Synthesis, Characterization and Gas Separation Properties of MOF-5 Mixed Matrix Membranes

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Abstract

With the rapid development of hydrogen economy and membrane science, membrane-based gas separation technology shows great potential for the hydrogen purification. Mixed matrix membranes (MMM) have been developed in order to increase the gas separation performance of a membrane. However, MMMs result in poor filler-polymer compabilities and filler segregation. Metal organic frameworks (MOFs) as new fillers with high surface area and pore volume overcome these drawbacks and enhance the H_2 gas adsorption properties. In this study, MOF- 5 was synthesized, characterized and incorporated into polyimide (PI) to investigate the effect of filler on the single gas permeation. MOF-5/PI MMMs were fabricated at different loading rates (5wt.%, 10wt.%, 15wt.% MOF-5). The characterization a membrane was performed by scanning electron microscopy (SEM), infrared spectroscopy (IR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). The prepared membranes with varying filller contents were used to investigate the H_2, CO_2 and CH_4 permeation properties and H_2/CO_2, CO_2/CH_4, H_2/CH_4 selectivities. The results showed that the single gas permeation experiments for all gases increased with MOF-5 loading at room temperature and pressure of 200 kPa. At higher loadings, ideal selectivity of H_2/CO_2, CO_2/CH_4, H_2/CH_4 were found less compared to the pure polymer. Consequently, the incorparation of MOF-5 into the polimer incresed the membrane gas permeation rates but decreased the selectivity.

Keywords: Metal organic framework, Polymer, Mixed matrix membrane, Permeability, Selectivity.

MOF-5 Bağlı Karışık Matriksli Membranların Sentezi, Karakterizasyonu ve Gaz Ayırma Özellikleri

Öz

Membran biliminin ve hidrojen ekonomisinin hızlı gelişimi ile hidrojen saflaştırmada membrane dayalı ayırma teknolojisi yüksek bir potansiyel göstermektedir. Gaz ayırma membranlarının performansını arttırmak için karışık matrisli membranlar (MMM) geliştirilmiştir. Fakat, MMM'lar, zayıf dolgu-polimer etkileşimine ve dolgu malzemesinin topaklanmasına neden olmaktadır. Yüksek yüzey alanı ve por hacmine sahip yeni bir dolgu malzemesi olan metal organik kafes sistemi (MOF) bu olumsuzlukların üstesinden gelmekte ve H_2 gas adsoprsiyon özellikleini iyileştirmektedir. Bu çalışmada, MOF-5 sentezlenerek, bu yapının karakteristik özellikleri incelenmiştir. Gaz geçirgenliği üzerinde dolgu maddesinin etkisini incelemek üzere, farklı yükleme oranlarında (0, %5, %10, %15) hazırlanan MOF-5 kristalleri poliimit membrane içine ilave edilmiştir. Karakterizasyonları, taramalı electron mikroskobu (SEM), kızık ötesi spektrometresi (IR), x ışını kırınım cihazı (XRD), termogravimetrik analiz (TGA) ile tayin edilmiştir. Farklı oranlarda hazırlanan membranlar, H_2, CO_2 ve CH_4 gazlarının geçirgenlikleri ile H_2/CO_2, CO_2/CH_4 ve H_2/CH_4 seçiciliklerini belirlemek üzere kullanılmıştır. Tüm gazlarda geçirgenlik 200 kPa ve oda sıcaklığında artış göstermiş fakat yükleme oranı arttıkça H_2/CO_2, CO_2/CH_4 ve H_2/CH_4 seçicilikleri saf polimere gore azalmıştır. Sonuç olarak, polimere MOF-5'in ilavesi geçirgenlik performansını arttırmasına rağmen, seçicilik azalma göstermiştir.

