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In situ Synthesis of Novel ZIF-8 Membranes on Polymeric and Inorganic Supports

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The fabrication of integrated ZIF-8 membranes via a direct *in situ* crystallization on a porous polyacrylonitrile material and a composite aluminum zirconate based support is performed for the first time. A novel free-seeding synthetic procedure was accomplished without an elevated temperature and autogeneous pressure. The proper choice of the support in combination with the appropriate synthesis procedure allowed the preparation of phase-pure polycrystalline ZIF-8 membranes. The gas permeation experiments indicated that dense ZIF-8 selective layers including multi-layer coating are perfectly grown on both supports. Our results revealed a strong impact of the support on the gas separation characteristics of the resulted ZIF-8 membranes.

Keywords: Zeolite-imidazolate framework; Selective layer; Composite membranes; Gas separation

Introduction

The modification of defined surfaces and interfaces by assemblies of porous crystals is a topic of pronounced technological importance, since this approach paves a way to the materials with potential application in the fields of catalysis, gas storage and separation, sensor devices, electronics and photonics.¹ Among the porous ordered solids suitable for the support modification, metal-organic frameworks (MOFs) have drawn an intense attention due to their outstanding characteristics: exceptionally high surface areas, large pore volume, high degree of crystallinity and tunable pore functionality.²⁻⁴ The ultrahigh porosity, well-defined pore size and shape of MOFs make them promising candidates for selective nanofiltration of various molecules⁵⁻⁷ by creating functional supported membranes for energy-efficient separation of gas mixtures^{1,5,9-11}

It is anticipated that metal-organic hybrid membranes combine the advantages of inorganic porous materials with those of organic polymers.^{6,12,13} Actually, very promising results were obtained concerning the achievement of selectivities higher than the Knudsen selectivity by some MOF membranes.¹⁴ Dense coating of the membrane surface provides permeation conducted only through the channels existing in the MOF crystal lattice.¹⁵ Under these conditions, transport of gas molecules does not occur through gaps or cracks due to uncontrolled porosity. However, one of the main problems of crystalline MOF (as well as zeolite) application in gas separation is the difficulty of preparation of a uniform defect-free selective layer over a large membrane area. Therefore these

materials are used mainly as fillers for polymeric matrixes and adsorbents in separation columns.¹⁶⁻²²

The general strategy used for fabricating metal-organic framework membranes is the direct growth of nanoscale MOFs on solid supports.¹ In contrast to the research achievements on bulky MOF materials, only limited progress was made in the field of supported MOF membranes. Growing a dense polycrystalline MOF layer on porous ceramic or metal supports, owing to the weak interfacial bonding between MOFs and the chemically inert substrate, is a serious challenge.^{13,23} The main problem accompanying this synthesis approach is an undesired nucleation in the solution or growth on top of previously formed crystals instead of the growth on the support, which results in an incomplete support coverage and uneven membrane thickness.¹⁵ Therefore, in many cases, it was reported that the nucleation density of MOF crystals on ceramic supports is very low, which makes it extremely difficult to fabricate the integrated membranes by an *in situ* solvothermal synthesis.⁷

Currently, a seeding procedure combined with a secondary (seeded) growth has been demonstrated to be a feasible and effective method to produce highly integrated MOF membranes with strong bonding to the support.^{5,23,25} The hydrothermally synthesized seeds offer nucleation centers and induce a better crystallization of the seeded support.^{11,23,26,27} Polymer binder-assisted seeding,^{6,23,28} thermal seeding,²⁷ reactive seeding (RS)^{29,30}, and *in situ* seeding methods³¹⁻³³ were developed for the formation of a homogeneous seeding layer, which assisted a secondary hydrothermal synthesis of well-intergrown MOF membranes.

