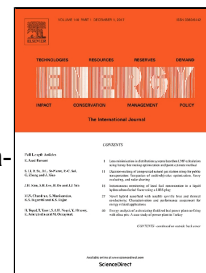


Accepted Manuscript

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PII: S0360-5442(17)31959-X

DOI: 10.1016/j.energy.2017.11.101

Reference: EGY 11889

To appear in: *Energy*

Received Date: 10 March 2017

Revised Date: 07 August 2017

Accepted Date: 17 November 2017

Please cite this article as: Mohammad Peydayesh, Toraj Mohammadi, Omid Bakhtiari, Effective Hydrogen purification from Methane via Polyimide Matrimid® 5218- Deca-dodecasil 3R zeolite mixed matrix membrane, *Energy* (2017), doi: 10.1016/j.energy.2017.11.101

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- DDR zeolite loaded Matrimid® mixed matrix membranes were prepared for H₂ purification.
- Semicrystalline neat polymer becomes more crystalline after thermal treatment.
- H₂ permeability and H₂/CH₄ selectivity up to 34.90 Barrer and 375.27 were obtained.

Effective Hydrogen purification from Methane via Polyimide Matrimid®**5218- Deca-dodecasil 3R zeolite mixed matrix membrane**

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Abstract

The demand for purified hydrogen as a new green energy source has dramatically increased during last years. In this study, different -Matrimid®- Deca-dodecasil 3R mixed matrix membranes were synthesized for Hydrogen purification from Methane. Results demonstrated that existence of Deca-dodecasil 3R into the Matrimid® matrix, as well as, high temperature thermal treatment enhances membrane crystallinity. Scanning electron microscope images of membranes showed uniform dispersion of zeolite in polymer matrix and well contact at polymer and zeolite interface. Gas permeation experiments exhibits that due to molecular sieving effect of Deca-dodecasil 3R membrane Hydrogen permeabilities and Hydrogen / Methane selectivity enhance for 20 wt. % loading of Deca-dodecasil 3R to 34.90 Barrer (100%) and 375.27 (189%), respectively.

Keywords: Hydrogen, Gas purification, Mixed matrix membranes, Polyimide Matrimid®, Deca-dodecasil 3R

1. Introduction

According to the World Energy Outlook in 15 past years, the basic world's energy demands from 10 billion ton of oil equivalent in 2000 have increased by 41 % to 14.1 billion in 2015 [1]. In recent years, due to worldwide climate changes, future energy need and environmental issues, the request for Hydrogen as a new green energy source has dramatically increased and this has stimulated more research to improve techniques of hydrogen separation, purification and production [1-6]. Hydrogen due to its high calorific value and environmental friendliness is the most emerging and suitable energy carrier, which can be used in portable or stationary fuel cells to substitute the non-sustainable fossil fuel to generate electricity [7]. Some hydrogen applications such as fuel cell technology and hydro-cracking process need high purity of hydrogen, therefore purification of this gas is necessary to meet different purity necessities [8]. There are several applications for H_2/CH_4 separation in various processes. Off-gas stream of refineries and petrochemical companies has large amount of CH_4 and H_2 , which can be recycled from flare stream to compensate the shortage of feedstock in some plants. Basically flare gas mixtures include 50% H_2 at pressure of 5-10 bar [9]. In addition, in the gas-cracking units, Hydrogen/Methane separation is essential for recovery of hydrogen from flare streams and pure methane production, which is used in Ethylene Oxide units as a balance gas [2].

Traditional processes for H_2 purification are absorption, cryogenic distillation and pressure and temperature swing adsorption, however, these processes are high-energy consuming in terms of equipment corrosion, regeneration of solvent, flow issues due to high viscosity of solvent and environmental contamination [3, 10]. Some of gas purification processes for hydrogen, have to use efficient, low cost and environment friendly techniques such as fast improving and spreading membrane processes [11]. Membrane processes compared to another gas separation

methods, consume lower energy, have easier scale up and operation, cost less in terms of capital and operating and are more friendly with environment [12-16].

Among all of the membranes types, polymeric membranes due to their low cost and ease of scale up are widely used in gas separation industries for Hydrogen, Methane, Carbon dioxide, Oxygen, Nitrogen, Paraffin and Olefin, etc. [17-21]. However, current commercial polymeric membranes suffering from low separation performances i.e. low flux and selectivity values and trade-off of these two parameters. Therefore, these limitation barricade the more use of these membranes in separation process industries [12, 13, 22, 23]. Incorporation of proper inorganic particles into the matrix of polymer is well known strategy among different approaches to enhance polymeric membrane separation performances [24-29]. Mixed matrix membranes (MMMs) with the aim of enhancing the separation performance are generally prepared by incorporation of inorganic particles such as metals, zeolites and carbons into the polymer matrix [30, 31]. With the aim of passing the Robeson upper bound limit, MMMS combine easy operation of polymeric membranes with promising separation performance of inorganic particles [13, 32-34].

Compared to other polymers, glassy polyimides due to excellent gas selectivity and thermal and chemical stabilities have been considered as an appropriate candidate for different gas separation processes, especially H_2 separation [34]. Condensation reaction of dianhydrides with diamines results in rigid polyimides with high glass transition temperature. Thermoplastic polyimide Matrimid® 5218 which based on the monomers of 3, 3', 4, 4'-benzophenone tetra carboxylic dianhydride (BTDA) and 5(6)-amino-1-(4'-aminophenyl)-1,3- tri methylindane (DAPI) is soluble in different solvents, such as Dimethyl acetamide (DMAC), 1-methyl-2-pyrrolidone (NMP), Dimethyl formamide (DMF) and Tetra hydrofurane (THF) [35].

