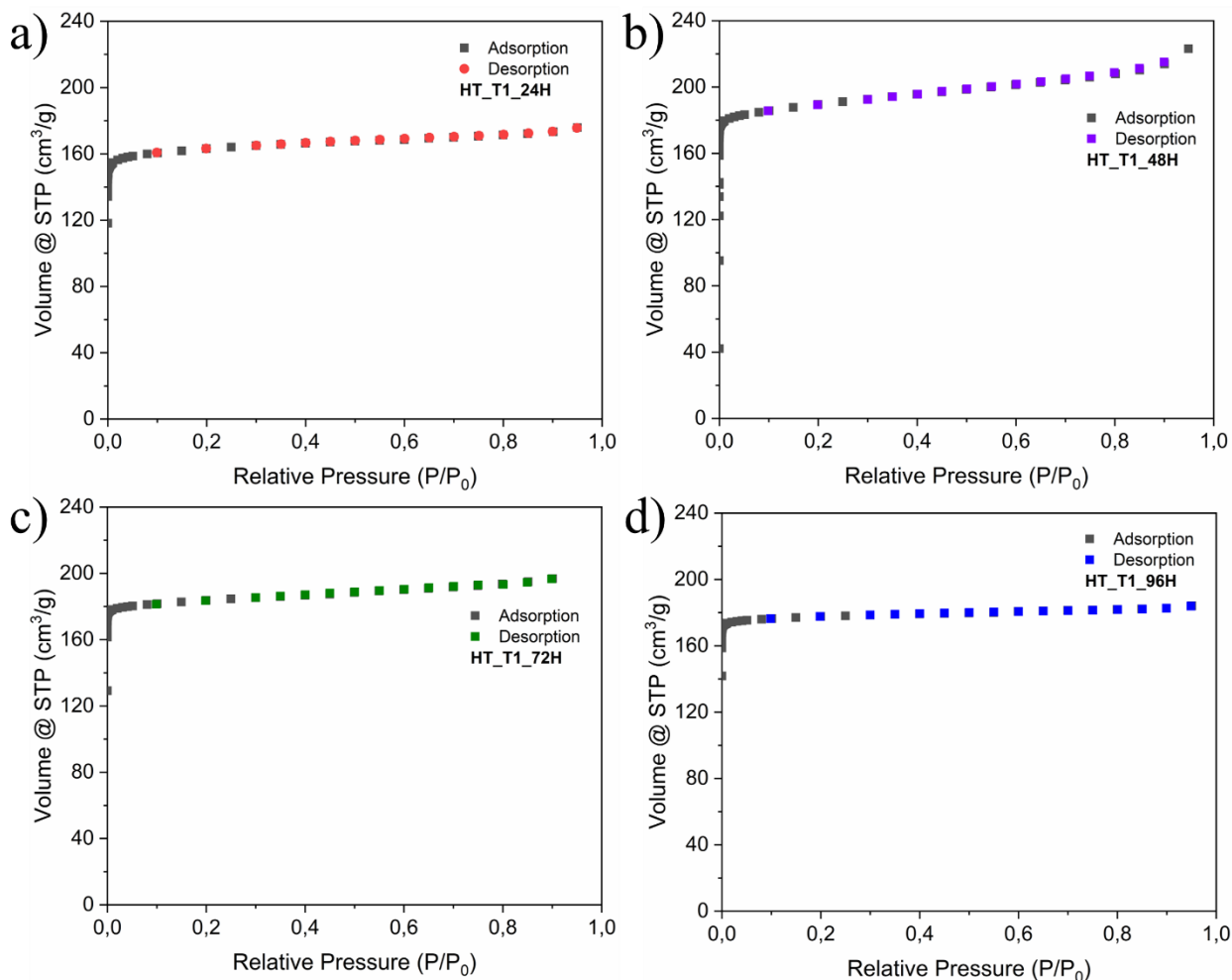


Figure 44. N₂ adsorption isotherms for samples produced via HT_T1.

For the samples synthesized via the HT_T2 methodology, the nitrogen adsorption–desorption isotherms can be seen in Figure 41.

Overall, according to IUPAC classification, the isotherms obtained for the HT_T2_24H and HT_T2_48H samples are a mix of Type I and Type IV(a) with H3-type hysteresis loops. Type IV isotherms are characteristic of mesoporous adsorbents (oxide gels, mesoporous molecular sieves, etc.). Adsorption behavior in mesopores is governed by both adsorbate-adsorbent interactions and interactions between molecules in the condensed state. In this case, the initial adsorption as a monolayer or multilayer on the mesopore walls is followed by capillary condensation. Capillary condensation is the phenomenon in which a gas condenses to a liquid-vapor critical phase within a pore at a pressure P lower than the saturation pressure P_0 of the bulk liquid. For a Type IV(a) isotherm, this capillary condensation is accompanied by hysteresis, which occurs when the pore width exceeds a certain critical width that depends on the adsorption system and

temperature.^{166,167} H3-loops are given by non-rigid aggregates of plate-like particles (e.g., certain clays) but also if the pore network consists of macropores which are not completely filled with pore condensate. This behavior further reinforces that, up to 48 hours of reaction, the T2 composition was not able to produce an effectively pure microporous material, likely due to microstructural deformations or the presence of amorphous phases in the material.^{36,165}

For the HT_T2_72H sample, a Type I isotherm is observed with a small H4-type hysteresis, typical of aggregated zeolitic crystals.^{36,165,168,169} This behavior indicates that significant microporous material formation occurs from 72 hours onward. The HT_T2_96H sample, in turn, again exhibits a Type I isotherm with a small H4-type hysteresis.

Considering these results, a comparison of the HT_T1 and HT_T2 isotherms shows that the T1 composition favored the formation of typical microporous structures without the hysteresis commonly observed in mesoporous materials. In contrast, HT_T2 exhibited such behavior in all tests, indicating the presence of mesoporosity in the material. Therefore, it can be inferred that longer hydrothermal treatment times would be necessary to eliminate impurities present in the T2 composition.

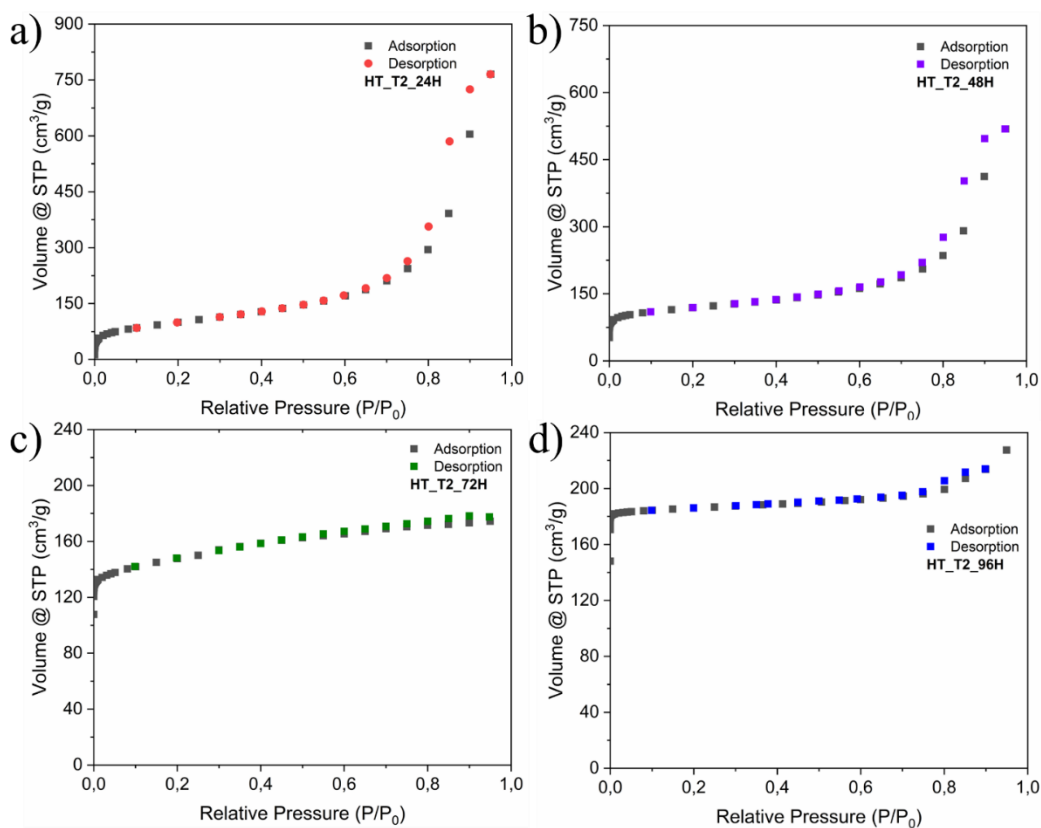


Figure 45. N₂ adsorption isotherms for samples produced via HT_T2.

The values of total surface area (S_{BET}), micropore area (S_{micro}), micropore volume (V_{micro}), external surface area (S_{ext}), and total pore volume (V_{T}) can be seen in Table 20. The graphs used to obtain these values are presented in Appendix section.

The results presented in Table 20 reveal that, on average, the samples synthesized via the HT_T1 route exhibited higher S_{BET} and S_{micro} values than those obtained via the HT_T2 route. However, at 96 hours, the HT_T2 sample was slightly superior in terms of micropore area ($754.7 \text{ m}^2/\text{g}$) and micropore volume ($0.275 \text{ cm}^3/\text{g}$), showing external surface area values similar to those observed for HT_T1_96H.

It is also noteworthy that the T1 composition reaches near-maximum values of S_{BET} , S_{micro} , and V_{micro} already within the first 24 hours of reaction. In contrast, the T2 composition exhibits a faster evolution of these parameters, indicating that longer synthesis times could produce materials with larger micropore areas and volumes than those observed for T1. However, as discussed previously, HT_T2_96H showed larger crystal sizes than those observed for T1. Therefore, extended crystallization times could lead to further crystal growth, compromising the direct formation of thin membranes. Nevertheless, with longer synthesis times, the material produced via HT_T2 could be promising as a seed, promoting faster crystallization in future syntheses.

Table 20. Textural properties calculated via BET method and t-plot of materials synthesized via hydrothermal route.

Sample	$S_{\text{BET}}^{\text{a}}$ (m^2/g)	$S_{\text{micro}}^{\text{b}}$ (m^2/g)	$S_{\text{ext}}^{\text{b}}$ (m^2/g)	$V_{\text{micro}}^{\text{b}}$ (cm^3/g)	$V_{\text{meso}}^{\text{c}}$ (cm^3/g)	V_{total} (cm^3/g)
HT_T1_24H	668.2	631.4	36.8	0.237	0.047	0.269
HT_T1_48H	776.0	706.6	69.3	0.264	0.076	0.332
HT_T1_72H	769.8	734.1	35.6	0.269	0.038	0.302
HT_T1_96H	749.7	732.5	17.1	0.268	0.023	0.283
HT_T2_24H	352.4	0	352.4	0	0.937	0.937
HT_T2_48H	434.2	225.3	208.9	0.093	0.556	0.639
HT_T2_72H	574.4	458.0	116.3	0.179	0.098	0.268
HT_T2_96H	786.1	754.7	31.3	0.275	0.059	0.331

Surface area $^{\text{a}}\text{BET}$; $^{\text{b}}S_{\text{micro}}$ (microporous area), S_{ext} (external surface area) e V_{micro} (microporous volume) determined by t-plot method. $^{\text{c}}V_{\text{meso}}$ (mesoporous volume) = $V_{\text{total}} - V_{\text{micro}}$; V_{total} determined by the penultimate adsorption point (P/P_0).

The samples produced by individually varying the molar amounts of P, Si, and structure-directing agent (based on the T1 methodology) were also subjected to nitrogen gas adsorption analyses. The results can be seen in Figure 42.

Overall, according to IUPAC classification, the isotherms obtained for the samples with a higher presence of amorphous phase (0.8 P, 2.8 T, and 3.5 T) are Type IV(a) with H3-type hysteresis. As previously mentioned, Type IV hysteresis is characteristic of mesoporous adsorbents. These results reinforce that the excessive reduction of phosphorus and structure-directing agent in the synthesis gel composition negatively impacted the formation of SAPO-34. The other samples (1.5 P, 0.3 Si, and 1.2 Si), however, exhibited isotherms typical of microporous materials.

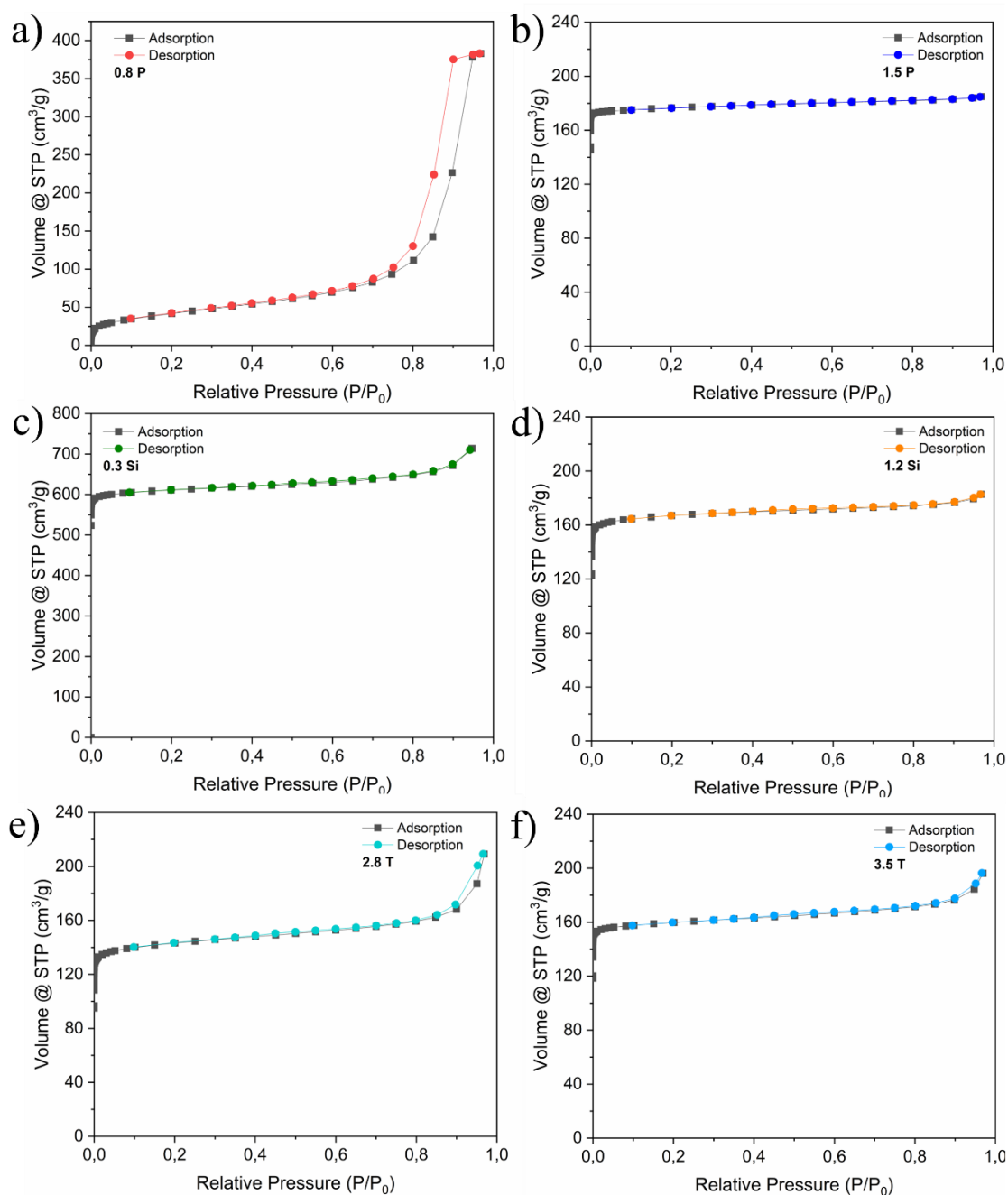


Figure 46. N₂ adsorption isotherms for samples which were produced changing the molar ratios of P, Si and organic-structure directing agent.

The values of total surface area (S_{BET}), micropore area (S_{micro}), micropore volume (V_{micro}), external surface area (S_{ext}), and total pore volume (V_{T}) can be found in Table 21. The graphs used to obtain these values are presented in the Appendix section. The results reveal that, on average, the synthesized samples exhibited good microporosity, with the exception of the 0.8 P sample. The 0.3 Si sample exhibited surface area and pore volume values that deviate from the trends observed for the other samples. This behavior may be partly attributed to the smaller particle size of this material.¹⁷⁰

Table 21. Textural properties calculated via BET method and t-plot of materials synthesized changing the molar ratios of P, Si and organic-structure directing agent.

Sample	$S_{\text{BET}}^{\text{a}}$ (m ² /g)	$S_{\text{micro}}^{\text{b}}$ (m ² /g)	$S_{\text{ext}}^{\text{b}}$ (m ² /g)	$V_{\text{micro}}^{\text{b}}$ (cm ³ /g)	$V_{\text{meso}}^{\text{c}}$ (cm ³ /g)	V_{total} (cm ³ /g)
0.8 P	139.5	0	139.5	0	0.587	0.587
1.5 P	746.7	718.0	28.7	0.259	0.026	0.285
0.3 Si	2551.9	2422.1	129.8	0.880	0.162	1.042
1.2 Si	683.9	645.2	38.7	0.239	0.039	0.278
2.8 T	576.5	509.1	67.4	0.187	0.103	0.290
3.5 T	662.3	614.4	47.9	0.223	0.063	0.286

Surface area ^aBET; ^b S_{micro} (microporous area), S_{ext} (external surface area) e V_{micro} (microporous volume) determined by t-plot method. ^c V_{meso} (mesoporous volume) = $V_{\text{total}} - V_{\text{micro}}$; V_{total} determined by the penultimate adsorption point (P/P_0).

5.2. Hydrothermal Synthesis: Application of a Dual Structure-Directing Agent

5.2.1. Microstructural Analysis

The X-ray diffraction patterns of the samples synthesized using the structure-directing agent mixtures MOR/TEAOH and DPA/TEAOH are presented below (Figure 47). By comparing the diffraction signals of the samples with the standard reference data from the ICSD database, it was observed that all results exhibited diffraction patterns characteristic of the chabazite structure corresponding to the SAPO-34 zeolite. The main diffraction peaks were identified in the 2θ regions and corresponding hkl indices at approximately: 9.6° (100); 13° (-110); 16.2° (-111); 17.9° (111); 19.2° (200); 20.8° (210); 23.3° (-121); 25.1° (211); 26.2° (-220); 31° (-311); and 31.3° (310).¹⁴⁷

All observed peaks can be attributed to the SAPO-34 zeolite structure, confirming that the syntheses were successful for most of the samples. Furthermore, X-ray diffraction analysis revealed no detectable impurities after the hydrothermal treatment and calcination steps.

Figure 47 also demonstrates that variations in the composition of the structure-directing agents used had significant effects on the crystallinity of the samples. Despite these changes, the preferential orientation of crystal growth occurred along the (100) plane, being more pronounced in the samples synthesized with the MOR/TEAOH mixture. Moreover, the molar increase in the MOR/TEAOH ratio led to an enhancement in peak intensities, evidencing greater unit cell symmetry and indicating a promotion of the SAPO-34 formation processes (nucleation and crystal growth).

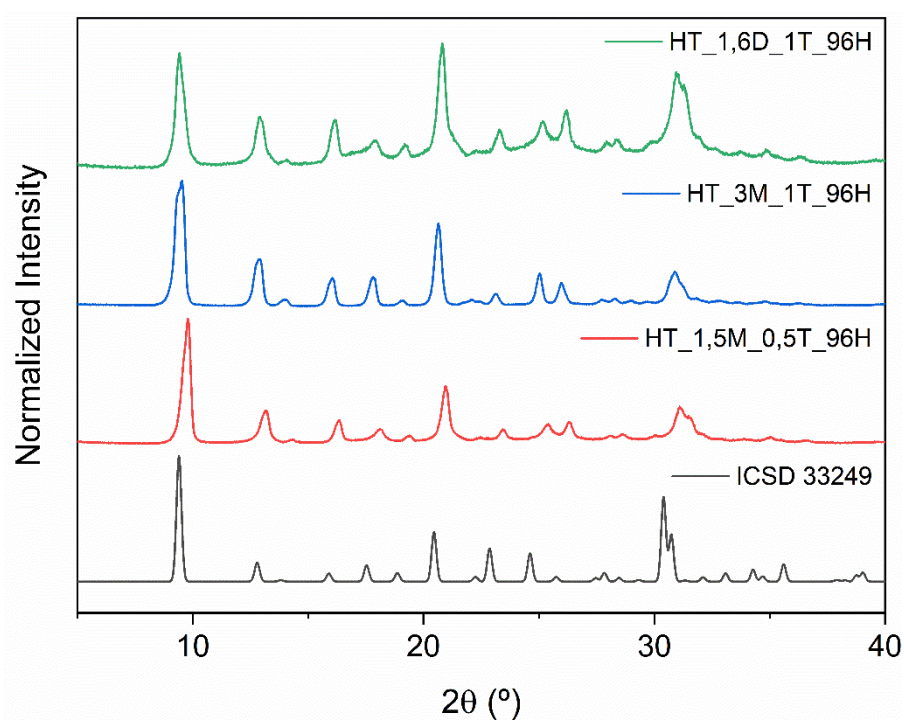


Figure 47. X-ray diffraction patterns (XRD) for samples synthesized via hydrothermal route at different organic structure-directing agents.

Based on the diffractograms presented in Figure 47, the crystallite size (S_c) was calculated using the Scherrer equation (Equation 34), along with the crystallinity percentage. The results are presented in Table 22.¹⁴²

The crystallite size values for all SAPO-34 samples range from 16.8 to 20 nm. These values fall within the range commonly reported in the literature for syntheses of

this zeolite.¹⁴³ It was observed that no clear trend of increase or decrease in S_c occurred with changes in the structure-directing agent compositions among the samples.

The crystallinity values, in turn, generally exhibit a clear increasing trend with changes in the type and molar ratio of the structure-directing agents used in the synthesis of the samples. It was observed that the use of DPA-TEAOH led to the formation of a less crystalline sample (54.1%) compared to the others, which may be associated with a reduction in crystal growth kinetics related to its use - a behavior consistent with what has already been reported in the literature.⁸³ Conversely, the use of morpholine resulted in the formation of more crystalline samples. In this case, increasing the molar ratios of MOR and TEOH in the hydrothermal syntheses led to an increase in crystallinity, from 67.3% to 81.8%, and a slight decrease in crystallite size.

As discussed in Section 5.1.1, the increase in the degree of crystallinity of the material is crucial and is directly related to the formation of more suitable and homogeneously distributed pore structures throughout the crystal. Therefore, the HT_3M_1T_96H sample appears to be promising for N_2/CH_4 separation from a microstructural standpoint.

Table 22. Crystallite sizes and crystalline fraction of SAPO-34 samples.

Sample	2 θ (°)	FWHM (°)	S_c (nm)	X_c (%)
HT_1.6D_1T_96H	9.42	0.444	17.9	54.1
HT_1.5M_0.5T_96H	9.78	0.399	20.0	67.3
HT_3M_1T_96H	9.54	0.476	16.8	81.8

5.2.2. Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

The FT-IR spectroscopy results of the samples synthesized via the hydrothermal route using the MOR/TEAOH and DPA/TEAOH mixtures are presented in Figure 48 and Table 23. In general, the samples exhibited spectra showing the characteristic bands of SAPO-34, which are consistent with those reported in the literature and discussed in Section 5.1.2.^{151,152}

It is noteworthy in Figure 48 that the bands observed in the regions of 490-574 cm^{-1} and 638 cm^{-1} are attributed, respectively, to the T-O bending vibrations of the AlO_4 | SiO_4 | PO_4 ring structures and to the bending vibrations of the D6R rings.^{151–153} As discussed previously, the presence of these bands is essential, as it provides strong evidence for the formation of the chabazite structure. Therefore, based on the X-ray

diffraction and FT-IR results, all samples discussed in this section are composed of SAPO-34.

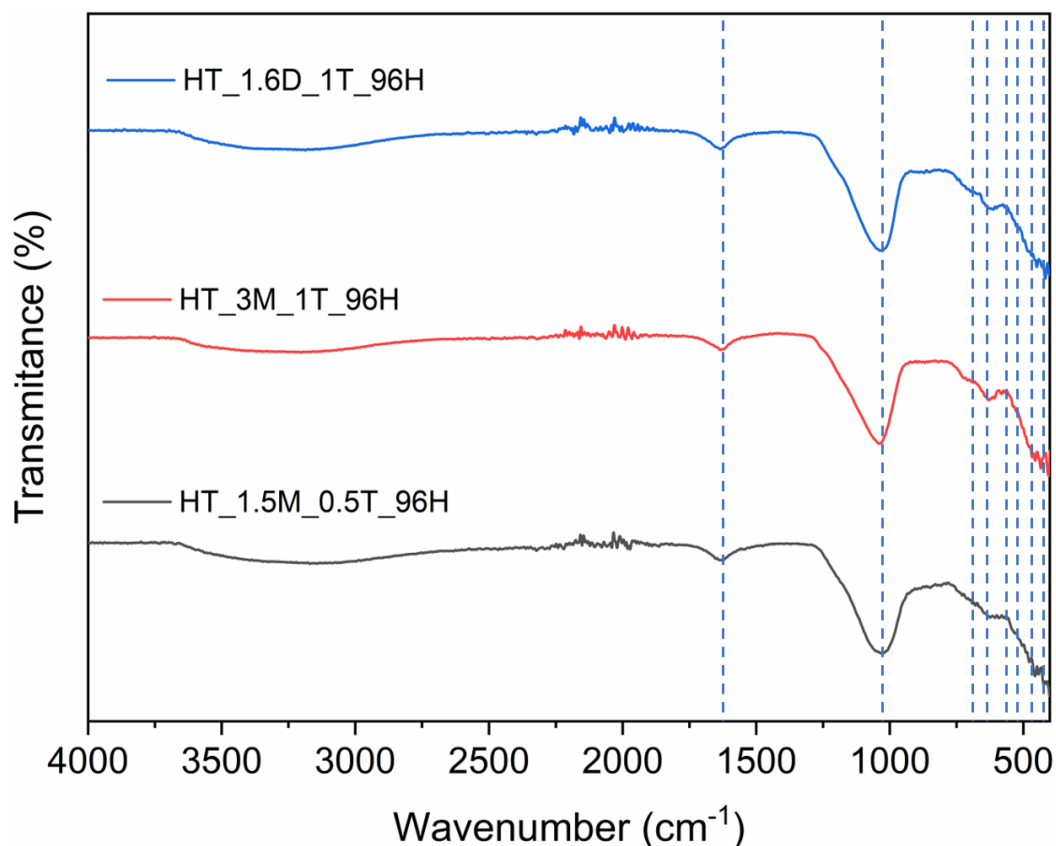


Figure 48. FT-IR spectra for samples synthesized via hydrothermal route and applying the use of DPA/TEAOH or MOR/TEAOH.

Table 23. Vibrational modes observed via FT-IR spectroscopy.

Wavenumber (cm ⁻¹)	Vibrational Modes
475, 530 e 574	T-O bending (SiO ₄ AlO ₄ PO ₄ rings)
638	Bending of D-6 rings
740	Symmetric stretching of P-O Al-O Si-O
1280-980	Asymmetric stretching of P-O Al-O Si-O
1640	Bending of physically adsorbed water
3000-4000	Stretching of bridged hydroxyl groups (Si-OH-Al and T-OH)

5.2.3. Crystal Morphology Analysis by SEM

The scanning electron microscopy (SEM) images of the samples synthesized via hydrothermal treatment using dual structure-directing agents are shown in Figure 49.