However, the synthesis of defect-free MOF-based membranes on a ceramic support is still a challenge despite the serious research efforts due to the difficulty in preparing suitable seed crystals and the complexity of the seeding process.³⁰ Another interesting approach involves the use of the MOF seeds in combination with other methods, for instance, enhancing the surface affinity of the support for one of the MOF precursors. Thus, based on physical interactions, ZIF-8 membranes were successfully prepared by depositing seeds on a substrate modified with layered double hydroxides (LDHs) walls before the secondary growth of the metal-organic framework layer.³⁴

According to a novel counter-diffusion approach, a number of integrated high-quality HKUST-1¹⁵ and ZIF-8³⁵ membranes were prepared. H.T. Kwon reported a synthesis method involved a simple one step *in situ* method based on a counter-diffusion concept to prepare well-intergrown ZIF-8 membranes on α -alumina supports with significantly enhanced microstructure.³⁶ The modification of the support surface with functional groups presents a useful tool to improve the nucleation density in the case of direct MOF crystallization.³⁷⁻⁴⁰ For instance, using 3-aminopropyltriethoxysilane (APTES) as a covalent linker to built a "bridge" between the porous ceramic support and the ZIF-8 layer, an improved seeding-free synthesis of a dense ZIF-8 membrane was carried out due to the promotion of the nucleation and growth of a continuous metal-organic framework layer on thus functionalized supports.^{37, 41-43}

A simple, versatile, and powerful synthesis strategy was developed to prepare highly reproducible and permselective molecular sieve membranes by using polydopamine as a novel covalent linker. Attributing to the formation of strong covalent and noncovalent bonds, ZIF-8 nutrients are bound to the surfaces of different supports, thus promoting the growth of well intergrown selective layer of zink-imidazolate framework.^{44,45} To improve the uniformity of the selective layer, this approach was combined successfully with layer-by-layer (LBL) deposition of a graphene oxide in order to seal a semicontinuous ZIF-8 layer.⁴⁶ The developed ZIF-8 membranes show high hydrogen selectivity and thermal stability.

According to LBL approach, by controlling the supramolecular assembly of inorganic and organic building blocks on the surface, nanocomposite membranes were prepared by liquid-phase stepwise deposition of reactants, which resulted in confinement of MOF material within the macropores of ceramic supports and thus a high-quality performance of the fabricated membranes.^{47,48}

The numerous examples of successful continuous MOF selective layer fabrication demonstrated an efficacy and prospects of multi-step approaches, however, to address the practical demands the non-sophisticated direct synthesis procedures are preferred. There are a limited number of works dealt with the MOF-based membrane preparation by one-step crystallization on the support. For instance, J. Caro and coworkers prepared a titania-supported ZIF-8 membrane through microwave-assisted solvothermal direct synthesis.¹³ The continuous MOF-5²⁴ and substituted imidazolate-based MOF (SIM-1)²⁵ membranes were synthesized by direct growth *in situ* on the alumina supports.

This paper is to show that through the proper support choice combined with the appropriate synthesis procedure, perfectly grown sodalite-type framework ZIF-8 selective layers (including multi-layer materials) can be obtained by *in situ* crystallization of on the surfaces of ultra-porous membranes without their preliminary modification. ZIF-8 as a member of the thermally and chemically stable family of zeolite imidazolate frameworks (ZIFs) is of particular interests for membrane applications, due to the monomodal pore size distribution and special diffusion pathways for guest molecules.⁴⁹⁻⁵⁵ Currently, numerous examples of successful

fabrication of ZIF-8 membranes and their testing for gas separations are known.^{11,13,26,38,48}

Taking into account the hybrid organic-inorganic ZIF-8 nature, we compared two types of supports providing the optimal affinity of ZIF-8 for their surfaces. The polymeric (Polyacrylonitrile (PAN)) material and a special composite inorganic support based on aluminum zirconate were used for the preparation of the integrated membrane with a selective zeolite-imidazolate layer. The reduction of the membrane thickness could be achieved by the fabrication of the supported MOF membrane on a porous substrate with a high stability.²³ Both supports used for the membrane preparation featured the high mechanical strength that is necessary for the fabrication of a highly integrated membrane with a MOF selective layer.

Noteworthy, the polymeric materials are used mainly as matrices for embedding the metal-organic framework nanoparticles in order to obtain thus MOF-based mixed matrix membranes (MMM). To the best of our knowledge, although various ceramic substrates have been used to prepare MOF films/membranes so far, there are only a few reports on the use of porous substrates, such as a nylon porous support.³⁵ Another example of the polymer-supported membranes is a growth of continuous ZIF-90 membranes on the Torlon hollow fibers by low-temperature processes.⁵⁶ As expected, the flexibility of the PAN material could provide favorable interactions between organic ligands of ZIF-8 and polymers, thereby increasing the metal-organic framework compatibility with the polymeric carrier.

