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Research Article

Hydrogen Separation Using Co-doped MOF-5/Polyimide Mixed Matrix Membrane for Energy Application

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Abstract

Hydrogen is the most abundant element in the universe, can be produced by water, stored easily, conversed into thermal, mechanical and electrical energy. Because of these properties, it can be considered as the energy carrier of the future. In order to use hydrogen as energy carrier, it must be separated from the gas mixture. Hydrogen separation using membrane method has the advantage over other separation methods due to its less energy intensive and environmental friendly properties. Mixed matrix membrane (MMM) has been developed so as to membrane properties become better and increase the performance of gas separation membranes. MOFs as a new fillers in MMM with high surface area and pore volume, enhance the H_2 gas separation properties**.** In this study, MOF-5 and Co-doped MOF-5 particles were synthesized, characterized and incorporated into polyimide to investigate the effect of filler on the H_2 gas permeation. Co-doped MOF-5/PI MMMs with different loading rate (5wt.%, 10wt.%, 15wt.%) were fabricated. The characterization was performed by different analysis techniques. The gas analyses results showed that permeability of H_2 gas in mixed matrix membrane including MOF-5 and Co-doped MOF-5 particules were enhanced with increasing the loading rate (5wt.%, 10wt.%, 15wt.%) at room temperature and pressure of 500 kPa. Furthermore, metal doped MOFs/PI is the highest gas permeation properties compared to pure PI and MOF-5/PI.

Key words: Hydrogen Energy, Mixed Matrix Membrane, Metal Organic Framework.

Enerji Uygulamasında Co katkılı MOF-5/Poliimit Karışık Matriksli Membranlar Kullanarak Hidrojen Ayrımı

Öz

Evrende bol miktarda bulunan hidrojen; su tarafından üretilebilmesi, kolayca depolanabilmesi, termal, mekanik ve elektrik enerjisine dönüşebilmesi özelliklerinden dolayı geleceğin enerji taşıyıcısı olarak düşünülebilmektedir. Hidrojenin enerji taşıyıcısı olarak kullanabilmesi için içinde bulunduğu gaz karışımından ayrılması gerekmektedir. Membran yöntemi kullanılarak hidrojen ayırma, diğer ayırma yöntemlerine göre daha az enerji yoğunluğuna sahiptir ve çevre dostudur. Gaz ayırma membranlarının performansının arttırılması ve membran özelliklerinin daha iyi hale gelmesi için karışık matriksli membranlar geliştirilmiştir. Karışık matriksli membranlarda dolgu maddesi olarak kullanılabilen, yüksek yüzey alanı ve gözenek hacmine sahip metal organik kafesler (MOF), H_2 gazı ayırma özelliklerini iyileştirmektedir. Bu çalışmada, MOF-5 ve Co katkılı MOF-5 partikülleri sentezlenmiş, karakterize edilmiş ve dolgu maddesinin H_2 gaz geçirgenliği üzerindeki etkisini araştırmak için poliimit(PI) içine ilave edilmiştir. Farklı yükleme oranlarına sahip katkılı MOF-5/PI karışık matriksli membranlar (ağırlıkça %5, %10 ve %15) üretilmiştir ve karakterizasyonları farklı analiz teknikleriyle gerçekleştirilmiştir. Gaz analiz sonuçları, MOF-5 ve Co katkılı MOF-5 dahil olmak üzere karışık matriksli membranda H_2 gazının geçirgenliğinin, oda sıcaklığında ve 500 kPa'lık basınç altında farklı yükleme oranlarında (ağırlıkça% 5,% 10,% 15) arttığını göstermiştir. Ayrıca, metal katkılı MOF/PI'in, saf PI ve MOF-5/PI ile karşılaştırıldığında en yüksek gaz geçirgenlik özelliklerine sahip olduğu görülmüştür.

