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정전분무법에 의한 결함없는 ZIF-7 박막의 제조

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Preparation of Crack-free ZIF-7 Thin Films by Electrospray Deposition

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요 약: ZIF 재료는 독특한 기체 분리 특성을 포함한 물리적, 화학적 특성 때문에 큰 관심을 받아왔다. 본 연구에서는 α-alumina 지지체 위에 결함 없고 연속적인 ZIF-7 막을 형성하는 새롭고 효율적인 방법이 연구되었다. 지지체 위에 시딩(seeding)을 하지 않고 직접 ZIF-7 박막을 합성하는데 정전분무법이 처음으로 적용되었다. 이 방법은 전구체 용액을 직접 정전분무함으로 α-alumina 지지체에 ZIF-7 박막을 형성할 수 있었다. ZIF-7 박막은 XRD, FE-SEM, 단일 기체 투과 장치 등을 이용해 분석하였다.

Abstract: Zeolitic imidazolate frameworks (ZIFs) have been the focus of interest for their physical and chemical properties, especially, for their extraordinary gas separation properties. In this study, a novel and efficient method for the fabrication of continuous ZIF-7 film on α-alumina substrate has been investigated. The electrospray deposition method was tried for the first time to prepare ZIF films directly without the necessity of prior substrate seeding. It has the advantage of depositing thin ZIF-7 films directly on the α-alumina substrate by electrospraying the precursor solution. The ZIF-7 films have been characterized through XRD, FE-SEM, and single gas permeation tests.

***Keywords**: zeolitic imidazolate frameworks, ZIF-7, electrospray deposition, hydrogen separation*

1. Introduction

The preparation of highly selective organic/inorganic composite membranes for gas separation is one of the current trends in nanomaterials research[1-5]. At present, large-scale hydrogen production generally occurs via steam reforming followed by water-gas shift (WGS) and the product contains primarily H_2 and CO_2[3]. Therefore, metal-organic frameworks (MOFs) have been the focus of interest for their extraordinary hydrogen separation properties[2,3]. In general, MOF films have been synthesized by *in situ* growth and secondary growth using the solvothermal method[3]. Although the solvothermal method is effective in preparing thin films of crystalline framework materials, it requires long processing time.

Electrospray deposition is a coating method that generates an extremely fine liquid aerosol through electrostatic charging. By applying high voltage to a solution, the charged liquid becomes unstable as it is forced to hold more and more charge. When the liquid reaches a critical point, at which it can hold no more electrical charge, it blows apart into a cloud of tiny, highly charged droplets at the tip of the nozzle. These tiny droplets fly about searching for an oppositely charged potential surface on which to land. Depending on the applied voltage, various shapes of electrospray jet can

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Table 1. Permeance and Ideal Selectivity Data of the ZIF-7 Film Synthesis

Synthesis Temperature (°C)	Permeance [mol · m^{-2} · s^{-1} · Pa^{-1}]		H_2/CO_2 Ideal Selectivity at 25°C
	CO_2	H_2	
160	3.27 × 10^{-7}	1.96 × 10^{-6}	6.03

be observed such as dripping mode, conejet mode, multijet mode, and ramified jet mode[6].

Zeolitic imidazolate frameworks (ZIFs), one of MOF species, show outstanding gas separation properties due to their thermal, and chemical stability[3,7,8]. In this study, defect-free continuous ZIF-7 films were prepared by electrospray deposition. The precursor solution for ZIF-7 was electrosprayed through the nozzle, and the electrically charged droplets were deposited uniformly onto a heated α-alumina substrate to facilitate the crystallization of ZIF-7. The effect of electrospray conditions was systematically investigated, and the synthesized ZIF-7 films were characterized by XRD, FE- SEM, and single gas permeation tests.

2. Experimental

2.1. ZIF-7 Films by Electrospray Deposition

First, the precursor solution was synthesized according to the literature[6]. In brief, 6.12 g of zinc nitrate hexahydrate ($ZnNO_3 \cdot 6H_2O$, 98%, Sigma-Aldrich) and 3.24 g of benzimidazole were dissolved in 80 mL of dimethylformamide ($HCON(CH_3)_2$, 99.8%, Sigma-Aldrich DMF) and stirred for 30 min at room temperature (solution A). 0.6 g of sodium formate (HCOONa, 99%, Sigma-Aldrich) was dissolved in 80 mL of DMF and stirred for 30 min at room temperature (solution B). The resulting solution obtained after mixing solutions A and B for 30 minutes was used for further electrospray deposition.