With regard to composite inorganic support, it is pointed out that the macroporous stainless-steel net (SSN) features the hardness in combination with remarkable texture properties allowing to use this material as the basis for the fabrication of the integrated membranes. For instance, SSN has a higher void volume than a conventional α -Al₂O₃ support, thus the permeability of the selective layer supported on SSN will show the high permeances.⁴⁵ To meet this objective completely, SSN needs in some modification before creating the MOF-membrane on its surface, because the pores are too large for providing a sufficient selectivity. J. Caro and coworkers invented SSN functionalization with polydopamine, which promotes the nucleation and growth of well intergrown ZIF-8 layers on membrane surface.⁴⁵ In contrast to this approach, in our work, a composite inorganic support fabricated by deposition of aluminum zirconate dense coating on SSN served for ZIF-8 layer *in situ* crystallization.

The performances of the integrated ZIF-8 membranes were evaluated in gas separation experiments of a number of gas mixtures.

Experimental

Materials

All reagents and solvents employed were commercial products (Acros). N,N'-dimethylformamide (DMF) was distilled over CaH₂ under a reduced pressure.

In this work, two ultra-porous disk-shaped supports ($d = 3$ cm) were used for composite ZIF-8 membrane preparation: a polymeric support based on polyacrylonitrile (PAN, GKSS, Germany) and a special composite support based on an aluminum zirconate layer deposited on a stainless-steel net (Association "ASPECT", Russia).

Synthesis of ZIF-8 membranes

ZIF-8 membranes on the polymeric and composite inorganic carriers were synthesized according to the following original procedures.

Synthesis of ZIF-8 membranes supported on PAN.

Sample 1. ZnCl₂ (1.08 g), HCOONa (0.54 g), and 2-methylimidazole (0.972 g) were dissolved in MeOH (50 mL). The PAN carrier was dipped in the reagent solution, and the reaction mixture was heated in a flask equipped with a Dean-Stark nozzle (12 h, 60°C, Ar) accompanied with the solvent gradual removal during the synthesis. After the end of the synthesis, the ZIF-8 membrane was activated under a vacuum (60°C, 5 h) until a constant weight.

XRD analysis of the crystals withdrawn from the reaction mixture revealed the pure ZIF-8 phase formation (Fig. 1).

Sample 2. ZnCl₂ (1.08 g), HCOONa (0.54 g), and 2-methylimidazole (0.972 g) were dissolved in MeOH (50 mL). The PAN carrier was dipped in the reagent solution, and the reaction mixture was heated in a flask equipped with a Dean-Stark nozzle (6 h, 60°C, Ar) accompanied with the solvent removal gradually during the synthesis. After the end of the synthesis, the ZIF-8 membrane was activated under a vacuum (60°C, 5 h) until a constant weight.

XRD analysis of the crystals withdrawn from the reaction mixture revealed the pure ZIF-8 phase formation.

Sample 3 was synthesized as samples **1**, **2** with a minor procedure modification involving a replacement of the Zn²⁺ source, i.e. ZnCl₂ was replaced for Zn(OAc)₂ as well as a solvent. Zn(OAc)₂ (1.74 g), HCOONa (0.54 g), and 2-methylimidazole (0.972 g) were dissolved in MeOH (25 mL). The PAN carrier was dipped in the reagent solution, and the reaction mixture was heated in a flask equipped with a Dean-Stark nozzle (6 h, 60°C, Ar) accompanied with the solvent removal gradually during the synthesis. After the end of the synthesis, the ZIF-8 membrane was activated under a vacuum (60°C, 5 h) until a constant weight.

XRD analysis of the crystals withdrawn from the reaction mixture revealed the pure ZIF-8 phase formation.

Synthesis of ZIF-8 membrane on the inorganic support.

Sample 4. The composite inorganic support was preliminarily treated with a solution of Zn(OAc)₂·2H₂O (0.87 g) in MeOH (10 ml) for 12 h. Zn(OAc)₂ (1.74 g), HCOONa (0.54 g), and 2-methylimidazole (0.972 g) were dissolved in MeOH (25 mL), and the pretreated support was dipped in the reagent solution. The reaction mixture was heated in a flask equipped with a Dean-Stark nozzle (6 h, 60°C, Ar) accompanied with the solvent removal gradually during the synthesis. The ZIF-8 membrane was activated under a vacuum (150°C, 5 h) until a constant weight.

XRD analysis of the crystals withdrawn from the reaction mixture revealed the pure ZIF-8 phase formation (Fig. 1).