The literature reports that neutral structure-directing molecules favor the formation of *van der Waals* interactions with the framework, filling the porous cavities

and contributing to the thermodynamic stability of the structure. On the other hand, protonated amines can neutralize the charge of the AlPO_4 framework.⁸³ Furthermore, the dimensions of the structure-directing molecules are expected to be compatible with the cavity sizes of the SAPOs. However, there is no obvious or direct relationship between the molecular size of the organic directing agent and the cavity dimensions. This behavior is explained by the flexibility of the carbon chains, which can allow the molecules to adapt to the available void space.¹⁷¹

Sastre *et al.* (1996) report that the small size of the organic directing agent allows multiple molecules to occupy a single intracrystalline cavity, consequently increasing the time and temperature required for crystallization and promoting the formation of undesirable phases.¹⁷²

Considering this, Figure 49 shows that the use of mixed directing agents MOR-TEAOH and DPA-MOR had a direct impact on the formation of SAPO-34 crystals, differing from syntheses using only TEAOH, as reported in previous sections. Morpholine is a small secondary amine ($90.4 \text{ \AA}^3$) that has been extensively studied for SAPO synthesis. Crystals formed with MOR-TEAOH generally exhibit much larger particle sizes compared to those produced with other alkylamines.^{78,83,84,104} Due to the presence of an oxygen atom, morpholine establishes strong hydrogen-bond interactions with Brønsted acid groups in the framework, thereby accelerating crystal growth.⁸³ Pastore *et al.* (2005) demonstrated that CHA cages contain water-MOR molecular complexes. Morpholine chains bind along multiple cages through hydrogen bonding with water molecules, which can lead to the formation of larger crystals, as observed in samples HT_1.5M_0.5T_96H and HT_3M_1T_96H. However, shorter synthesis times may result in the formation of competing phases.⁶⁸

The HT_1.6D_1T_96H sample, in turn, exhibited smaller cubic crystals with high uniformity, characteristic of syntheses using dipropylamine. However, it is observed that its use involves a slower SAPO-34 formation kinetics, requiring longer synthesis times and higher thermal treatment temperatures. This characteristic, nonetheless, is particularly advantageous for membrane growth, as it allows greater control over the zeolite formation process.

Although TEAOH is the most commonly used directing agent for SAPO-34 synthesis - due to its high stability under different pH conditions and its strong ability to facilitate the formation of smaller and purer crystals - it exhibits high toxicity,

corrosiveness, and cost. Therefore, the combined use of morpholine and dipropylamine with TEOAH may be a key strategy to enable the formation of seeds and membranes using more affordable raw materials, with reduced environmental and human health impacts.

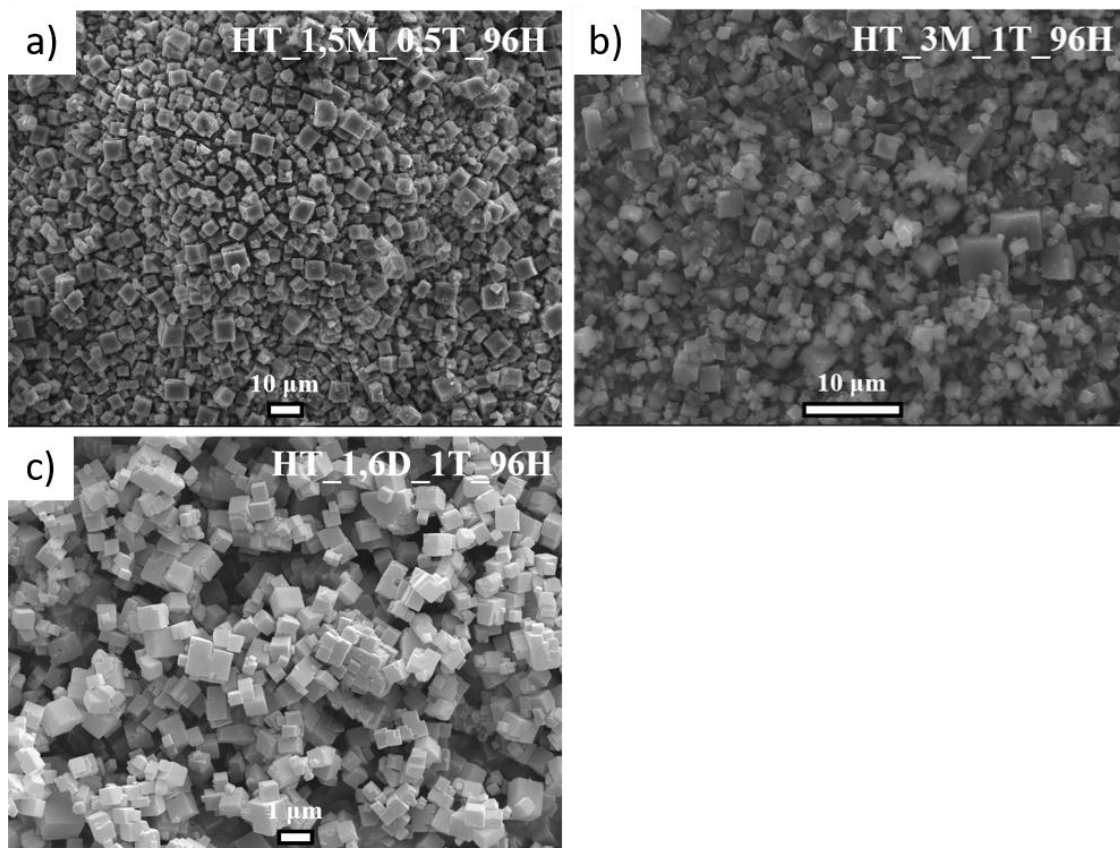


Figure 49. SEM images of samples produced from hydrothermal treatment and composition of (a) HT_1.5M_0.5T_96H, (b) HT_3M_1T_96H and (c) HT_1.6D_1T_96H.

Figure 50 presents the histograms corresponding to the crystal size distributions of the samples discussed in this section. It can be observed that the samples synthesized using MOR-TEAOH exhibited larger average crystal sizes, ranging from 1.60 μm (HT_3M_1T_96H) to 7.67 μm (HT_1.5M_0.5T_96H). In contrast, the use of DPA-TEAOH resulted in the formation of more uniform crystals, with an average size of 0.74 μm . Notably, the HT_3M_1T_96H and HT_1.6D_1T_96H samples displayed crystal sizes promising for thin membrane production tests for gas separation.

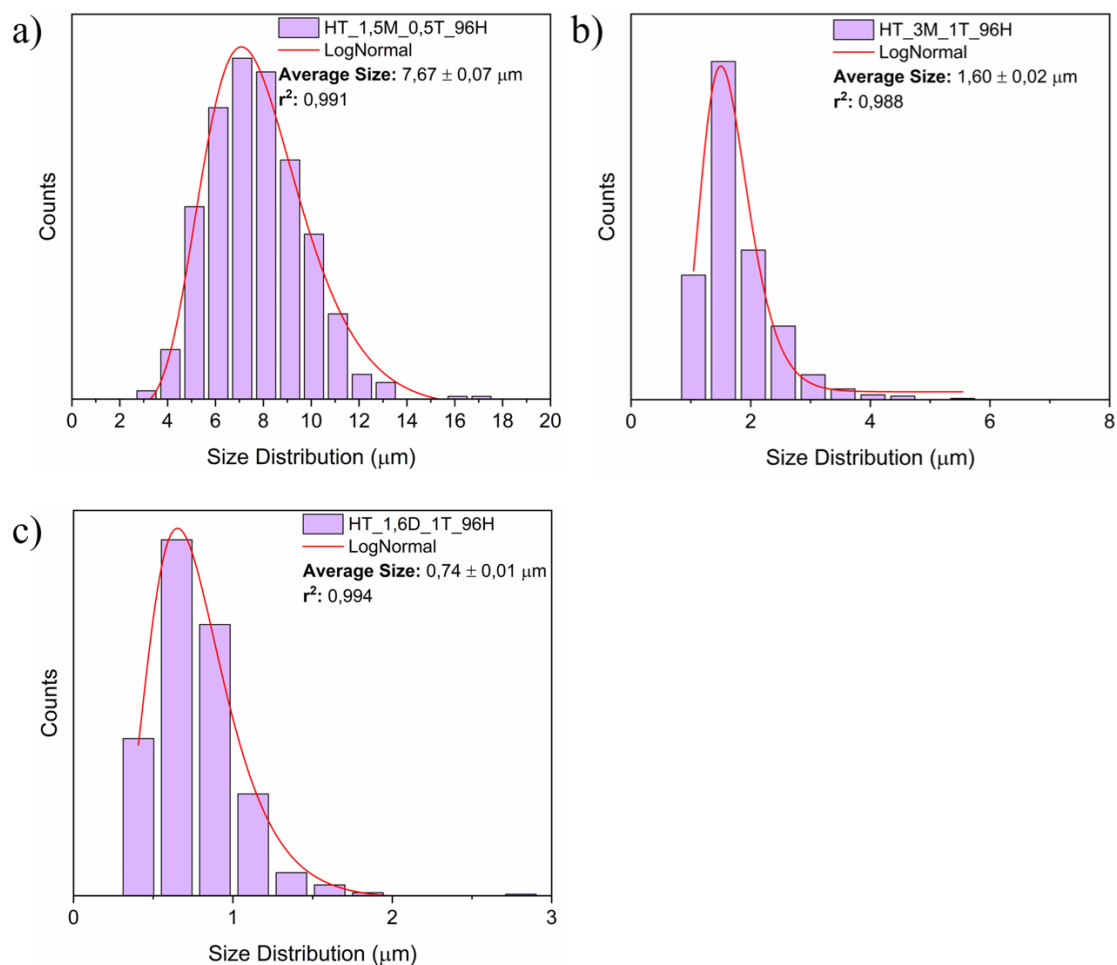


Figure 50. Histograms of samples produced from hydrothermal treatment (a) HT_1.5M_0.5T_96H, (b) HT_3M_1T_96H and (c) HT_1.6D_1T_96H.

5.2.4. Elemental Mapping by Energy-Dispersive X-ray Spectroscopy (EDS)

Elemental analysis of the samples synthesized via hydrothermal treatment using dual structure-directing agents was performed using EDS. The results are compiled in Table 24.

The processed EDS data indicate that there was no clear trend of increased Si incorporation in the SAPO-34 crystals with higher MOR/TEAOH molar ratios in the synthesis mixture. In contrast, the DPA/TEAOH composition exhibited Si/Al and Si/(Al+P+Si)_{obs} ratios closer to the theoretical values. Overall, the EDS results suggest that more Si was incorporated into the framework in the DPA/TEAOH system than in the samples synthesized using morpholine.

Table 24. Compilation of data collected via EDS.

Sample	Si/Al _{gel}	Si/Al _{obs}	Si/(Al+P+Si) gel	Si/(Al+P+Si) obs
HT_1.6D_1T_96H	0.30	0.27	0.13	0.12
HT_1.5M_0.5T_96H	0.30	0.18	0.09	0.08
HT_3M_1T_96H	0.30	0.17	0.09	0.08

*obs = observed value in SAPO-34 crystals.

*gel = theoretical value expected in the composition of the synthesis gel.

5.2.5. Analysis by MAS-NMR Spectroscopy

Considering the proposed synthesis of SAPO-34 zeolite using binary mixtures of structure-directing agents, Figure 51 presents the solid-state NMR spectra for the ^{27}Al , ^{29}Si , and ^{31}P nuclei of the HT_3M_1T_96H and HT_1.6D_1T_96H samples. The effects of each composition on the chemical environments of Al, P, and Si in the synthesized samples were investigated.

The NMR spectra show that the different compositions (MOR/TEAOH and DPA/TEAOH) induced distinct chemical environments for the species studied, which constitute the crystalline structures of the materials.

In the HT_3M_1T_96H sample, the ^{27}Al NMR signals (Figure 51(a)) are observed at 76.2, 43.5, 18.5, -11.2, and -45.2 ppm. The prominent signal at -11.2 ppm corresponds to Al^{VI} species interacting with two water molecules. The peak at 18.5 ppm can be attributed to pentacoordinated aluminum interacting with one water molecule. The signal at 43.5 ppm indicates the presence of tetrahedrally coordinated Al^{IV} within the zeolitic framework.^{160–162} In this case, the Al^{IV} and Al^{VI} peaks exhibited similar intensities. As discussed in Section 5.1.5, the downfield peak at 76.2 ppm can be assigned to the formation of a tetrahedral Al^{IV} variant within aluminosilicate domains, where Si is the closest neighboring atom.¹⁶² Based on these results, it is evident that a significant portion of the aluminum was incorporated into the SAPO-34 framework.

In the HT_1.6D_1T_96H sample, the solid-state ^{27}Al NMR signals (Figure 51(d)) are observed at 78.5, 45.4, 15.8, -9.7, and -46.2 ppm. As in the previous sample, the intense signal at -9.7 ppm corresponds to Al^{VI} species. The peak at 15.8 ppm can be attributed to pentacoordinated aluminum interacting with one water molecule. The signal at 45.4 ppm indicates the presence of tetrahedrally coordinated Al^{IV} within the zeolitic framework.^{160–162} Again, the Al^{IV} and Al^{VI} peaks exhibited similar intensities, although with a slight predominance of Al^{VI} species. The higher presence of Al^{VI} may suggest that

aluminum incorporation into the zeolitic framework was lower than that observed in the HT_3M_1T_96H sample.

The results described above may be related to the lower availability of phosphorus in the synthesis mixture to stabilize tetrahedral aluminum sites.¹⁷³ Furthermore, the size, geometry, and nature of morpholine allow it to fit appropriately into the CHA cavities, stabilizing the structure during crystallization. The presence of an oxygen atom in the morpholine structure, for example, can contribute to the establishment of stronger interactions between the molecule and the forming crystal framework, facilitating species incorporation via the SM2 mechanism. In contrast, comparative studies among different structure-directing agents indicate that DPA is less effective as a structural director compared to other organic agents.^{83,171}

The ³¹P NMR spectra (Figures 51(b) and (e)) display behaviors indicative of distinct chemical environments between the two samples. For HT_3M_1T_96H (Figure 51(b)), the signals at -7.2 and -48.7 ppm are attributed to rotating sidebands. The intense central peak at -28.7 ppm is assigned to the P(OAl)₄ species.¹⁶¹ The peak at -23.8 ppm corresponds to a distorted P(OAl)₄ species, while the weak signal at -17 ppm is associated with P(OAl)_x(H₂O)_y species.^{162–164}

The HT_1.6D_1T_96H sample, in turn, exhibited a distinct ³¹P NMR spectrum, with central band intensities different from those observed for the sample synthesized using MOR/TEAOH. The peaks at -28 and -23.5 ppm are attributed to the P(OAl)₄ and distorted P(OAl)₄ species, respectively. A signal at -17.1 ppm corresponds to P(OAl)_x(H₂O)_y species.^{162–164} The remaining side peaks can be attributed to noise originating from the analysis.^{163,164}

The ²⁹Si NMR spectra are presented in Figures 51(c) and (f). The ²⁹Si spectrum for the HT_3M_1T_96H sample exhibits signals at -84.9, -88.9, -94.4, -98.8, -105.5, -109.9, -117.8, and -121.6 ppm. The peak at -84.9 ppm likely arises from Si(OAl)₃(OH) or Si(OAl)(OSi)(OH)₂ species resulting from the cleavage of some Si-OH-Al bonds, disordered Si(4Al) linkages, or partially hydrated Si species located at Si domain boundaries. The peaks at -88.9, -94.4, -98.8, -105.5, and -109.9 ppm are assigned to Si(4Al), Si(3Al), Si(2Al), Si(1Al), and Si islands (Si(0Al)), respectively. The signals at -117.8 and -121.6 ppm can be attributed to distorted Si(0Al) species.^{161,165}

The ²⁹Si spectrum for the HT_1.6D_1T_96H sample shows signals similar to those of the previous sample. However, the peak near -83 ppm, corresponding to

Si(OAl)₃(OH) or Si(OAl)(OSi)(OH)₂ species, disordered Si(4Al) linkages, or partially hydrated Si species, was not observed. The peaks at -89.7, -93.5, -99.6, -104.9, and -109.3 ppm are assigned to Si(4Al), Si(3Al), Si(2Al), Si(1Al), and Si islands (Si(0Al)), respectively. The signals at -114.3 and -118.8 ppm can be attributed to distorted Si(0Al) species.^{161,165}

It can be observed that the HT_3M_1T_96H sample exhibited a slight decrease in the amount of Si(0Al) species compared to HT_1.6D_1T_96H. As discussed in Section 5.2.3, the CHA cavity has an internal free diameter of 9.2 Å, accessed through eight-membered ring windows of 3.8 Å. TEOH and DPA molecules occupy these spaces individually, whereas the smaller morpholine allows the packing of two molecules - one oriented “up” and the other “down” - within the same channel.¹⁷⁴ The presence of two directing molecules in a single cavity tends to reduce the formation of silicon islands in the framework and favor the formation of Si(4Al).¹⁷⁵ The two molecules, in the “up” and “down” orientations, distribute positive charges at opposite positions within the chabazite, forcing Si⁴⁺ ions to disperse to neutralize each charge center. Statistically, this effect suppresses Si aggregation and preserves Si(4Al) species.¹⁷⁴ In other words, as observed, the nature of the directing agent indeed impacted the silicon distribution within the lattice.^{174,176}

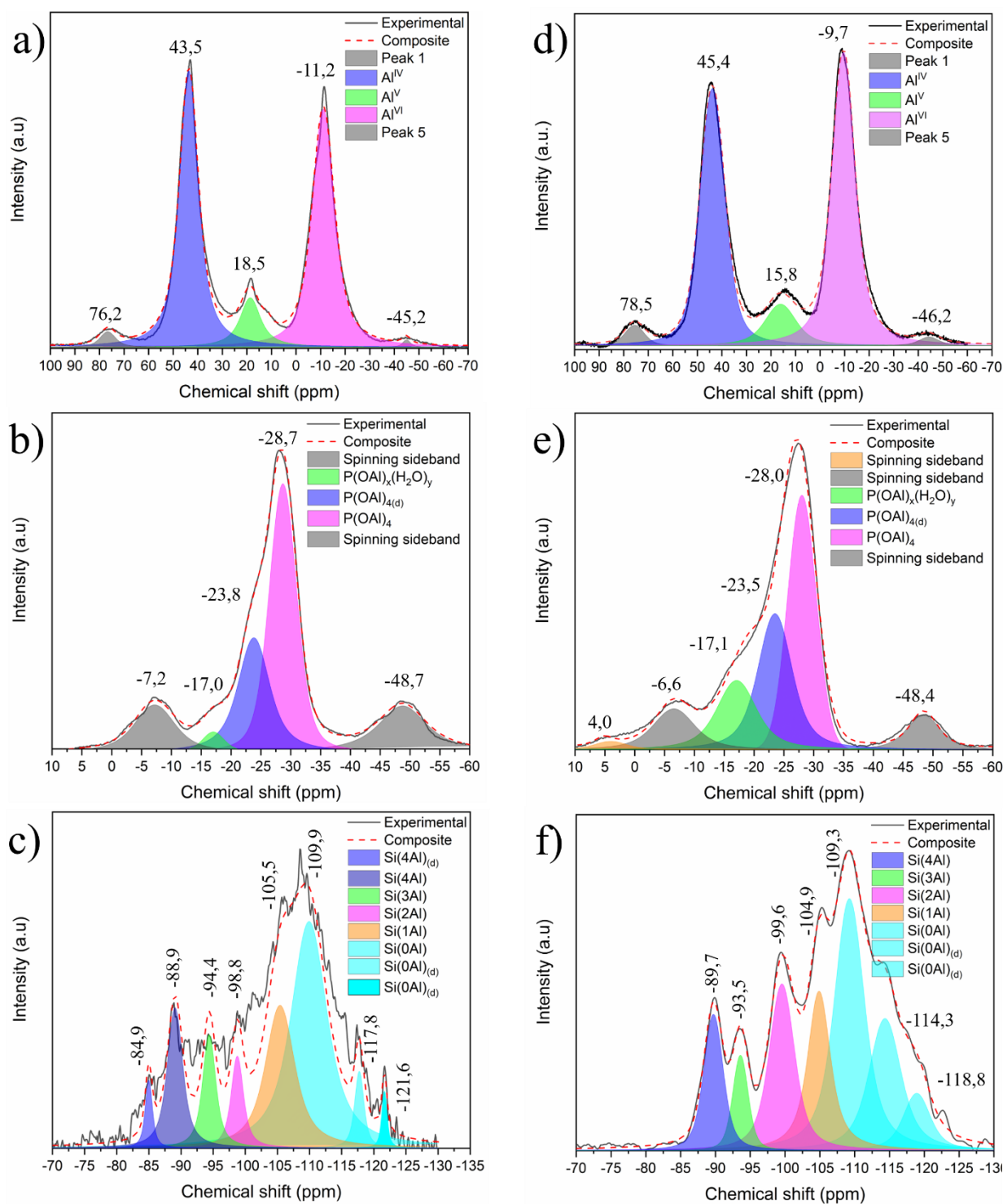


Figure 51. MAS-NMR spectra of ^{27}Al , ^{31}P and ^{29}Si for samples HT_3M_1T_96H (a, b, c) and HT_1.6D_1T_96H (d, e, f).

Based on the spectra shown in Figure 51, a quantitative analysis was performed to determine the percentages of the species identified in the samples. For this purpose, Equation 35 was used.

The results are shown in Figure 52. For the HT_3M_1T_96H sample, the ^{27}Al and ^{31}P analyses indicate that the expected groups, Al^{IV} (45.1%) and $\text{P}(\text{OAl})_4$ (67.3%), are predominant, demonstrating satisfactory incorporation into the SAPO-34 framework. The ^{29}Si analysis reveals a significant presence of $\text{Si}(4\text{Al})$ at 11.5%. However, 44.2% of the species correspond to $\text{Si}(0\text{Al})$ sites, indicating the formation of silicon islands, which reduce the overall acid site density in the framework but increase acid strength at the edges of the islands.¹⁷²

In the HT_1.6D_1T_96H sample, the ^{27}Al analysis shows the expected groups Al^{IV} (44.9%) and Al^{VI} (49.8%). This indicates that most of the aluminum interacts with water, suggesting a lower incorporation of aluminum into the zeolitic framework. The ^{31}P analysis reveals an increase in hydrated species, $\text{P}(\text{OAl})_x(\text{H}_2\text{O})_y$ (16.9%), compared to $\text{P}(\text{OAl})_4$ species (63.2%). These results are consistent with the X-ray diffraction and SEM data, as the DPA/TEAOH composition exhibited lower crystallinity and smaller zeolitic crystal sizes. The ^{29}Si analysis indicates that the SM2 and SM3 substitution mechanisms occur simultaneously during SAPO-34 framework formation. However, a higher percentage of silicon islands is observed relative to the other species.

The results presented allow us to affirm that the MOR/TEAOH composition provided better utilization of the aluminum (Alip), phosphorus (H_3PO_4), and silicon (SiO_2) sources. It is noted that, in this composition, the presence of undesired species in the ^{27}Al , ^{31}P , and ^{29}Si Raman spectroscopy analyses was significantly lower. However, much larger crystals were observed by scanning electron microscopy. To date, there are no studies addressing the production of zeolite membranes for N_2/CH_4 separation using the proposed composition. On the other hand, it is well established in the literature that the use of the DPA/TEAOH mixture as structure-directing agents provides excellent control over membrane growth processes, as it promotes slower reaction kinetics. Additionally, the predominance of silicon islands is advantageous, as it helps reduce interactions between the zeolitic framework and ambient moisture.

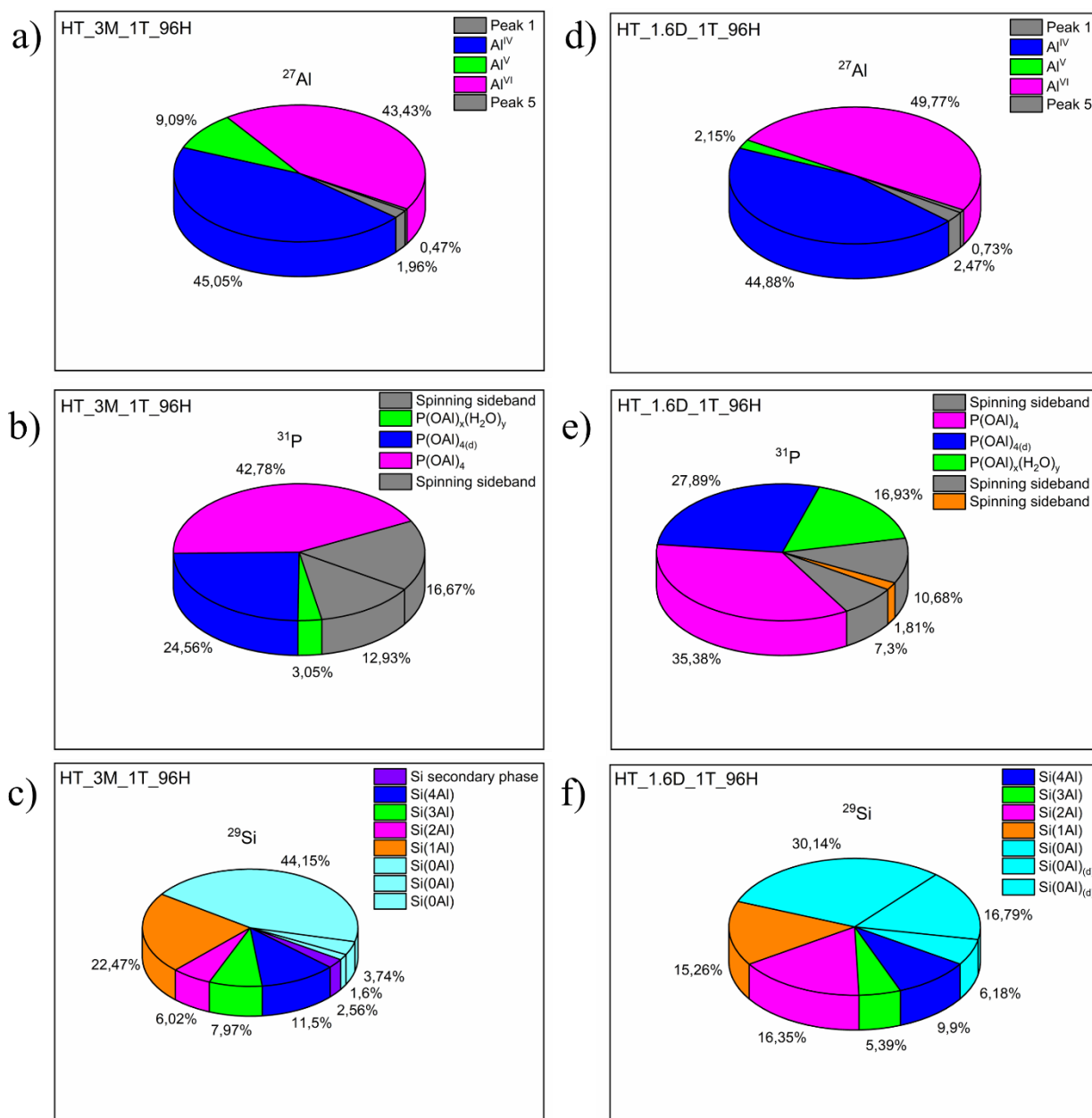


Figure 52. Percentages of species identified via MAS-NMR spectroscopy for the samples HT_3M_1T_96H (a, b, c) and HT_1.6D_1T_96H (d, e, f).

5.2.6. Gas Adsorption Analysis

The nitrogen adsorption-desorption isotherms for the samples discussed in this section are shown in Figure 53. The behavior observed for the samples synthesized using MOR/TEAOH and DPA/TEAOH corresponds to IUPAC type I isotherms, characteristic of microporous materials. The HT_1.5M_0.5T_96H sample exhibited a slight H4-type hysteresis, common in materials forming non-rigid aggregates of zeolitic crystals.

Similarly, the HT_3M_1T_96H sample displayed a small H4-type hysteresis too, which can be associated with the filling of micropores in aggregated particles.¹⁶⁷

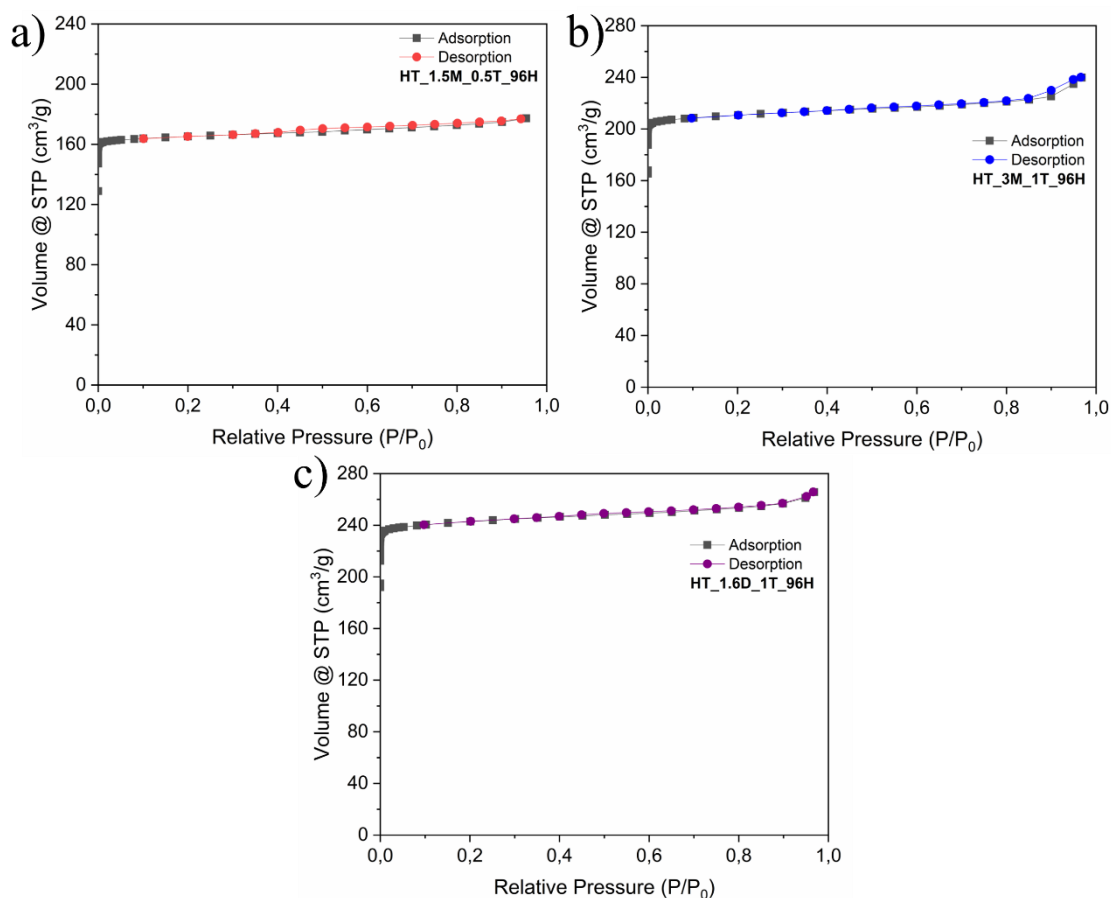


Figure 53. N₂ gas adsorption isotherms of samples: (a) HT_1.5M_0.5T_96H, (b) HT_3M_1T_96H, and (c) HT_1.6D_1T_96H.