Crystalline zeolites due to having unique surface properties and having uniform well-defined pores are widely used in separation and catalytic processes in industries [36, 37]. Deca-

dodecasil 3R type zeolites with 8-ring windows and aperture of $3.6 \times 4.4 \text{ \AA}$ have a high potential to separate H_2 (2.89 \AA) from CH_4 (3.8 \AA) based on their kinetic diameter difference [2, 22, 31, 38]. Zeolites of the DDR structure type include DD3R clathrasil and two isotopes of zeolites ZSM-58 and Sigma-1 [39].

In the current study, with the aim of enhancing the neat polymeric membrane Hydrogen separation performance, as well as, its thermal and mechanical properties, Sigma-1 DDR zeolite was incorporated into polyimide Matrimid[®] 5218 matrix. Effects of DDR (as a zeolite with good gas separation properties) loading on properties and gas separation performance of the MMMs were examined.

2. Experimental

2.1. Materials

Polyimide Matrimid[®] 5218 (Huntsman Chemical Company, USA) and 1-methyl-2-pyrrolidone (NMP) with boiling point of $204 \text{ }^\circ\text{C}$ (Merck) were used to synthesize polymeric membranes. For synthesis of DDR zeolite, hydrophilic Aerosil[®]200 fumed silica was supplied from Evonik and sodium aluminate and sodium hydroxide were purchased from Merck. 1-adamantamine hydrochloride (1-ADA) was used as template of zeolite structure and provided from Alfa Aesar.

2.2. DDR synthesis

The molar composition of Sigma-1 DDR zeolite solution for hydrothermal synthesis was $3\text{Na}_2\text{O}:201\text{-ADA}:\text{Al}_2\text{O}_3:60 \text{ SiO}_2:2400\text{H}_2\text{O}$ [40]. The synthesis gel was prepared by combination of aqueous solution of sodium aluminate and sodium hydroxide to a mixture of fumed silica, water and 1-ADA with stirring for 30 min. The resulting gel was poured in rotating Teflon lined autoclave and heated at $180 \text{ }^\circ\text{C}$ for 140 h in an oil bath. Then the autoclave

was cooled down to ambient temperature and the resulting residue was collected by centrifugation followed by drying in air. In order to remove the organic template, the powder was calcined at 500 °C for 48 h.

2.3. Membrane preparation

DDR particles (2, 5 10, 15, 20, 22% of polymer content) and a portion of 10 % of total Matrimid® were dispersed in NMP solvent and the resulting mixture was stirred at ambient temperature for one day. Then the remaining polymer was added and the mixture was stirred for another day. In order to ensure well and uniform dispersion of zeolite particles in the polymer solution, sonication of suspension was applied. Furthermore, to remove the bubbles from the solution, degassing of the solution under vacuum was performed. Then the solutions were casted on clean glass plates with casting knife-gap of 200 µm and dried at 170 °C to obtain MMMs. After peeling the membranes from the plates, they were treated thermally at 250 °C in nitrogen environment. Finally, the resulting membranes with thickness of 80-100 µm were stored in desiccators for further applications.

2.4. Membranes characterization

VEGA\\TESCAN scanning electron microscope (SEM) was used to investigate structural properties and morphology of powder and MMMs, fractured in liquid nitrogen and coated with gold. An INEL model EQUINOX3000, France X-ray diffractometer was used for X-ray diffraction (XRD) analysis of powder and MMMs. Glass Transition Temperatures (T_g) of the synthesized membranes were measured using a PerkinElmer-pyris6 Differential Scanning Calorimetry (DSC). Heating and cooling rates were 10 °C/min under nitrogen environment. Thermal Stabilities of synthesized membranes were evaluated using a PerkinElmer-pyris diamond Thermogravimetric analysis (TGA). Heating range was 30 to 600 °C with rate of 10 °C/min under nitrogen environment. An electronic-controlled tensile apparatus was used to examine mechanical properties of the neat Matrimid® 5218 and the DDR zeolite -Matrimid®

5218 MMMs in terms of tensile strength and elongation. All measurements were performed two times with $5 \times 20 \text{ mm}^2$ membrane strips size and stretching rate of 1 mm h^{-1} . Then tensile modulus was calculated by fitting the stress-strain plot in the linear regime.

2.5. Synthesized zeolite gas adsorption capacity measurements

Before the adsorption experiments, in order to remove water and other impurities, zeolite powder was kept one day under vacuum at 200°C . To investigate the adsorption capacity of synthesized zeolite, volumetric approach [2] was carried out applying a common static-volumetric adsorption setup as illustrated in Figure 1.

2.6. Membrane gas permeation measurements

Pure gas permeabilities were evaluated for H_2 and CH_4 using a permeation measurement setup as described in our previous work [33] at temperature of 308 K and pressures 10 bar . NX series control & monitoring program was used to record the steady state permeation data. Gas permeations were measured via constant volume method. Permeate side volume and cell effective area for membranes were 295.65 cm^3 and 11.95 cm^2 , respectively.