Characterization of ZIF-8 membranes

For N₂ adsorption measurements and XRD examinations, the ZIF-8 powder samples were collected from the bulk solution after the membrane syntheses. N₂ adsorption data were obtained at 78 K by a volumetric method.⁵⁷ The powder XRD patterns were measured in a transmission mode using a Huber G670 Guinier camera diffractometer (Cu K_{α1} radiation, λ=1.54059 Å) at 295 K. Scanning electron microscopy (SEM) performed by using a LEO 1455 VP with an XR microanalyzer (Carl Zeiss) was used to determine the ZIF-8 thin layer morphology.

Diffusion reflectance Fourier transform infrared (DRIFT) spectra of synthesized ZIF-8 samples and integrated membranes were recorded at room temperature with a Nicolet 460 Protégé spectrometer supplied with a diffuse reflectance attachment. To obtain a satisfactory signal-to-noise ratio, 500 scans were collected. The spectra were measured from 400 to 2000 cm⁻¹ with a resolution of 4 cm⁻¹.

Gas permeability experiments

The single gas permeance for He, N₂ (gas purity 99.9% vol.), CO₂ (gas purity 98.9% vol.) was measured by a volumetric method (high flux samples) and a differential method with gas chromatography analysis (medium flux samples) using two techniques:

- sweeping of a permeate by a carrier gas (He, Ar),
- evacuation of a permeate ($p_{\text{perm}} \sim 10^{-2}$ atm).

Experiments were carried out at room temperature; the partial pressure drop was equal to 1 atm. The volumetric method was applied as well for measurements in the range of the pressure drops 0.5-3.5 atm at room temperature.

It was found that evacuation and volumetric methods allowed us to obtain more reproducible data in studying the gas permeance through the membranes than the technique with a gas-carrier. This can be probably accounted for by the gas-carrier transfer in the reverse direction through the highly permeable selective layer. This effect can influence seriously the penetrant permeance, especially for low permeable gases.

The permeance of single gases was calculated as:

$$Q = \frac{J}{A \cdot \Delta p}, \quad (1)$$

where J is the gas flux through the membrane, mol/s; A is the membrane area, m², Δp is the pressure drop, Pa.

The ideal selectivity of single gases was defined as:

$$\alpha_{ij} = \frac{Q_i}{Q_j}, \quad (2)$$

where Q_i and Q_j are the permeances of i-th and j-th gases, respectively.

Results and Discussion

ZIF-8 Membrane preparation and characterization

The numerous studies reported the membrane surface preliminary modification for inducing the preferred attachment of MOF crystals.^{15,24} However, in this work, no special treatment of the carrier was made, except for the pretreatment of a composite inorganic support with a solution of Zn(OAc)₂·2H₂O in MeOH. We expected that the terminal nitrile functionalities homogeneously distributed throughout the structure of the PAN material could provide the appropriate affinity of the ZIF-8 imidazolate linker with the surface of the polymeric support. It could facilitate the seeding-free one-step preparation of continuous zinc-imidazolate metal-organic framework layer on the top of the integrated membrane. On the other hand, the PAN material features an ultra-microporous structure, which can contribute to the formation of a homogeneous ZIF-8 layer on its surface.

As it can be concluded from the published permeation results relevant to this topic, the preparation method of the metal-organic selective layer is a critical issue for MOF membranes. Simultaneously, it was pointed out that common solvothermal syntheses are difficult to scale-up and expensive.⁴⁷ Since the polymeric PAN material is decomposed at temperatures exceeded 150-200°C, a novel synthetic procedure accomplished at the atmospheric pressure and moderate temperatures (about 60°C) was developed. This protocol involved a partial solvent removal for increasing the reagent concentration in a reaction mixture and shifting the crystallization process towards ZIF-8 crystallization on the support surface.

Moreover, one of serious hurdles accompanied a solvothermal synthesis of integrated membranes is a difference between the

thermal expansion coefficients of the metal-organic framework layer and the support, which can produce cracks while cooling the composite membrane back to ambient temperature.⁴⁷ Probably, that is why a poor reproducibility of the synthesis of ZIF-8 dense coating on inorganic supports by the solvothermal reaction has been reported so far. Actually, the preliminary tests made in this work revealed that the solvothermal reaction did not afford the reproducible synthesis of ZIF-8 dense coating on the inorganic support. It prompted us to apply a novel “non-solvothermal” procedure for ZIF-8 membrane fabrication on the aluminum zirconate surface (sample 4). This synthesis protocol is described above for polymer-based membrane preparation with minor modifications involving the support pretreatment with the Zn^{2+} salt solution (see above).