Key words: Hidrojen Enerjisi, Karışık Matriksli Membran, Metal Organik Kafes

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1. Introduction

Hydrogen is considered as a possible solution for future energy economy because of its light weight and high energy. Furthermore, it produces only water and is conversed into electrical energy easily (Dincer, 2002; Jain, 2009; van den Berg & Arean, 2008; Züttel, 2003). There are mainly three different ways that hydrogen separation can be carried out namely, pressure swing adsorption, cryogenic distillation and membrane processes. Although pressure swing adsorption and cryogenic systems supply high purity of H_2, they have some drawback such as high capital and operational cost, use of special adsorbents and considerable amount of energy consumption (Adhikari & Fernando, 2006; Shao et al., 2009). On the contrary, membranes have been competitive with other technologies in terms of ease of operation, low investment cost, low energy consumption and cost effectiveness (Adatoz, et al., 2015; Adhikari & Fernando, 2006). However, there is a tradeoff between permeability and selectivity which is why cannot obtain high selectivity and permeability for these membranes. The selectivity of the gases increases while their permeability decreases or vice versa. Mixed matrix membranes (MMMs) composed of inorganic filler and polymer matrix are promising way to overcome inverse relationship between permeability and selectivity (Feijani et al., 2015). However, their cost, fragility and voids at the polymer–filler interface remain important challenges (Shu, Husain, & Koros, 2007). Recently, metal organic frameworks (MOFs) were found to be good candidates to fabricate MMMs, because MOFs are flexible in structure variability, could change pore size and adjustable internal surface properties and also enhance MMM’s performance (Li et al., 2012). Thanks to these unique features, MOFs have been synthesized and investigated frequently in recent years. MOF-5 consist of four $[Zn_4O]^{+6}$ clusters in octahedral subunits that are connected to each other by benzene-1,4-dicarboxylate (BDC) groups, to form a porous cubic framework is one of the most popular frameworks of these materials (Li et al., 2009).

Many scientific researches have been studied with mixed matrix membranes prepared with MOF-5 and the gas separation performance of MMM has been investigated. Perez et al. (2009) have increased gas permeabilities of mixed matrix membranes by 120% by adding MOF-5 to Matrimid membranes. In another study reported that H_2 permeability of the MOF-5/PEI mixed matrix membrane was increased by 40% compared to pure PEI membrane (Arjmandi & Pakizeh, 2014). However, MOF-5 is sensitive to moisture and causes structure collapse. To solve this issue, researchers focused on the enhancement of hydrostability of MOF-5 and found that doping metals into MOF-5 improve these drawbacks (Botas et al., 2010; Li et al., 2012; Yang et al., 2014b). There are only a few works reported on the enhacement of hydrostability for MOF-5. Yang and co-workers demonstrated that Ni-doped MOF-5 microcrystals have higher Langmuir specific surface areas and larger pore volume, they enhance the structural stability of MOFs towars moisture and hydrogen adsorption properties (Yang et al., 2014b). Li and co-workers found that Ni-doped MOF-5s not only exhibit larger Langmuir specific surface areas and larger pores than the undoped MOF-5, but also significantly enhance water resistance of the framework. The H_2 uptake capacity of undoped MOF-5 drops rapidly when exposed to the ambient air, whereas the H_2 adsorptions of the Ni-doped MOF-5s remain stable for 4 days (Li et al., 2012).

The objective of this paper is to synthesize and characterize MOF-5 and Cobalt-doped MOF-5 and incorporate into polyimide matrix to investigate the effect of filler on the single gas permeation. MOF-5 has been chosen due to its uniform microporous structure and good thermal stability. Cobalt transition metal has been used in order to understand metal’s effect on gas permeation.

2. Material and Method

In this study, MOF synthesis, pure polymeric and mixed matrix membranes fabrication, characterization and permeation test were carried out.

2.1. Reagents

The polyimide resin $(C_8O_2N)_n$ was purchased from Alfa Aesar. The physical properties of the polyimide are given in Table 1.

Table 1. Polyimide properties used in this study.