The values of total surface area (S_{BET}), micropore surface area (S_{micro}), micropore volume (V_{micro}), external surface area (S_{ext}), and total pore volume (V_{T}) are presented in Table 25. The graphs used to obtain these values can be found in the Appendix section.

Table 25 shows that the synthesized samples exhibited significant microporosity. The HT_1.6D_1T_96H sample may have behaved similarly to the 0.3 Si sample. Its specific micropore surface area (968.2 m²/g) and micropore volume (0.351 cm³/g) could have been overestimated due to kinetic blocking effects, where adsorbed N₂ molecules block micropore entrances and hinder complete gas diffusion into the pores. As discussed previously, this phenomenon causes the adsorbed volume in the external region to appear larger when using the BET and t-plot methods.¹⁷⁰

The results obtained for the HT_3M_1T_96H and HT_1.6D_1T_96H samples stand out for combining over 95% micropore surface area with smaller particle sizes. Moreover, these samples exhibited properties similar to the HT_T1_96H and HT_T2_96H zeolites, making them promising candidates for comparative tests in membrane production applications.

Table 25. Textural properties calculated via BET method and t-plot of materials synthesized hydrothermally and using double organic-structure directing agent.

Sample	S _{BET} ^a (m ² /g)	S _{micro} ^b (m ² /g)	S _{ext} ^b (m ² /g)	V _{micro} ^b (cm ³ /g)	V _{meso} ^c (cm ³ /g)	V _{total} (cm ³ /g)
HT_1.5M_0.5T_96H	698.5	668.8	29.7	0.241	0.030	0.271
HT_3M_1T_96H	883.8	837.1	46.7	0.303	0.061	0.364
HT_1.6D_1T_96H	1017.9	968.2	49.7	0.351	0.053	0.405

Surface area ^aBET; ^bS_{micro} (microporous area), S_{ext} (external surface area) e V_{micro} (microporous volume) determined by t-plot method. ^cV_{meso} (mesoporous volume) = V_{total} - V_{micro}; V_{total} determined by the penultimate adsorption point (P/P₀).

5.3. Microwave-Assisted Synthesis: Application of Single and Mixed Organic Structure-Directing Agents

5.3.1. Microstructural Analysis by X-ray Diffraction

Based on the results observed in Sections 5.1 and 5.2, the most promising methodologies were selected for microwave-assisted syntheses. Accordingly, tests were carried out varying synthesis times between 0.5 and 24 hours using the compositions 1 Al₂O₃ : 2 P₂O₅ : 0.6 SiO₂ : 4 TEAOH : 150 H₂O (MW_T1); and 1 Al₂O₃ : 2 P₂O₅ : 0.6 SiO₂ : 3 MOR: 1 TEAOH : 75 H₂O (MW_3M_1T).

Figures 54(a-b) present the results for both studied compositions. When comparing the X-ray diffraction signals with the corresponding ICSD database standard, it is observed that, after 12 hours of thermal treatment, all MW_T1 samples exhibited the typical diffraction pattern of SAPO-34 zeolite, similar to the HT_T1_96H sample. For these samples, the main signals are observed at 2θ values and hkl indices approximately at: 9.6° (100); 13° (-110); 16.2° (-111); 17.9° (111); 19.2° (200); 20.8° (210); 23.3° (-121); 25.1° (211); 26.2° (-220); 31° (-311); and 31.3° (310).¹⁴⁷ The MW_T1_6H, MW_T1_3H, and intermediate samples exhibited a mixed profile, with predominance of the CHA phase (SAPO-34) and a minor contribution of AEI phase peaks (SAPO-18). The

presence of SAPO-18 was evidenced by subtle peaks at 2θ values near 10.6° and 16.8° .

150

Figure 54(b) presents the X-ray diffraction signals compared with the corresponding ICSD database standard for samples with the MW_3M_1T composition. After 6 hours of treatment, signals corresponding predominantly to the AFI phase of SAPO-5 are observed. With 12 hours of microwave treatment, a clearer competition between the formation of SAPO-5 and SAPO-34 is evident. However, extending the treatment time to 24 hours resulted in the formation of only the chabazite phase. For this phase, the main signals are again observed at 2θ values and hkl indices approximately at: 9.6° (100); 13° (-110); 16.2° (-111); 17.9° (111); 19.2° (200); 20.8° (210); 23.3° (-121); 25.1° (211); 26.2° (-220); 31° (-311); and 31.3° (310).¹⁴⁷

As discussed in Section 5.2, Sastre *et al.* (1996) demonstrated that small-molecule organic structure-directing agents (e.g., morpholine), when present in pairs within the same cavity, exhibit repulsive interactions that increase the nucleation free energy and prolong the crystallization time required for SAPO-34 formation. Additionally, they promote the appearance of competing phases at shorter times (e.g., SAPO-18 or SAPO-5). This explains the need for higher synthesis times or temperatures when using MOR compared to TEAOH.¹⁷² Furthermore, a direct solid-state topotactic transformation from the AFI to the CHA framework is unlikely, given the substantial differences between their intracrystalline structures and the large structural rearrangement required. It is far more probable that partial dissolution of SAPO-5 occurred, followed by nucleation and growth of SAPO-34 from the dissolved species, a mechanism commonly referred to as dissolution-recrystallization.

Nevertheless, the results are highly promising and demonstrate that the change in heating methodology was able to accelerate SAPO-34 formation. Microwave energy enhances molecular collisions, promoting better dispersion of the synthesis gel. Additionally, the nucleation stage tends to produce denser crystal nuclei. Simultaneously, the suspension is heated rapidly and uniformly, which generally results in accelerated crystallization rates and high phase purity. For this reason, the crystals tend to exhibit smaller particle sizes and a more uniform size distribution.⁷⁶

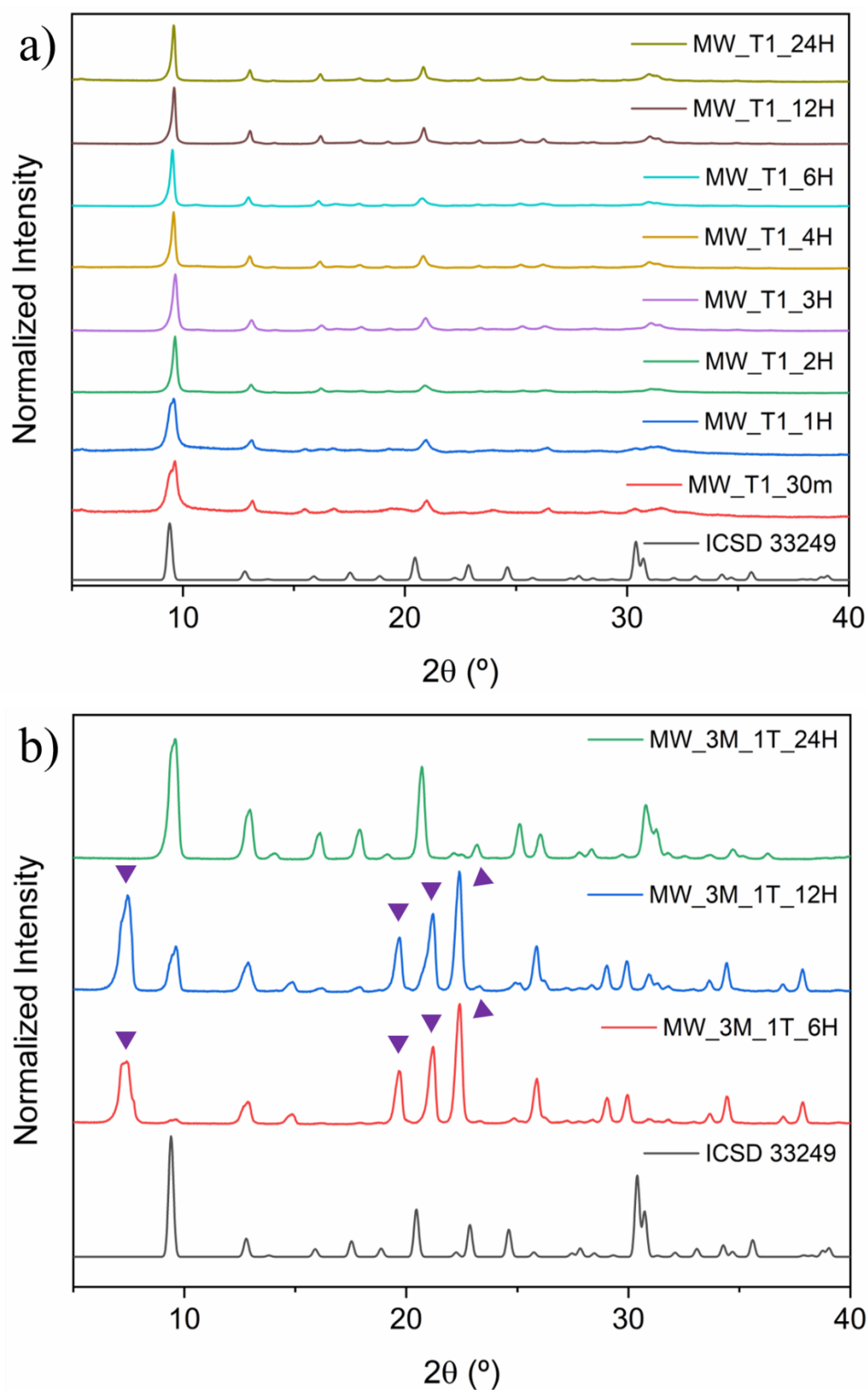


Figure 54. X-ray diffraction pattern for the single-component variation tests based on the T1 reaction ratio. The purple triangles indicate the main signals observed and attributed to the AFI phase (SAPO-5).

The diffraction results presented in Figure 54 were used to calculate the crystallite size (S_c) using the Scherrer equation (Equation 34) and to determine the percentage of crystallinity. The results for the MW_T1_12H, MW_T1_24H, and MW_3M_1T_24H samples are presented in Table 26.¹⁴²

The crystallite size values for the samples synthesized using the microwave technique range from 17 to 42 nm. It was observed that the zeolites synthesized via the MW_T1 methodology exhibited larger crystallite sizes than those produced using MOR/TEAOH. This pattern is also evident when comparing the results from Sections 5.1.1 and 5.2.1. This phenomenon can be explained based on the characteristics of the organic structure-directing agents used. TEAOH is known as an ideal molecule for SAPO-34 synthesis because it induces controlled and orderly growth of crystal domains. Therefore, the T1 methodology likely contributed to increased long-range ordering of the crystals, which may be attributed to a lower incidence of intracrystalline defects.^{174–177} Morpholine, in contrast, promotes faster crystal growth, which may lead to packing defects. Nonetheless, the crystallite sizes remain within the range reported in the literature.¹⁴³

However, for samples MW_T1_12H and MW_T1_24H, a decreasing trend in crystallite size can be observed. During conventional hydrothermal heating, the temperature rise is governed by heat transfer through the autoclave walls, resulting in a relatively slow and uniform nucleation process. This controlled regime favors the formation of a moderate number of nuclei, followed by a diffusion-limited growth stage, during which the nutrient species (Si, Al, and P) are gradually incorporated into the developing crystals. Under these conditions, characterized by slow nucleation and diffusion-controlled growth, the crystalline framework remains only minimally distorted, allowing atoms to occupy well-defined lattice positions in accordance with the symmetry and periodicity of the SAPO-34 structure. Consequently, a uniform and well-ordered lattice parameter is achieved. As the hydrothermal treatment time increases, the dissolution of smaller nuclei in favor of larger ones promotes the gradual enlargement of coherent intraparticle domains, as were observed for HT_T1 and HT_T2 samples.^{178,179}

In contrast, microwave-assisted synthesis selectively excites polar molecules, leading to a nearly instantaneous temperature rise. This rapid and volumetric heating induces massive and simultaneous nucleation, generating localized supersaturation within the reaction medium. As a result, numerous nucleation centers are formed in a very short

time. Under these highly supersaturated conditions, crystal growth proceeds rapidly through the incorporation of nutrient species at multiple sites simultaneously. The non-uniform and accelerated incorporation process may introduce localized distortions within the crystalline lattice, which may account for the progressive reduction in crystallite size, even as the relative proportion of the crystalline phase increases.^{178,179}

The crystallinity values were generally promising, as they were comparable to those obtained for the samples subjected to conventional oven treatment for 96 hours. The MW_T1_24H sample exhibited a crystallinity of 71.3%, a value close to that of HT_T1_72H (71.9%). The MW_3M_1T_24H sample showed the highest crystallinity in this study, exceeding 90%. This result can be attributed to the contribution of morpholine in accelerating the formation and growth processes of the zeolitic crystals.

The results observed are highly promising, as they demonstrate a clear reduction in the synthesis time required to obtain SAPO-34 zeolite while maintaining well-structured crystal formation. As discussed in previous sections, increasing the material's degree of crystallinity is crucial and is directly related to achieving more suitable and homogeneously distributed pore structures, a key factor for gas separation applications.

Table 26. Crystallite sizes and crystalline fraction of SAPO-34 samples synthesized by microwave heating.

Sample	2 θ (°)	FWHM (°)	S _c (nm)	X _c (%)
MW_T1_12H	9.56	0.188	42.4	65.1
MW_T1_24H	9.58	0.345	23.1	71.3
MW_3M_1T_24H	9.56	0.465	17.2	92.2

5.3.2. Analysis by Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectroscopy results for the samples synthesized via microwave heating using the MW_T1 and MW_3M_1T compositions are presented in Figure 55 and Table 27. The behavior observed for these samples was similar to that seen in previous sections: samples with growth times of 6 hours or longer exhibited spectra displaying the characteristic bands of SAPO-34, consistent with those reported in the literature and discussed in Sections 5.1.2 and 5.2.2.^{151,152}

In Figure 55, the appearance of bands in the regions 490-574 cm⁻¹ and 638 cm⁻¹ is again observed, which are attributed, respectively, to the T-O bending of the AlO₄ | SiO₄ | PO₄ rings and the bending of the D6R rings.¹⁵¹⁻¹⁵³ As noted previously, the presence of

these bands is essential, as they provide strong evidence for the formation of the chabazite structure.

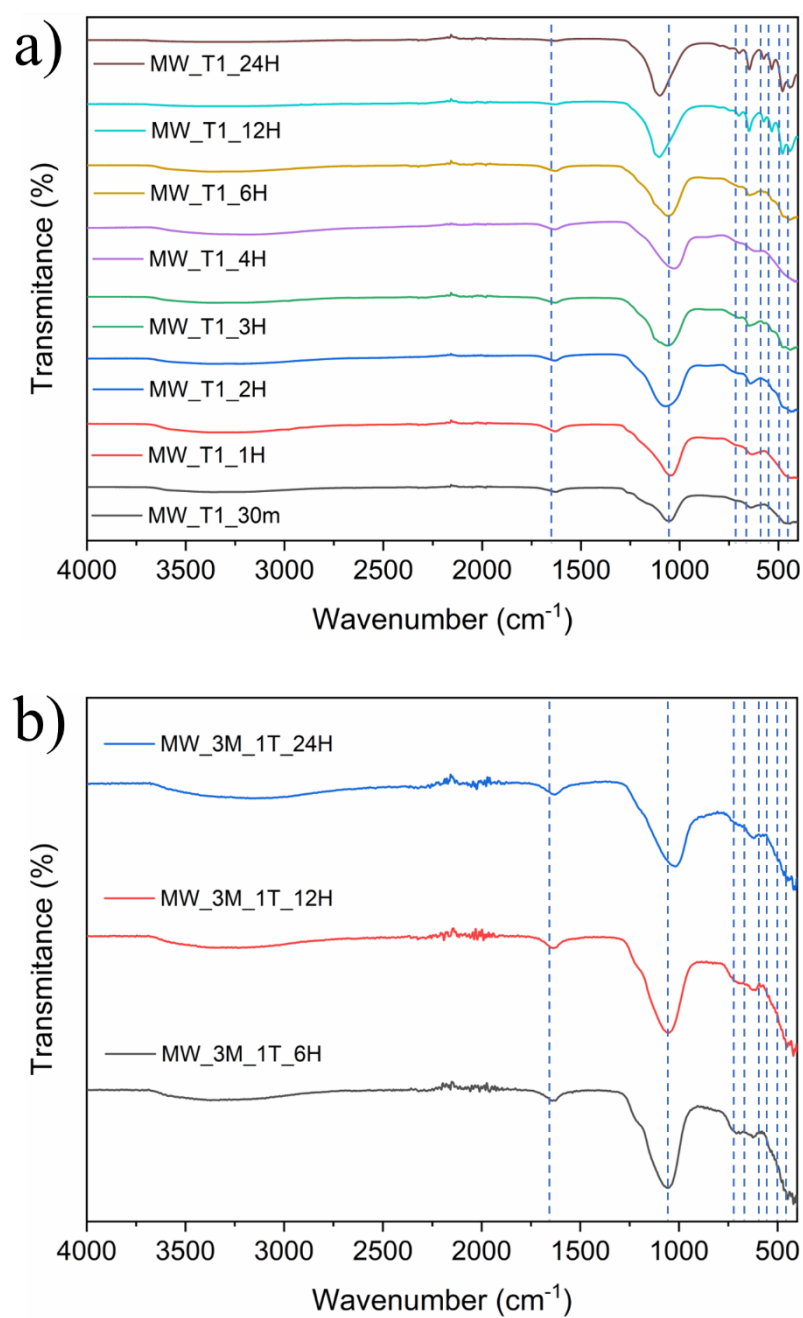


Figure 55. FT-IR spectra for samples synthesized via microwave route.

Table 27. Vibrational modes observed via FT-IR spectroscopy.

Wavenumber (cm ⁻¹)	Vibrational Modes
475, 530 e 574	T-O bending (SiO ₄ AlO ₄ PO ₄ rings)
638	Bending of D-6 rings
740	Symmetric stretching of P-O Al-O Si-O
1280-980	Asymmetric stretching of P-O Al-O Si-O
1640	Bending of physically adsorbed water
3000-4000	Stretching of bridged hydroxyl groups (Si-OH-Al and T-OH)

5.3.3. Analysis by Scanning Electron Microscopy

The scanning electron microscopy (SEM) images of the samples synthesized via microwave treatment, using either single or dual structure-directing agents, are shown in Figures 56 and 57.

Figure 56 shows the results for the MW_T1 samples. It was observed that, after only 6 hours of thermal treatment, the formation of some cubic crystals was already evident. However, the sample also exhibited aggregated spherical particles. These structures can be attributed to the presence of amorphous or semi-crystalline phases, as indicated by baseline shifts in the diffraction peaks and peak broadening.

The MW_T1_12H sample still shows the presence of spherical particles in the material; however, cubic structures with more uniform and well-formed sizes predominate. After 24 hours of crystallization, only well-defined, regular cubic crystals were observed, which are typical of the chabazite (SAPO-34) structure.

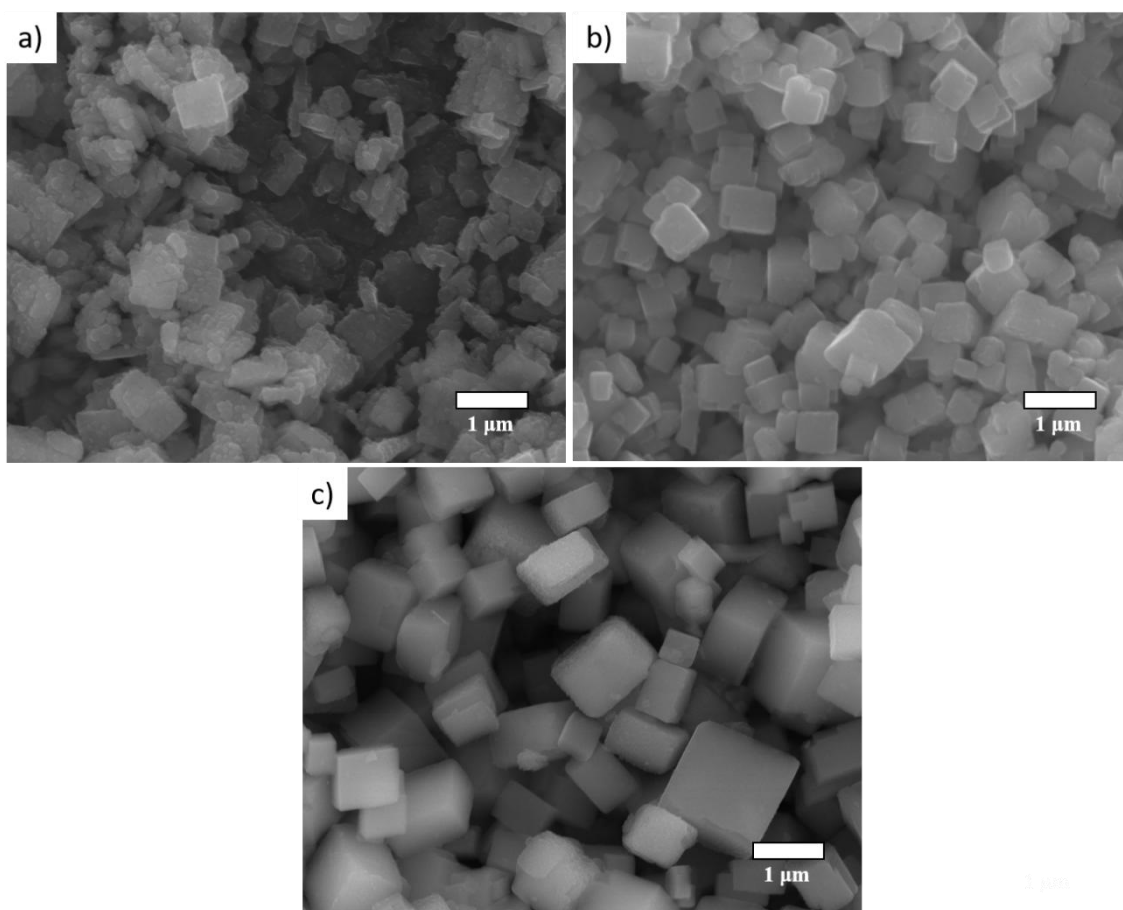


Figure 56. SEM images of samples (a) MW_T1_6H, (b) MW_T1_12H and (c) MW_T1_24H.

Figure 57 presents the results for the MW_3M_1T samples. For the sample subjected to 12 hours of crystallization, the formation of large cubes, conical structures, and hexagonally faceted structures was observed. These impure phases can be attributed to SAPO-5 (AFI) crystals. The pronounced appearance of the AFI phase can be explained by the combination of the morpholine's nature (in a majority proportion) and the accelerated nucleation and growth induced by the microwave technique. Nevertheless, after 24 hours of thermal treatment, a high-purity material composed of large cubic crystals (CHA) was obtained.^{157,180}

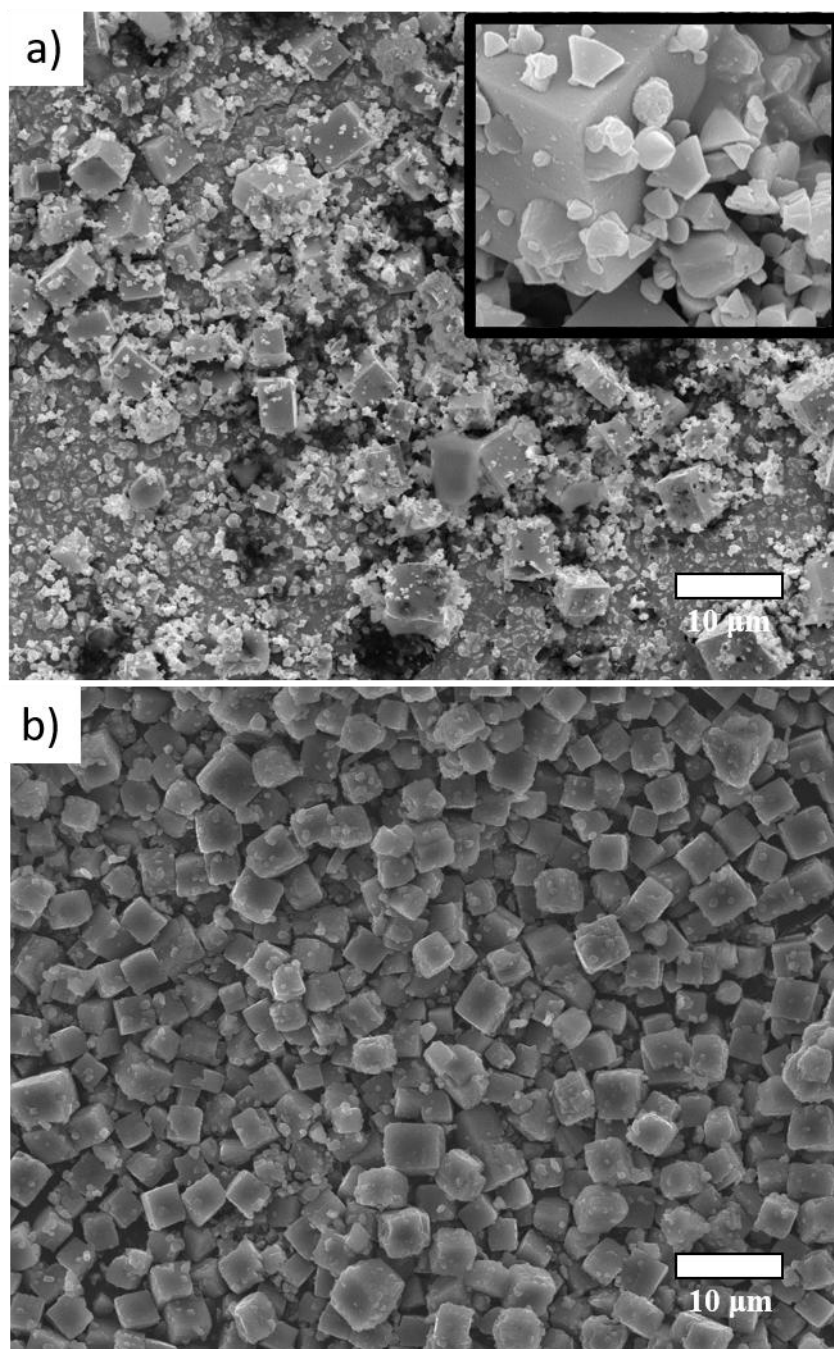


Figure 57. SEM images of (a) MW_3M_1T_12H and (b) MW_3M_1T_24H samples.

Figure 58 presents the histograms of the average particle size measurements for the samples discussed in this section. The samples synthesized via the MW_T1 methodology exhibited smaller particle sizes, ranging from an average of 0.71 μm (MW_T1_12H) to 2.77 μm (MW_T1_24H). The use of the MOR-TEAOH mixture led to the formation of larger crystals, reaching an average size of 4.38 μm (MW_3M_1T_24H). It is evident that the MW_T1_24H sample is highly promising for thin membrane production, as it displayed smaller cubic crystals with excellent size

uniformity. However, the deposition of SAPO-34 seeds produced with the MOR/TEAOH mixture onto porous substrates is scarcely explored, opening opportunities for innovation in gas separation film production methods.