XRD results revealed (Fig. 1b, 1c, samples 1, 4) that the crystal structures of the powder products obtained by preparation of the ZIF-8 membrane on both supports were consistent with the reported calculated XRD pattern (Fig. 1a) obtained by simulation. Noteworthy, preliminary tests revealed that the use of $Zn(OAc)_2 \times H_2O$ as a Zn^{2+} source in the integrated membrane synthesis resulted in a significant improvement of the purity of the ZIF-8 crystalline phase as compared to selective layer preparation with $ZnCl_2 \times 6H_2O$. The impact of inorganic salt in the MOF crystalline phase quality was pointed out previously.^{58,59}

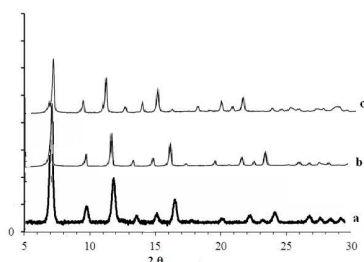


Fig. 1. (a) XRD pattern simulated from crystal structure data for ZIF-8; experimental XRD pattern of ZIF-8 sediment powder collected during preparation of (b) the ZIF-8 membrane on PAN (sample 1), (c) the ZIF-8 membrane on the composite inorganic support (sample 4).

After membrane syntheses, extra crystals were taken from the mother liquor. N_2 adsorption measurements (BET) for these crystals yielded a specific surface areas ranged within $1100\text{--}1300\text{ m}^2/\text{g}$. The high surface areas confirmed the formation of the ZIF-8 structure on both carriers and were in a good accordance with corresponding values measured for ZIF-8 samples synthesized without a support.

The SEM micrographs reveal the significant difference between surface structures of both supports, which impacts very much the ZIF-8 layer formation. The surface of PAN support is smooth, whereas composite inorganic support consists of the aluminum zirconate particles with average size of $150\text{--}200\text{ nm}$ deposited on steel net (Fig. 2a, b).

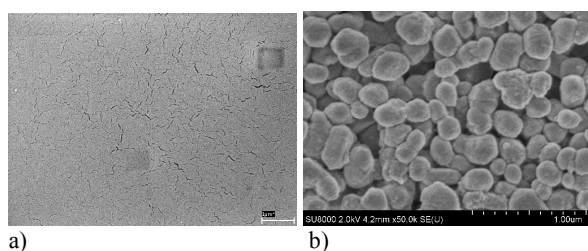


Fig. 2. SEM micrographs of (a) surface of PAN support; (b) surface of composite inorganic support.

A thin and highly integrated MOF layer is desired for high permeation flux and selectivity, and crystal size and shape are also of paramount importance to the integrated membrane performance.^{24,60} A smaller grain size is preferred since it can help to reduce the overall membrane thickness, and consequently increase the permeation flux.²³ The SEM images show the polycrystalline, well-intergrown layers of ZIF-8 crystals on top of both supports (Fig. 3a, b). No cracks, pinholes or other defects in continuous membrane coatings were observed. SEM micrographs revealed that a most homogeneous dense coating has been achieved on polymeric support as compared with ZIF-8 layer on composite inorganic substrate. It can be seen that the surface of integrated membrane on PAN support is smooth, while the surface of aluminum zirconate based-support has been completely covered with randomly oriented spherical grains featured a rather small size, i.e. about $200\text{--}330\text{ nm}$ (Fig. 3b, sample 4). It indicates a good compatibility of hybrid ZIF-8 layer with flexible organic PAN substrate and its smooth surface.

It is interesting to note that the synthesis time extension over 9 h did not lead to any further increase of the supported ZIF-8 quantity. Moreover, weighing synthesized integrated membranes showed that one-step *in situ* syntheses of ZIF-8 crystals on the PAN support repeated in the same conditions resulted in the formation of a selective layer of a similar thickness. It probably indicated that nitrile functionalities of the PAN material could provide the anchoring sites for the ZIF-8 layer direct growth, and specific interaction between the polymeric surface and the imidazolate linker play a decisive role in a dense coating formation.