Keywords: Metal organik kafes, Polimer, Karışık matrisli membran, Geçirgenlik, Seçicilik

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1.   **Introduction**

Gas separation membranes take place in literature for many applications, especially in hydrogen separation and storage. In order to investigate membrane performance, researchers concentrated on inorganic and organic polymers. Although inorganic membranes have good selectivity and permeability, these materials are higher cost than organic membranes to fabricate, fragile and need certain thicknesses [1]. Latter result in lower energy consumption, higher mechanical stability and easy to manufacturing compared to inorganic membranes. On the other hand, they have relationship between permeability and selectivity, inversely, in other words, the selectivity decreases with increasing permeability and vice versa, reported by Robeson in 1991 and 2008 [2 and 3]. Many techniques have been investigated to improve the productivity of polymeric membranes. Nowadays, a new group membrane MMMs became main topic to eliminate trade-off between permeability and selectivity of polymeric membranes. Mixed-matrix membranes (MMMs) were prepared in the 1980s are formed an inorganic or organic filler incorporated into a polymeric matrix [4 and 5].

Performance of MMMs depends on the choosing of a proper polymeric material, inorganic filler and compatibility between material and filler. Poor filler-polymer compatibilities can lead to formation of voids and filler blocking are the main reason for the degradation of performance of these membranes [6]. Recent advances have tended towards the addition of new fillers such as MOFs into the polymeric matrix. Mixed matrix membranes prepared by using MOFs have received significant attention as gas separating membranes. MOFs consist of transition metal ions linked and organic ligands are good candidates to improve incompability between filler and polymer (Figure 1) [7].
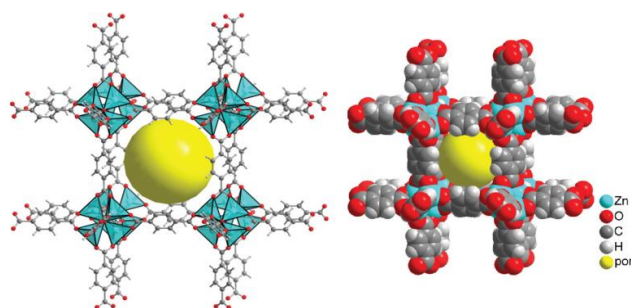

Figure 1. Shematic representation of MOF-5 [6].

MOF-5 or IRMOF-1 which is basically $Zn_4O_{13}C_{24}H_{12}$ framework reported firstly by Yaghi [8] is the most important framework. MOF-5 built up $[Zn_4O]^{+6}$ and benzene-1,4-dicarboxylate (BDC) groups, to get a porous cubic structure. This specific framework makes MOF-5 higher surface area, exceptional pore volume and better thermal stability, endless variety of ordered structure, and functional groups [9 and 10]. Because of these properties, MOF-5 has been studied in the literature commonly.

Yaghi et al. [8] indicated in their first paper published in 1999 that MOF-5 presented hydrogen uptake, 4.5 wt% at 77 K and pressure of 0.8 bar. They changed operation conditions (room temperature and 20 bar) at the next step and were found 1 wt% hydrogen storage capacity . Another study explained that the hydrogen storage of MOF-5 was 1.32 wt% at 1 bar and 77 K [11]. Panella and co-worker [12]

showed a hydrogen uptake capacity of 1.6 wt% for MOF-5 at 77 K and pressures above 10 bars. Hydrogen uptake of MOF-5 reaches up 5.1 wt% at 77 K and over 80 bar [13].

In this study, MOF-5 particles were succesfully formed, identified and incorporated into the polyimide to determine the impact of filler on the single gas permeation in mixed matrix membranes. The MOFs and membranes were characterized by scanning electron microscopy (SEM), infrared spectroscopy (IR), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and single gas permeation analyses.

2.   Materials and Methods

This study comprises three steps, namely MOF production, pure polymeric and mixed matrix membranes manufacturing, and membrane characterization. Chemical such as benzene-1,4-dicarboxylic acid (H_2BDC), zinc nitrate hexa-hydrate ($Zn(NO_3)_2.6H_2O$), N,N-dimethylformamide (DMF), polyimide (PI), and N-methyl-2-pyrrolidone (NMP) obtained and used without further purification.