The experimental set-up for electrospray deposition is shown in Fig. 1. Before the electrospray deposition, a disk shaped α-alumina substrate (diameter : 20 mm, thickness : 2 mm, pore diameter : 0.12 µm, porosity : 40%) was heated to a desired temperature (160°C). The precursor solution was fed into a nozzle by a syringe pump at various flow rates from 0.5 to 2.0 mL/h. The voltage that was applied to the nozzle was varied from 5 to 15 kV. The distance between the nozzle tip and the substrate was varied from 3 to 6 cm.

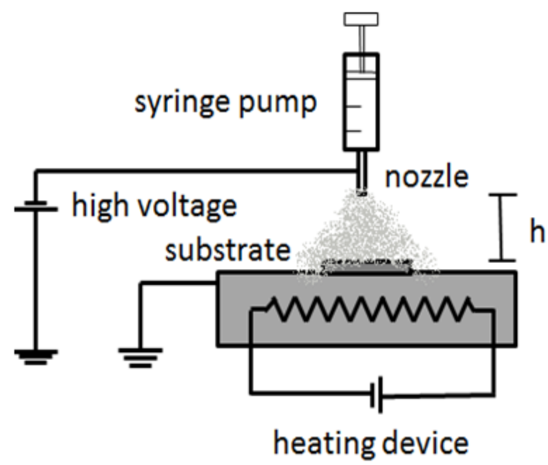

Fig. 1. Experimental set-up for electrospray.

The as-synthesized ZIF-7 films were activated by solvent exchange. They were immersed in methanol for 1 h. Afterwards, the ZIF-7 films were dried at 45°C under saturated conditions overnight to prevent cracking.

2.2. Characterization

The XRD (M18XHF-SRA, Mac Science, Japan) was employed to identify crystal phases. The morphology and thickness of the films were observed by a field-emission scanning electron microscope (Leo-Supra 55, Carl Zeiss STM, Germany). The gas permeation properties through the film were investigated using a home-made permeation set-up at room temperature[9].

3. Results and Discussion

The optimum experimental conditions were set through experimentation. For a given flow rate of 1.5 mL/h, as

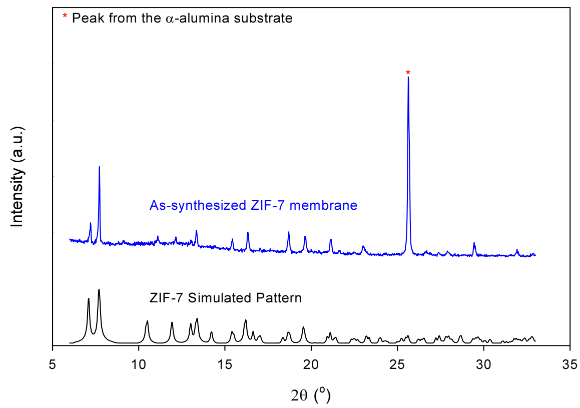

Fig. 2. XRD pattern of the ZIF-7 film prepared by electrospray deposition.

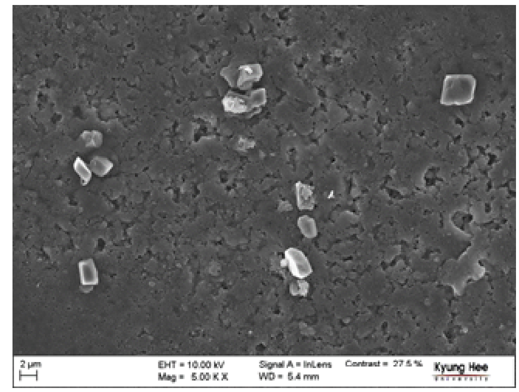

Fig. 3. FE-SEM top view image of the ZIF-7 film prepared by electrospray deposition.

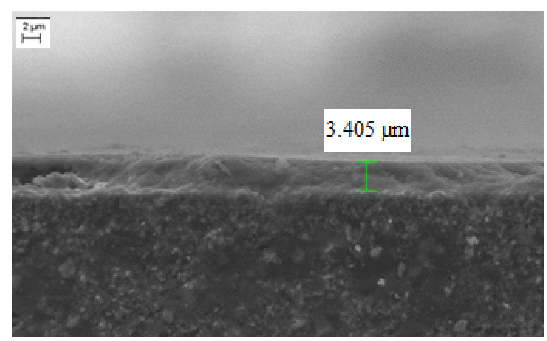

Fig. 4. FE-SEM cross section view of the ZIF-7 film prepared by electrospray deposition.

the voltage was increased from 5 to 15 kV, the different electrospray modes were observed : dripping, microdripping, conejet, multijet, and ramified jet modes. After varying the applied voltage, the optimum conditions to obtain the conejet mode or Taylor-cone mode were determined to be a voltage of 12 kV at a feed rate of 1.5 mL/h. In addition, the optimum height of the nozzle tip over the substrate was determined to be 4 cm to completely cover the α-alumina substrate with the ZIF-7 film.