Steady state MMMs permeability values were calculated by means of pressure rate (dp/dt) according to Equation (1) and then membrane selectivity was calculated from equation (2):

$$P = \frac{V.T_s.l}{A.\Delta P_{Upst}.T.P_s} \frac{dp}{dt} \quad 1$$

$$\alpha = P_i/P_j \quad 2$$

Where P and α are permeability coefficient ($\text{cm}^3 \text{ cm cm}^{-2} \text{ s}^{-1} \text{ mmHg}^{-1}$) and selectivity coefficient for components i and j , respectively. V , A and l are volume of permeate side (cm^3), membrane effective surface (cm^2), thickness of membrane (cm). dp (bar) is pressure difference during permeation time of dt (s), ΔP_{Upst} (mmHg) is pressure difference across the membrane

and P_S is standard pressure equal to 1 bar. T and T_S are operating temperature (K) and standard temperature of 298.15 K, respectively [41]. It must be mentioned that each membrane was prepared twice and the results were presented on average.

3. Results and discussion

3.1. Synthesized DDR zeolite

A Scanning Electron Microscope image of the DDR zeolite is shown in Figure 2 (a). Powder morphology depicts a sphere with average particle size of 20 μm for DDR zeolite. As observed, small hexagonal crystals are also formed that can be characterized as ZSM-5, one of the DDR zeolite neighbors [40, 42]. The same observations were reported for many other synthesized zeolites which their neighbors were formed and the synthesized powders were a mixture of close zeolite crystals [40, 42]. ZSM-5 crystal also is a proper selection for gas separation [23]. Figure 2 (b) shows Sigma-1 DDR zeolite powder XRD patterns of the as-synthesized (which include speaks of minor ZSM-5 crystals) with the sharpest peak at $2\theta = 17$. The main peaks are close to those described by Stewart et al. [40].

H_2 and CH_4 adsorption isotherms of DDR zeolite crystals at 300 K were shown in Figure 3. As observed adsorbed amounts of H_2 into the zeolite is more than those for CH_4 . The reason for this phenomenon is that DDR zeolite pore diameter is 3.6×4.4 Å. Thus small H_2 molecules with critical diameter of 2.89 Å can inter to the structure windows of zeolite and be trapped there while big molecules of CH_4 with critical diameter of 3.8 Å cannot enter the zeolite structure easily. Therefore, adsorption capacity of DDR zeolite for H_2 is higher than that for CH_4 [2].

3.2. MMMs structure characterization

Figure 4 shows SEM images of surface and cross section of the prepared membranes with different loadings. As observed in Figure 4 (a) and (b) for pure Matrimid® 5218 membranes, surface is smooth, clean and uniform.

Figure 4 (c-h) shows SEM images of DDR zeolite -Matrimid® 5218MMMs. Existence of the particles in the polymeric matrix can be seen in cross-section images. The images indicate that for loadings below 20%, due to use of ultrasonic waves the filler particles are distributed well enough. Although no modifier agent was used, "filler particles - polymer chains" interface as observed in SEM images and subsequently proved by gas separation experiments are well interacted. Thermal treatment at high temperature can accelerate rearranging of polymer chains around the filler resulting in prepared defect free membranes. As observed in Figure 4 (h) for filler loading of 22%, aggregation of the particles occurs resulting in more passage of gases through the membrane and less selectivity [43]. In addition, it can be seen that due to fracturing stress in liquid N₂ for some of zeolite particles, their surface becomes segregated [41].

Effects of thermal treatment and incorporation of zeolite particles on XRD patterns of the membranes are shown in Figure 5. In fact, thermal treatment causes annealing of the polymer, resulting in membranes with higher polymeric crystalline segments.

Furthermore, by adding the zeolite particles, which have crystalline structures, XRD pattern of membranes with more sharp peaks approaches to zeolite XRD patterns [44].

The polymeric macromolecules interchain movements and segmental flexibilities strongly influence separation mechanism and performance of membranes. At temperature of near 50 °C below T_g , polymer segmental flexibility is more limited, thus interchain movements are hindered and diffusive selectivity which is based on size and shape, is dominated and polymer matrix acts as pseudo molecular sieves. Incorporation of zeolite particles within the polymeric matrix could affect the chain movements and flexibility by means of rigidification around

zeolite particles and/or polymer entrance into zeolite pores and subsequently affect structural properties and separation performance of the membranes. Aforementioned phenomena could be evaluated by structure characterization methods like DSC and TGA [45].

The DSC results of neat Matrimid® 5218 membrane, annealed neat Matrimid® 5218 membrane and MMMs are shown in Table 1. T_g values of the membranes after annealing at high temperature increase confirming polymer crystalline segments increment. For glassy polymers like polyimide which regards as pseudo molecular sieves, this crystalline increment can result in better gas separation performance. Furthermore as mentioned before this thermal treatment causes better polymer chains movements and flexibility, resulting in chain rearrangement around the filler, which subsequently leads to have defect free polymer-zeolite interface [41]. In addition, as observed by increasing DDR zeolite loading in the MMMs, T_g values enhance. By adding more zeolite particles, polymer chains to the zeolite particles connection and/or polymer entrance into the zeolite pores increases and subsequently the polymer chain free volume decreases. As aforementioned this phenomena restricts polymer chains movements and flexibility, which results in MMMs T_g values enhancement [45].