2.1.   Synthesis of MOF-5

MOF-5 crystals were obtained by solvotermal method. In a typical synthesis, 5.1 mmol of Zn metal salts and 1.7 mmol H_2BDC was dissolved in 16mL of DMF in a glass tube under strong agitation in a ultrasonic water bath. Then the prepared solution was placed in an oven (105°C for 24 h). Glass tube was then removed from the oven and ensure to be cooled down to ambient atmosphere. MOF-5 crystals were gotten by filtering the solution and then the white particles washed three times using ethanol of 5mL. The white particles were retained (1 d at 60°C) in a vacuum oven in order to get dry particles. MOF-5 powders were stored in a capped vial.

2.2.   Fabrication of Pure PI Membrane.

0.5 g of the PI was added in 4.5 g of NMP and this solution stirred (12h at 70°C) until homogeneous solution was obtained. The uniform solution was casted on a clean glass surface with the help of casting rod to get thin film, then placed in a vacuum oven (70°C) for 12 h to permit the solvent to evaporate completely. After that, the membrane was immersed into a water bath to separate the membrane from glass surface. Finally, the membrane was heat treated in a vacuum oven at 220°C for 1 d.

2.3.   Fabrication of Mixed Matrix Membrane Containing MOF-5 Particles

Preparation of mixed matrix membrane is comparable to the pure polymer membrane fabrication with the additional process which includes introducing of MOF-5 crystals into the polymeric solution. Two different solutions were prepared for the manufacturing of a MMM. The first solution includes 0.5 g of PI dissolved in 4.5 g of NMP to get a 10 wt.% solution. The second solution includes MOF-5 added in NMP. Different MMMs were prepared using different MOF-5 loadings; for example, 0.025 g (for 5 % loading), 0.050 g (for 10% loading), and 0.075 g (for 15% loading) of MOF-5 were added to 4.5 g of NMP. The two solutions were sonicated in a water bath for 3 h then were mixed by adding the polymer solution into the MOF-5 solution. The solution was stirred in the sonicator for 5 h. Other steps for the fabrication of MMMs similar to pure polymer membrane preparation. The uniform solution was slightly poured on a clean glass surface with the help of casting rod to get thin film, then placed in a vacuum oven (70°C) for 12 h to allow the solvent to evaporate completely. After that, the membrane was immersed into

a water bath to separate the membrane from glass surface and the membrane was annealed in a vacuum oven at 220°C for 1 d.

2.4.   Characterization of PI and MOF-5 MMMs

The spectrum of MOF-5 obtained by infrared spectroscopy (IR) was recorded at room temperature using a Perkin-Elmer MIRacle Single Reflection Diamond ATR and IR spectra were collected at wave-number between 650 cm^{-1} and 4000 cm^{-1}. Scanning electron microscopy (SEM) images of MOFs and MMMs were taken using a JSM-7001F Field Emission Scannig Electron Microscope. Thermogravimetric analyses (TGA) performed to determine weigh loss of samples by temperature using a TGA instrument(SDT Q600 V20.9 Build 20) under the nitrogen atmosphere with a heating rate of 20 °C min^{-1}. To explain crystal characterization of samples, RIGAKU, SMARTLAB X Ray Diffraction (XRD) equipment was used.

3.   Findings

In this study, pure polymeric membrane, MOF-5 and MMMs were prepared and characterized, and gas permeation and separation performances of these membranes were investigated.