The temperature of the substrate was fixed at 160°C. High temperatures are required to promote the bonding between the deposited organic linkers and the α-alumina substrate as well as the crystallization of ZIF-7[8]. However, the substrate temperature should not exceed the decomposition temperature of organic linkers of the ZIF structure. As a result, the substrate temperature was set at 160°C to favor the DMF evaporation since its normal boiling point is 153°C. At this substrate temperature, the prepared film was colorless, indicating the characteristics of the ZIF-7 crystals[10].

Fig. 2 shows the XRD pattern of the as-synthesized ZIF-7 films and the simulated pattern of ZIF-7[10]. The peaks of the ZIF-7 film clearly indicate that it has pure ZIF-7 crystal phase. The marked peak with an asterisk corresponds to the α-alumina substrate phase onto which the ZIF-7 film was deposited.

Fig. 3 shows the morphology of the ZIF-7 films, indicating a well intergrown, crack-free, and continuous layer. This is a consequence of the addition of sodium formate in the precursor solution. Sodium formate acts as a deprotonator by increasing the pH of the solution and consequently by fully depronotating the benzimidazole, resulting in growth occurring in all directions and yielding larger, well-intergrown crystals[8]. The well-intergrowth of the crystals and the continuity of the ZIF-7 film are important for effective gas separation and high selectivity of H_2 and CO_2. They favor the sieving effect shown in the zeolitic imidazolate frameworks, and increase the value of the ideal selectivity in the H_2 and CO_2 separation.

Fig. 4 exhibits a clear distinction between the film and the α-alumina substrate with a ZIF-7 film thickness of 3.5 μm. It is very important to synthesize very thin ZIF-7 films to permit high H_2 permeance values as well as a high gas separation selectivity of H_2/CO_2. In addition, Fig. 4 shows a clear boundary between the α-alumina substrate and the ZIF-7 film. It implies that the film consists of only ZIF-7 crystals, free of impure phases.

The single gas permeation measurements show that the ZIF-7 films prepared are promising alternatives for H_2 separation from CO_2. The H_2/CO_2 selectivity for Knudsen diffusion is 4.7. From the gas permeation results, the ZIF-7 films synthesized at 160°C exhibit a higher ideal H_2/CO_2 selectivity of 6.03, calculated as the ratio of single-gas permeances, than that of Knudsen diffusion.

The ideal H_2/CO_2 selectivity at 25°C of ZIF-7 films prepared at 160°C surpasses that of Knudsen diffusion significantly, in 28.3%. This is the result of the molecular sieving effect shown in the zeolitic imidazolate frameworks (ZIFs)[7]. The ZIF-7 films exhibit a high permeance for H_2 and have the potential to be used in industrial applications to separate hydrogen and then use this gas as an alternative energy for energy needs. Furthermore, ZIF-7 films have outstanding hydrophobic properties, which make them ideal for H_2 separation in the presence of steam due to their excellent hydrothermal stability in comparison to zeolite membranes and sol-gel-derived silica membranes[7].

ZIF-7 is a promising candidate as a H_2-selective film. The pore size of ZIF-7 is about 0.3 nm, which is between the size of H_2 (0.29 nm) and CO_2 (0.33 nm). Consequently, there is high selectivity of H_2 over CO_2 due to its molecular sieving effect. ZIF-7 crystallizes in the sodalite structure with a hexagonal arrangement of the cavities octahedrally interconnected by narrow windows interconnecting the cavities, which are responsible for the molecular sieving effect. One of the advantages that ZIF-7 films have is that their pore size is near that of the molecular size of H_2. Consequently, a high H_2 selectivity can be achieved without any pore modification.

Previous studies by Li *et. al.* show that H_2/CO_2 selectivity for ZIF-7 increases with temperature. In fact, they present a H_2/CO_2 selectivity of 5.4 at 50°C[11], which is exceeded by the ZIF-7 films prepared at 160°C even when the single gas permeation tests were carried at 25°C.

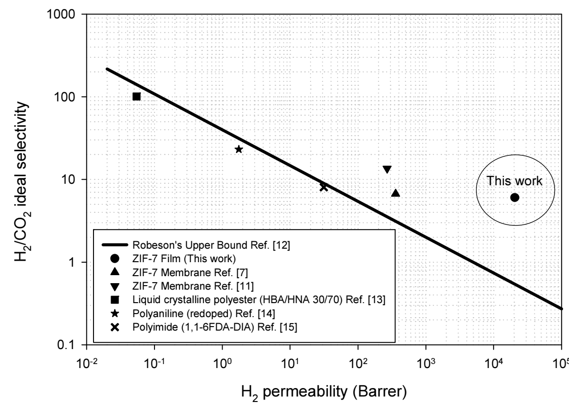

Fig. 5. Comparison of this work with the Robeson's upper bound for H_2/CO_2 separation.