To study the effect of DDR zeolite loading on the MMMs thermal stability and the MMMs weight loss during heating, TGA was performed. As observed in Figure 6, after 500 °C, the membranes lose their weights, while thermal stability of the MMMs is slightly higher than that of the neat Matrimid® 5218. As can be measured, Neat Matrimid® 5218, Matrimid® 5218/10% DDR and Matrimid® 5218/20% DDR loss 34.51, 32.23 and 27.86% of their weights, respectively. This enhanced thermal stability may be due to the polymer chain stabilization by interactions between the DDR and the Matrimid® matrix [45].

Mechanical stability of the prepared membranes in terms of Young's Modulus, tensile strength and tensile strain are presented in Table 2. As observed, by increasing the filler loading both tensile strength and strain decrease, indicating more rigid structure of MMMs due to the

presence of DDR particles. Also, the neat Matrimid® Young's module is 2310 MPa which increases to 2621 MPa for the Matrimid® 5218/20% DDR MMM, The Young's module enhancement is attributed to well interfacial adhesion between the DDR particles and Matrimid® chains [46]. However, due to aggregation of the particles, it decreases to 2126 MPa for the Matrimid® 5218/22% DDR MMM.

3.3. Gas separation performance

Table 3 shows the H₂/CH₄ separation performance comparison between this work and other works. As observed, the separation performance of membranes depends on operating condition parameters such as pressure and temperature and preparation conditions such as procedure and solvent type.

The membrane selectivity coefficient depends on properties of solvent, concentration of polymer and filler and preparation approaches [33]. In MMMs, transport consists of two mechanisms, solution and diffusion in polymer matrix and molecular sieve of fillers. At low- to intermediate loading of zeolite, permeation occurs via diffusion across the polymer matrix and the zeolite particles and at very high zeolite loading, permeation occurs mainly through the zeolite pores [22]. Gas separation performance of membranes including permeability and selectivity are listed in Table 4. By increasing the zeolite particles loading, H₂ and CH₄ permeabilities increase and decrease, respectively. The reason for this phenomenon is that the pores aperture of DDR zeolite ($3.6 \times 4.4 \text{ \AA}$) is between molecule sizes of H₂ (2.89 \AA) and CH₄ (3.8 \AA). So the zeolite acts like molecular sieve and small molecules of H₂ could easily pass through the membrane while big molecules of CH₄ do not [51]. By increasing the zeolite loading, separation mechanism shifts more from polymeric solution diffusion to zeolite molecular sieving [22]. Figure 7 illustrates the membranes ideal selectivity as a function of DDR zeolite loading. As observed, by increasing the zeolite loading up to 20% the membrane H₂/CH₄ selectivity increases. For the best membrane with 20% loading, H₂ permeability and

H₂/CH₄ selectivity are 34.90 Barrer and 375.27, respectively. As observed in DDR high loading of 22%, permeability of both gases increases while selectivity decreases. This phenomenon could be due to the agglomeration of DDR particles at high loading and formed interface voids and non-selective passage for both gases [43].

The H₂/CH₄ separation performance regarding H₂/CH₄ Robeson upper bound limit is shown in Figure 8. As observed, although MMMs separation performance is still below the Robeson upper bound limit, by increasing DDR zeolite loading, H₂/CH₄ separation performance trend approaches this bound confirming potential of the prepared MMMs. In fact, the results showed that selecting proper filler type and content could enhance permeability and selectivity of polymeric membrane simultaneously.

4. Conclusion

Incorporation of inorganic particles like zeolites into the matrix of polymeric membranes is one of the major approaches to enhance gas separation performance of polymeric membranes. In this study Sigma-1 zeolite was synthesized successfully and applied to prepare different loadings Polyimide Matrimid® 5218- DDR mixed matrix membranes. The membrane characterization showed uniform dispersion of particles and well-defined zeolite polymer interface morphology. The results showed that thermal treatment plays an important role to increase polymer crystallinity and compatibility of polymer with filler. The gas separation performance results showed simultaneous increment of permeability and selectivity of the membranes up to 100% and 189%, respectively.

Acknowledgment

The authors would like to thank Iran National Science Foundation (INSF) (940110) for supporting the research

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List of Symbols

Symbol	Variable / Parameter	Unit
V_{Perm}	permeated volume	cm^3
V	permeate side volume	cm^3
Δp	pressure increment in time duration of t	Bar
P_s	standard pressure	Bar
Δp_{Upst}	pressure difference across the membrane	mmHg
T	operating temperature	K
T_s	standard temperature	K
L	membrane thickness	Cm
A	membrane area	cm^2
α	selectivity coefficient	-
t	permeation time	S
P	permeability coefficient	Barrer