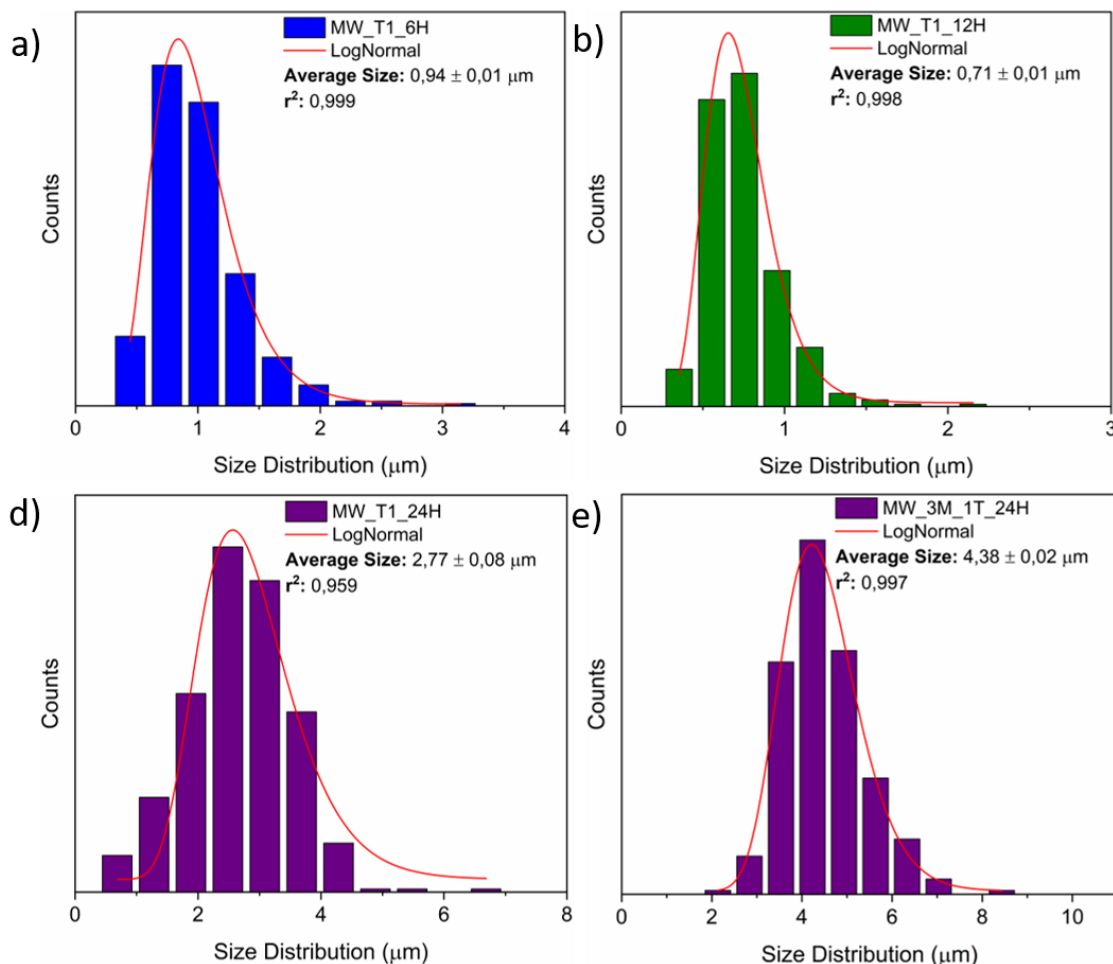


Figure 58. Histograms constructed to evaluate the average particle size of the main samples synthesized via microwave-assisted heating.

5.3.4. Elemental Analysis by Energy-Dispersive X-ray Spectroscopy

The elemental analysis by energy-dispersive X-ray spectroscopy (EDS) for the main samples synthesized via microwave heating using single or dual structure-directing agents is presented in Table 28.

The processed data show a trend of increasing Si incorporation into the SAPO-34 crystals with longer crystallization times for the MW_T1 methodology. Comparing the MW_T1_12H and MW_T1_24H samples, the observed Si/Al_{obs} ratio increased from 0.22 to 0.30, reaching the same level as the initial synthesis gel. Similarly, the

MW_3M_1T_24H sample exhibited $\text{Si}/\text{Al}_{\text{obs}}$ and $\text{Si}/(\text{Al}+\text{P}+\text{Si})_{\text{obs}}$ ratios closer to the theoretical values. These results indicate that, after 24 hours of microwave treatment, it is possible to achieve the maximum possible silicon incorporation - given the initial gel compositions - into the SAPO-34 crystalline structure, regardless of whether a mixed organic structure-directing agent is used.

Table 28. Compilation of data collected via EDS.

Sample	$\text{Si}/\text{Al}_{\text{gel}}$	$\text{Si}/\text{Al}_{\text{obs}}$	$\text{Si}/(\text{Al}+\text{P}+\text{Si})_{\text{gel}}$	$\text{Si}/(\text{Al}+\text{P}+\text{Si})_{\text{obs}}$
MW_T1_12H	0.30	0.22	0.09	0.09
MW_T1_24H	0.30	0.30	0.09	0.12
MW_3M_1T_24H	0.30	0.30	0.09	0.13

*obs = observed value in SAPO-34 crystals.

*gel = theoretical value expected in the composition of the synthesis gel.

5.3.5. Analysis by Nuclear Magnetic Resonance (NMR) Spectroscopy

The MW_T1_24H and MW_3M_1T_24H samples were subjected to solid-state NMR spectroscopy, and the spectra for the ^{27}Al , ^{29}Si , and ^{31}P nuclei are shown in Figure 59.

The NMR spectra show that the different compositions induced significant changes in the chemical environments of the species forming the crystalline frameworks of these materials.

The MW_T1_24H sample shows ^{27}Al NMR signals (Figure 59(a)) at 76.7, 44.5, 16.7, -9.5, and -43.4 ppm. As discussed in Sections 5.1.5 and 5.2.5, the three intermediate signals correspond to Al^{IV} , Al^{V} , and Al^{VI} , respectively. The same signal patterns are observed in the ^{27}Al spectrum of the MW_3M_1T_24H sample (45.6, 15.9, and -9.9 ppm; Figure 59(d)). However, in MW_T1_24H, a closer intensity balance between Al^{IV} and Al^{VI} was noted, along with a slight increase in the Al^{V} intensity.^{160–162} Ambas as amostras apresentaram pequenas bandas nas faixas de 76 à 78 ppm e -43 à -46 ppm. Both samples exhibited minor bands in the ranges of 76–78 ppm and -43 to -46 ppm. The former may be related to tetrahedrally coordinated aluminum bonded to silicon groups, while the latter may be associated with Al^{IV} linked to silicon nuclei.¹⁸¹ Based on these results, a substantial portion of the aluminum was incorporated into the SAPO-34 structure.

The ^{31}P NMR spectra showed similarities for both samples (Figures 59(b) and (e)). The signals indicate a significant presence of $\text{P}(\text{OAl})_x(\text{H}_2\text{O})_y$ in both samples,

observed at -17.5 ppm (MW_T1_24H) and -16.5 ppm (MW_3M_1T_24H).^{162–164} Peaks around 3.0, -6.0, and 48.0 ppm were assigned to spinning sidebands, which constitute noise in NMR analysis.^{162–164} Both compositions exhibited similar signals for hydrated phosphorus species (≈ 20 ppm) and for distorted or undistorted phosphorus tetrahedra.

The ^{29}Si NMR spectra are shown in Figures 59(c) and (f). For the MW_T1_24H sample, the ^{29}Si spectrum exhibits signals at -76.6, -83.2, -89.1, -94.5, -98.9, -104.1, -108.8, -113.1, and -121.7 ppm. The peaks at -76.6 and -83.2 ppm likely arise from $\text{Si}(\text{OAl})_3(\text{OH})$ or $\text{Si}(\text{OAl})(\text{OSi})(\text{OH})_2$ species, resulting from the cleavage of some Si-OH-Al bonds, disordered $\text{Si}(4\text{Al})$ linkages, or partially hydrated Si species located at Si domain boundaries. Peaks at -89.1, -94.5, -98.9, -104.1, -108.8, -113.1, and -121.7 ppm are attributed to $\text{Si}(4\text{Al})$, $\text{Si}(3\text{Al})$, $\text{Si}(2\text{Al})$, $\text{Si}(1\text{Al})$, and $\text{Si}(0\text{Al})$, respectively. The signals at -113.1 and -121.7 ppm may correspond to distorted $\text{Si}(0\text{Al})$ species.^{161,165}

The ^{29}Si spectrum for the MW_3M_1T_24H sample exhibits signals similar to those of MW_T1_24H. However, the peaks near -76 and -83 ppm, associated with disordered $\text{Si}(4\text{Al})$ species or partially hydrated Si species, were not observed. Peaks at -90.7, -94.9, -100.2, -105.7, and -111.6 ppm are assigned to $\text{Si}(4\text{Al})$, $\text{Si}(3\text{Al})$, $\text{Si}(2\text{Al})$, $\text{Si}(1\text{Al})$, and $\text{Si}(0\text{Al})$, respectively. Signals at -116.4 and -119.9 ppm may correspond to distorted $\text{Si}(0\text{Al})$ species.^{161,165}

It can be observed that the MW_T1_24H sample exhibited a marked decrease in the quantity of species representing silicon islands – $\text{Si}(3\text{Al})$, $\text{Si}(2\text{Al})$, $\text{Si}(1\text{Al})$, and $\text{Si}(0\text{Al})$ (distorted or not) – compared to MW_3M_1T_24H. Thus, the MW_T1 methodology favored SM2-type substitution mechanisms, which lead to the formation of $\text{Si}(4\text{Al})$ species. According to the literature, the acidity strength of silicon species follows the order: $\text{Si}(1\text{Al}) > \text{Si}(2\text{Al}) > \text{Si}(3\text{Al}) > \text{Si}(4\text{Al})$. The higher presence of $\text{Si}(4\text{Al})$ promotes moderately strong and better-distributed Brønsted acid sites, conferring greater structural stability, hydrolysis resistance, and resistance to dealumination.^{174,182}

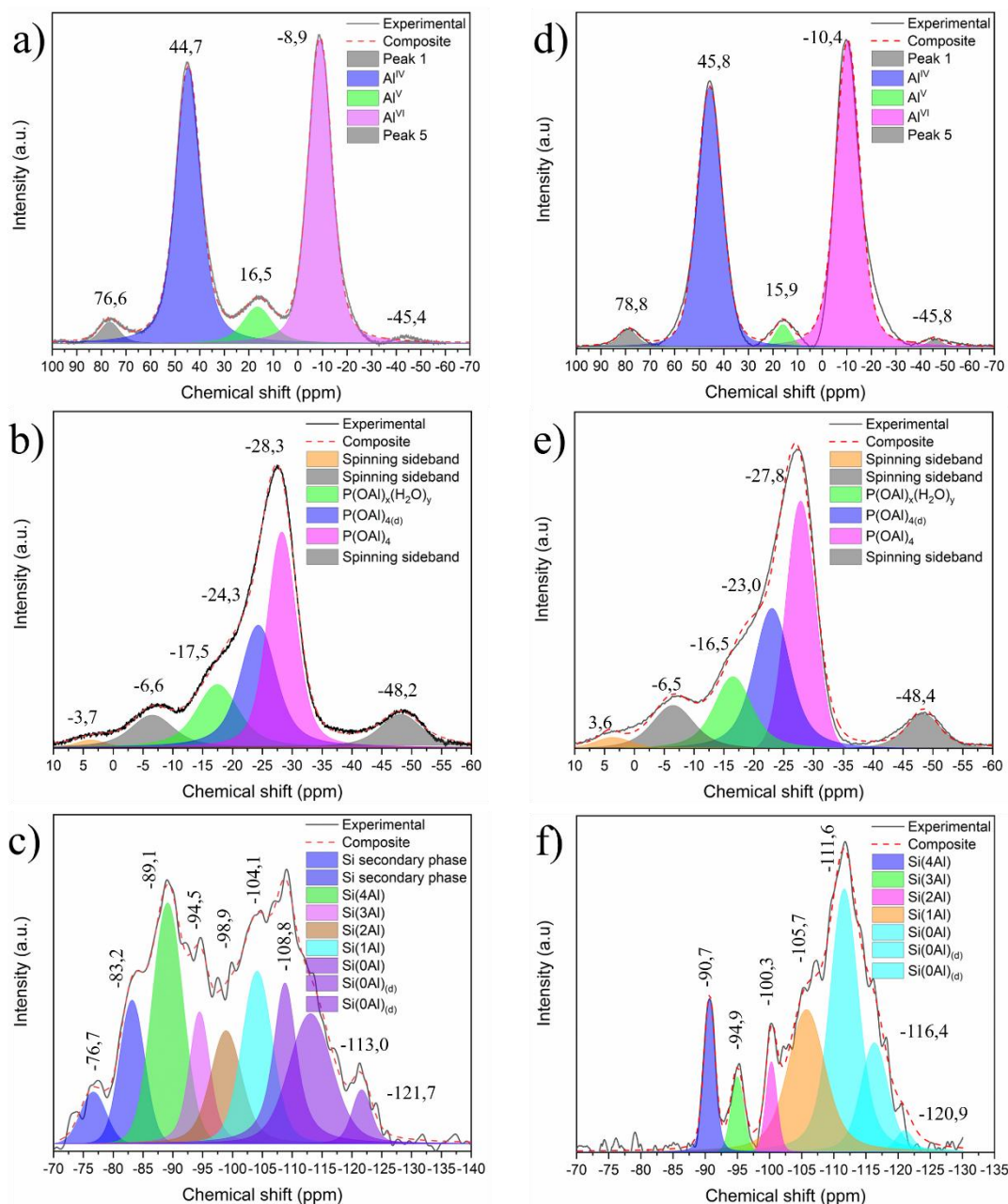


Figure 59. MAS-NMR spectra of ^{27}Al , ^{31}P and ^{29}Si for samples MW_T1_24H (a, b, c) and MW_3M_1T_24H (d, e, f).

The quantitative results from the solid-state NMR analyses are shown in Figure 60. For the MW_T1_24H sample, it is observed that the predominant species for ^{27}Al and ^{31}P are Al^{IV} (44.8%) and $\text{P}(\text{OAl})_4$ (63.9%), indicating satisfactory incorporation of these elements into the SAPO-34 framework. The ^{29}Si analysis reveals a significant presence of $\text{Si}(4\text{Al})$ species, accounting for 28% of the total silicon environment.

In the MW_3M_1T_24H sample, for ^{27}Al , the most abundant species were Al^{VI} (51.2%), indicating that a larger fraction of aluminum interacted with water. The ^{31}P

analysis shows a similar trend to the previous sample, with hydrated species $P(OAl)_x(H_2O)_y$ accounting for 16.2% compared to 62.4% of $P(OAl)_4$. The ^{29}Si analysis reveals a greater contribution of the SM3 mechanism in the incorporation of silicon into the SAPO-34 framework.

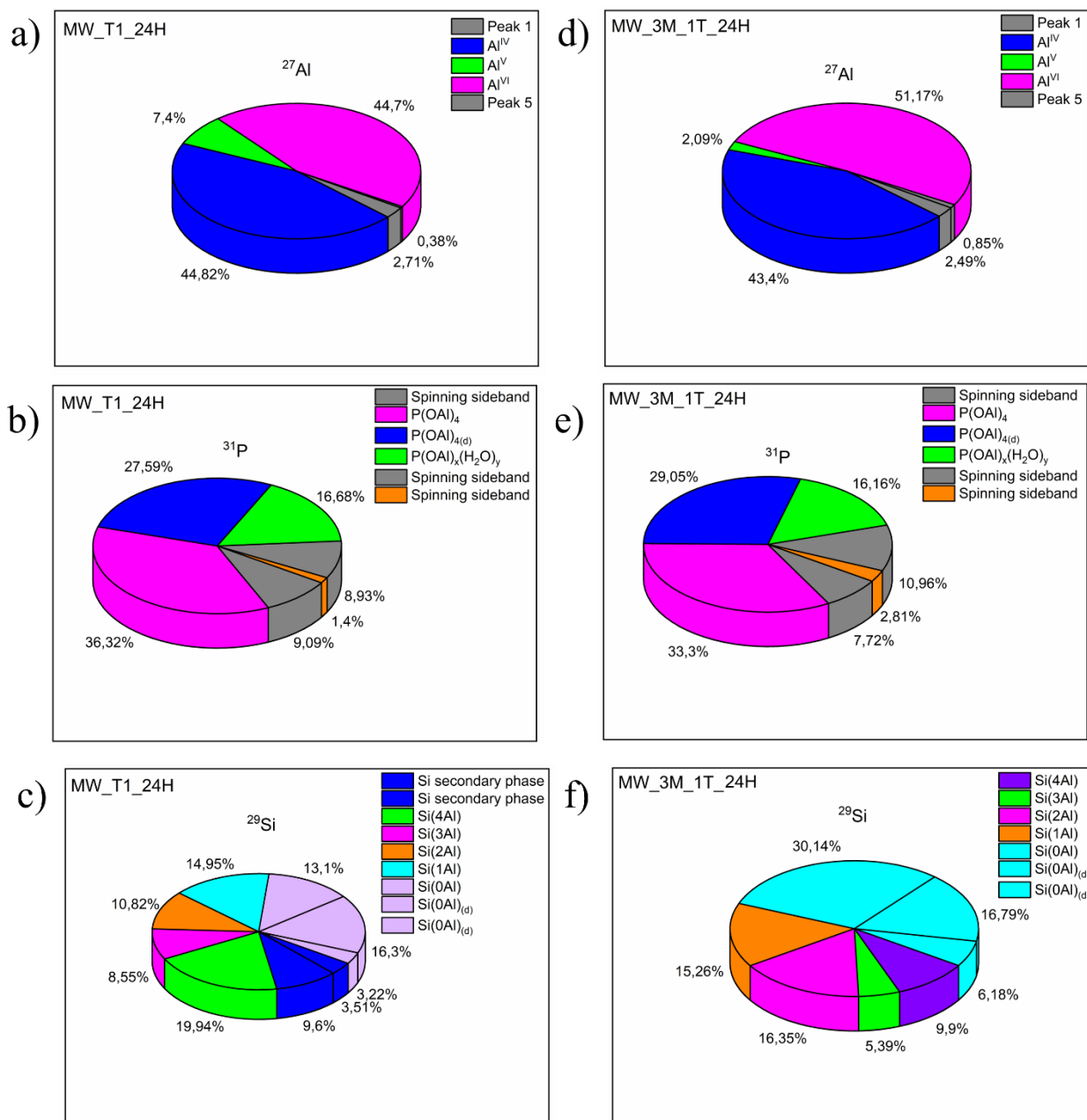


Figure 60. Percentages of species identified via MAS-NMR spectroscopy for the samples MW_T1_24H (a, b, c) and MW_3M_1T_24H (d, e, f).

5.3.6. Nitrogen Gas Adsorption

The nitrogen adsorption-desorption isotherms for the samples discussed in this section can be seen in Figure 61. The observed behavior of the samples synthesized via microwave using TEAOH and MOR/TEAOH follows the IUPAC classification of Type I isotherms, typical of microporous materials. The MW_T1_12H sample exhibited H4-type hysteresis, which may be caused by aggregation of the zeolite crystals.¹⁶⁷ Materials synthesized with 24-hour treatments, which exhibited higher crystallinity as measured by XRD, displayed isotherms with an almost complete absence of hysteresis, with the adsorption and desorption branches showing negligible divergence.

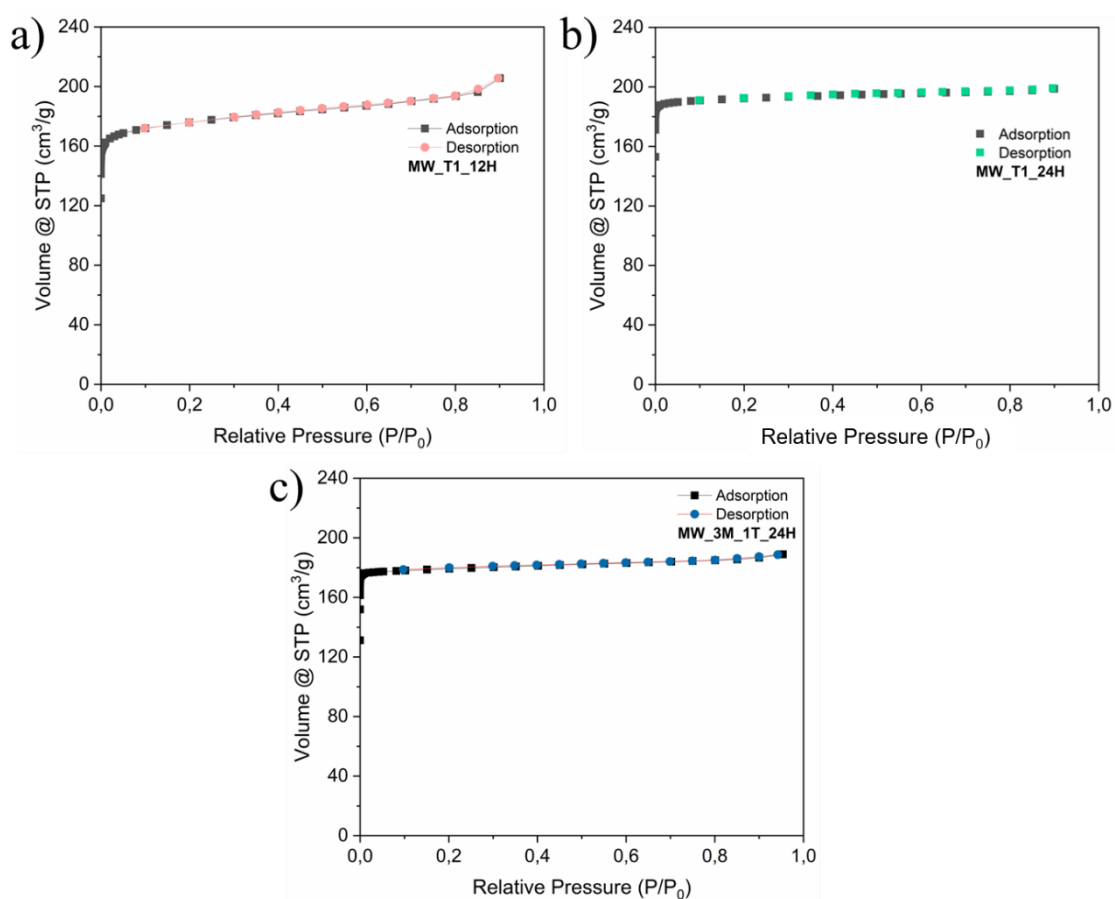


Figure 61. N₂ gas adsorption isotherms of samples: (a) MW_T1_12H, (b) MW_T1_24H, and (c) MW_3M_1T_24H.

The values of total surface area (S_{BET}); micropore area (S_{micro}), micropore volume (V_{micro}), and external surface area (S_{ext}); as well as total pore volume (V_{T}) can be found in Table 29. The graphs used to obtain these values are presented in the Appendix section.

Table 29 shows that the synthesized samples exhibited high BET specific surface areas and large micropore areas. Sample MW_T1_12H presented a S_{BET} of 706.6 m²/g and a micropore area of 639.0 m²/g, corresponding to 90% of the BET area. Increasing the microwave thermal treatment time to 24 hours resulted in a significant increase in S_{BET} and S_{micro} , rising to 810.6 and 789.3 m²/g, respectively, in which these values indicate that 98% of the BET-estimated area is attributable to micropores presence.

The results obtained for sample MW_3M_1T_24H were somewhat lower than those observed for samples HT_3M_1T_96H and MW_T1_24H. The decreases in S_{BET} and S_{micro} can be attributed to the larger average particle size of this sample compared with the others. Nevertheless, the microporous fraction remains significant, corresponding to approximately 96% of the BET surface area.

Table 29. Textural properties calculated via BET method and t-plot of materials synthesized by microwave heating using a single or dual organic structure-directing agent.

Sample	$S_{\text{BET}}^{\text{a}}$ (m ² /g)	$S_{\text{micro}}^{\text{b}}$ (m ² /g)	$S_{\text{ext}}^{\text{b}}$ (m ² /g)	$V_{\text{micro}}^{\text{b}}$ (cm ³ /g)	$V_{\text{meso}}^{\text{c}}$ (cm ³ /g)	V_{total} (cm ³ /g)
MW_T1_12H	706.6	639.0	67.6	0.243	0.061	0.304
MW_T1_24H	810.6	789.3	21.3	0.289	0.018	0.307
MW_3M_1T_24H	760.4	732.5	27.9	0.263	0.026	0.289

Surface area ^aBET; ^b S_{micro} (microporous area), S_{ext} (external surface area) e V_{micro} (microporous volume) determined by t-plot method. ^c V_{meso} (mesoporous volume) = $V_{\text{total}} - V_{\text{micro}}$; V_{total} determined by the penultimate adsorption point (P/P_0).

The use of dual templates (TEAOH/MOR) produced materials with good crystallinity and mean particle sizes equal to or smaller than those observed for the T1 composition. Under hydrothermal conditions, a MOR/TEAOH molar ratio of 3:1 yielded a material with 82% crystallinity and a mean particle size of approximately 1.60 μm. Mixed-template strategies can reduce production costs, as TEAOH is a relatively expensive structure-directing agent. The use of DPA/TEAOH resulted in a material with lower crystallinity (~54%), but with a smaller mean particle size (0.74 μm) and low size dispersity. These results indicate that different organic structure-directing agents (OSDAs) directly affect the nucleation and growth kinetics during the zeolite formation process. The use of DPA/TEAOH, for example, exhibited slower growth kinetics, which may be advantageous for membrane growth applications. In the secondary-growth method for membrane development, the hydrothermal step is ideally conducted under

slow-growth conditions, promoting the formation of a homogeneous and dense membrane with a high degree of crystal intergrowth, thereby minimizing the formation of intercrystalline porosity.

The application of microwave heating enabled the synthesis of materials with high crystallinity (up to 92%), reduced mean particle sizes, and narrow size distributions, while requiring thermal treatment times three to four times shorter (24 h) than those needed for the conventional hydrothermal route (96 h). Notably, sample MW_3M_1T_24H exhibited the highest crystallinity in this study (~92%); however, it also presented a relatively large mean particle size of 4.38 μm .

CHAPTER 6 – SAPO-34 MEMBRANES PRODUCTION AND SEPARATION PERFORMANCE ANALYSIS

Chapters 4 and 5 address, respectively, different strategies for producing macroporous supports aimed at developing materials that exhibit an optimal trade-off between porosity and mechanical strength, and distinct methodologies for synthesizing the SAPO-34 zeolite with the objective of obtaining products of high phase purity, pronounced crystallinity, and controlled particle size.

This section describes the use of seeds produced in this study to grow SAPO-34 membranes on commercial α -alumina tubes and on α -alumina tubes fabricated by the freeze-casting method.

6.1. Fabrication of Membranes on Commercial α -Al₂O₃ Tubes

In light of the discussions set out in Chapter 5, three seed crystals were selected to guide the experiments related to the fabrication of SAPO-34 membranes. The selection of the seeds was based on the following criteria: crystallinity (X_c), average particle size (A_s), micropore area measured by the t-plot method (S_{micro}), and the absence of competing phases in the samples. Accordingly, the chosen seeds were HT_T1_96h ($X_c = 85.2\% \mid A_s = 2.3 \mu\text{m} \mid S_{\text{micro}} = 732.5 \text{ m}^2 \cdot \text{g}^{-1}$), MW_T1_24H ($X_c = 71.3\% \mid A_s = 2.8 \mu\text{m} \mid S_{\text{micro}} = 789.3 \text{ m}^2 \cdot \text{g}^{-1}$), and MW_3M_1T_24H ($X_c = 92.2\% \mid A_s = 4.4 \mu\text{m} \mid S_{\text{micro}} = 732.5 \text{ m}^2 \cdot \text{g}^{-1}$).

The following SEM images correspond to the deposition of the different seeds listed above onto α -alumina substrates via the dip-coating technique. The characteristics of the seeds (crystal size, purity, geometry, and crystallinity) are of great importance and contribute significantly to the final quality of the membrane.⁴¹ In this context, Figure 62 shows that the HT_T1_96H and MW_T1_24H seeds produced more effective coatings compared to the MW_3M_1T_24H seed.

Seeds with smaller sizes and low size dispersion are able to pack more efficiently and homogeneously than larger crystals. Consequently, the occupied regions tend to exhibit a higher crystal density, which reduces intercrystalline voids and enhances the intergrowth. As a result, the growth of thinner and more uniform membranes is favored.^{41,183} Thus, it was observed that the tubes coated with the MW_3M_1T_24H seed exhibited lower crystal adhesion on the alumina surface, with the macroporous structure of the substrate clearly visible in the images.