Fig. 5 shows a comparison between the results of this study and the Robeson's upper bound for H_2/CO_2 separation. The graph includes the performance of some membranes and films that have been synthesized for H_2/CO_2 separation[12-15]. As it can be observed, for the H_2 permeability through the synthesized ZIF-7 films, the ideal H_2/CO_2 selectivity upper bound has been surpassed. This shows that these results are promising for industrial applications not only in terms of ideal H_2/CO_2 selectivity but also of H_2 permeability.

4. Conclusion

Crack-free, uniform and thin ZIF-7 films on porous α-alumina substrates by electrospray deposition have been prepared successfully. The XRD pattern confirms the synthesis of ZIF-7 crystals and the FE-SEM images show crack-free uniform layer of ZIF-7 with thickness of 3.5 μm. The thickness of ZIF-7 film can be controlled by the amount of the precursor solution electrosprayed on the α-alumina substrate. The permeation tests show that an ideal selectivity H_2/CO_2 of 6.03 is obtained when the film is prepared at 160°C, exceeding in 28.30% that of Knudsen diffusion, as well as the Robeson's upper bound.

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References

1. N. E. Kim, T. B. Kang, and S. L. Hong, "Preparation and characterization of PTMSP/PDMS-zeolite composite membranes for gas separation", *Membrane Journal*, **22**, 342 (2012).
2. S. J. Noh and J. Kim, "Solvothermal synthesis and gas permeation properties of nanoporous HKUST-1 membranes", *Membrane Journal*, **22**, 435 (2012).
3. M. Shah, M. C. McCarthy, S. Sachdeva, A. Lee, and H. K. Jeong, "Current status of metal-organic framework membranes for gas separations : Promises and challenges", *Ind. Eng. Chem. Res.*, **51**, 2179 (2012).
4. B. R. Jung, Y. Son, Y. T. Lee, and N. Kim, "Preparation of organic-inorganic hybrid PES membranes using Fe(II) clathrochelate", *Membrane Journal*, **23**, 80 (2013).
5. K. K. Lee, T. H. Kim, T. S. Hwang, and Y. T. Hong, "Novel sulfornated poly(arylene ether sulfone) composite membranes containing tetraethyl orthosilicate (TEOS) for PEMFC applications", *Membrane Journal*, **20**, 278 (2010).
6. B. Kwon, J. Kim, and J. H. Park, "Preparation of thin YSZ film by electrostatic spray deposition", *J. Korean Ind. Eng. Chem.*, **19**, 117 (2008).
7. Y. Li, F. Liang, H. Bux, A. Feldhoff, W. Yang, and J. Caro, "Molecular sieve membrane : supported metal-organic framework with high hydrogen selectivity", *Angew. Chem. Int. Ed.*, **49**, 548 (2010).
8. M. C. McCarthy, V. V. Guerrero, G. V. Barnett, and H.-K. Jeong, "Synthesis of zeolitic imidazolate framework films and membranes with controlled microstructures", *Langmuir*, **26**, 14636 (2010).
9. H. T. Kwon and J. Kim, "Synthesis and characterization of sol-gel derived mesoporous titania/alumina membranes", *Membrane Journal*, **21**, 229 (2011).
10. K. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, and O. M. Yaghi, "Exceptional chemical and thermal stability of zeolitic imidazolate frameworks", *PNAS*, **103**, 10186 (2006).
11. Y. Li, F. Liang, H. Bux, W. Yang, and J. Caro, "Zeolitic imidazolate framework ZIF-7 based molecular sieve membrane for hydrogen separation", *J. Membr. Sci.*, **354**, 48 (2010).
12. L. M. Robeson, "The upper bound revisited", *J. Membr. Sci.*, **320**, 390 (2008).
13. D. H. Weinkauf and D. R. Paul, Gas transport properties of thermotropic liquid-crystaline copolyesters. II. The effects of copolymer composition, *J. Polym. Sci.: Part B: Polym. Phys.* **30**, 837 (1992).
14. G. Illing, K. Hellgardt, M. Schonert, R. J. Wakeman, and A. Jungbauer, "Towards ultra-thin polyaniline films for gas separation", *J. Membr. Sci.*, **253**, 199 (2005).
15. M. E. Rezac and B. Schoberl, "Transport and thermal properties of poly(ether imide)/acetylene- terminated monomer blends", *J. Membr. Sci.*, **156**, 211 (1999).