3.1.   Membrane Characterization

The MOF-5 characterization was performed by XRD, IR, SEM and TGA methods. As shown in Figure 2, XRD pattern of MOF-5 showed similar trend with the literature [14]. The peak at 2θ=9.87 corresponding to the MOF-5 crystal plane, explain that MOF-5 particles were successfully synthesized using solvothermal method. Another characteristic peaks appear at 2θ =17.84 for MOF-5 in the sample. The last peak for the MOF-5 crystal plane at 2θ=24.85 is shown in the sample demonstrated that presence of MOF-5 crystals in this sample.
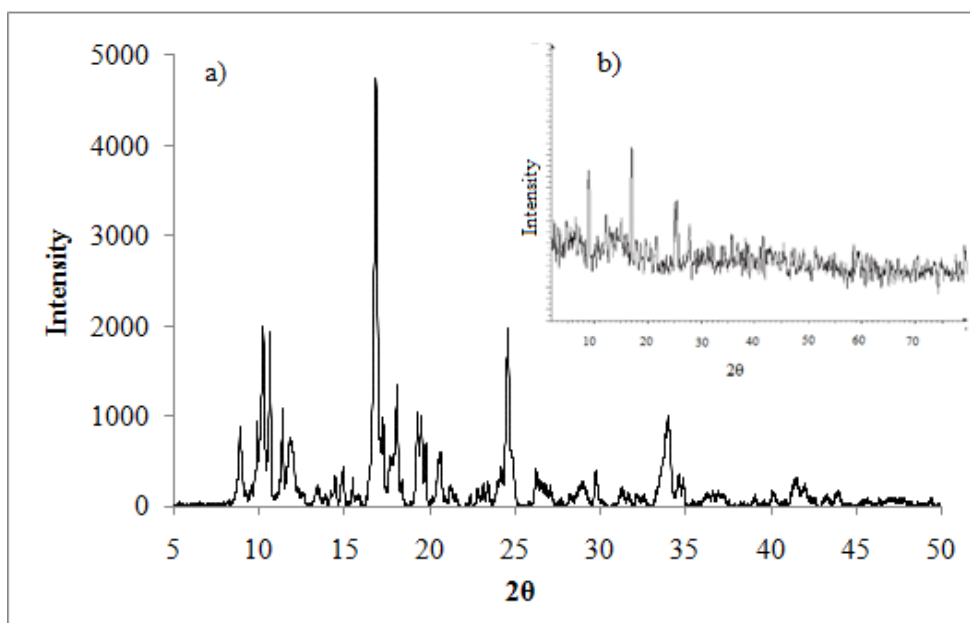

Figure 2. XRD of MOF-5 a) obtained from this study b) Reference (Ullah et al, 2012)

Figure 3 shows IR spectra for MOF-5. The MOF-5 exhibits one peak at 1580-1500 cm^{-1} range and one peak at 1400-1300 cm^{-1} range correspond to the symmetric and asymmetric stretching of COO groups in carboxylic, respectively [15]. The vibration bands at 700–1200 cm^{-1} represent the fingerprint of terephthalate compounds [16]. The peaks in the range of 1250–1010 cm^{-1} correspond to the C–H group present in the benzene ring of the BDC linker. The peaks take place between the range of 400–530 cm^{-1} are characteristic of ZnO molecules. The broad bands at 2800–3600 cm^{-1} exhibit the presence of water in the metal coordination sphere [15 and 16]. As a result, in this study, the main IR vibration bands indicate same values with previous studies and confirm the existence of MOF-5 [1].
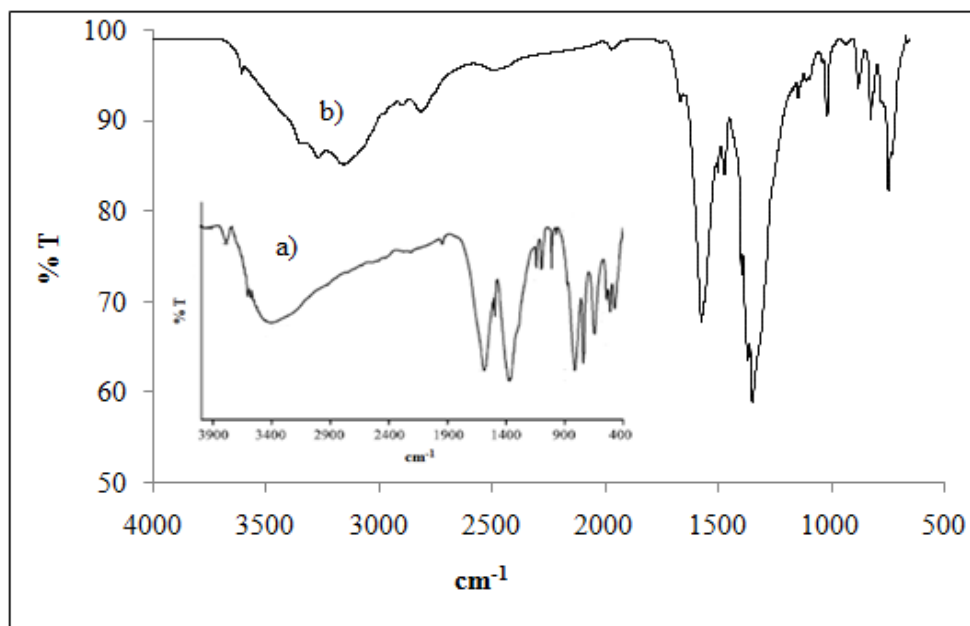