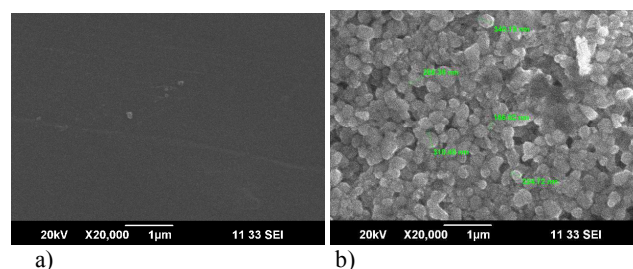


Fig. 3. SEM micrographs of surface of (a) the ZIF-8 membrane on the PAN support, (b) the ZIF-8 membrane on composite inorganic support (sample 4).

DRIFT study confirmed the supported ZIF-8 selective layer formation. The spectrum of the membrane on PAN substrate is in a good agreement with that of the ZIF-8 crystallites obtained from the synthesis solution (see Fig. 4). The main band positions in ZIF-8/PAN spectrum are consistent with the previous report.⁶¹

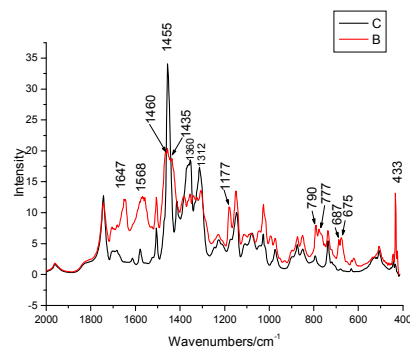


Fig. 4. DRIFT spectra of (C) PAN support, (B) the ZIF-8 membrane on PAN support.

In spectrum of ZIF-8 selective layer supported on PAN substrate the peak at 1568 cm^{-1} can be assigned as the $C=N$ stretch mode

specifically, while Zn–N band is observed at 433 cm^{-1} .⁶² The convoluted bands at $1300\text{--}1500\text{ cm}^{-1}$, which are associated with the entire heteroaromatic ring stretching, overlap the bands from the polyacrylonitrile support, and for this reason could not be identified properly.

It could conclude that most pure ZIF-8 phase was formed on PAN support due to better adherence of ZIF-8 selective layer and polymeric substrate as compared to inorganic composite substrate.

The results of the repeated syntheses of the ZIF-8 selective layer on different types of supports revealed that defect-free polycrystalline coating could be obtained for both types of supports, but the PAN material provided more reproducible data due to its flexibility, polymeric nature and functionality.

Gas Permeability

The adherence of ZIF-8 selective layers to both types of supports was strong enough for the gas permeability tests. The permeability decreases for supported ZIF-8 layers as compared with starting supports (Table 1), for example for PAN based support the permeability decreases in some orders for most selective samples in comparison with support, for Aluminium zirconate membrane it is in two times approximately due to gas resistance of selective layer.

Nevertheless, the ZIF-8 membranes synthesized according to the novel “non-solvothermal” procedures demonstrate high gas permeances, for example, the He permeance through the composite membranes with the selective layer on the inorganic support was equal to $6.8 \cdot 10^{-5}\text{ mol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$ and the N_2 permeance was equal to $3.5 \cdot 10^{-5}\text{ mol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$ (Table 1). This permeability level is higher than that found for most gas separation membranes including ceramic-based and zeolite based membranes, for example, the permeability level of the composite membranes with the ZIF-8 selective layer for H_2 was about $2.7 \cdot 10^{-5}\text{ mol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$ and for $\text{N}_2 - 1.8 \cdot 10^{-6}$.⁴⁵ It should be noted that the synthesis procedure influences more seriously the gas permeability level in the case of the PAN material (Table 1) in comparison with the inorganic support. For instance, the synthesis time prolongation from 6 h (sample 2) to 12 h (sample 1) resulted in a permeability decrease for He and CO_2 . Probably, this observation could be explained by more thick ZIF-8 layer formation on the membrane surface (sample 1). ZIF-8

The pressure dependences of the gas flux and permeability were studied for the prepared membranes as well (Fig. 4, sample 4).

Table 1. Gas permeability of composite membranes with the selective layer based on ZIF-8.