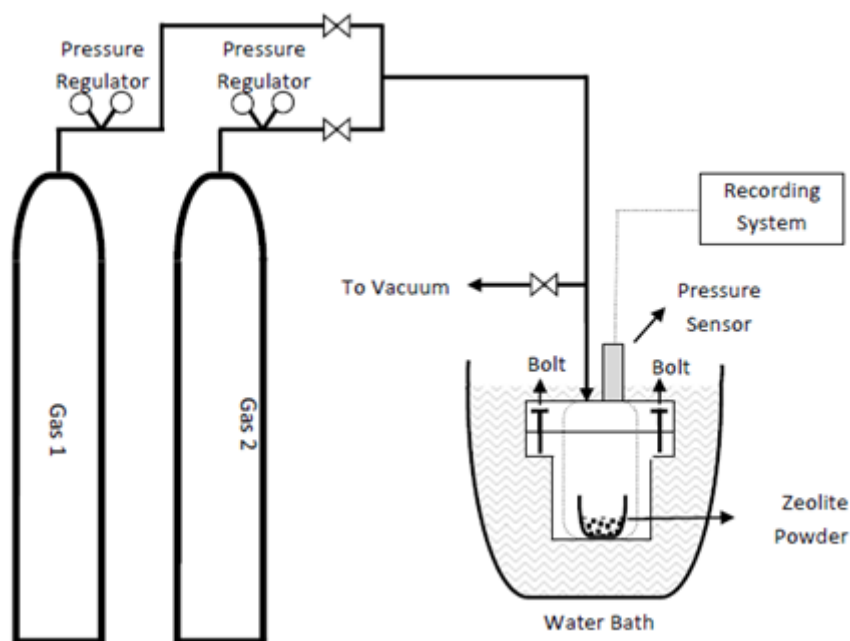


Figure 1: Schematic diagram of zeolite powder gas adsorption measurement setup.

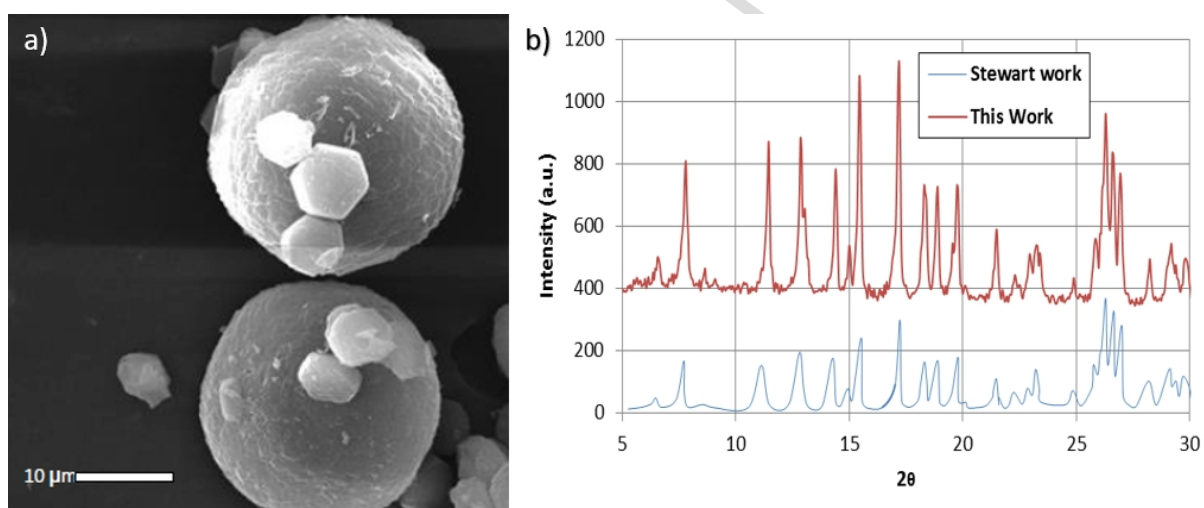


Figure 2: Characterization of synthesized DDR zeolite crystals a) SEM image, b) X-ray diffraction patterns compared to Stewart work

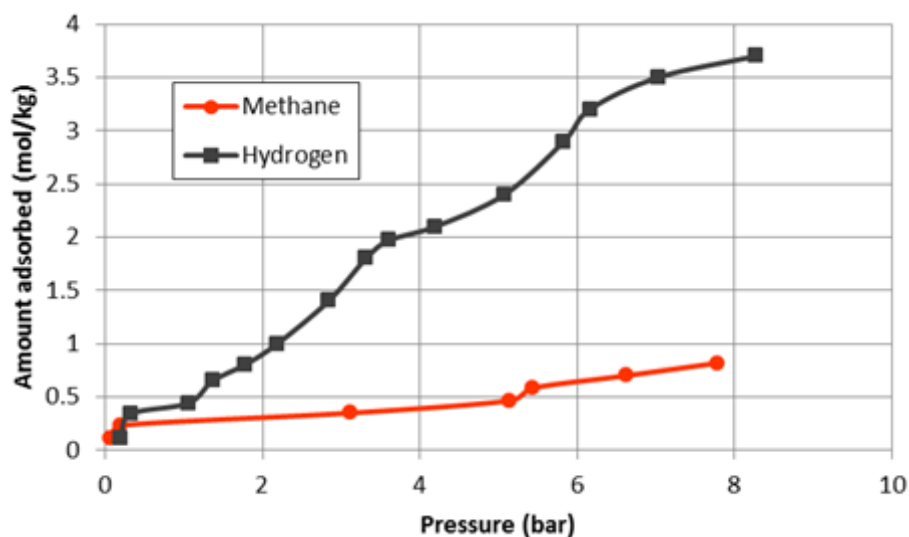


Figure 3: Adsorption isotherms of H₂ and CH₄ at 300 K.