The images in Figure 62 also demonstrate that depositing multiple layers can significantly enhance the coverage of the substrate surface. Once again, the MW_3M_1T_24H seed did not achieve high surface coverage, even after three successive depositions. In contrast, the other seeds exhibited excellent coverage with increasing numbers of depositions. These results suggest that crystal size is a fundamental characteristic for the formation of homogeneous films on the substrate.

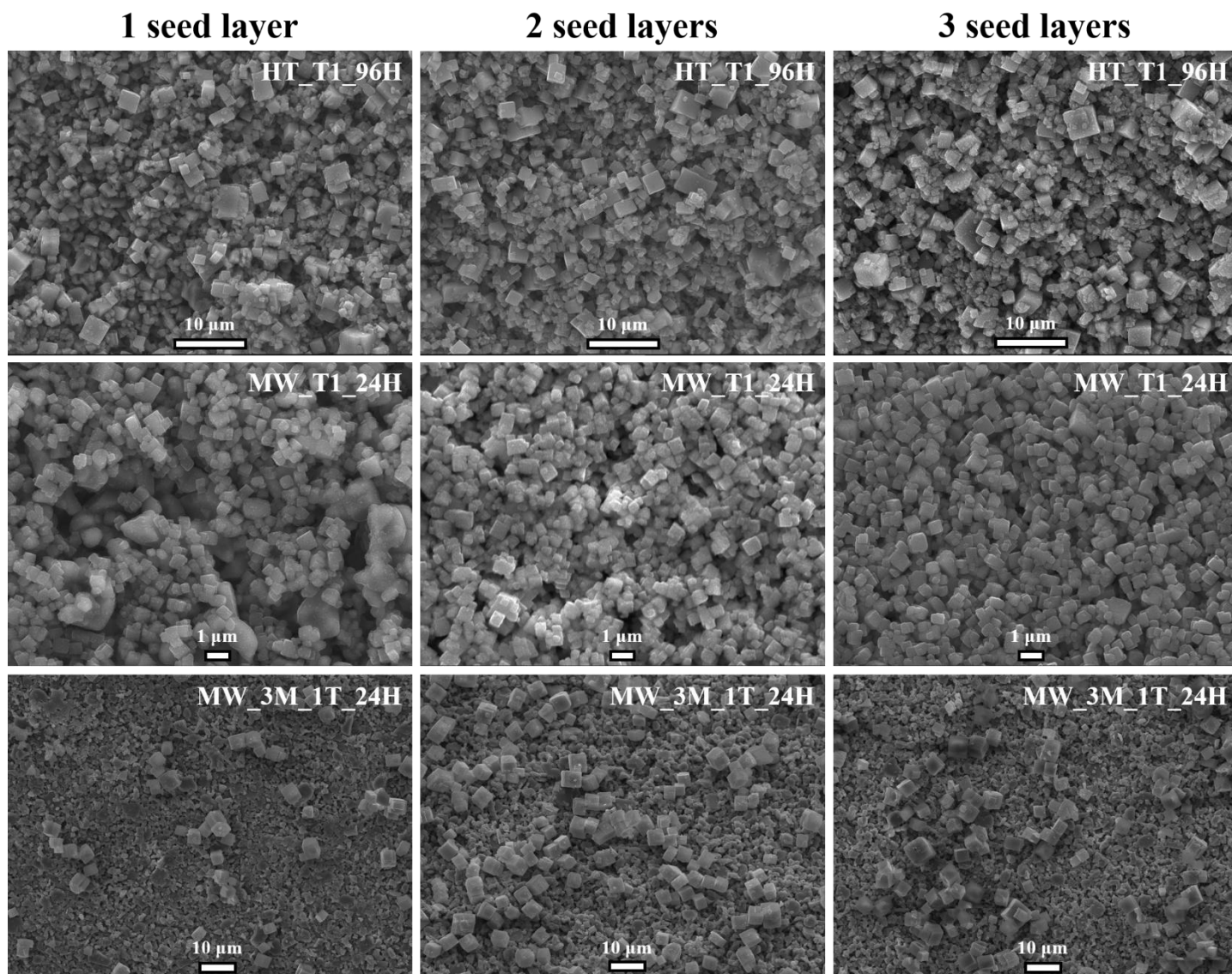


Figure 62. SEM analysis of α -alumina substrates coated with one to three layers of the selected SAPO-34 seed materials.

In view of the results from seeding the commercial tubes, the growth of membranes via the hydrothermal method was subsequently carried out. The results obtained using the HT_T1_96H seed are shown in Figure 63.

After applying 6 hours of hydrothermal treatment, it is observed that the coverage of the commercial tube surfaces remains poor, even when coated with two or three layers of pre-secondary-growth seed. Furthermore, this condition was insufficient to promote the formation of well-structured, interconnected crystals, indicating a likely high presence of defects in the membrane. Intergrowth or crystal connectivity is crucial, as it minimizes the formation of non-selective intercrystalline pores. These pores are considered non-selective because they generally have dimensions on the meso or macropore scale, in contrast to intracrystalline pores. Consequently, permeation pathways are created within the membrane structure that are incapable of selectively separating N_2 and CH_4 , thereby impairing the overall separation performance.

This outcome is similarly observed for the sample with two seed layers and 12 hours of hydrothermal treatment (HT1962c_12H). However, the sample with three seed layers (HT1962c_12H) exhibited an excellent coverage of the support surface. The image clearly shows the interconnection between the faces and edges of the zeolitic cubic particles. This structure is highly desirable, as it contributes to an increased membrane density and a reduction in intercrystalline defects.

When the hydrothermal treatment was extended to 24 hours, it was observed that tubes coated with two or three seed layers exhibited satisfactory coverage and good interconnectivity between zeolitic particles. However, despite the longer treatment duration, the application of only a single seed layer was insufficient to promote intergrowth, as evidenced by the pronounced presence of separated zeolitic cubes on the surface. It is likely that the seeding process with only one layer promoted a low density of crystals on the surface of commercial tubes, creating larger spaces between particles. This fact may have contributed to the lower intergrowth seen in the images. In addition to the aforementioned factor, literature reports indicate that the type of zeolite and the thermal treatment conditions can also influence the quality of the coverage.¹⁸⁴

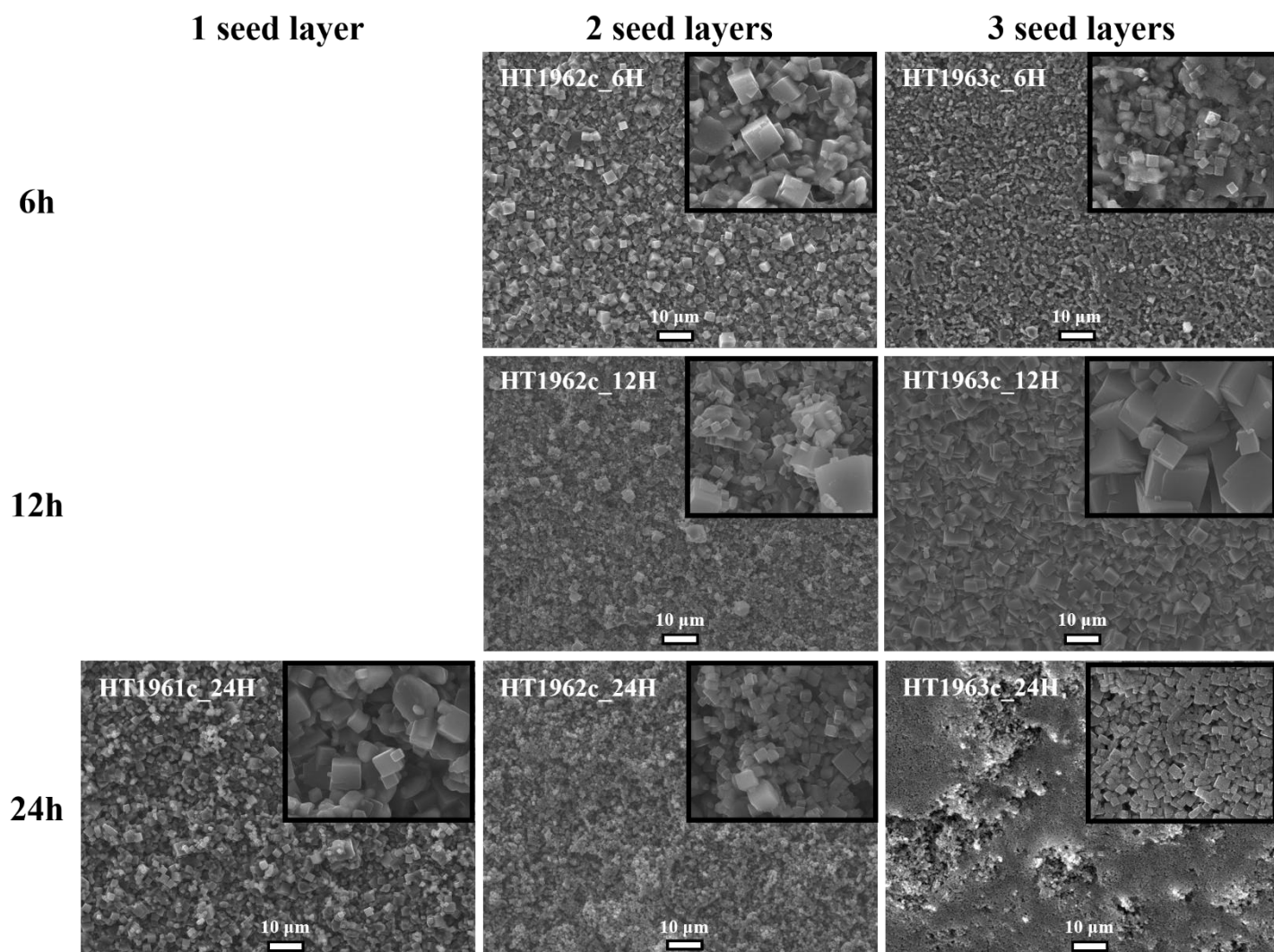


Figure 63. SEM analysis of commercial α -alumina substrates coated with SAPO-34 membranes applying HT_T1_96H seed. Applied magnifications of 500x and 2000x (highlighted).

Figure 64 presents cross-sectional images of tubes produced with the HT_T1_96H seed. It can be observed that membranes grown for 24 hours exhibited average thicknesses — from one to three seed layers — ranging from 4.5 to 44.8 μm , respectively. For the 12-hour growth period, membranes with two and three seed layers displayed average thicknesses between 6.8 and 11.2 μm , respectively. The change in growth time had a more pronounced effect on tubes coated with three seed layers than on those with two layers. In the first case, the 12 hours increase in the autoclave resulted in a membrane four times thicker, whereas in the latter case, the increase was more modest, corresponding to approximately 1.2 times.

Thus, the results presented in Figure 63 indicate that both the number of seed layers and the duration of hydrothermal treatment influence the final membrane thickness,

with the former being the parameter exerting the greatest impact. Moreover, with the exception of the HT1963c_24H membrane, due to its considerable thickness, all other membranes exhibited values consistent with those reported in the literature.^{13,14,50,90} Considering the results shown in Figures 62 and 63, the HT1963c_12H membrane stands out for combining excellent surface coverage with moderate membrane thickness. Although reduced thicknesses were observed in samples with fewer seed layers, these membranes appear to present surface defects in the images, which could significantly compromise the performance during permeation and the separation of the N₂/CH₄ gas mixture.

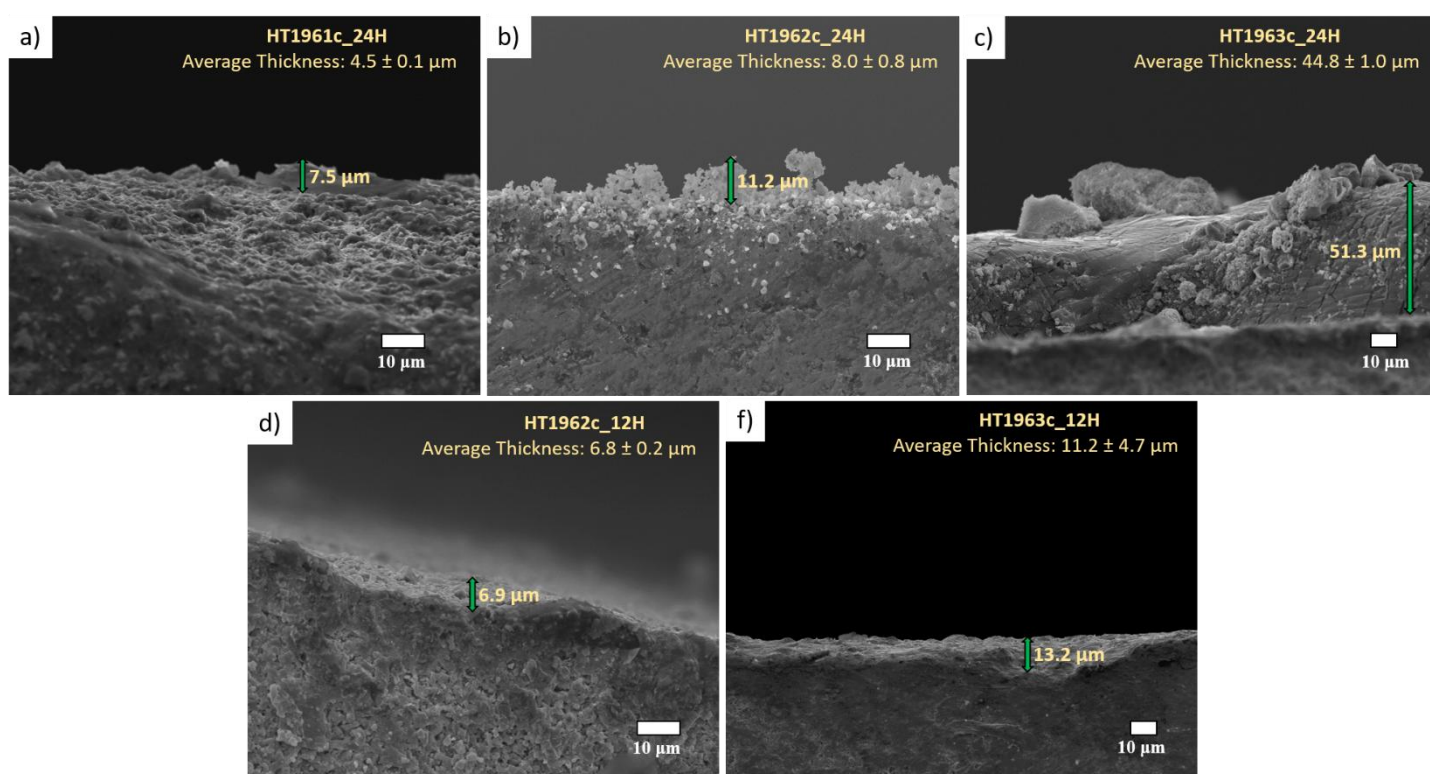


Figure 64. SEM images of the cross-sections of the commercial tubes synthesized with the HT_T1_96H seed. The corresponding thickness distributions are presented in the Appendix section.

The results regarding the use of the MW_T1_24H seed are shown in Figure 65. The coverage observed after only 6 hours of hydrothermal treatment appears to be more effective than that observed in the case shown in Figure 63. However, elongated structures with a hexagonal base, indicative of SAPO-5 formation, are evident. These structures were not observed in the MT1243c_6h membrane. Despite the improved coverage, it is again noted that intergrowth was insufficient to prevent the presence of defects on the membrane surface.

Applying 12 hours of hydrothermal treatment, it was observed that deposits resulting from two or three seed coatings of MW_T1_24H were capable of promoting formation of the desired membrane structure. Both micrographs clearly show that the conditions favored the growth of interconnected crystals, which led to a reduction in nonselective pores. The same behavior was observed for samples synthesized with 24 hours of hydrothermal treatment, including cases in which only a single seed coating was applied.

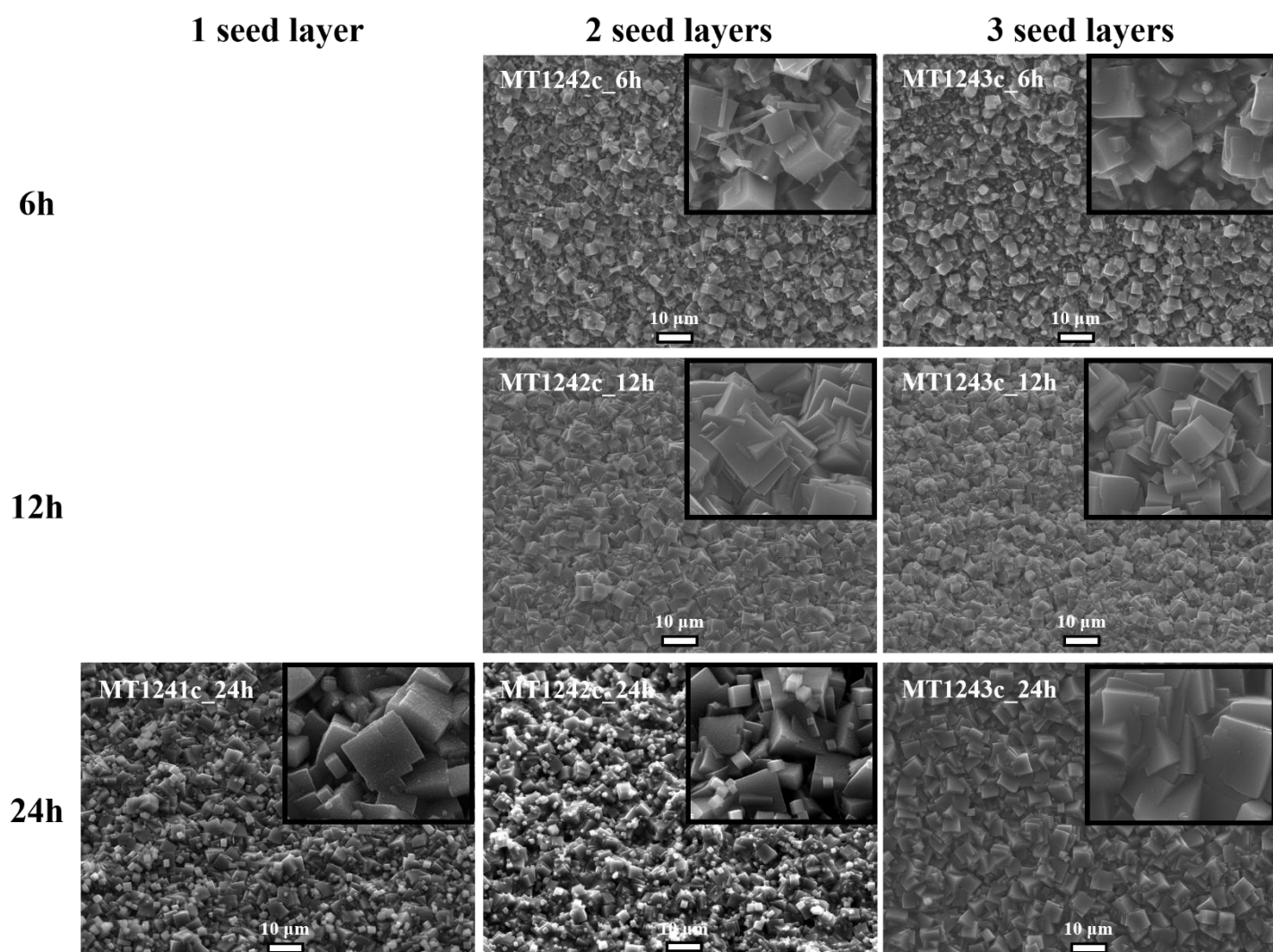


Figure 65. SEM analysis of commercial α -alumina substrates coated with SAPO-34 membranes applying MW_T1_24H seed. Applied magnifications of 500x and 2000x (highlighted).

Figure 66 shows cross-sections of the tubes produced using the MW_T1_24H seed. Membranes synthesized with a growth time of 24 hours exhibited average thicknesses, from one to three seed coatings, in the range of 9.0 to 47.9 μm , respectively. For a growth time of 12 hours, the membranes exhibited average thicknesses — for two

and three seed coatings — between 5.2 and 13.8 μm , respectively. Again, the change in growth time had a greater impact on tubes deposited with three seed coatings than on those with two layers.

Thus, the results in Figure 66 indicate that the number of seed coatings and the duration of the hydrothermal treatment affect the final membrane thickness. Furthermore, with the exception of membrane MT1243c_24H, whose thickness is markedly high, the other membranes displayed thickness values consistent with those reported in the literature.^{14,41,80,90,93} Li *et al.* (2015) synthesized SAPO-34 membranes for N_2/CH_4 separation using secondary growth times from 6 to 24 hours and a synthesis temperature of 220 $^\circ\text{C}$. The study reports membrane thicknesses in the range of 3 to 9 μm . For membranes with a thickness of 8.2 μm , the group reported an N_2/CH_4 selectivity of 6.0 ± 0.5 . Considering the results presented in Figure 65, membranes MT1242c_12H and MT1243c_12H stand out for exhibiting excellent surface coverage, moderate thicknesses, short production times, and the absence of undesirable phases (SAPO-5/SAPO-18).

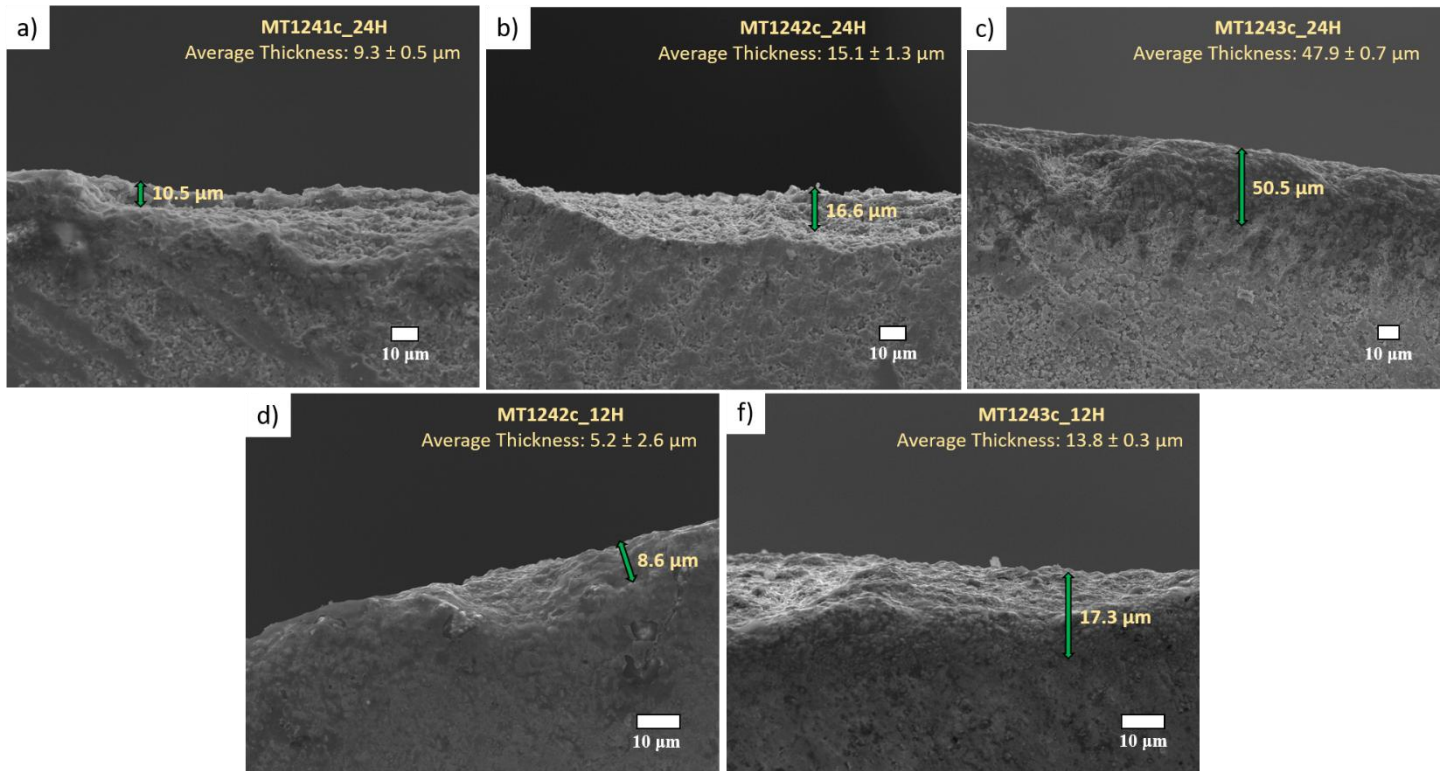


Figure 66. SEM images of the cross-sections of the commercial tubes synthesized with the MW_T1_24H seed. The corresponding thickness distributions are presented in the Appendix section.

Figure 67 shows that membranes produced using the MW_3M_1T_24H seed exhibited highly homogeneous coverage of the α -alumina surfaces in samples

M3M242c_6h and M3M243c_6h after only 6 hours of hydrothermal treatment. However, both membranes displayed substantial occurrences of the competing SAPO-5 phase across the material surface. This result is noteworthy because, among the three seeds tested, the one prepared with a double organic structure-directing agent provided the best coverage at a short secondary growth time.

For samples subjected to 12 hours of hydrothermal treatment, deposits from two or three seed coatings of MW_3M_1T_24H were also able to promote formation of the desired membrane structure. However, the SAPO-5 phase remained present, albeit with lower intensity, in sample M3M242c_12h. Similarly, membranes synthesized with 24 hours of hydrothermal treatment, even when only a single seed coating was applied, exhibited excellent coverage and an absence of undesirable phases. The application of this seed proved effective for the formation of interconnected crystals that reduce nonselective pores. However, it exhibited greater issues related to the appearance of secondary phases.

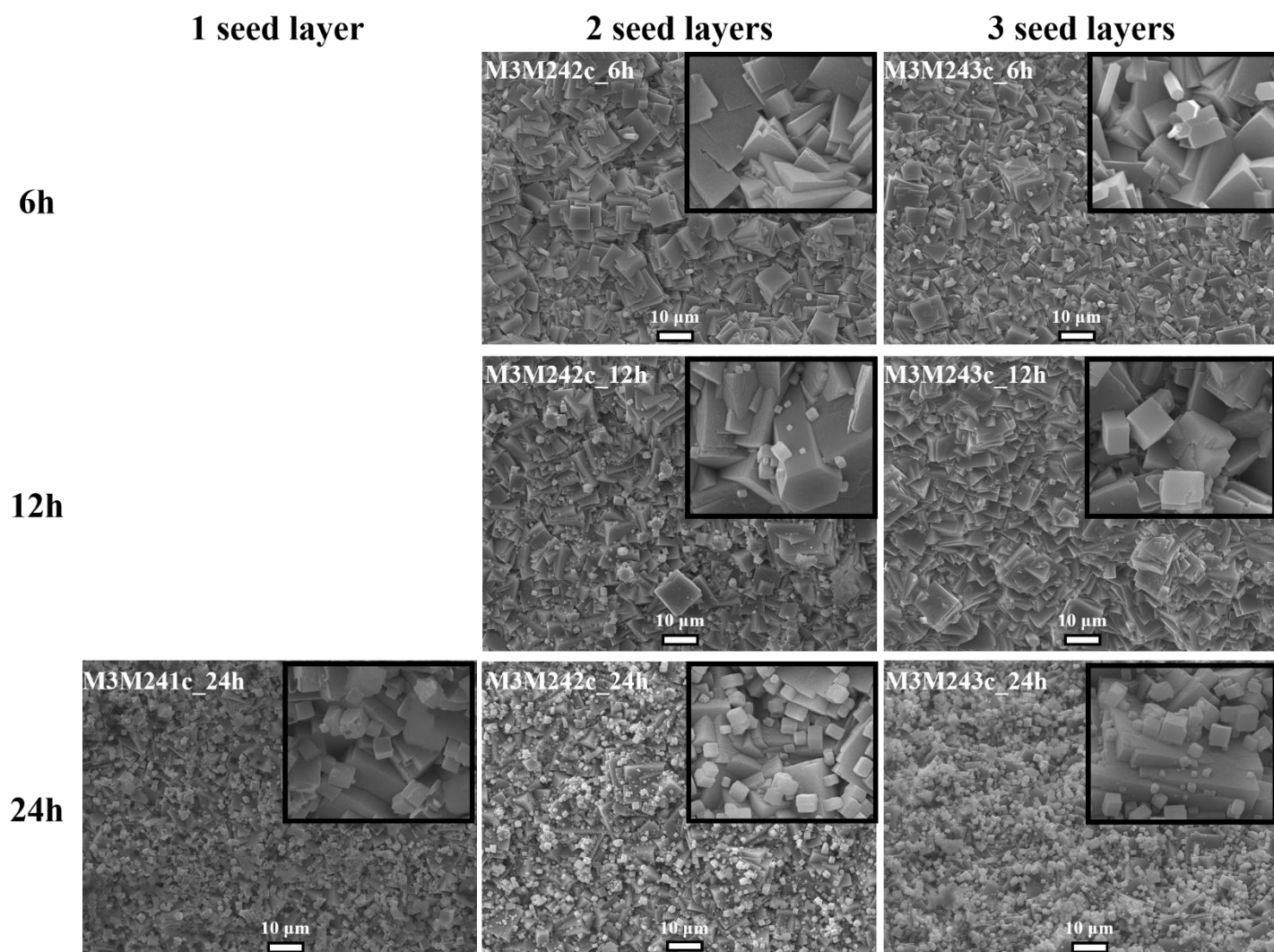


Figure 67. SEM analysis of commercial α -alumina substrates coated with SAPO-34 membranes applying MW_3M_1T_24H seed. Applied magnifications of 500x and 2000x (highlighted).

