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# Seeding-free aqueous synthesis of zeolitic imidazolate framework-8 membranes: How to trigger preferential heterogeneous nucleation and membrane growth in aqueous rapid reaction solution

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## ABSTRACT

Zeolitic imidazolate frameworks (ZIFs) have received attention for membrane separation applications due to their zeolite-like permanent porosity and tunable uniformly-sized micropores. Although aqueous room temperature synthesis has apparently opened up environmental friendly and efficient ways to synthesize ZIFs, it poses challenges for membrane preparation including unavoidable homogeneous nucleation. Many ZIF membranes prepared in an aqueous system are based on conventional secondary seeded growth techniques for zeolite membranes in spite of well-recognizing that the coordination chemistry of ZIFs is fundamentally different from the covalent chemistry of zeolites. In this study, we first applied a support-surface activation approach to promote heterogeneous nucleation followed by crystal growth in the aqueous system. Continuous well-intergrown ZIF-8 membranes were successfully grown on  $\alpha$ -alumina porous support using zinc acetate and showed relatively-high hydrogen permeance of  $6.9 \times 10^{-7}$  mol/m<sup>2</sup> s Pa with corresponding ideal separation selectivity of 13.6 for the hydrogen/methane. The competitive interaction between the coordination of constructing framework and zinc-acetate interaction by carboxylate functionality of acetate anions is essential to control heterogeneous nucleation and membrane growth. Avoiding the seeding process and reducing the use of organic solvents can provide potential for improving a reproducible, scalable, and commercializable process configuration for membrane preparation.

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## 1. Introduction

Supported porous layers are of interest for various potential applications as separation membranes, chemical sensors, and optical and electrical devices. Zeolitic imidazolate frameworks (ZIFs) constructed from tetrahedral building blocks, in which each bivalent metal cation (e.g., Zn, Co) joins four imidazole-derived ligands to form neutral open framework structures adopting zeolite topologies, [1–3] have been recognized as promising candidates for use in membrane-based liquid and gas separations [4–6]. So far, diverse

synthesis protocols have been used to prepare polycrystalline ZIF membranes, including in situ and secondary seeded growth techniques along with others. Most of the protocols are generally derived from those devised for zeolite membrane preparation although the coordination chemistry of ZIFs is fundamentally different from that of the covalent chemistry of zeolites. Since the secondary seeded growth techniques are widely prevalent in ZIF membrane preparation as in the case of zeolite membrane preparation, [7–21] one can expect that ZIF membranes will face similar challenges as zeolite membranes have faced for their practical applications, including reproducibility and scalability issues. Unlike zeolites that could be covalently-immobilized on the support, the imidazole-derived ligands of ZIFs cannot form covalent bonds with surface OH groups of the commonly-used  $\alpha$ -alumina support, thereby causing poor membrane adhesion [5]. Furthermore, it must be noted that typical synthesis of ZIFs is

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carried out in toxic and flammable organic solvents, such as *N,N*-dimethylformamide and methanol [1–3,7–15,21–42].

On the other hand, *in situ* growth techniques have been developed to improve ZIF deposition by using surface-activated supports [28–31,43,44]. For *in situ* growth, porous supports are typically modified with an organosiloxane possessing an unshared electron pair, such as an amino end group, to promote heterogeneous nucleation followed by crystal growth under solvothermal conditions [28–31]. The organosiloxanes are grafted on the support-surface and act as a covalent linker for immobilization of ZIF crystals. Due to the organic–inorganic hybrid nature of ZIFs, the chemical modification approach is effective to facilitate ZIF crystallization at the solid–liquid interface and modifying ZIF surface. However, this approach has been deemed unsuitable for aqueous synthesis of ZIF membranes because unfavorable homogeneous nucleation predominantly occurs due to the extremely-fast formation rate of ZIF crystals in the aqueous system [16–20]. The only exceptions are the ZIF-8 membranes reported by Huang et al., which were grown on a modified alumina support in the aqueous system [43]. Their process requires two different solutions, a seeding synthesis solution and a secondary growth solution, for heterogeneous nucleation and crystal growth, respectively, in order to supply sufficient nutrients for crystal growth. However, an increased number of steps make the membrane preparation process complicated, potentially causing basic cost increase and reproducibility issues. For the preparation of continuous well-intergrown polycrystalline membranes, it is crucial to favor heterogeneous nucleation and crystal growth of ZIFs on the support surface over homogeneous nucleation and crystal growth in solutions. Indeed, *in situ* grown ZIF membranes could still not be achieved in the aqueous system, even though the aqueous room temperature synthesis is more economical and greener compared to other synthesis procedures requiring organic solvents and high synthesis temperature.

