Supporting Information

Defect-induced Ripening of Zeolitic-Imidazolate Framework ZIF-8 and Its Implication to Vapor-phase Membrane Synthesis

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Experimental details:

Chemicals: Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98%, Sigma-Aldrich), 2-methylimidazole ($C_4H_5N_2$, 97%, Sigma-Aldrich), sodium formate (HCOONa, 99%, Sigma-Aldrich), and methanol (99.8%, Alfa Aesar) were purchased and used without further purification.

Preparation of α-Al_2O_3 supports: In a typical symmetric support preparation, 10 g of α-Al_2O_3 powder with primary particle size of 250 nm (Baikowski) was blended with 1 ml of an aqueous PVA solution. The PVA solution was prepared by dissolving 3 g of PVA 500 (Duksan) in a mixture of 5 ml of 1 M HNO_3 and 95 ml of D.I. water. Then, 2.1g of the alumina powder blend was injected into a mold and pressed at 10 ton for 1 min, followed by sintering at 1100 ^oC for 2 h. Finally, all supports were polished using a sand paper (#1200) and sonicated in methanol for 1 min before usage. For asymmetric supports, fine α-Al_2O_3 nanopowder (Inframat Advanced Material) was manually rubbed on polished symmetric supports multiple times and subsequently sintered at 1100 ^oC for 2 h before usage.

Microwave-assisted seeding: A metal precursor solution was prepared by dissolving 2.43 g of zinc nitrate hexahydrate in 40 ml of methanol while a ligand precursor solution by dissolving 2.59 g of 2-methylimidazole and 0.125 g of sodium formate in 30 ml of methanol. Then, a polished support was vertically loaded in a home-made Teflon holder and soaked in the metal solution for 1 h. Afterward, the metal solution-saturated support was inserted into a microwave-inert pyrex tube containing the ligand solution, which was then placed in a microwave oven (Discover, CEM Co.) and immediately exposed to microwave with the powder of 100 W for 1.5 min for the microwave-assisted seeding. Finally, the seeded support was submerged in a 30 ml methanol and kept under gentle rocking for 3 days. Methanol was replenished every 12 h. The seed layer was then dried at 70 ^oC for 24 h before usage.

Synthesis of ZIF-8 crystals: A precursor solution was prepared by mixing separately-prepared metal and ligand solutions. The metal solution was obtained by dissolving 0.2 g of zinc nitrate hexahydrate in 20 ml of methanol while the ligand solution by dissolving 0.44 g of 2-methylimidazole and 0.06 g of sodium formate in 20 ml of methanol. For rapid synthesis, the metal and ligand solution were mixed for 30 s, followed by microwave irradiation at 100 W for 1.5 min. Then the sample was naturally cooled for 20 min and washed with methanol multiple times. For slow synthesis, the metal and ligand solutions were mixed for 2 min and subsequently kept without stirring for 4 h at room temperature, followed by methanol washing. As-prepared crystals were finally dried in a vacuum oven at 70 ^{o}C for 12 h and kept in a desiccator before usage.

Ripening of ZIF-8 crystals: A support with ZIF-8 crystals deposited under microwave was vertically loaded in a custom-made Teflon holder. The seeded support was inserted into a Teflon-lined autoclave which contained an aqueous solution of 2-methylimidazole (1.5 g of 2-methylimidazole in 1 ml of D.I. water). The seeded support was placed in the autoclave such that it was never in direct contact with the aqueous ligand solution. Then, the autoclave was sealed and kept in an oven at 145 ^{o}C for 9 h. Finally, the sample was submerged in 30 ml of methanol and kept under gentle rocking for 3 days and dried at 70 ^{o}C for 24 h before usage. Methanol was replenished every 12 h during the washing step.

Characterizations: A Rigaku Miniflex II powder X-ray diffractometer with Cu-Kα radiation (λ = 1.5406 Å) was used to collect the XRD patterns of samples. Electron micrographs were obtained using A JEOL JSM-7500F operated at 5 keV acceleration voltage and 15 mm working distance. A Varian INOVA 400 MHz solid-state NMR spectrometer equipped with a 7.5 mm CP/MAS probe was employed to collect the ^{13}C (100.58 MHz) and ^{15}N NMR (40.52 MHz)

spectra. The spinning frequency was held constant at 10 kHz with a pulse delay time of 4 s, and the contact time was 1 ms. Samples were packed into 7.5 mm zirconia rotors and sealed with Kel-F short caps. To obtain the ^{67}Zn (37.5 MHz) spectra, a Varian VNMRS 600 MHz spectrometer was used with constant spinning frequency of 10 kHz, pulse delay time of 5 s, and a contact time of 2 ms. A Nicolet iS 10 FT-IR spectrometer was used to obtain the IR spectra of the samples. TGA-Q50 (TA Instruments) and ASAP 2020 (Micrometrics) were used for thermogravimetric and N_2 adsorption analyses, respectively.