Polyimide Properties		
Moleculer weight	Mw	588,60 g/mol
Glass transition temperature	Tg	305°C
Melting point	Mp	>300°C
Density	ρ	1,2 g/mL
Flash point	-	>93°C

Zinc (II) nitrate tetrahydrate $(Zn(NO_3)_2.4H_20)$, Cobalt (II) nitrate hexahydrate $(Co(NO_3)_2.6H_20)$, 1-methyl-2-pyrrolidone (C_5H_9NO), Terephthalic acid and Ethanol (C_2H_5OH) were obtained from Merck. N-N-dimethylformamide (DMF, 98% purity) was provided from Carlo Erba. All chemicals and solvents were used without further purification. Permeability experiments were carried out using H_2 gas with purity is greater than 99.99 %.

2.2. Synthesis of MOF-5

MOF-5s were synthesized by solvotermal method. In a typical synthesis, 5.1 mmol of $Zn(NO_3)_2 \cdot 4H_2O$ and 1.7 mmol terephthalic acid were dissolved in 16mL of DMF in a glass tube. Then the prepared solution was placed in an oven (105°C for 24h). After that, glass tube was allowed to be cooled to room temperature. The white solution was filtered and then washed three times with 5mL aliquots of DMF to obtain MOF-5 crystals. The white crystals were placed (24h at 60°C) in a vacuum oven to get dry MOF-5. It was stored in moisture proof glass bottle (Figure 1a).

2.3. Synthesis of Co-doped MOF-5

Co-doped MOF-5 was synthesized by procedure published previously (Yang et al., 2014a). Equimolar quantities (0.05 mmol) of $Zn(NO_3)_2.4H_2O$, $Co(NO_3)_2.6H_2O$ and terephthalic acid were dissolved in 16mL of DMF in a glass tube under strong agitation. Then the prepared solution was placed in an oven (105°C for 24h). After ensuring sample to be cooled down room temperature, particles were derived from the solution by filtration. The particles were retained (60ºC for 24h) in a vacuum oven in order to get dry particles. Finally, Co-doped MOF-5 particles were stored in a capped vial (Figure 1b).

Figure 1. Picture of MOFs a) MOF-5, b)Co-doped MOF-5

2.4. Fabrication of Pure Polyimide Membrane

Membrane was prepared using the solution casting method as mentioned previous study (Ozturk & Demirciyeva, 2013). Figure 2 shows the flow diagram of membrane preparation.

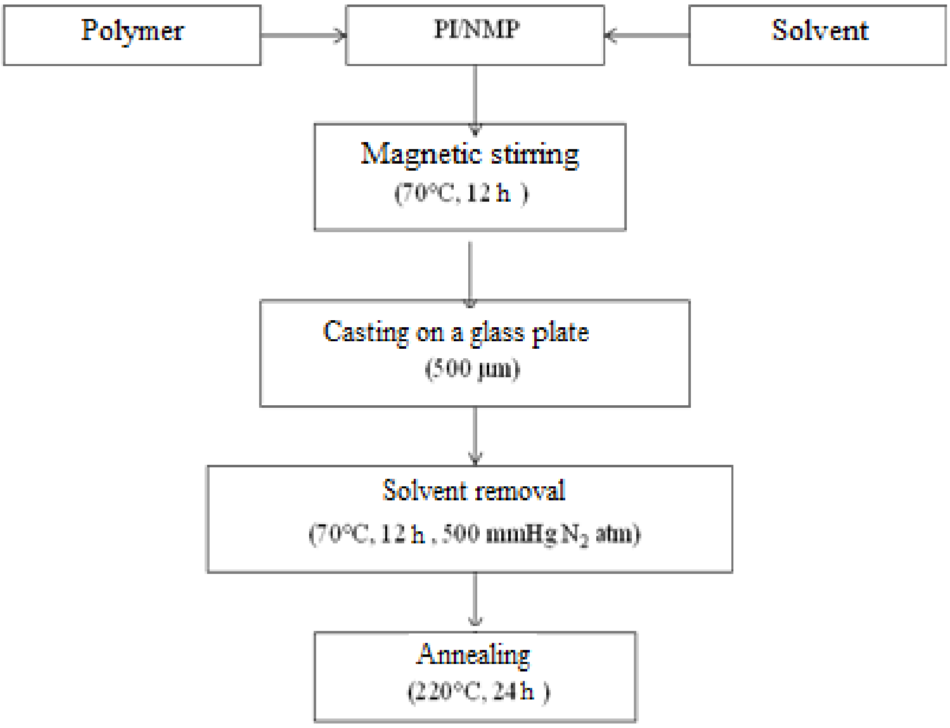

Figure 2. The Flow Diagram of Pure Polymer Membrane Preparation.