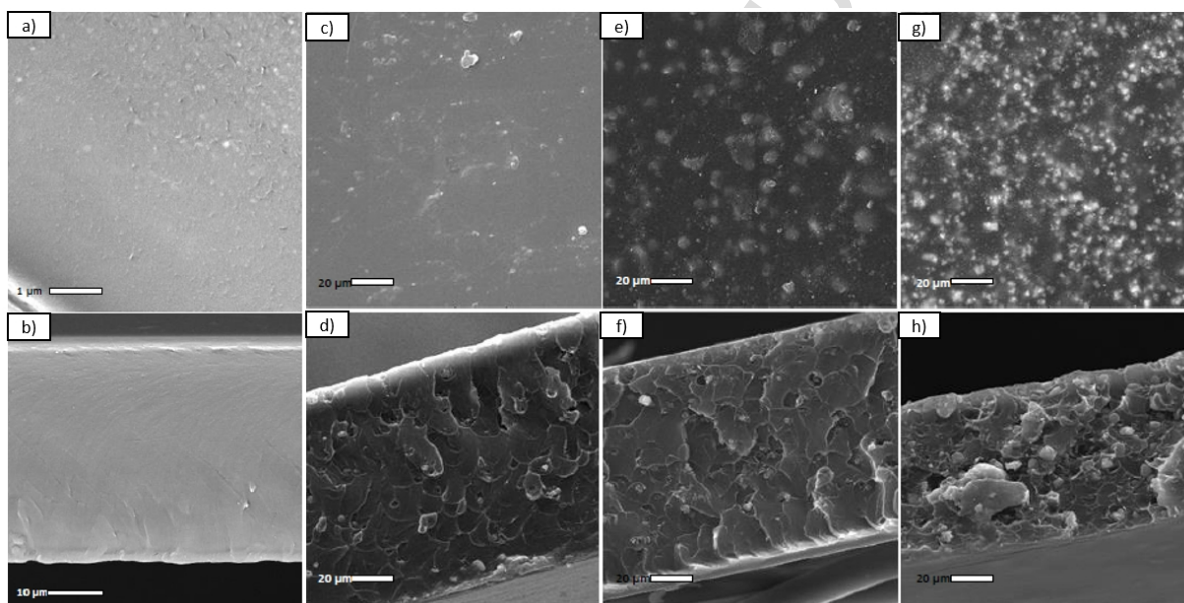


Figure 4: SEM images of DDR - Matrimid® 5218 MMMs with different filler loadings, surface of 0% (a), 10% (b), 20% (c), 22% (d) and cross section of 0% (e), 10% (f), 20% (g), 22% (h).

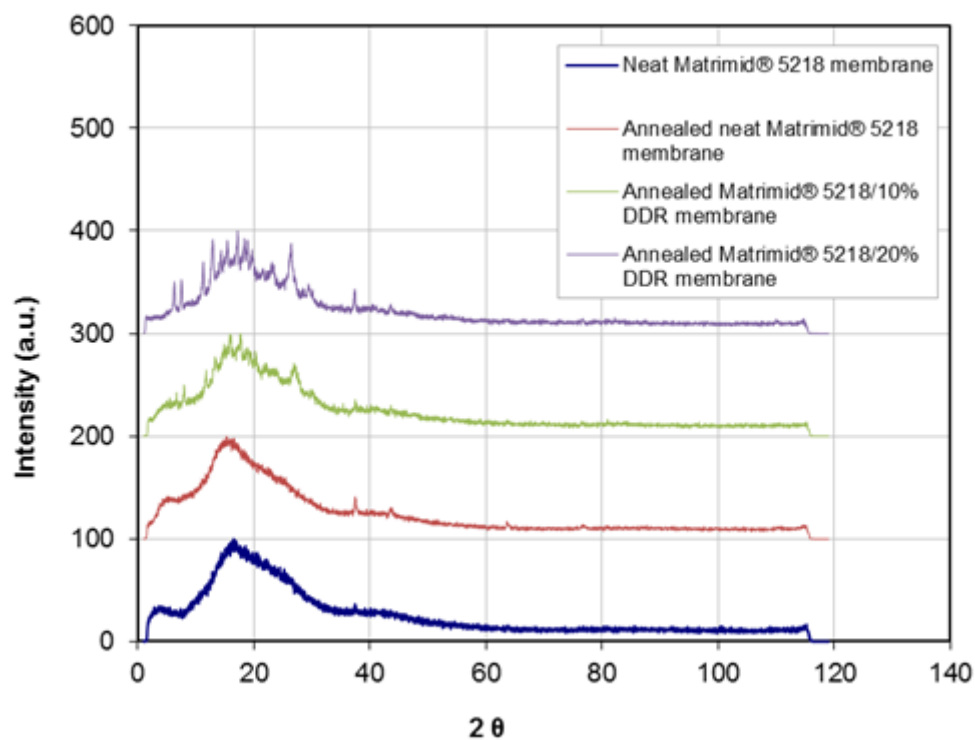


Figure 5: XRD patterns of the MMMs with different DDR zeolite loadings.