Sample	Q, mol/(m ² ·s·Pa)		
	He	N ₂	CO ₂
PAN support			
Sample 01	$3.3 \cdot 10^{-5}$	$1.6 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$
PAN support + ZIF-8			
Sample 1	$1.6 \cdot 10^{-9}$	$6.0 \cdot 10^{-10}$	$1.2 \cdot 10^{-10}$
Sample 2	$6.0 \cdot 10^{-9}$	$6.9 \cdot 10^{-10}$	$6.5 \cdot 10^{-10}$
Sample 3	$2.4 \cdot 10^{-5}$	$9.1 \cdot 10^{-6}$	$7.0 \cdot 10^{-6}$
Aluminium zirconate support			
Sample 02	$1.2 \cdot 10^{-4}$	$7.1 \cdot 10^{-5}$	$6.5 \cdot 10^{-5}$

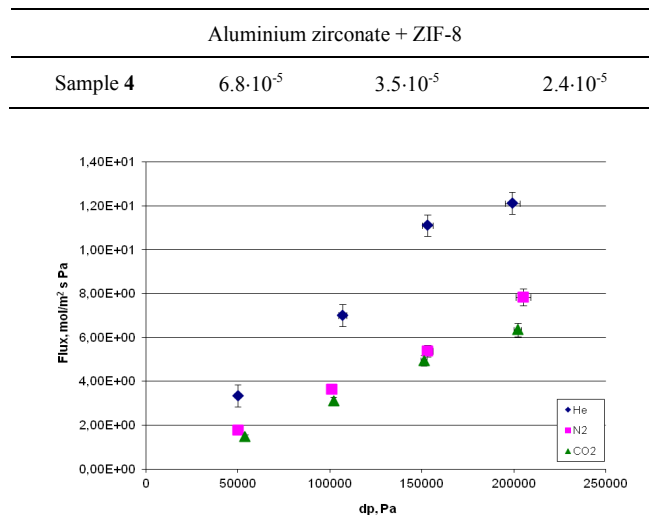


Fig. 4. The dependence of gas flux on drop pressure for composite membrane with ZIF-8 selective layer on composite inorganic support (sample 4).

It is important to note that the gas flux linearly increases with the pressure for all the studied gases and the gas permeability does not depend significantly on the pressure drop which is in agreement with eq. 3-4 for the Knudsen molecular flow J_{Kn} and the gas permeability Q_{Kn} .⁶³

$$J_{Kn} = Q_{Kn} \cdot \Delta p \quad (3)$$

where Q_{Kn}

$$Q_{Kn} = \frac{4\epsilon d_p}{3\tau l} \sqrt{\frac{1}{2\tau MRT}} \quad (4)$$

where d_p is the pore diameter, ϵ is the porosity factor, R is the universal gas constant, M is molecular mass, Δp is the partial pressure drop, τ is the tortuosity factor, l is the thickness of the membrane.

This shows the molecular flow prevalence in the general gas flux through the membrane. Molecular flow is notable for gas separation as opposed to viscous flow, for example. During the experiments, it was found that CO_2 demonstrated a specific behavior, particularly significantly longer times to achieve the steady state flux in comparison with other gases. This fact can be explained by specific interaction of CO_2 molecules with ZIF-8.⁴⁹ Thus it can be suggested that CO_2 sorption can influence seriously the permeability of other gases in gas mixtures.

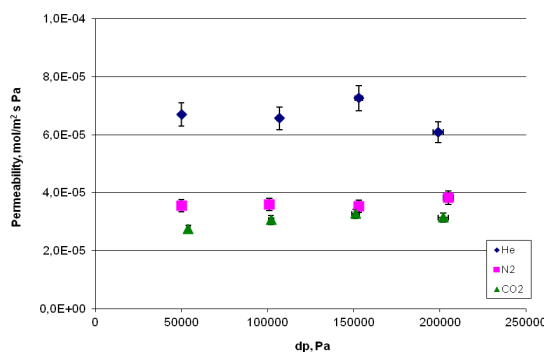


Fig. 5. The dependence of gas permeability on drop pressure for composite membrane with ZIF-8 selective layer on inorganic support (sample 4).

The ideal gas selectivity for all studied samples was calculated (Table 2). The obtained values for composite membranes are higher than supports selectivity. It is seen that the achieved level of the membranes gas selectivity is equal to or higher than the Knudsen selectivity depending of the synthesis conditions and the support nature. It should be noted that for porous membranes gas mixture selectivity can differ from ideal value that it is needed additional study.