Firstly, PI (0.5 g) was dissolved in 4.5 g of 1-methyl-2-pyrrolidone (NMP) and stirred for 12h at 70°C until a clear uniform viscous solution was obtained. Then solution was casted on a clean glass plate using a casting rod. The glass plate was placed in a vacuum oven at 70°C and low pressure for 12h to allow the solvent to evaporate completely. The glass plate was immersed into a water bath to separate membrane from glass plate. After that, the membrane was annealed in a vacuum oven at 220°C for 24h. The average membrane thickness was 40 µm.

2.5. Fabrication of MMMs

Flow diagram of preparation of MMMs have been shown in Figure 3. Initially, MOF-5 containing 5, 10 and 15wt.% particles were dispersed the NMP in separate beakers. PI polymer and NMP solvent mixed in same separate beaker for each percentage. After getting uniform mixing MOF-5/NMP solutions poured into PI/NMP solutions, then sonicated in a ultrasonic bath and stirred (12h at 70°C) to get homogeneous solution. After getting thorough uniform solution, they were casted on a clean glass surface and got thin films using casting rod. Then, they were placed in a vacuum oven at 70°C for 12h to allow the solvent to evaporate completely. After that, the membranes were immersed into a water bath to separate the membrane from glass surface. Finally, the membranes were kept in a vacuum oven at 220°C for 24h. Similar procedure was carried out preparing Co-doped MOF-5/PI membranes. Finally, six different MMMs have been manufactured to be used permeation tests.