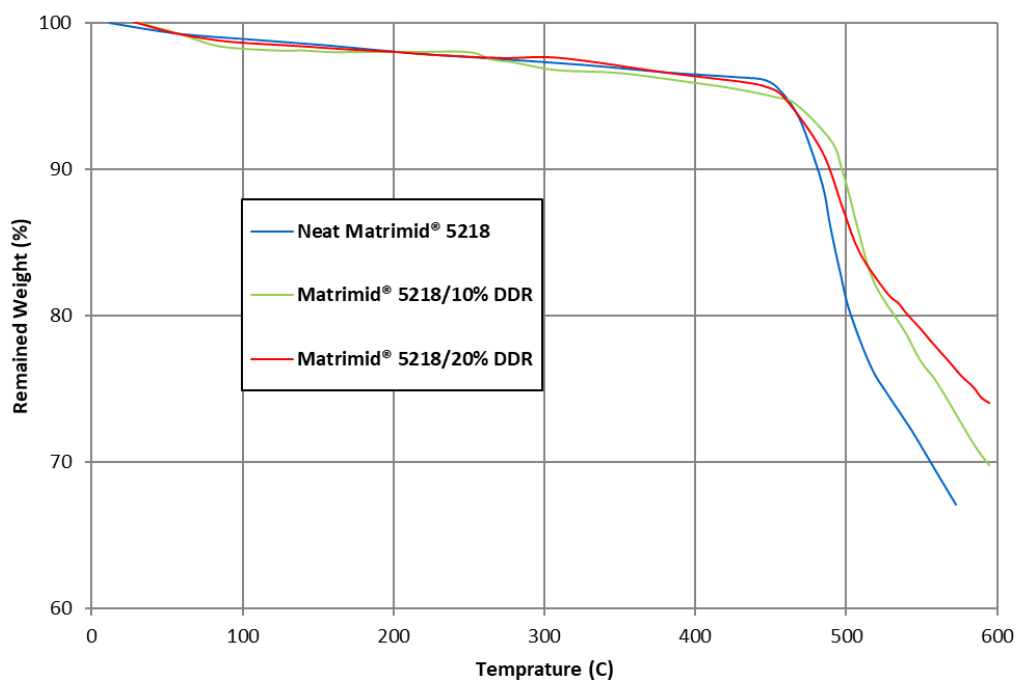


Figure 6: Effect of DDR zeolite loading on the MMMs thermal stabilities.

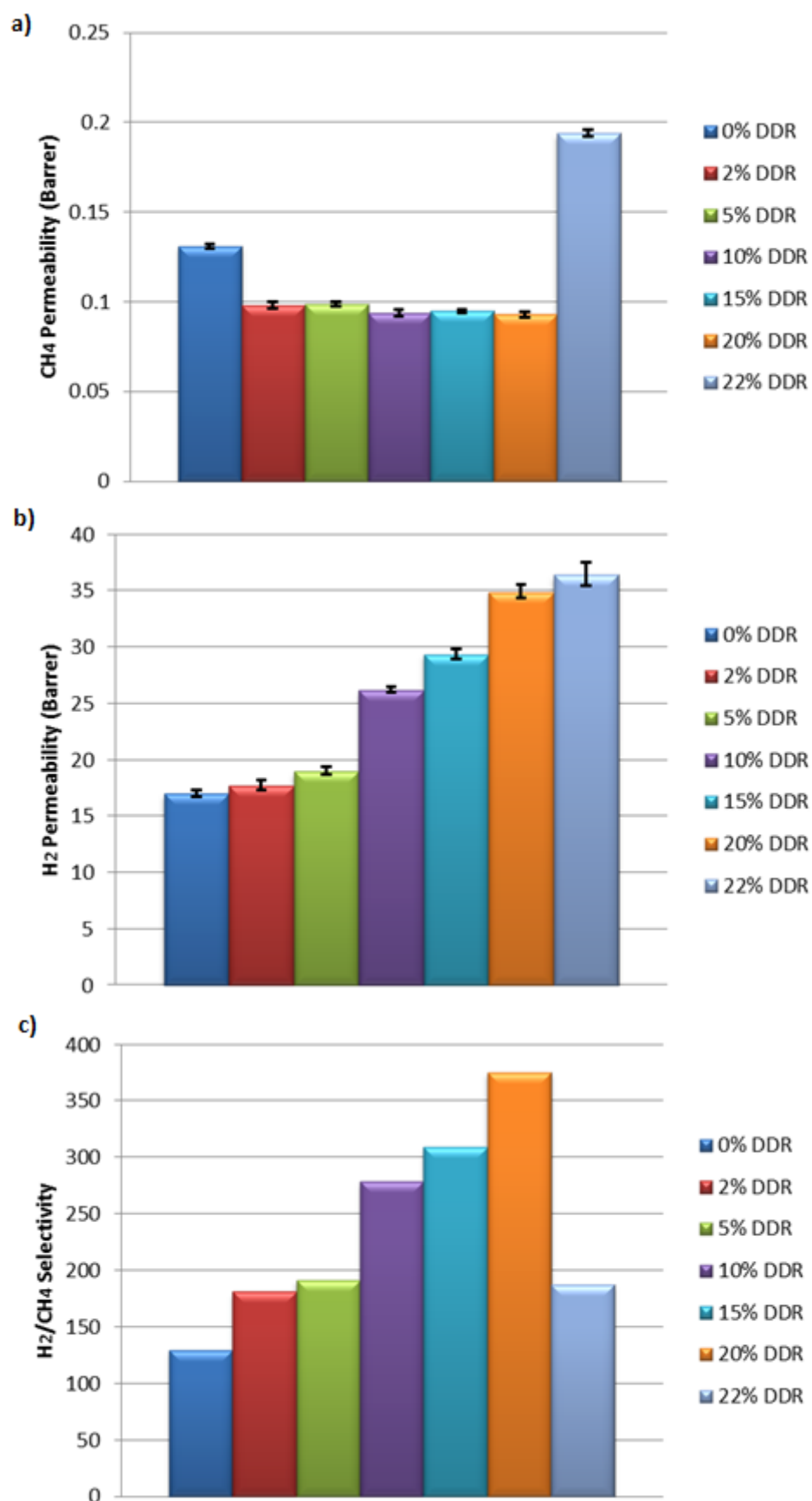


Figure 7: Separation performance of the membranes as a function of DDR zeolite loading.