Table 2. Ideal gas selectivity of composite membranes with the selective layer based on ZIF-8.

Sample	Selectivity			
	He/CO ₂		He/N ₂	
	α_{Kn}	$\alpha_{exp.}$	α_{Kn}	$\alpha_{exp.}$
PAN support				
Sample 01	3.3	2.0	2.6	2.2
PAN support + ZIF-8				
Sample 1		3.6		2.7
Sample 2	3.3	9.2	2.6	8.7
Sample 3		3.3		2.6
Aluminium zirconate support				
Sample 02	3.3	1.7	2.6	1.9
Aluminium zirconate + ZIF-8				
Sample 4	3.3	2.8	2.6	2.0

Using ZIF-8 membranes prepared by the “non-solvothermal” procedures, a good selectivity was not achieved in He/N₂ separation. Probably, the selectivity decrease in the case of the He/N₂ pair separation is not connected with the selective layer quality and can be explained by molecular dimensions of ZIF-8 (pore size ca. 3.4 Å diameter), which exceed very small kinetic diameters of the studied gases (~2.89 Å for He, 3.64 Å for N₂, and 3.30 Å for CO₂). Obviously, molecular sieving separation did not work in this case.

On the other hand, the inertness of both gases did not provide the specific interaction between these molecules and the supported membrane, which played an important role in separation of gas mixtures containing CO₂ molecules. The permeability results revealed that the most selective supported membranes were obtained using the PAN material. For example, the achieved He/CO₂ selectivity of the ZIF-8 membrane on the polymeric support (sample 2) was equal to 9.2, which is above the calculated level of the Knudsen parameter for nanoporous membranes. Probably, such a high selectivity is provided by the quality of polycrystalline ZIF-8 coating formed under conditions of the appropriate combination of the synthesis time and solvent quantity. Gas permeance examination revealed that a subtle variation of the synthesis conditions affected very much the ZIF-8 layer permselectivity.

It can be suggested that a more regular structure of the ultra(micro)porous polymeric support in comparison with the aluminium zirconate layer provided more dense and uniform ZIF-8 coating. Additionally, a flexibility of the PAN material and its nitrile functionalities provided a very good compatibility with the imidazolate linker of ZIF-8 crystals.

We suggested that the inorganic support structure could provide ZIF-8 crystallization both in the pores and on the surface. In the case of inorganic membranes, the synthetic procedure involving a solvent removal led to the permeate flux drop (sample 4, Table 1) caused probably by the partial pore blocking of the inorganic support by the zinc-imidazolate framework. Simultaneously, a subtle selectivity increase was observed. Blocking the pores by intrusion of the ZIF-8 crystals into the pores of the inorganic matrix confirmed a good adherence of the ZIF-8 layer to the inorganic support.

The repeated growth is one of the most effective methods to produce continuous and dense membranes.^{26,35} According to the developed synthetic protocol involving a partial solvent removal, multi-layer ZIF-8 based uniform coating on the aluminium zirconate surface can be prepared by repeated *in situ* synthesis. The two-layer membrane obtained by this route demonstrated a significant selectivity increase. Such an impact on the membrane performance could be probably explained by “smoothing” of the surface due to the formation of the first layer of ZIF-8 in the pores. Actually, in the case of three or more ZIF-8 layers coating, the flux drop occurred due to the support pore blocking. Thus, ZIF-8 membranes on an inorganic support can be considered as hierarchically ordered macro-/microporous hybrid materials.⁶⁴

Conclusions

In summary, we can conclude that ZIF-8 polycrystalline membranes were successfully synthesized for the first time by the *in situ* growth technique on PAN and aluminum zirconate-based composite supports. Despite of different structure of polymeric and inorganic substrate, the novel procedure accomplished under mild conditions resulted in a reproducible fabrication of a crack-free, well-intergrown zinc-imidazolate coating on their surfaces. Our findings revealed that the support nature (organic/inorganic) and texture (microporous and macroporous) determined the differences in the morphology of ZIF-8 selective layers on the membrane surfaces: a most homogeneous dense coating has been achieved on polymeric support. The prepared ZIF-8 membranes demonstrated a significant selectivity level and simultaneously high fluxes. The integrated novel ZIF-8 membranes may find a potential application in gas separation technology, including He and CO₂ separation from gas fluxes.

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Notes and references

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In situ synthesis of novel ZIF-8 membranes on polymeric and inorganic supports

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