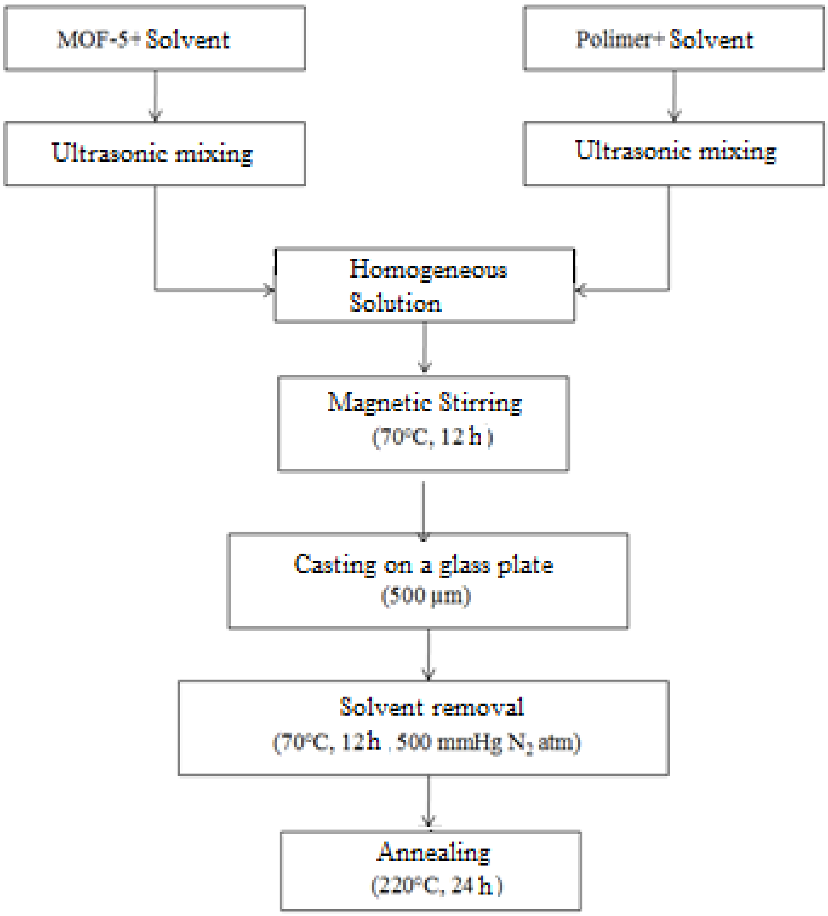

Figure 3. The Flow Diagram of Mixed Matrix Membrane Preparation

2.6. Permeability experiment

To perform permeability analysis, variable pressure-constant volume method was used. The gas separation system consists of membrane cell, pressure transducer, vacuum pump, temperature gauge and gas tank (Figure 4). The typical membrane module is shown in Figure 5. Membrane area located at test cell was 49.2 cm^2 and permeate side volume was 30.2 mL. Membrane was placed in permeation apparatus and held under vacuum to remove residual gases. All measurements were performed at room temperature and pressure of 500 kPa. Single gas permeabilities of the prepared membranes were determined for H_2 gas.

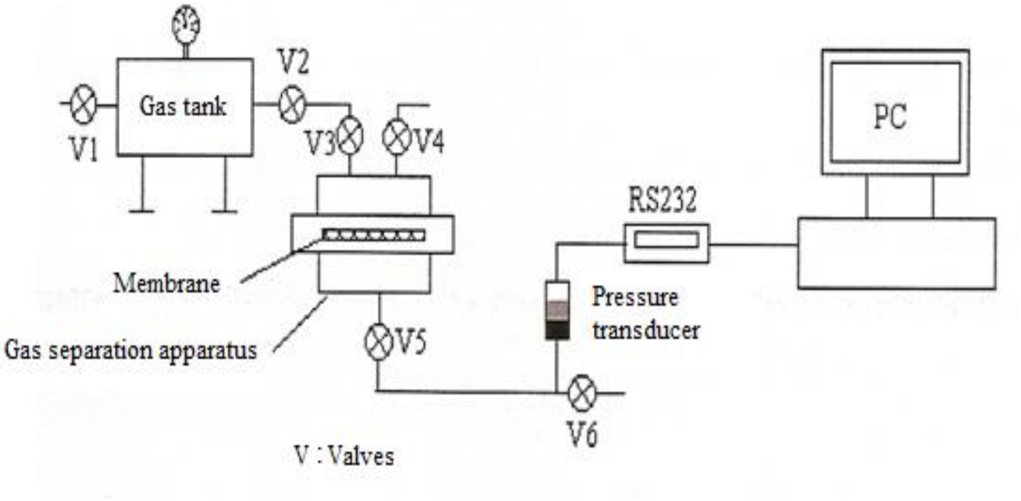

Figure 4. Gas Separation System

Figure 5. Membrane module

The gas permeability (P) was calculated by the slope of curve of permeate pressure vs. time (dp/dt) using the Daynes-Barrier time lag equation as follows (Weng et al., 2010):

$$P=\left(\frac{dp}{dt}\right)\frac{V\,T_0}{A\Delta P}\times\frac{L}{TP_0} \tag{1}$$

where P is the permeability coefficient expressed in 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 at which permeation pressure increases with time on the downstream side, V (cm^3) is the calibrated downstream volume, ΔP (cmHg) is the trans membrane pressure difference between the two sides, A (cm^2) is the effective area of the membrane, L (cm) is the membrane thickness, T (K) is the measure temperature, and T_0 and P_0 are the standard temperature and pressure, respectively

2.7. Characterization of MOF-5s and MMMs

The spectrum of MOF-5 and Co-doped MOF-5 obtained by Fourier transformed infrared spectroscopy (FTIR) were recorded at room temperature using a Perkin-Elmer MIRacle. FTIR spectra were collected at wave-number between 650 cm^{-1} and 4000 cm^{-1}. Scanning electron microscopy (SEM) images of MOFs were taken using a JSM-7001F Field Emission Scanning Electron Microscope. Thermal analyses were performed to determine weigh loss of samples by temperature using a Shimadzu DTG-60 instrument under the nitrogen atmosphere with a heating rate of 20 °C min^{-1}.

3. Results and Discussion

3.1. MOF-5 and Co-doped MOF-5 characterization

Characterization of MOF-5 and Co-doped MOF-5 were examinated byFT IR, TGA and SEM methods. FTIR spectrum of MOF-5 and Co-doped MOF-5 were shown in Figure 6.