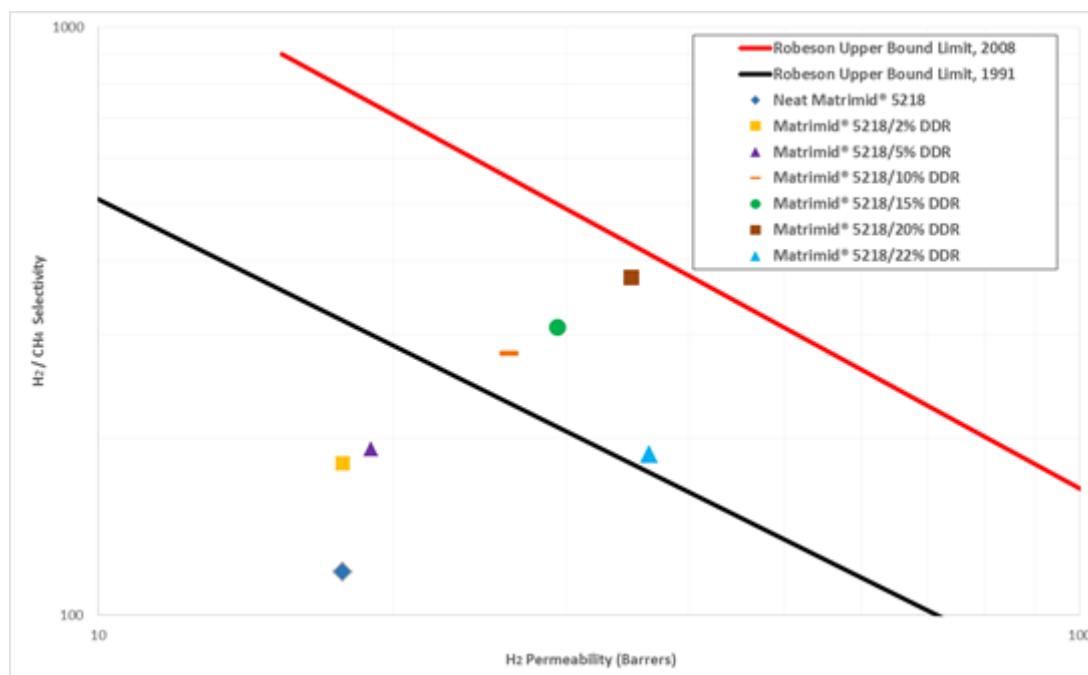


Figure 8: Robeson plot of DDR - Matrimid® 5218 MMMs for H₂/CH₄ separation.

Table 1: DSC analysis of the neat membrane and the MMMs.

Membrane	Glass Transition Temperature, T _g (°C)
Neat Matrimid® 5218 membrane	294.12
Annealed neat Matrimid® 5218 membrane	299.88
Annealed Matrimid® 5218/5% DDR membrane	302.13
Annealed Matrimid® 5218/10% DDR membrane	305.43
Annealed Matrimid® 5218/15% DDR membrane	306.65
Annealed Matrimid® 5218/20% DDR membrane	309.84

Table 2. The prepared membranes Young's Modulus, tensile strength and tensile strain

Membrane	Young's Modulus (MPa)	Tensile strength (MPa)	Tensile strain (%)
	E	σ	ε
Neat Matrimid® 5218	2310 \pm 0.04	84.12	20.10
Matrimid® 5218/10% DDR	2472 \pm 0.08	76.43	7.44
Matrimid® 5218/20% DDR	2621 \pm 0.03	72.01	5.47
Matrimid® 5218/22% DDR	2126 \pm 0.09	62.33	2.71

Table 3: Comparison of H₂/CH₄ separation performance of this work with the other works.

Sample	Pressure (bar)	H ₂	H ₂ /CH ₄ pure selectivity	Ref.
		Permeability (Barrers)		
This work	10	17.01	129.8	
Y. Zhang et al.	4	17.50	83.3	[46]
Rösler	3.5	28.10	112.4	[47]
S.S.Hosseini et al.	3.5	27.16	129.3	[48]
H. Zhao et al.	2	17.75	118.3	[49]
S. Shishatskiy et al.	-	24.00	109.1	[50]

Table 4: Pure gas permeabilities and ideal selectivities for the neat membrane and the MMMs.

Membrane	Permeability(Barrer) (R ² =regression coefficient)		H ₂ /CH ₄ Ideal selectivity
	H ₂	CH ₄	
Neat Matrimid [®] 5218	17.01 (0.9833)	0.131 (0.9916)	129.85
Matrimid [®] 5218/2% DDR	17.76 (0.9763)	0.098 (0.9813)	181.22
Matrimid [®] 5218/5% DDR	18.98 (0.9822)	0.099 (0.9878)	191.72
Matrimid [®] 5218/10% DDR	26.2 (0.9904)	0.094 (0.9796)	278.72
Matrimid [®] 5218/15% DDR	29.37 (0.9854)	0.095 (0.9901)	309.16
Matrimid [®] 5218/20% DDR	34.9 (0.9832)	0.093 (0.9856)	375.27
Matrimid [®] 5218/22% DDR	36.43 (0.9712)	0.194 (0.9912)	187.78