Figure 3. IR spectra of MOF-5 a) obtained from this study b) reference [1].

Figure 4 shows the surface morphology of MOF-5 and MOF-5/PI MMM. The pure MOF-5 morphology is defined as cubic crystals which is comparable with literature [17]. It can be seen in Figure 4 that MOF-5 particles were well dispersed on the membrane surface and how membrane morphology changed with loading of MOF-5.

Figure 4. SEM pictures of MOF-5 and MOF-5/PI mixed matrix membrane

TGA analysis of MOF-5, PI and MOF-5/PI are shown in Figure 5. MOF-5 structure displayed two weight loss in TGA plot. It is supposed that the weight loss below 250°C is due to the evaporation of the solvent DMF in the structure and mass loses above 250°C indicates the collapse of the framework [18 and 19]. Polyimide membranes have durable structure in terms of mechanical, thermal and chemical; hence, TGA analysis of PI showed a smooth line which consistent with the literature [20].
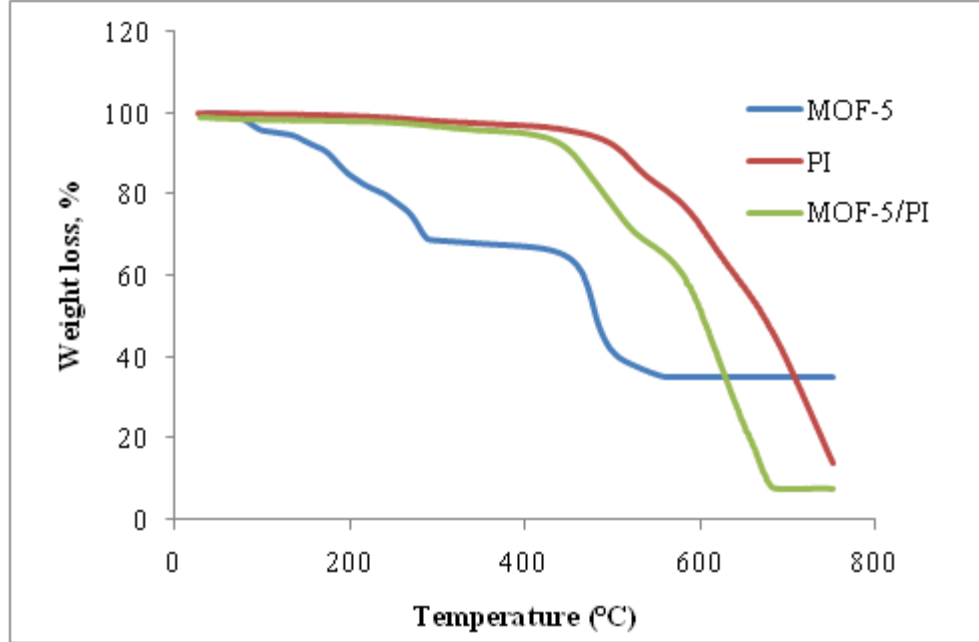