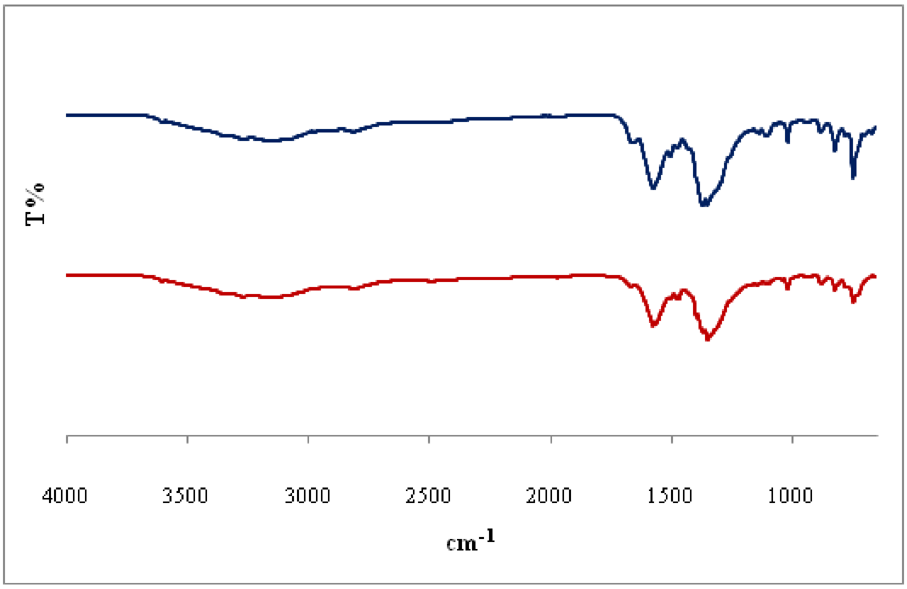

Figure 6. FTIR spectra of MOF-5 and Co-doped MOF-5 crystals.

FTIR spectra of MOF-5 exhibited characteristic peaks at 1580-1500 cm^{-1} corresponds to asymmetric stretching of COO groups and at 1400-1300 cm^{-1} corresponds to the symmetric stretching of COO groups in BDC^{2-} (Huang et al., 2003) The peaks indicating terephthalate compounds were shown 700–1200 cm^{-1}(Sabouni et al., 2010). The peaks in the range of 1250–1010 cm^{-1} assigned to the C–H group present in the benzene ring (Arjmandi & Pakizeh, 2014). The broad band at 2800–3600 cm^{-1} demonstrates the presence of water in structure. These results show consistency with the literature (Huang et al., 2003). FTIR spectra of Co-doped MOF-5 showed similar trends with FTIR spectra of MOF-5 indicating isostructure has not change doping metal into MOF structure.

Thermo gravimetric analysis (TGA) curve of MOF-5 display two main steps of weight loss (Figure 7). The first step of weight loss in the temperature below 250°C can be attributed to the loss of guest molecules (water vapour and solvent). The second weight loss occurred in the endothermic process between 398-601°C correspond to the decomposition of organic linkers.