Figure 68 shows cross sections of the tubes produced using the MW_3M_1T_24H seed. Membranes synthesized with a growth time of 24 hours exhibited average thicknesses, for one to three seed coatings, in the range of 15.1 to 37.1 μm , respectively. For a growth time of 12 hours, the membranes exhibited average thicknesses, for two and three seed coatings, between 12.6 and 15.1 μm , respectively. The use of this seed produced different trends, with the change in growth time having a similar impact on tubes deposited with three and with two seed coatings. Increasing the hydrothermal treatment time from 12 to 24 hours resulted in thickness increases of approximately 2.2 times in both cases.

Thus, the results shown in Figure 64 indicate that the number of seed coatings and the duration of the hydrothermal treatment again affect the final membrane thickness.

Moreover, with the exception of membranes M3M242c_24H and M3M243c_24H, due to their elevated thicknesses, the remaining membranes exhibited values consistent with those reported in the literature. Membrane M3M243c_12H can be highlighted for exhibiting excellent surface coverage, moderate thickness, a short production time, and the absence of secondary phases.

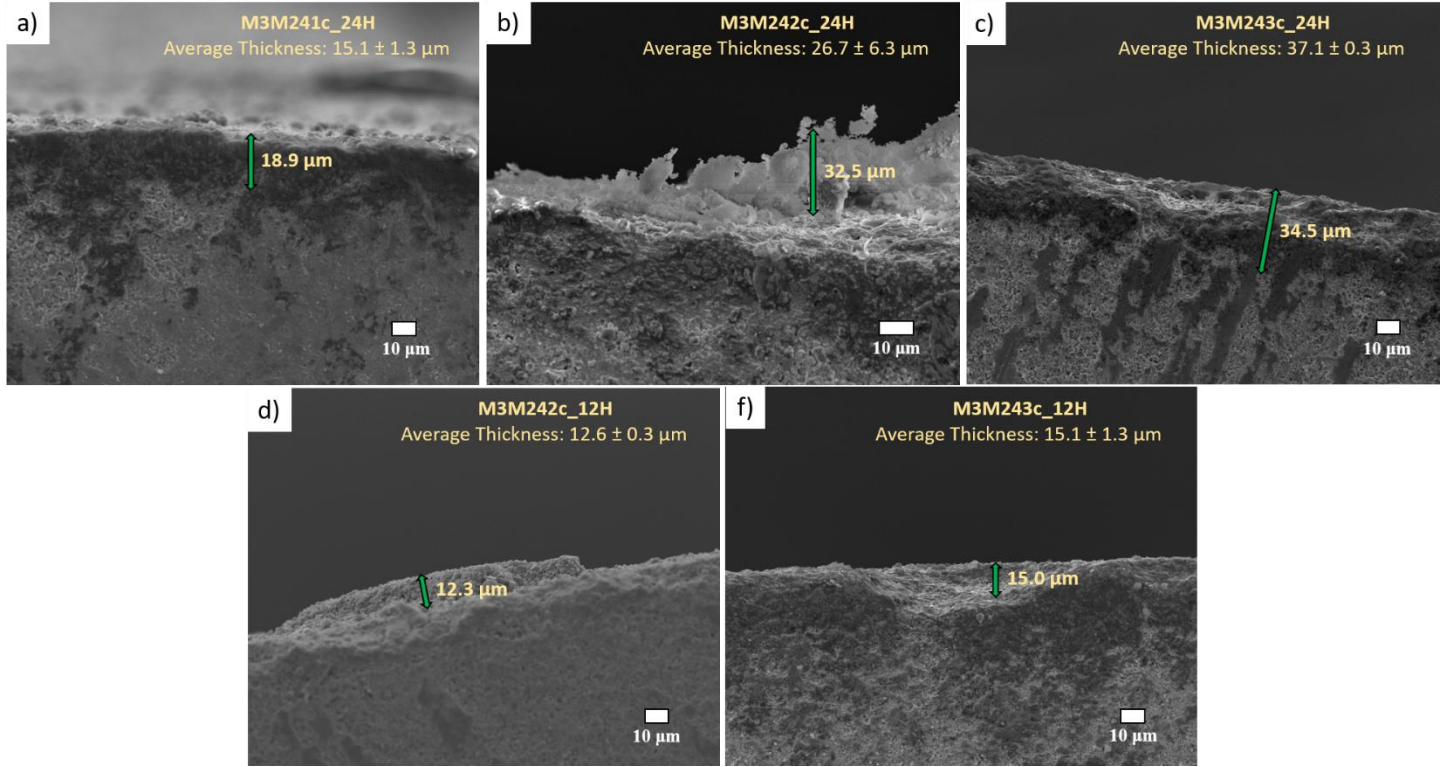


Figure 68. SEM images of the cross-sections of the commercial tubes synthesized with the MW_3M_1T_24H seed. The corresponding thickness distributions are presented in the Appendix section.

6.2. Synthesis of membranes on α -alumina tubes produced via freeze-casting

The definition of the substrate type is fundamental because it plays an important role in ensuring the quality of the formed membrane. The macroporous support must exhibit hydrothermal, chemical, and mechanical stability for application under realistic operating conditions. In addition, it is desirable that its coefficient of thermal expansion be compatible with that of the selective material. A mismatch between the thermal expansion coefficients of the substrate and the zeolite layer can lead to delamination of the zeolite layer from the substrate during temperature variation.⁴¹

Surface properties of the substrate, such as roughness, are relevant factors for the development of uniform SAPO-34 films. To ensure the formation of a high-quality,

interconnected zeolite layer, the substrate surface should be smooth and exhibit a small, homogeneous pore size distribution. However, excessively smooth surfaces can reduce adhesion of the zeolitic film and increase the likelihood of cracks or defect formation during removal of the organic structure-directing agent. Moreover, as discussed in Chapter 2, the substrate should offer low mass-transfer resistance to facilitate permeation through the membrane. Therefore, for membrane growth it is ideal to use a thin, highly porous substrate with a reasonably smooth surface.^{41,185}

The discussions presented in Chapter 4 indicated substantial potential for producing ceramic α -Al₂O₃ tubes by freeze-casting using the naphthalene-camphor binary composition and two-hour sintering cycles. This potential arises because that composition demonstrated an excellent balance between compressive strength and open porosity.

Having selected the tubular substrate production method and based on the results presented in Section 6.1, the initial test was chosen to produce membranes on freeze-cast tubes by depositing three seed layers of MW_T1_24H followed by a 12-hour hydrothermal secondary growth. This choice was justified by the seed's excellent surface coverage, intermediate thickness, and absence of adverse phases compared with the other seeds tested on commercial tubes.

Figure 69 presents SEM images of the surface (a-b) and the cross section (c) of sample FCMT1243c_12H. Based on the results observed for sample MT1243c_12H (Section 6.1), it is apparent that the change of substrate had a significant impact on crystal intergrowth and on the formation of a high-quality membrane. In Figures 69 (a-b) the crystals retained the cubic morphology expected for SAPO-34 but were arranged as isolated crystals. Consequently, the formation of a continuous multifaceted film, as observed in Figure 61, was not detected.

This zeolitic film configuration can be problematic because failure to form a dense, interconnected-crystal membrane may produce gaps between crystals with dimensions larger than the target gas molecular sizes. Consequently, the membrane's ability to selectively separate the target gas can be compromised. Although the formation of a multifaceted continuous layer is not clearly observed, Figure 69 (b) shows that the entire imaged surface is covered with SAPO-34. Furthermore, Figures 69 (c-d) reveal that the average thickness of the formed membrane was 12.3 μm , slightly smaller than that observed on commercial tubes.

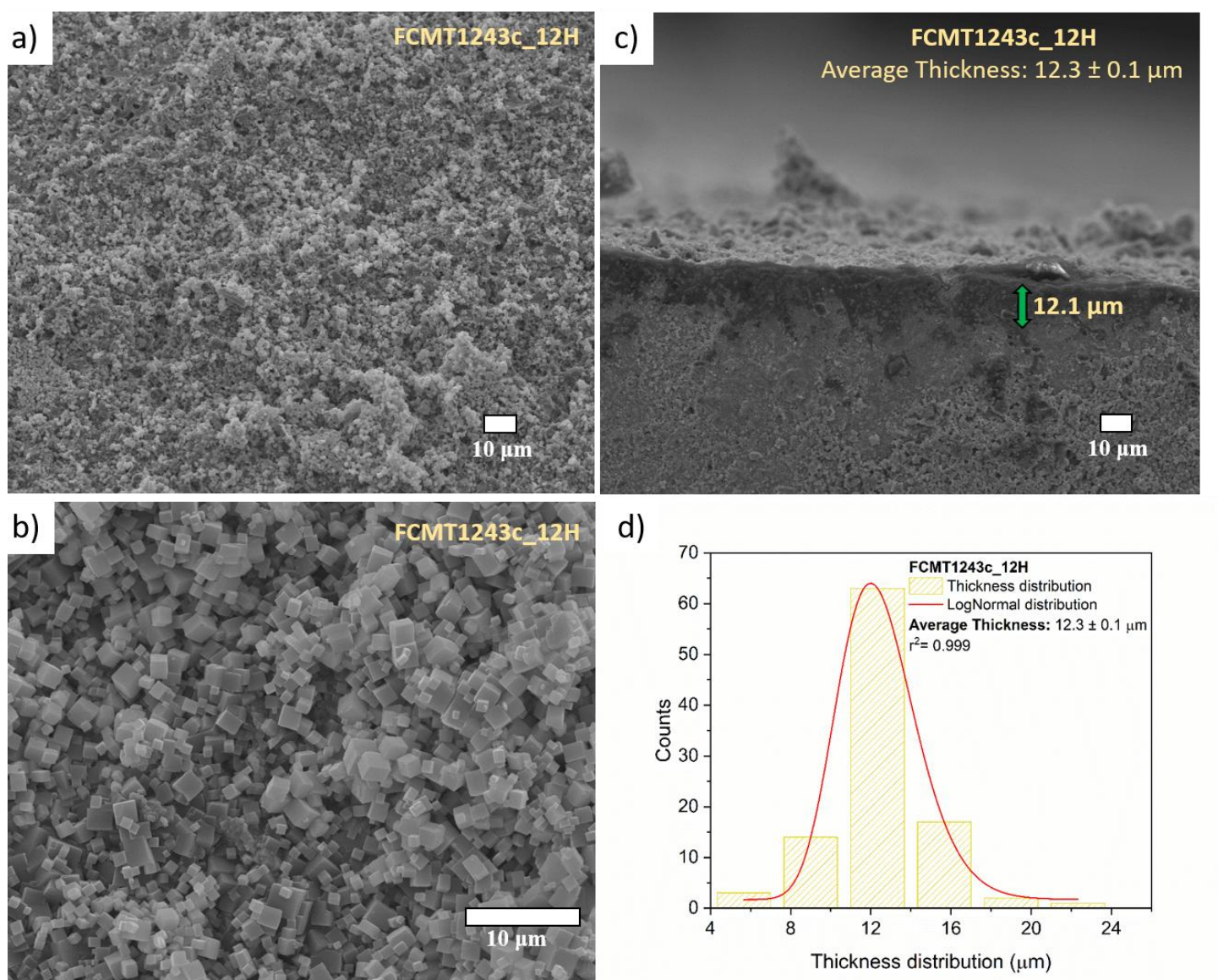


Figure 69. SEM images of the surficial (a-b) and cross-section areas (c) of the membranes synthesized with the MW_T1_24H seed and deposited in freeze-casting tubes produced with hypereutectic camphor-naphthalene composition.

6.3. Application of the Ideal Adsorbed Solution Theory (IAST) method for evaluating adsorption selectivity

Based on the results presented in Sections 6.1 and 6.2, this section will address the effect of the adsorption phenomenon on the process of gas mixture separation. In this context, this study explores results obtained from adsorption experiments with the gases N_2 , CO_2 , and CH_4 .

Figure 70 (a–b) presents the absolute and molar adsorption isotherms fitted with the Langmuir model for N_2 , CO_2 , and CH_4 at 298.15 K for the MW_T1_24H sample.

Under these conditions, CO₂ exhibited the highest adsorption capacity, followed by CH₄ and N₂. The obtained isotherms indicate that both N₂ and CH₄ display weak adsorption at this temperature, suggesting that the contribution of adsorption to the N₂/CH₄ separation process is minor compared to the diffusional mechanism.¹⁴ In contrast, CO₂ shows a markedly higher adsorbed volume, evidencing its stronger interaction with the adsorbent surface.

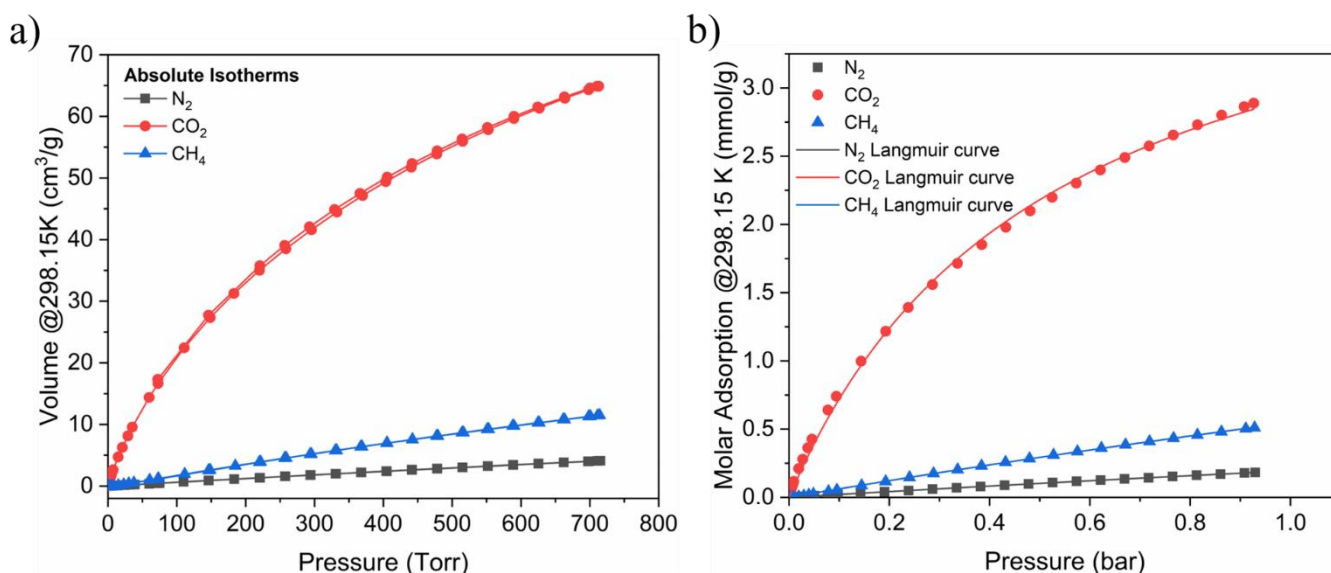


Figure 70. Langmuir-fitted adsorption isotherms of N₂, CO₂, and CH₄ at 298.15 K for the MW_T1_24H sample.

The Langmuir fitting parameters presented in Table 30 show that the maximum adsorption capacity ($q_{\max}$) follows the expected trend when comparing N₂, CO₂, and CH₄. Overall, considering the physicochemical characteristics of both gases and the SAPO-34 zeolite, the observed behavior is: $q_{\max, \text{CO}_2} > q_{\max, \text{CH}_4} > q_{\max, \text{N}_2}$. This trend is consistent with the higher polarizability and quadrupole moment of CO₂, which lead to stronger interactions with the polar sites of SAPO-34. Methane, being less polarizable, exhibits intermediate adsorption capacity, whereas N₂, with the lowest polarizability and weakest interaction potential, shows the smallest $q_{\max}$ among the three gases. Furthermore, a similar trend is observed for the affinity constant (b). However, the maximum adsorption capacities obtained for methane and carbon dioxide were unexpectedly close. This result can be attributed to the fact that, under the pressure and temperature conditions applied, the CH₄ isotherm did not reach the adsorptive saturation region (plateau), which may have led to an inaccurate extrapolation in the Langmuir fitting.

Table 30. Langmuir fitting parameters obtained from adsorption isotherms of N₂, CO₂, and CH₄ at 298.15 K.

Parameters	N ₂	CO ₂	CH ₄
$q_{\max}$ (mmol.g ⁻¹)	2.01 ± 0.03	4.41 ± 0.06	4.13 ± 0.32
b (bar ⁻¹)	0.11 ± 0.01	1.95 ± 0.05	0.15 ± 0.01
R ²	0.999	0.999	0.999

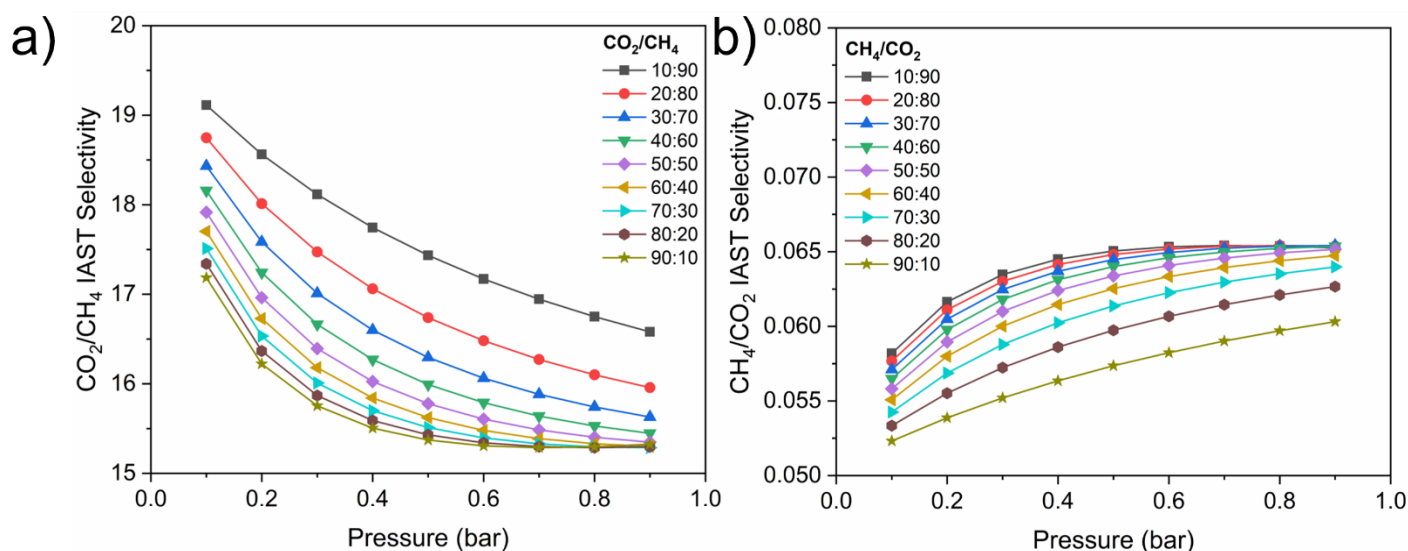
Figure 71 presents the adsorption selectivity curves calculated using the Ideal Adsorbed Solution Theory for the binary gas mixtures CO₂/CH₄, CH₄/CO₂ (a–b); N₂/CH₄, CH₄/N₂ (c–d); and N₂/CO₂, CO₂/N₂ (e–f). To apply the IAST model, the individual adsorption isotherms were fitted with the Dual-Site Langmuir (DSL) equation. The DSL model was chosen due to its ability to describe heterogeneous adsorption sites in the SAPO-34 structure. All isotherms were measured at an experimental temperature of 298.15 K, and the corresponding fitting parameters for each gas are provided in the Appendix.

For the CO₂/CH₄ separation, Figure 71 (a), adsorption selectivities above 15 were obtained, exhibiting a decreasing trend with increasing pressure or CO₂ molar fraction in the feed mixture. This behavior is consistent with expectations, as CO₂ exhibits a significantly higher affinity toward SAPO-34 due to strong quadrupolar interactions with its framework. At low pressures, adsorption is dominated by CO₂; however, as the pressure rises, CH₄ molecules may compete for the available adsorption sites, leading to partial site saturation and, consequently, a reduction in selectivity. As the CO₂ molar fraction in the gas mixture increases, the saturation effect becomes more pronounced, further influencing the calculated selectivity. Figure 71 (b) shows the reciprocal selectivity (CH₄/CO₂), with values well below one, confirming that CO₂ is preferentially adsorbed.

Figure 71 (c) illustrates the IAST-predicted selectivity trend for the N₂/CH₄ gas mixture. The selectivity values are below unity, indicating that the material exhibits a higher affinity for methane. The selectivity decreases with increasing pressure and decreasing nitrogen fraction in the feed mixture. This behavior can be explained by the fact that, under the experimental conditions (temperature and pressure) at which the absolute adsorption isotherms were obtained, neither N₂ nor CH₄ adsorption reached the saturation plateau. Consequently, as CH₄ possesses a larger kinetic diameter and higher

polarizability, the increase in pressure enhances its adsorption by promoting greater occupation of the available adsorption sites. This trend is consistent with the reciprocal case (CH_4/N_2), where the selectivity increases with both pressure and methane molar fraction, reaching values as high as 3.3. This result is consistent with previous reports in the literature. For instance, Shang et al. (2019) observed similar adsorption selectivity values for a 50:50 molar ratio mixture, reaching selectivity values of 2.9 for CH_4/N_2 .¹⁸⁶

Figure 71(e) presents the adsorption selectivity results for the N_2/CO_2 binary mixture. The observed behavior is interestingly opposite to that obtained for the CH_4/CO_2 system. CO_2 molecules exhibit a strong affinity toward the Brønsted acid sites of the zeolite framework. In contrast, CH_4 , although non-polar, possesses a higher polarizability than N_2 , enabling slightly stronger interactions and limited competition for adsorption sites at higher pressures. Conversely, N_2 shows considerably lower adsorption capacities that are nearly independent of pressure at 298.15 K, which can be attributed to its weak quadrupole moment and low polarizability. Therefore, even at elevated pressures, N_2 is unable to effectively compete for adsorption sites. This trend is further confirmed by the reciprocal selectivity (CO_2/N_2), which increases with both pressure and CO_2 molar fraction, reaching values of approximately 85 for a CO_2/N_2 mixture with a 90:10 mmol% ratio.



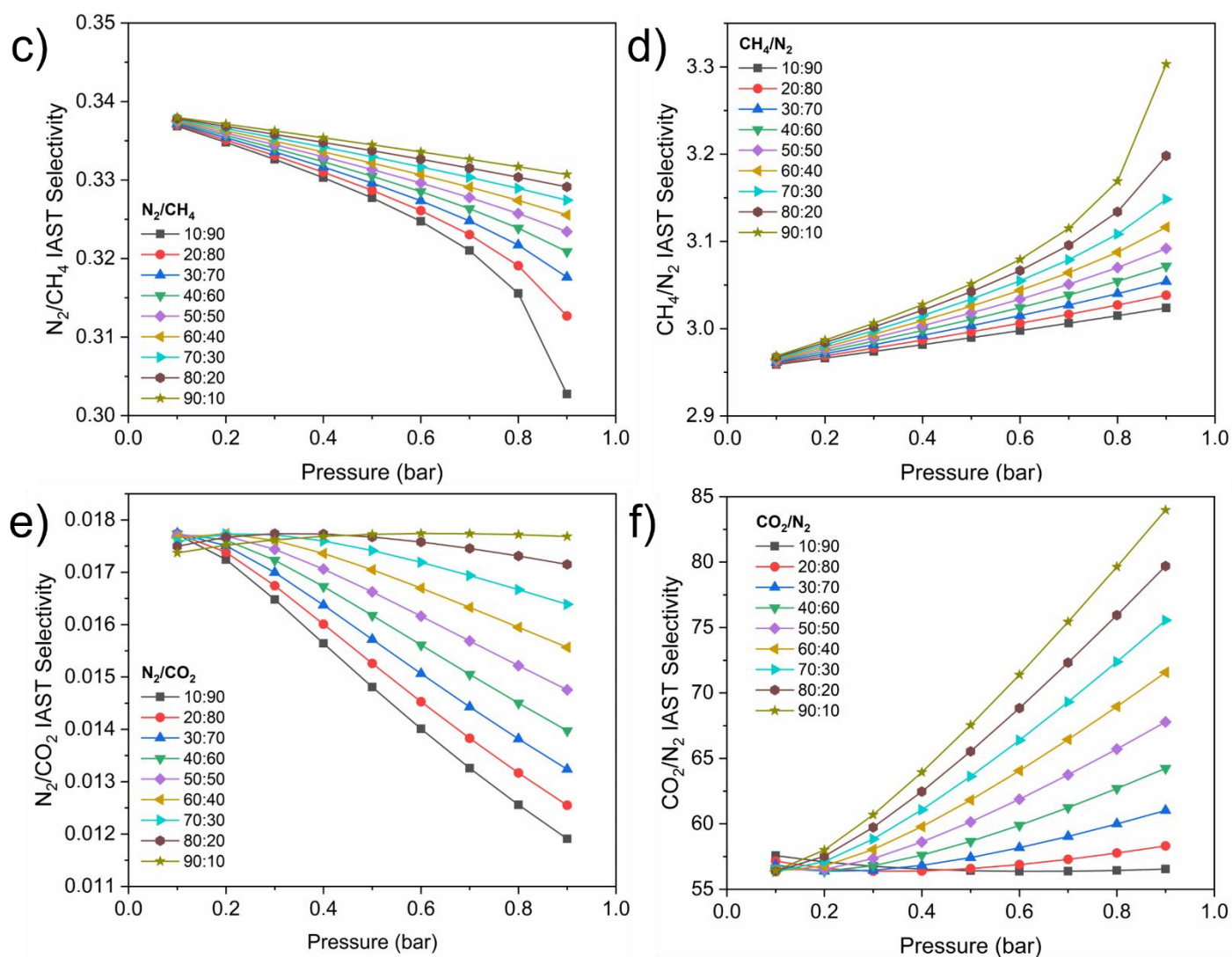


Figure 71. Adsorption selectivity results estimated using the Ideal Adsorbed Solution Theory (IAST) for the binary gas mixtures CO_2/CH_4 , CH_4/CO_2 (a-b); N_2/CH_4 , CH_4/N_2 (c-d); N_2/CO_2 , and CO_2/N_2 (e-f).

CONCLUSION

Given the challenges faced by industrial natural gas treatment processes in achieving methane purification through removal of the gases CO₂ and N₂, this study contributes by proposing the fabrication of SAPO-34 selective membranes supported on commercial and in-house produced macroporous substrates for the separation of mixtures present in natural gas.

The synthesis of ceramic supports by freeze casting enabled the controlled fabrication of monoliths with high total porosity (65-70%) and distinct pore morphologies through adjustment of solvent composition and sintering time while maintaining a fixed solid loading of 20 vol%. Alumina monoliths exhibited open porosities of 49-60%. Increasing sintering time generally produced larger grain sizes, reduced open porosity, and an increased proportion of isolated pores. These trends were not observed for alumina monoliths prepared using the Hypo_3H system. In those samples, microstructural defects appear to have induced the formation of macroscopic holes in the material, leading to higher open porosity and lower relative density.

The solvent composition influenced pore orientation and directionality: hypoeutectic compositions produced porous architectures characterized by discontinuous void segments, whereas eutectic compositions yielded lamellar structures aligned parallel to the freezing front. Mechanical strength depended on these pore architectures and on the fraction of open versus closed porosity. The eutectic composition, which produced a lamellar porous structure, exhibited the highest open porosity (52-58%); nevertheless, its compressive strength remained among the lowest (1.5-4.8 MPa), even after sintering for 3 h, likely due to the lamellar morphology and high open-porosity connectivity.

The hypereutectic composition exhibited distorted dendritic porosity and, with a sintering time of 2 h, achieved the best balance between open porosity (~ 53%) and compressive strength (~ 16 MPa). Production of single-channel tubes with the same composition yielded a porous architecture similar to that observed for the corresponding monoliths; however, the open-porosity fraction of the material decreased to approximately 40%.