Figure 5. TGA plot of MOF-5, PI and MOF-5/PI

3.2. Gas Permeation

Gas permeation tests for pure polyimide and MMMs were carried out by a constant-volume/variable pressure method. All measurements performed at room temperature and 200 kPa of pressure. Permeability was estimated using Daynes-Barrier time-lag method as given equation:

$$P = \left(\frac{dp}{dt}\right)\frac{VT_0}{A\Delta P} x \frac{L}{TP_0}$$

P: the permeability coefficient (Barrer) [1 Barrer = 1×10^{-10} cm^3 cm (STP) cm^{-2} s^{-1} cmHg^{-1}]

dp/dt: is the slope of the straight line in the steady-state region

V: downstream volume (cm^3),

ΔP : the transmembrane pressure difference between the two sides, (cmHg)

A: the area of the membrane (cm^2),

L : the thickness of membrane (cm),

T : the measure temperature(K)

T_0 : standard temperature

P_0 : standard pressure

The ideal separation factor of pure gas A over B (α_{AB}) is described as the ratio of the permeation rates of A and B, which can be represent as:

$$\alpha_{AB} = P_A/P_B$$

Permeabilities and selectivities of pure polymeric and MOF-5/PI mixed matrix membranes have been determined for H_2, CH_4 and CO_2 gases. Gas permeability tests were carried out in the order CH_4, H_2 and CO_2 because of plasticisation effect of CO_2 on polymeric membrane [21].The results showe that permeabilities of MOF-5/PI membranes for all gases (H_2, CH_4 and CO_2) incerased with increasing the MOF-5 particle loading (5wt.%, 10wt.%, 15wt.%) at room temperature and pressure of 200 kPa. Permeability results of pure PI and MOF-5/PI with different loadings are shown in Figure 6.

H_2 permeability was increased from 10.33 barrer (pure PI) to 13.90 barrer at 15 wt% MOF-5 loading. Although CO_2 permeability of pure PI was 2.11 barrer, 5 wt% MOF-5/PI, 10wt.% MOF-5/PI and 15wt.% MOF-5/PI were found 3.49, 4.62 and 6.07 barrer, respectively. Incorporation of MOF-5 into PI with different loading increased the permeability of CH_4. These result explained that MOF-5 crystals were faciliting the gas transport.
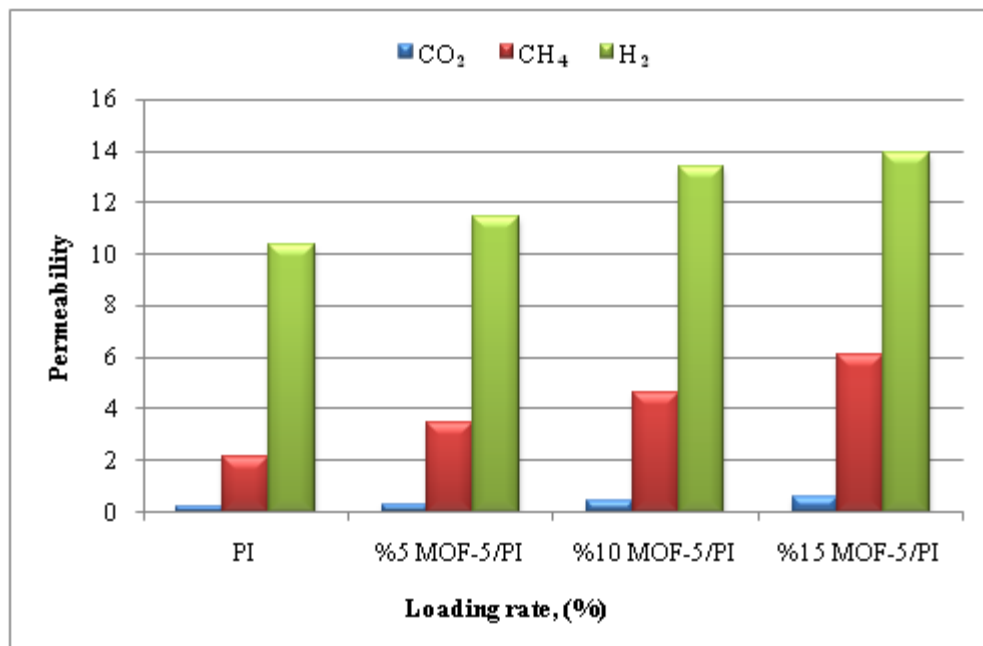

Figure 6. Permeabilities of MOF-5/PI at different loadings.