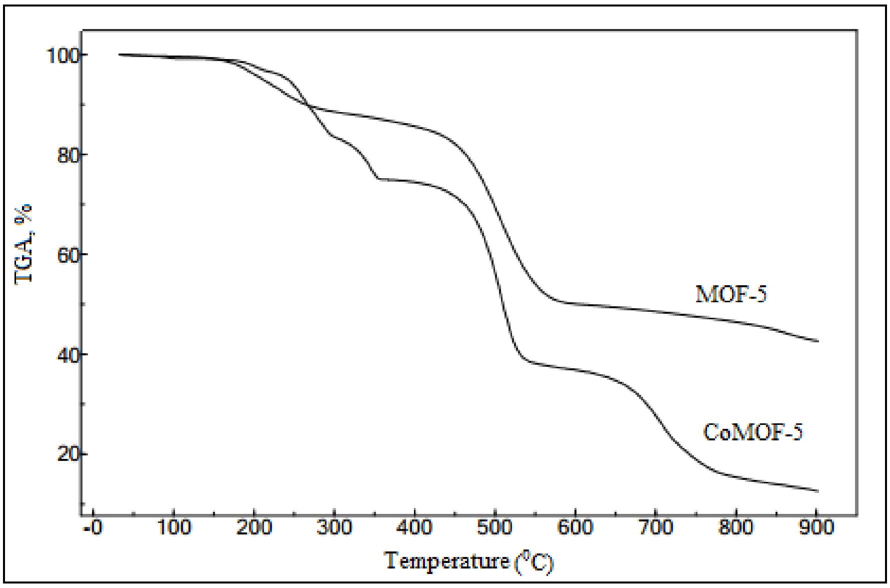

Figure 7. TGA plots of MOF-5 and Co-doped MOF-5.

Since the MOF-5 structure degrades at this temperature range, the initial value (398°C) of this step determine the thermal stability of structure. This mechanism of degradation of step is due to the breakage of the bridges between carboxylate ZnO_4 clusters and benzene rings. The weight loss values obtained in the first and second stages of the curve are in agreement with the values reported in the literature (Liu et al., 2009).

The thermal analysis curve of the Co-doped MOF-5 structure exhibits a three-stage weight loss. The initial weight loss (below 370°C) corresponds to the removal of water and solvent molecules in the pores. The decomposition of the Co-doped MOF-5 structure and ZnO/CoO formation are associated with the removal of the organic ligands in the second step between 408-559°C. The mass loss between 628-800°C is the third stage, the carbon based species remaining from the degradation of the ligand and the low boiling point zinc metal are removed in this step. The residue considered to be cobalt oxide or cobalt oxide-zinc oxide

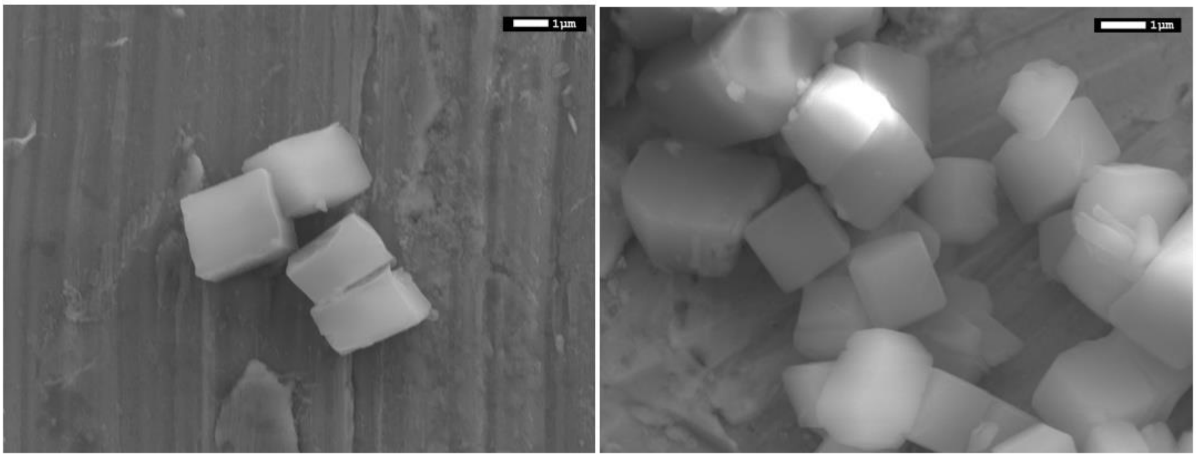

Figure 8. SEM pictures of MOF-5 and Co-doped MOF-5

3.2. H_2 permeation measurement

Gas permeation measurements for pure polymeric membrane and MMMs were conducted using a constant volume-variable pressure. All measurements were carried out at room temperature and 500 kPa of pressure.