Considering the feasibility and ease of controlling multiple variables in the synthesis of porous ceramics, this study demonstrates that the binary naphthalene-camphor solvent combined with the freeze-casting method is highly versatile and enables

fine control over the fabrication of macroporous materials that can be tailored as membrane supports.

In the second stage, the influence of precursor ratios and the use of single or dual-organic structure-directing agents on the hydrothermal synthesis of the SAPO-34 zeolite were investigated.

Using a single organic structure-directing agent, tetraethylammonium hydroxide (TEAOH), an increase in the concentrations of the Si, P, and template precursors promoted the formation of a more crystalline material (~85%), as observed for sample HT_T1_96H, and a reduced mean particle size (~2.3 μm). Solid-state NMR-MAS analyses further indicated that this composition favored formation of a material less susceptible to hydration than composition T2, preserving the tetrahedral Al and P units that comprise the SAPO-34 intracrystalline framework. The T1 methodology achieved approximately 60% crystallinity within the first 24 h of synthesis, whereas T2 required 72 h of hydrothermal treatment to reach comparable crystallinity.

The use of dual templates, TEAOH/MOR or TEAOH/DPA, produced materials with good crystallinity and mean particle sizes equal to or smaller than those observed previously. Under hydrothermal conditions, a molar ratio of 3:1 MOR/TEAOH yielded a material with 82% crystallinity and a mean particle size near 1.60 μm . Use of DPA resulted in a less crystalline material (~ 54%) but with a mean particle size of 0.74 μm and low size dispersity. The study shows that different OSDAs directly affect the kinetics of product formation, with DPA exhibiting a slower growth kinetics. Mixed-template strategies can reduce production costs because TEAOH is a relatively expensive structure-directing agent.

Applying microwave heating enabled the synthesis of materials with high crystallinity (up to 92%), reduced mean particle sizes, and narrow size distributions after a thermal treatment time four times shorter (24 h) than that required by the hydrothermal route (96 h). Notably, sample MW_3M_1T_24H exhibited the highest crystallinity in this study (~ 92%) but had a relatively large mean particle size of 4.38 μm .

Among the synthesized zeolites, three were selected to serve as seeds for secondary growth membrane fabrication on both commercial and freeze-cast tubes. The chosen zeolites were HT_T1_96H, MW_T1_24H, and MW_3M_1T_24H.

Membranes prepared with 12 h of hydrothermal treatment and three seed depositions exhibited excellent surface coverage of the tubes, particularly when seeded

with MW_T1_24H, which produced an total coating of the tube surface and an average membrane thickness of 13.8 μm . The MW_3M_1T_24H seed, however, showed poor adhesion to the tubes, which can be attributed to its larger particle size. Although its use enabled the formation of well-covered membranes during the first 6 h of hydrothermal treatment, hexagonal phases were observed alongside the cubic SAPO-34 structures. This finding indicates the formation of SAPO-5, which persisted up to 12 h of hydrothermal treatment.

Finally, adsorption selectivities calculated by IAST for the MW_T1_24H seed were determined. For equimolar (50:50 mol%) CO_2/CH_4 and CH_4/N_2 mixtures, the selectivity values were 16 and 3, respectively. These results are consistent with literature reports, indicating that species with larger quadrupole moments and greater polarizability tend to interact more strongly with the zeolite adsorption sites. Although permselectivity tests have not yet been performed, the study demonstrates that the proposed method can produce well-covered membranes using only 12 h of hydrothermal treatment and three seed layers. These materials therefore show clear potential for separations of mixtures such as CO_2/CH_4 and N_2/CH_4 .

FUTURE WORKS

- a) Publication of scientific articles exploring the research conducted on the development of selective materials and their application in gas separation membranes;
- b) Implementation of deposition tests on ceramic tubes using an intermediate layer of alpha- or gamma-alumina, with the aim of minimizing fouling during the membrane fabrication process;
- c) Applying advanced strategies, such as the use of ball milling techniques or growth-inhibiting agents, to achieve a controlled reduction in the particle size of seed crystals synthesized through the most promising methodologies of this research. This approach is expected to enhance the homogeneity and surface properties of the seeds, thereby improving the reproducibility and efficiency of subsequent membrane fabrication processes. In a broader perspective, such optimization may contribute to the design of membranes with superior selectivity and durability, reinforcing the potential of these materials for large-scale applications in energy and environmental technologies;
- d) Development of membranes deposited on ceramic hollow fibers, aiming to exploit their high surface-area-to-volume ratio and mechanical robustness. This strategy is expected to enable the fabrication of compact and efficient separation modules, thereby enhancing process intensification and scalability;
- e) Execution of permselectivity tests for the separation of gas mixtures such as N_2/CH_4 , CO_2/CH_4 , and N_2/CO_2 ;
- f) Evaluation of the regenerability and service life of the membranes;
- g) Scale-up of membrane production using larger ceramic supports.

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APPENDIX

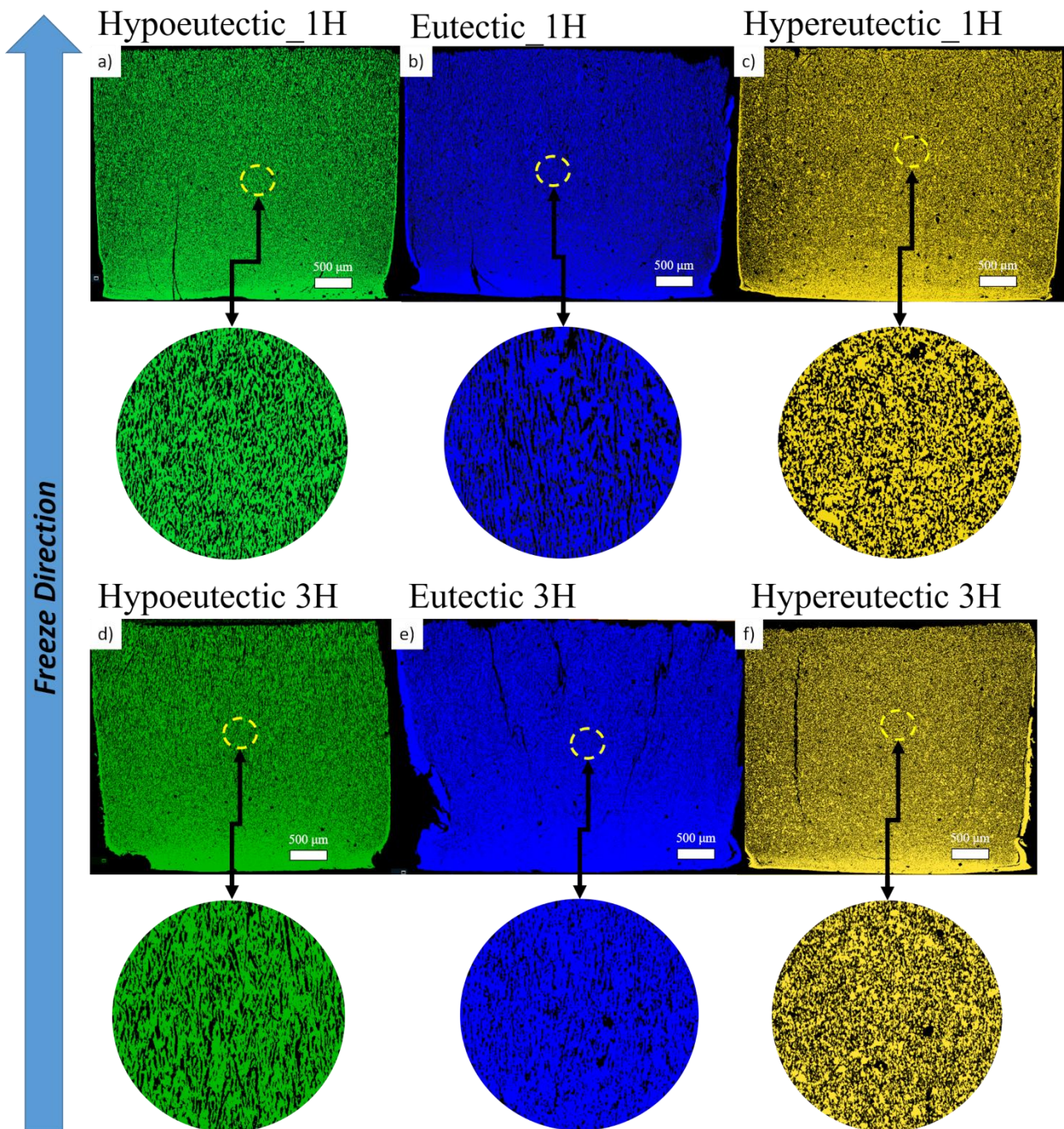


Figure A 1. Pore morphology from microtomography images of samples produced with sintering times of 1 h (a-c) and 3 h (d-f).

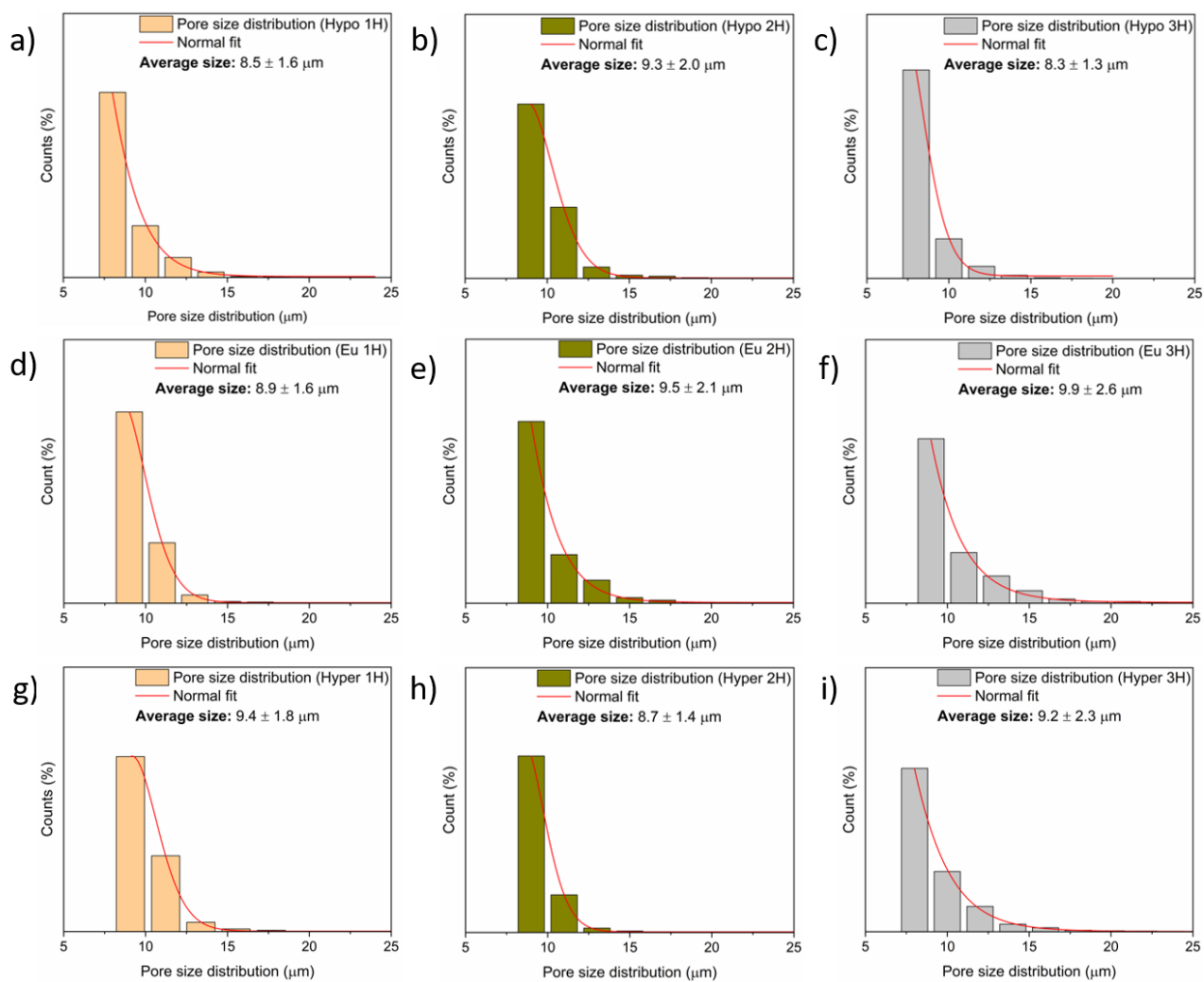


Figure A 2. Pore width distribution curves calculated via Avizo[®] 3D software for α -alumina monoliths.

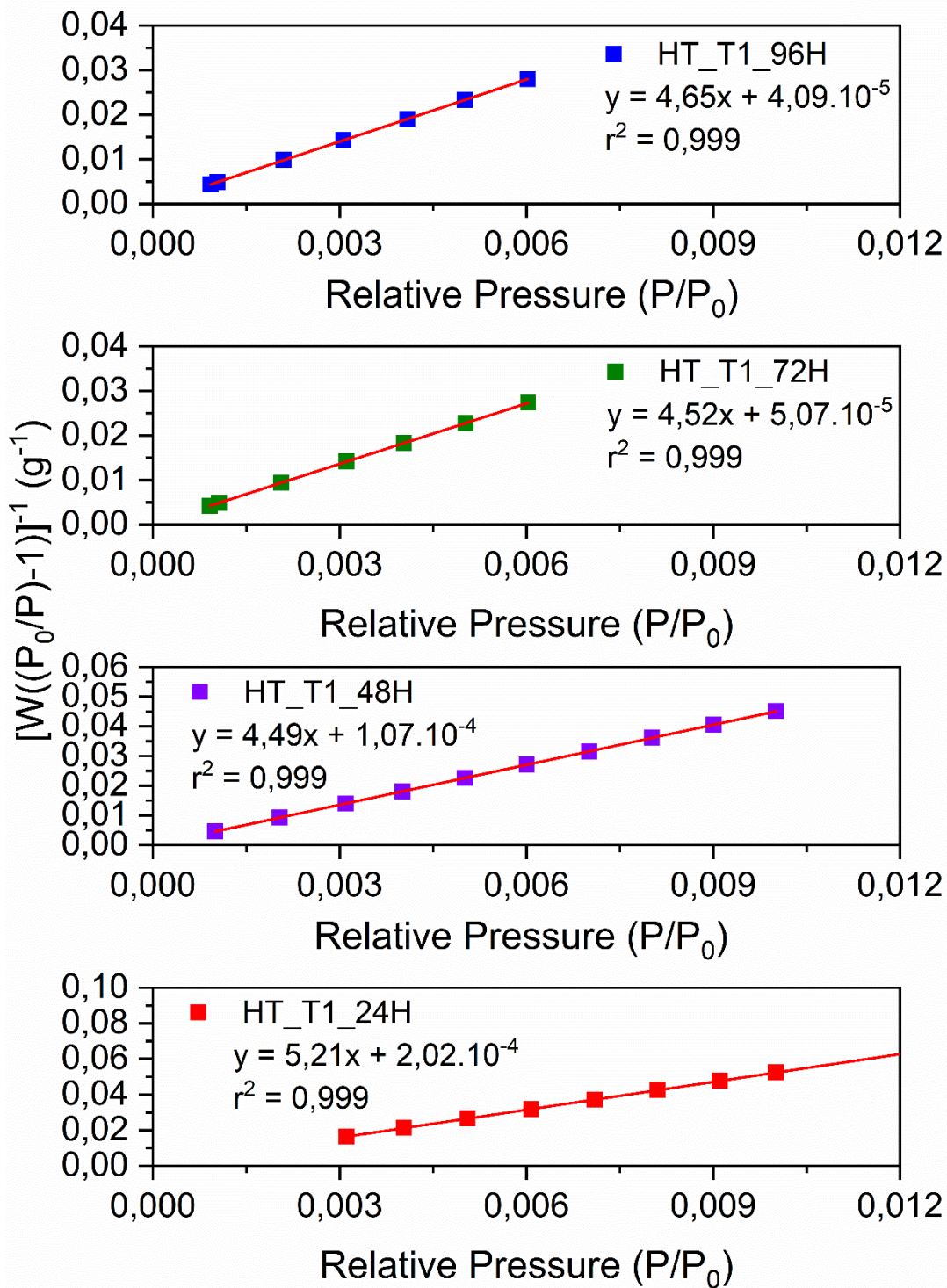


Figure A 3. Curves produced via BET method for samples HT_T1.

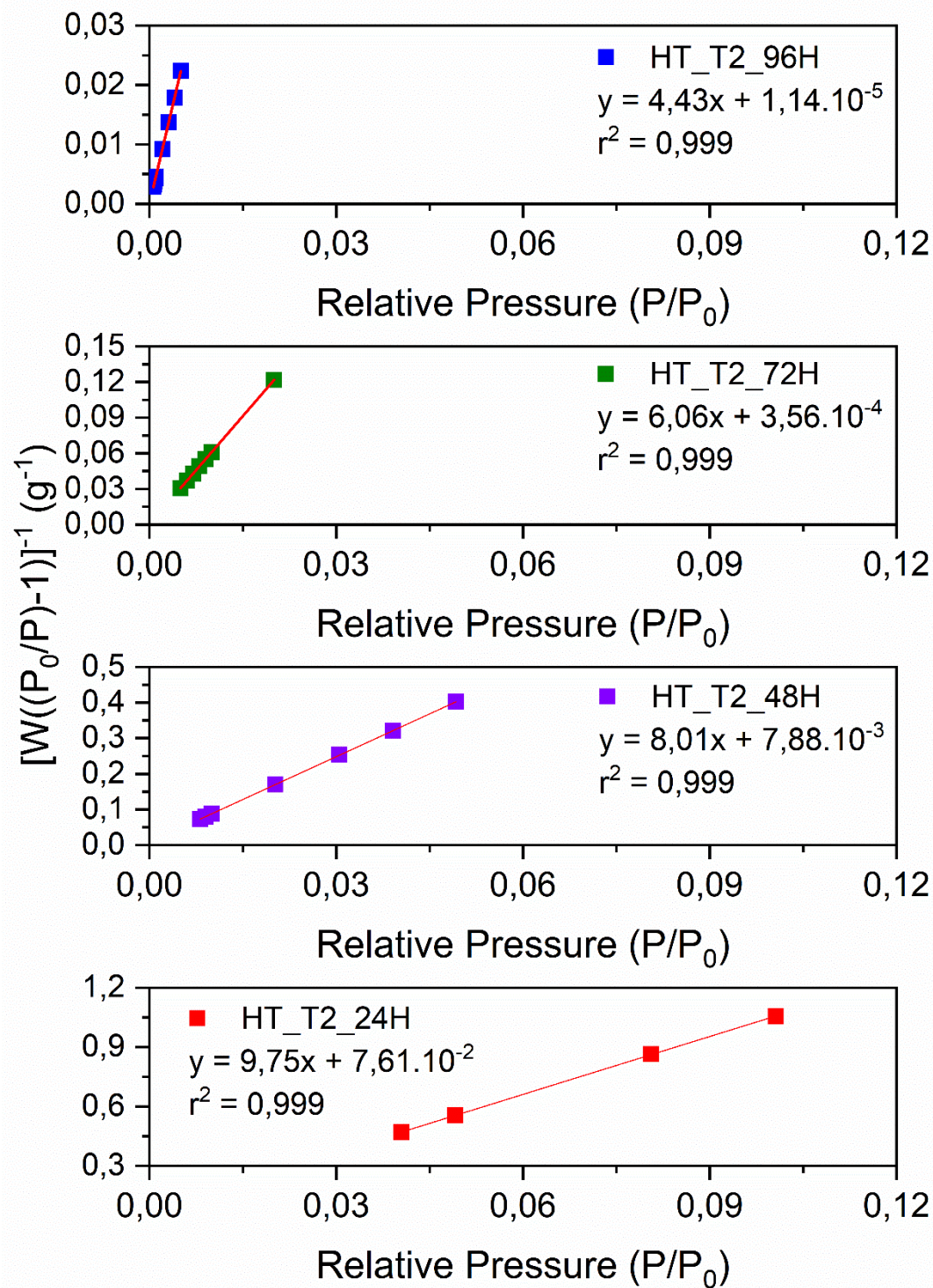


Figure A 4. Curves produced via BET method for samples HT_T2.

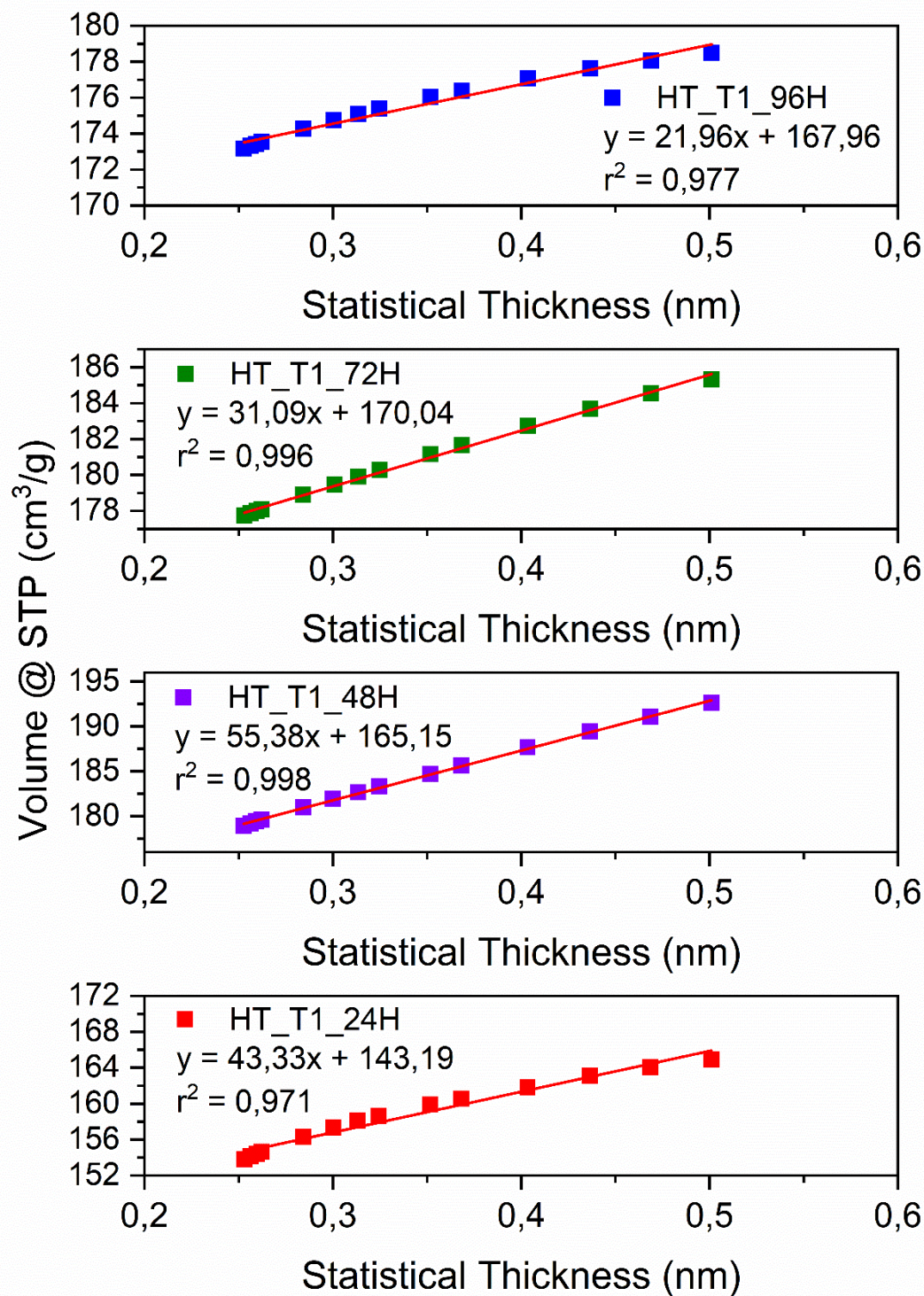


Figure A 5. Curves produced via t-plot method for samples HT_T1.

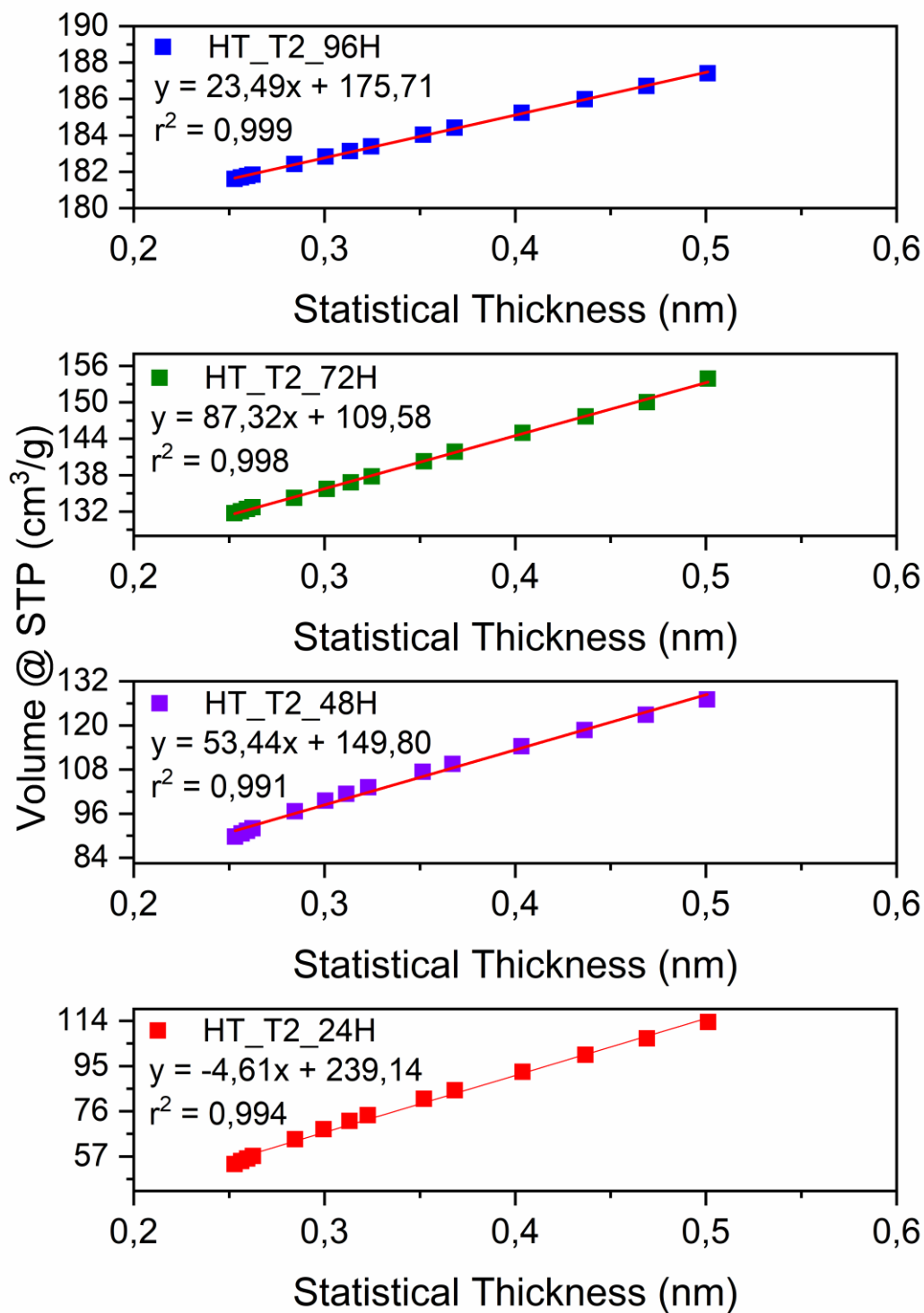


Figure A 6. Curves produced via t-plot method for samples HT_T2.