Since the permeabilities of all the gases increased proportionally with different loading, the ideal selectivities showed fluctuation (Fig. 7). For example, while H_2/CO_2 seperation of pure PI was found 4.90, it was determined as 3,29, 2,90 and 2,29 at 5wt%, 10 wt% and 15 wt% of MOF-5 loadings, respectively. When CO_2/CH_4 selectivity is considered, pure PI and 15 wt% MOF-5/PI exhibited 9.33 and 9.93, respectively. While H_2/CH_4 selectivity of PI was 45.72, %15 MOF-5 loading caused 22.76 of H_2/CH_4.
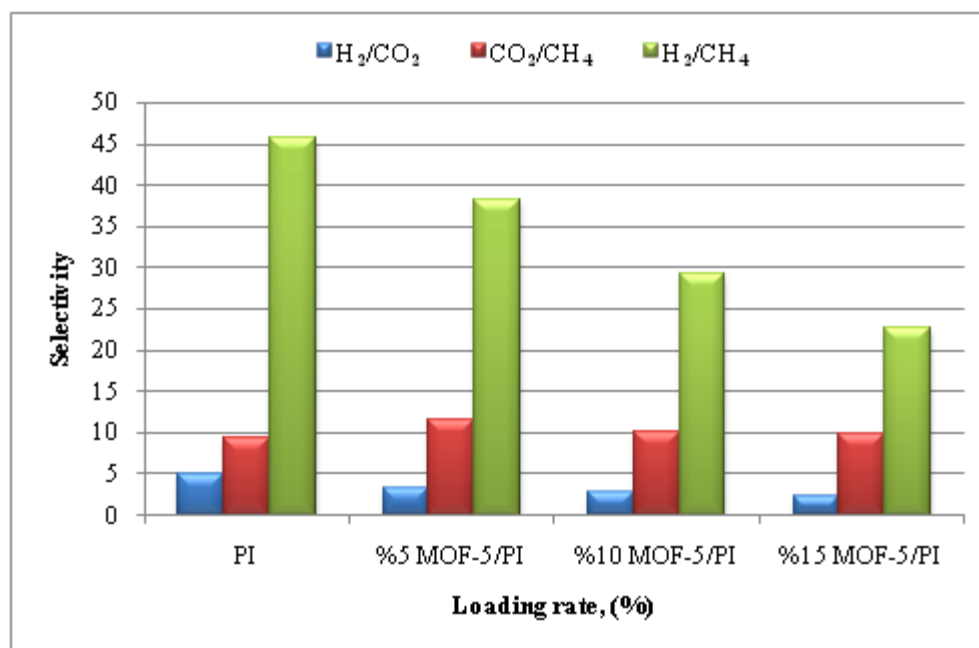
Figure 7. Selectivities of MOF-5/PI at different loadings.

4. Conclusion

In this study, MOF-5 particles were succesfully formed, identified and incorporated into the polyimide to determine the impact of filler on the single gas permeation in mixed matrix membranes. The prepared membranes and MOF-5 were defined by powder X-ray diffraction (XRD), infrared spectroscopy (IR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA). Incorparation of 5wt.%, 10wt.%, 15wt.% MOF-5 into pure PI resulted in 11.04%, 29.43 %, 34.56 % increase in H_2 permeability, 30.44%, 100%, 165.22% increse in CH_4 permeability and 65.40%, 118.96%, 187.68% increase in CO_2 permeability, compared to pure PI. Consequently, pure gas permeation increased when MOF-5 introduced into the pure polymer, but the separation factor of H_2/CO_2, CO_2/CH_4, H_2/CH_4 decreased with the MOF-5 loadings.

5. References

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