Here, we now wish to report a simple aqueous route for *in situ* synthesis of well-intergrown ZIF-8 membranes with significantly enhanced microstructure. Our synthesis method is based on the support-surface activation concept in which the 3-(2-imidazolyl)propyltriethoxysilane (IPTES) is used to first form a pseudo-surface of ZIF-8 on porous  $\alpha$ -alumina tubular support followed by heterogeneous nucleation and crystal growth. Furthermore, in order to supply sufficient nutrients for crystal growth from the same solution as for heterogeneous nucleation, the reactivity of growth solution was optimized using zinc source  $\text{Zn}(\text{CH}_3\text{COO})_2$  without any additives such as crystal growth modulator, coupling agent, and catalyst; sodium formate, [11,14,15,25,27,35,36,40] diethylamine, [32] *N,N*-dimethyl acetamide, [45] polyethyleneimine, [9] and ammonia [46–48]. Our strategy is based on the expectation that acetate anion  $\text{CH}_3\text{COO}^-$  acts as monodentate [49–51] or perhaps bidentate ligand, [52–54] and further can control the deprotonation of imidazole linkers, [55] thus enabling the control nucleation rate. Avoiding the use of seed crystals and reducing the use of organic solvents and additives can provide an improvement of membrane preparation reliability and a decrease in environmental load, providing potential for improving a scalable and commercializable process configuration for membrane preparation.

## 2. Experiment

### 2.1. Materials

All commercially available chemicals were used without further purification. Zinc nitrate hexahydrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( $\geq 98\%$ , Sigma-Aldrich Japan), and zinc acetate dihydrate,  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$

( $\geq 98\%$ , Sigma-Aldrich Japan), were used as zinc source. 2-methylimidazole (Hmim;  $\geq 99\%$ , Sigma-Aldrich Japan) was used as ligand. 3-(2-imidazolyl)propyltriethoxysilane (IPTES;  $\geq 97\%$ , Sigma-Aldrich Japan) was used as silylation reagent. Methanol ( $\geq 99.7\%$ ) and 0.1 M hydrochloric acid (HCl) were purchased from Wako Pure Chemical Industries. Porous  $\alpha$ -alumina tubular supports (outer diameter: 10 mm; inner diameter: 7 mm; length: 400 mm; average porosity: 35%; average pore size: 0.15  $\mu\text{m}$ ) were purchased from Noritake Co. and cut into 20 mm long pieces. One side of the tubular supports was connected to a dense glass plate with epoxy-based sealant prior to surface modification.

### 2.2. IPTES modification of the support surface

Porous  $\alpha$ -alumina tubular supports with dead-end structure were treated with IPTES (0.04 M in 50 mL of 0.01 M HCl) at 60 °C for 10 min with the aid of microwave irradiation using  $\mu$ Reactor Ex (Shikoku Instrumentation), followed by washing with deionized water and methanol.

### 2.3. Preparation of ZIF-8 membranes

ZIF-8 membranes were grown on the IPTES-modified supports as follows: the supports were vertically immersed in a precursor solution consisting of deionized water, zinc salt, and Hmim at room temperature. The molar composition of the solution was  $\text{Zn}^{2+}:\text{Hmim}:\text{water}=1:30\text{--}60:2228$ . The obtained membranes were washed with methanol for 24 h and then dried at room temperature under vacuum.

### 2.4. Characterization of ZIF-8 membranes

X-ray diffraction (XRD) patterns were recorded on a RINT-TTR III X-ray diffractometer (Rigaku, Japan) using  $\text{Cu K}\alpha$  radiation at 40 kV and 20 mA. Diffraction data were collected in the range of  $2\theta=5\text{--}60^\circ$  with  $0.02^\circ$  steps. Field emission scanning electron microscopy (FESEM) images of membrane surfaces were obtained using an S-4800 electron microscope (Hitachi High-Tech, Japan) operated at an acceleration voltage of 1–10 kV. The cross-sectional structure of membranes was analyzed using FESEM S-5000 (Hitachi High-Tech, Japan) equipped with an energy-dispersive X-ray spectroscopy (EDS).

### 2.5. Characterization of growth solutions and ZIF-8 crystals

UV spectra were recorded on an UVmini-1240 (Shimadzu, Japan). The visible light transmittance of the growth solutions was recorded at a wavelength of 500 nm as a function of time. Nitrogen adsorption/desorption isotherms were measured at 77 K using a BELSORP-max (Bel Japan). The samples were degassed at 200 °C under vacuum. Langmuir model surface area was calculated from the nitrogen adsorption branch. The micropore volume was calculated by the  $\alpha_s$ -plot method. The diameters of more than 200 particles in the FESEM images were measured to determine the number-based particle size distribution. The average particle size,  $d_n$ , and coefficient of variation,  $C_v$ , are calculated by the following equations:

$$d_n = \frac{\sum n_i d_i}{\sum n_i} \quad (1)$$

$$C_v = 100 \times \sqrt{\frac{\sum (d_i - d_n)^2 / \sum n_i}{d_n}} \quad (2)$$

### 2.6. Evaluation of gas permeation

Single gas permeation measurements were carried out for gases,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , at 30 °C. The  $\alpha$ -alumina-supported ZIF-8 membranes were activated at 80 °C under

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