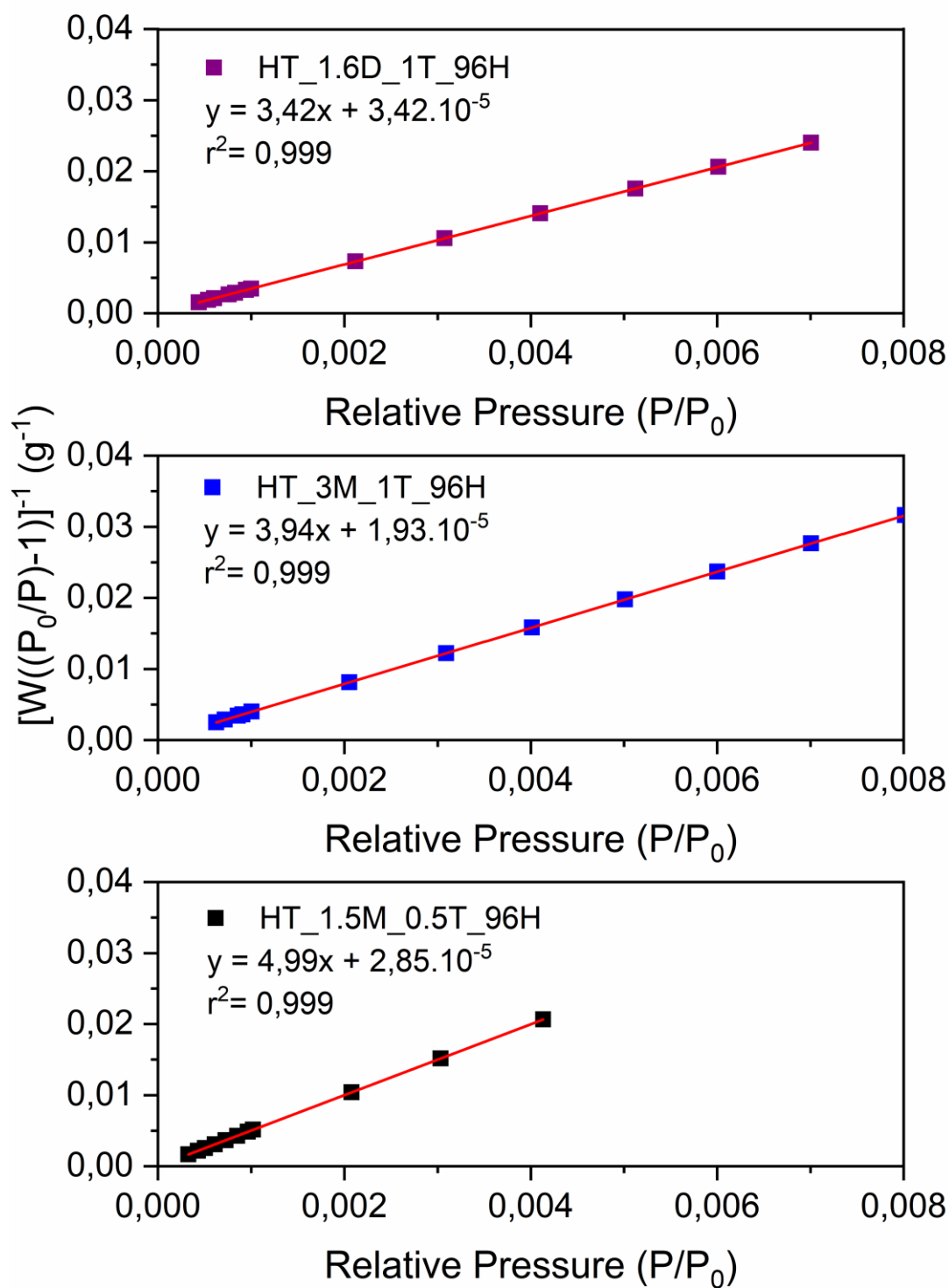


Figure A 7. Curves produced via BET method for samples produced with HT method and using dual OSDA's.

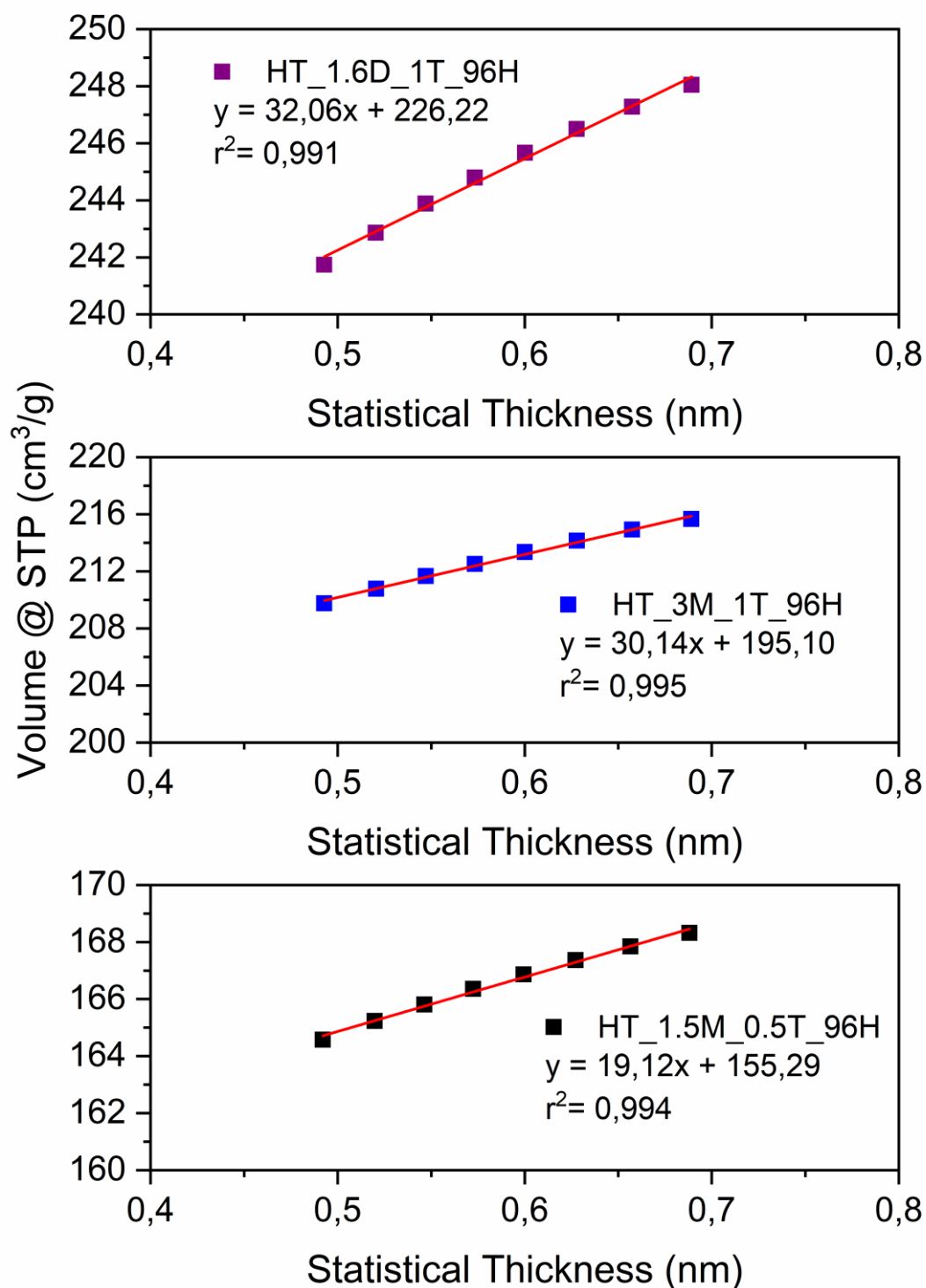


Figure A 8. Curves produced via t-plot method for samples produced with HT method and using dual OSDA's.

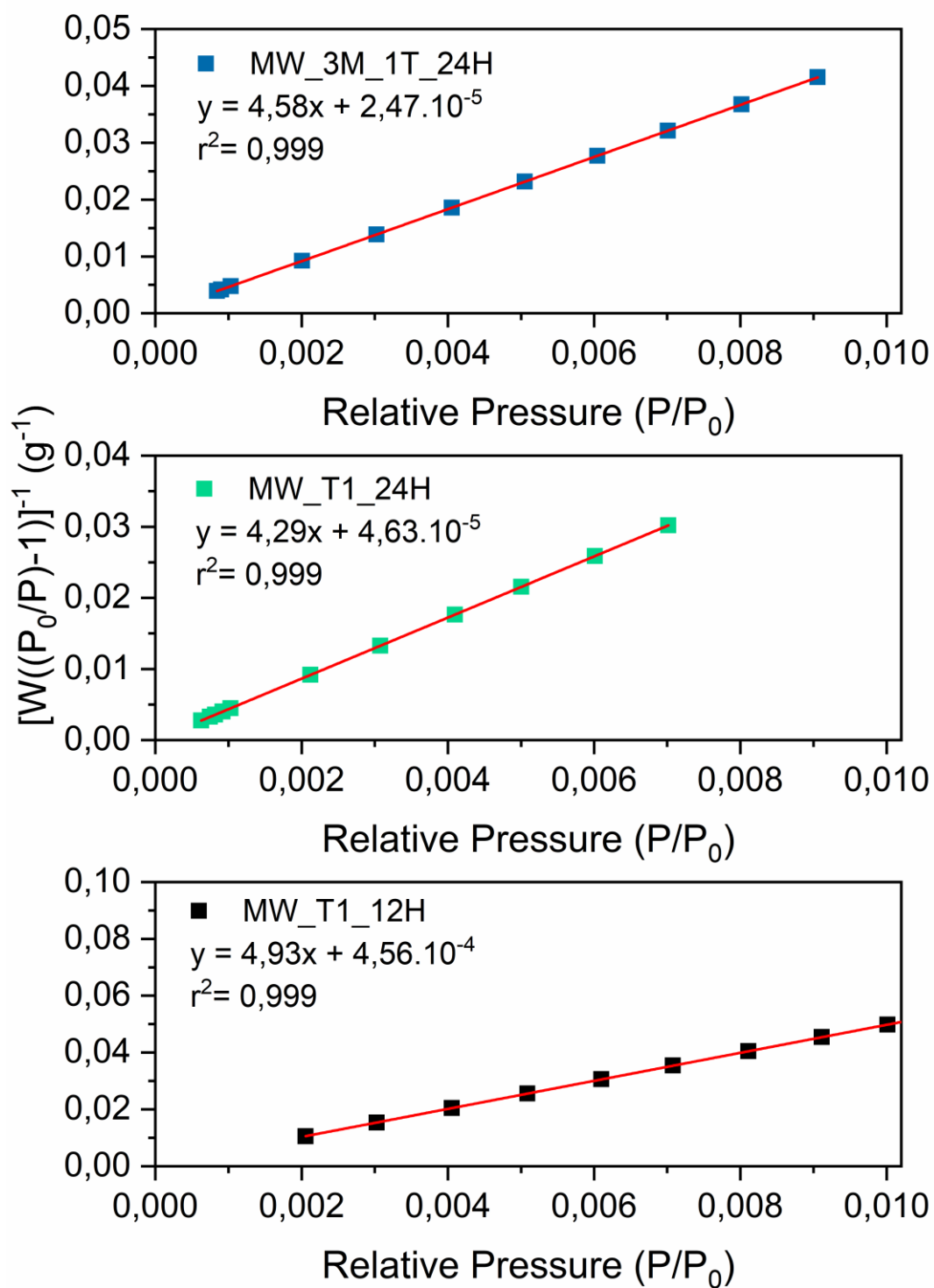


Figure A 9. Curves produced via BET method for samples produced with MW method and using single or dual OSDA's.

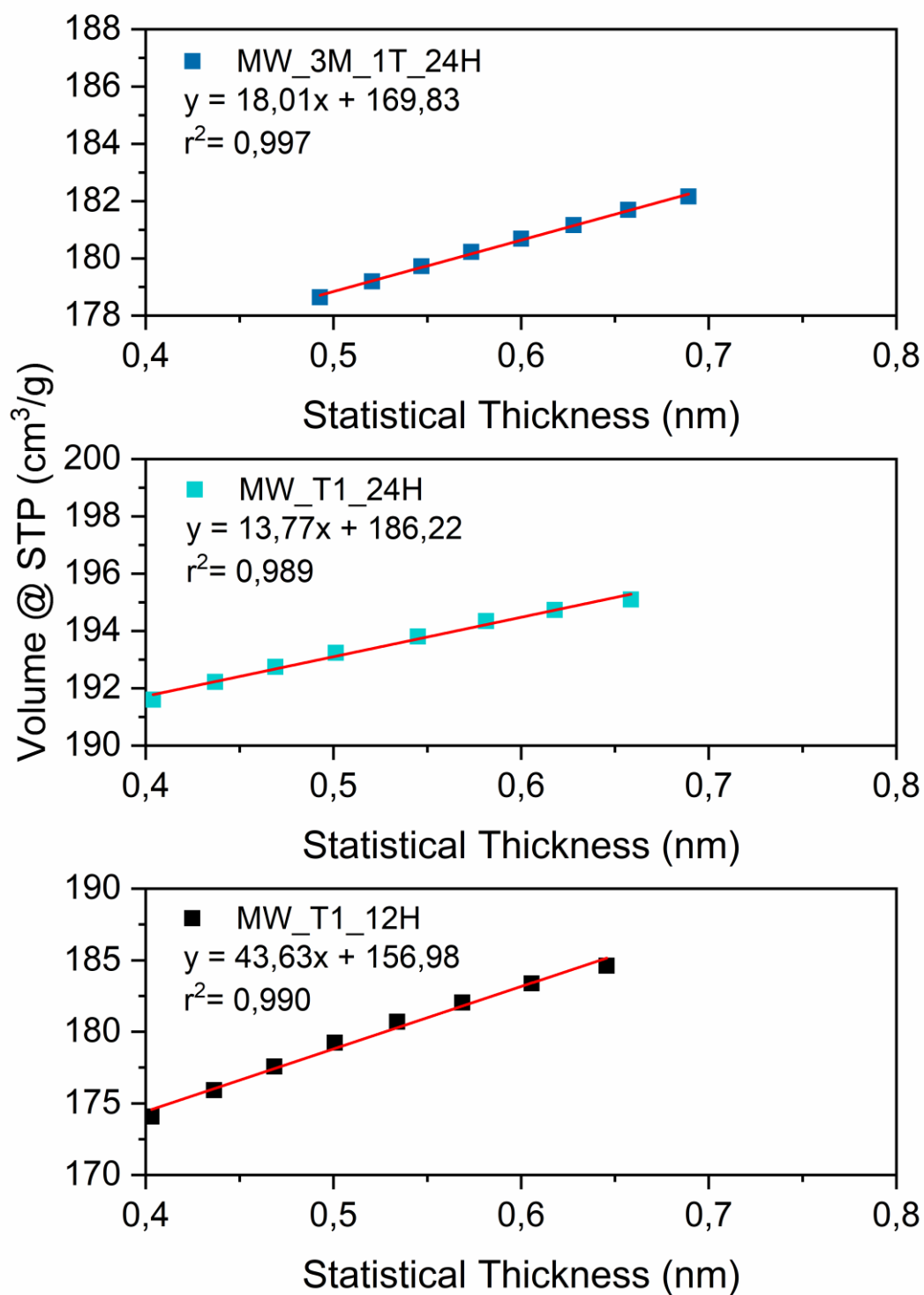


Figure A 10. Curves produced via t-plot method for samples produced with MW method and using single or dual OSDA's.

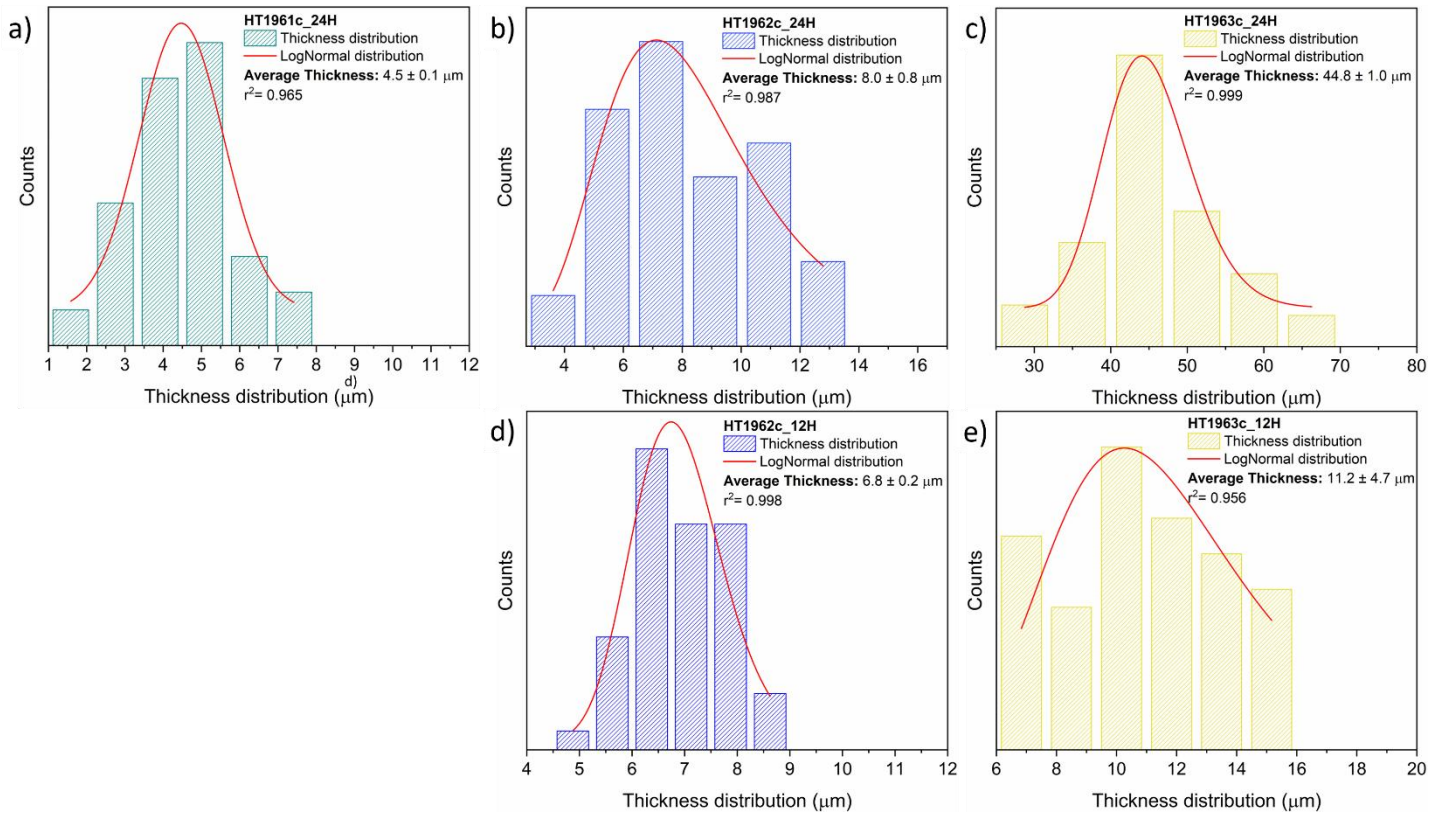


Figure A 11. Log-normal fitting of thickness distributions for the HT_T1_96H seeded samples.

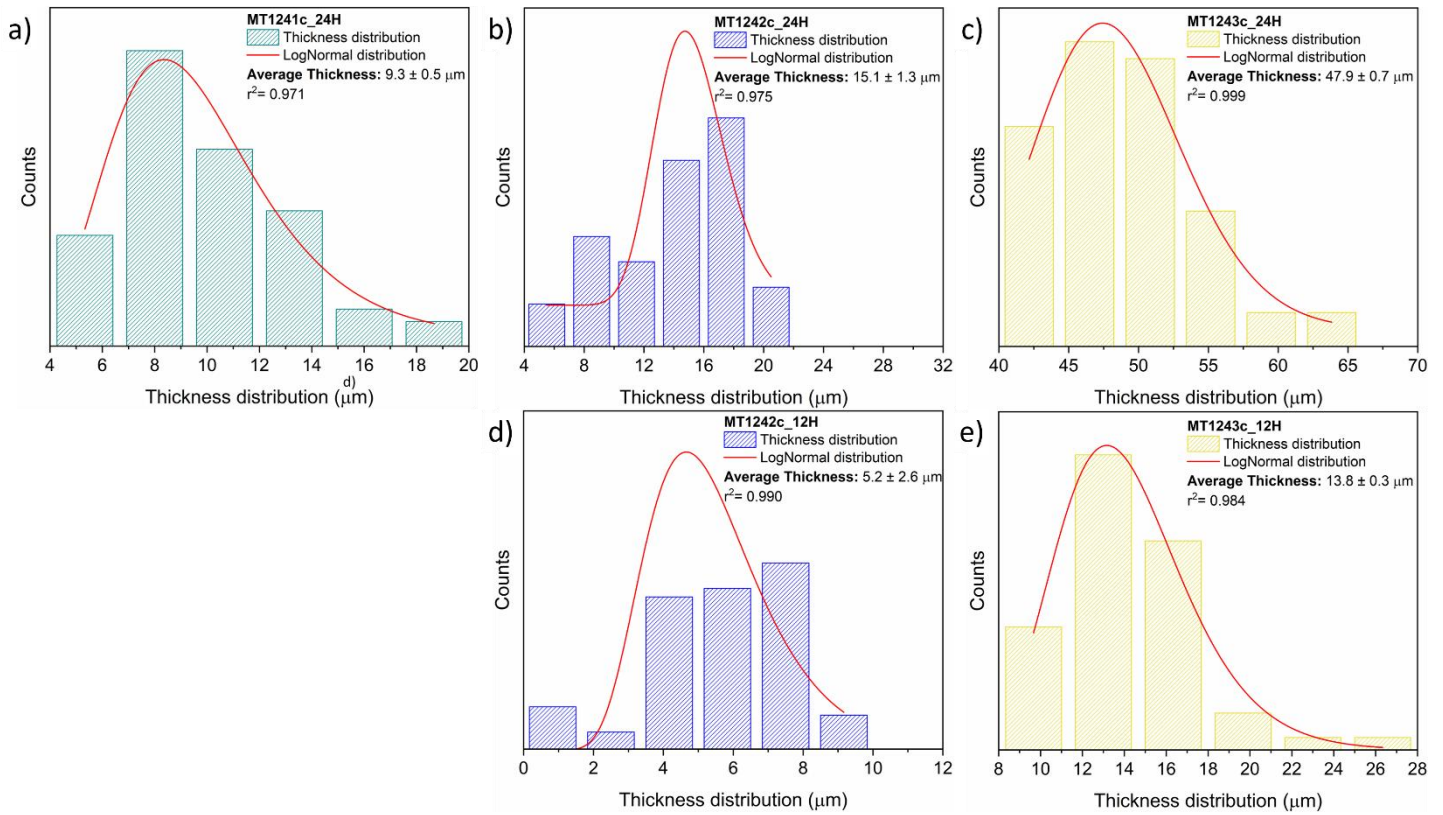


Figure A 12. Log-normal fitting of thickness distributions for the MW_T1_24H seeded samples.

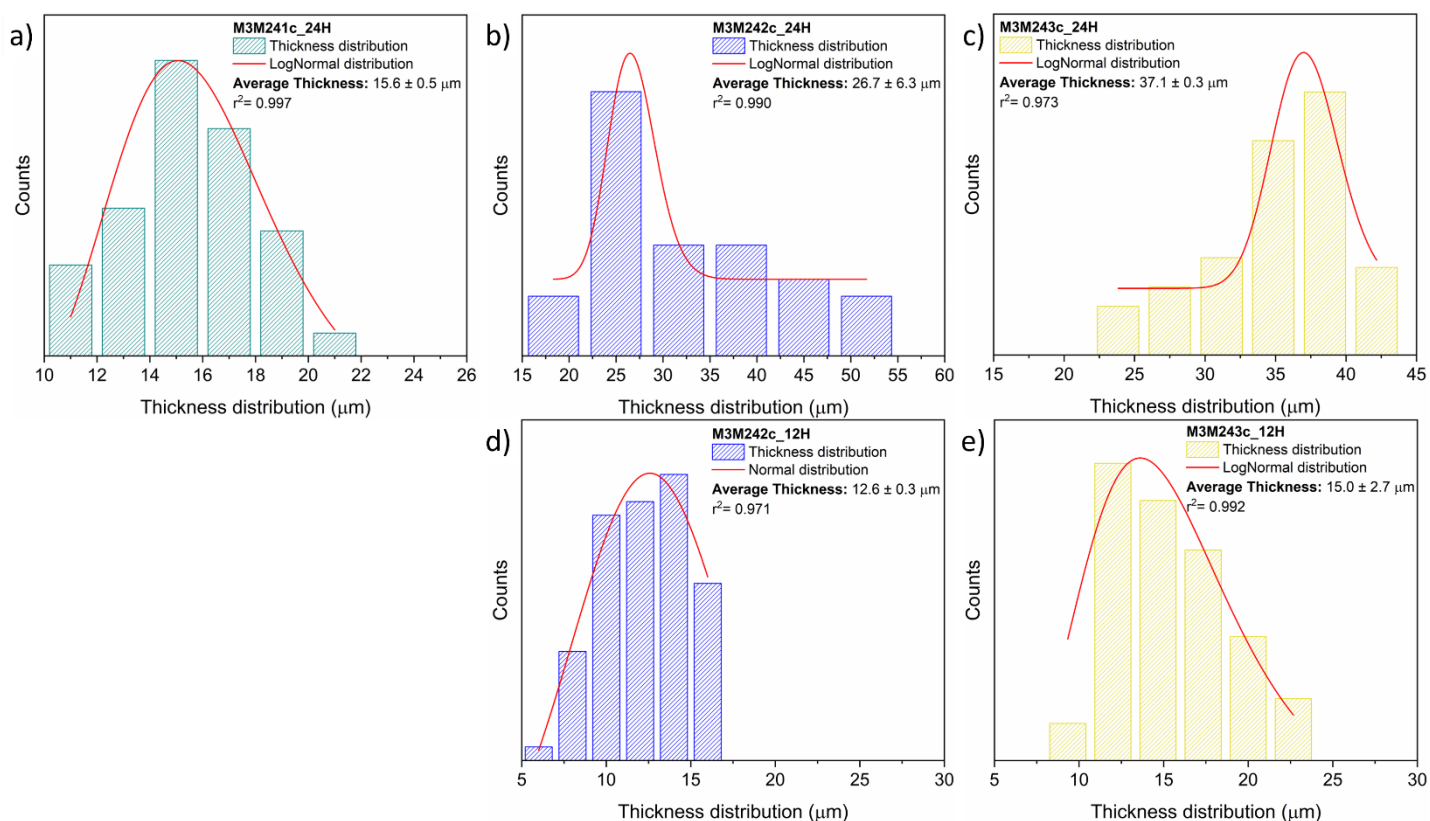


Figure A 13. Log-normal fitting of thickness distributions for the MW_3M_1T_24H seeded samples.

Table A 1. Dual-Site Langmuir model fitting parameters for N_2 , CO_2 , and CH_4 .

Parameters	N_2	CO_2	CH_4
$q_{\text{max},1} \text{ (mmol.g}^{-1}\text{)}$	2.01	4.67	1.88
$b_1 \text{ (bar}^{-1}\text{)}$	0.07	14.17	0.16
$q_{\text{max},2} \text{ (mmol.g}^{-1}\text{)}$	0.30	0.50	2.16
$b_2 \text{ (bar}^{-1}\text{)}$	0.19	1.16	0.16

Role of solvent composition and sintering time on the porosity of α -alumina monoliths produced by freeze casting

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Funding information

PETRONAS, Grant/Award Number: 07082

Abstract

The present study reports the investigation of the influence of naphthalene–camphor binary solvent and the densification process on the pore structure formation of α -alumina monoliths using the freeze-casting technique with a freezing temperature control mechanism. Freeze-casting technique allowed a controlled production of monoliths with high porosity (65%–70%) and distinct pore morphologies based on the adjustment of solvent composition (hypoeutectic, eutectic, and hypereutectic) and sintering time. In general, the longer the sintering time, the greater the average pore diameter (8–10 μm), the larger the grain size (~ 319 – 596 nm), the higher the material density (~ 1450 – 1650 kg/m^3), the lower the open porosity ($\sim 60\%$ – 49%), the higher the closed porosity (5%–18%), and the greater the compressive strength of the monoliths (hypoeutectic: 23.56 MPa; eutectic: 4.81 MPa; hypereutectic: 23.49 MPa). The study also reveals that the solvent composition directly influenced the alignment of the pore structure, as the pores of the final monolith resemble frozen solvent crystals. Hydraulic tortuosity varied from 1.30 to 1.53 for selected samples. Finally, solvent composition and sintering time proved to be important parameters that should be considered in the manufacturing process of porous ceramic structures via freeze casting.

KEYWORDS

densification, freeze casting, naphthalene–camphor, pore network model, α -alumina

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Programa: Programa de Pós-Graduação em Química

Nome completo: Saulo Lucas Pereira da Silva

Título do Trabalho: DEVELOPMENT OF SAPO-34 ZEOLITE MEMBRANES
SUPPORTED ON α -Al₂O₃ FOR GAS SEPARATION

Nível: () Mestrado (x) Doutorado

Orientador/a: Prof. Dr. Alysson Martins Almeida Silva