The gas permeation performances of MMMs were measured by single gas permeation test of H_2. Table 2 indicates that H_2 permeation of MOF-5/PI and Co-doped MOF-5/PI mixed matrix membranes results**.** The results showed that permeabilities of MOF-5/PI membranes for H_2 gas incerased with increasing the loading (5wt.%, 10wt.%, 15wt.% MOF-5) at room temperature and pressure of 500 kPa. The average pore size of MOF-5 is approximately 8.67 A˚ which is greater than H_2 molecular diameter (2.9 A˚). Thus, it can be expected that the MOF-5 crystals increase the gas permeation through the MMMs relative to dense pure PI membrane.

Table 2. H_2 permeability with different MOF-5 and Co doped MOF-5 loadings in PI at room temperature and 500 kPa.

Membrane	MOF loading, %			
	0	5%	10%	15%
	Permeability (barrer)			
PI	12.18	-	-	-
MOF-5/PI	-	12.75	14.65	15.48
Co-doped MOF-5/PI	-	17.98	19.59	20.39

In gas permeability analysis, permeability of pure polyimide was found 12.18 barrer at 500 kPa and room temperature. Incorparation of 5wt.% MOF-5 into polyimide changed the results as 12.75 barrer. At 10 wt% and %15 wt% loading rate, permeabilities were found 14.65 and 15.48 barrer. In other words, incorparation of 5wt%., 10wt.%, 15wt.% MOF-5 into pure PI resulted in 4.68%, 20.28%, 27.09% increase in H_2 permeability compared to pure polymer, respectively. Recently, Perez and coworkers found permeability results that support this study, they synthesized MOF-5 crystal and added matrimid membrane to form MMM and reported the permeability of H_2 gas increased with different MOF-5 loading rate (Perez et al., 2009). Another study explained that incorporation of 5 wt.% of MOF-5 into pure polyetherimide conclued in 40% increase in H_2 permeability (Arjmandi & Pakizeh, 2014).

Single gas permeability results clarified that MOF-5 doped with Co metal enhance the permeability of H_2 compared to pure polymer. For instance, incorporation of 5 wt.% of Co-doped MOF-5, 10 wt.% of Co-doped MOF-5 and 15 wt.% of Co-doped MOF-5 to polyimide increase H_2 permeability as 17.98, 19.59 and 20.39 barrer. The results showed that permeability of H_2 gas incerased with mixed matrix membrane including Co-doped MOF-5 crystals relative to pure polyimide.

In comparison Co-doped MOF-5/PI with MOF-5/PI, permeability results represent that Co metal doped MOF-5 into polyimide showed better permeability values than undoped MOF-5. Indeed, 5 wt% of Co-doped MOF-5, 10 wt.% of Co-doped MOF-5/PI and 15 wt.% of Co-doped MOF-5/PI were enhance H_2 permeation results by 41.02%, 33.7% and 31.72% respectively, when compared to MOF-5 polyimide. Because the atomic diameter of cobalt is greater than the atomic diameter of zinc, has influenced result of H_2 permeability. This consequence implies that the MMM containing Co-doped MOF-5/PI produced highest permeability suggesting that the Co-doped MOF-5 crystals were facilitating gas transport tested under the same conditions.

4. Conclusion

In order to improve gas permeability of MOF/PI membranes, in this work metal doped MOF-5 was sytnhesized and its effect was investigated on permeation of H_2. First of all, MOF-5 and MOF-5 doped with Co metal were successfully synthesized. Then, the structure of MOF-5 and Co-doped MOF-5 were characterized by FTIR, TGA and SEM analyses. Characterization results displayed that doping metal into MOF-5 structure does not change its morphology, and determined same functional groups. Afterwards, mixed matrix membranes containing MOF-5 and Co-doped MOF-5 were fabricated successfully via casting solution method. MMMs were performed for the permeation of H_2 as a function of various filler loadings at room temperature and 500 kPa of pressure. The experimental gas permeation exhibited that H_2 permeability increased with increasing filler loading compared to unfilled membrane. Furthermore, metal doped MOF-5 increase permeability of H_2 and ease the gas transport when compared to undoped MOF-5. The differences in permeability can be better realized by the contributions of atomic diameter of Co metal. In conclusion, polymer membrane with metal doped MOF-5 encourage in gas separation and are said to be promising candidates to separate H_2 for energy application.

5.Acknowledgements

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