Gas permeation test: A Wicke-Kallenbach technique was used to conduct binary propylene/propane separation measurements. A 50/50 binary mixture of propylene/propane was supplied to a membrane side while a permeate side was constantly swept with argon gas, which was connected to a gas chromatography (Agilent GC 7890A) for composition analysis. The total pressures and temperature of both feed and permeate sides were atmospheric pressure and room temperature, respectively. The volumetric flow rates of the feed and sweeping gases were kept at 100 cc/min.

Fig. S1

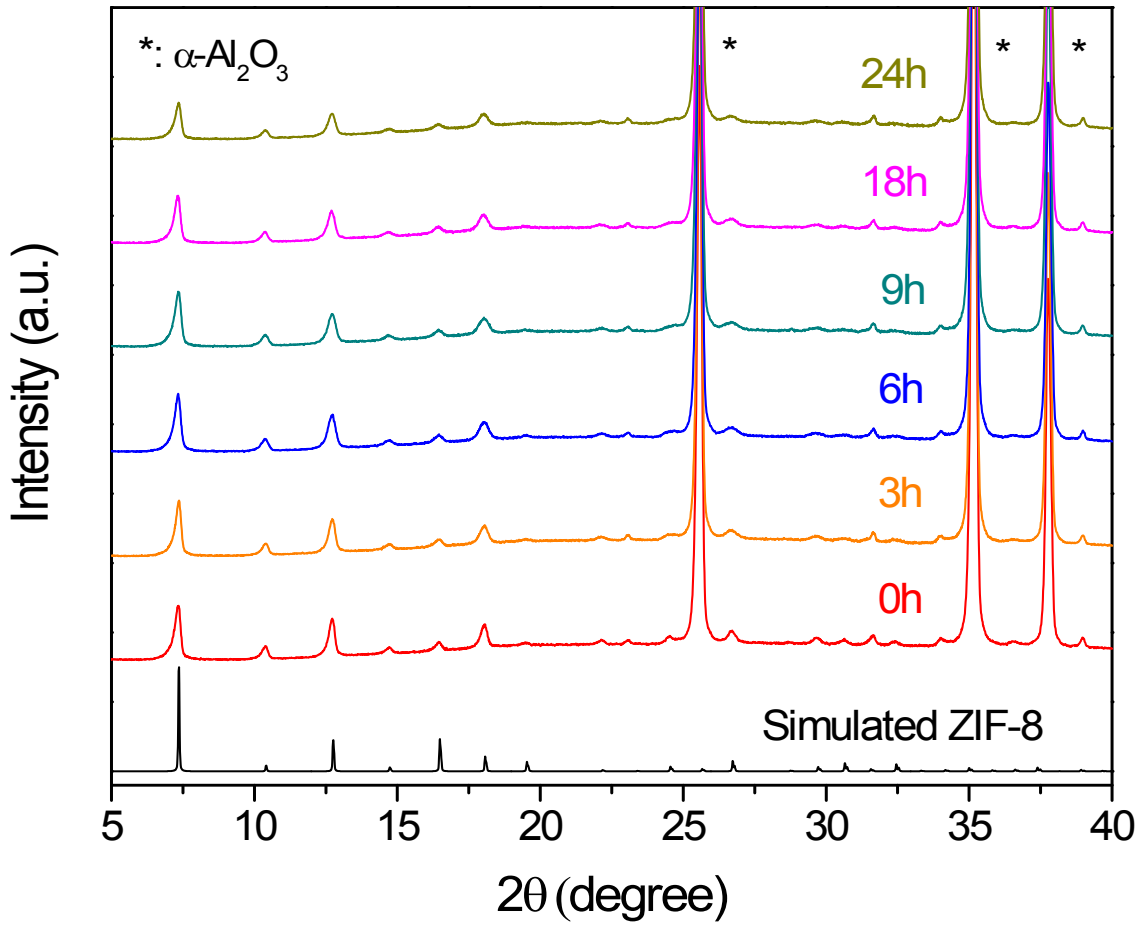

Fig. S1 X-ray diffraction patterns of supported ZIF-8 seed crystal layers prepared by the microwave-assisted seeding that are exposed to a mixture of ligand and water vapors at 145 ^{o}C for varied time .

Fig. S2

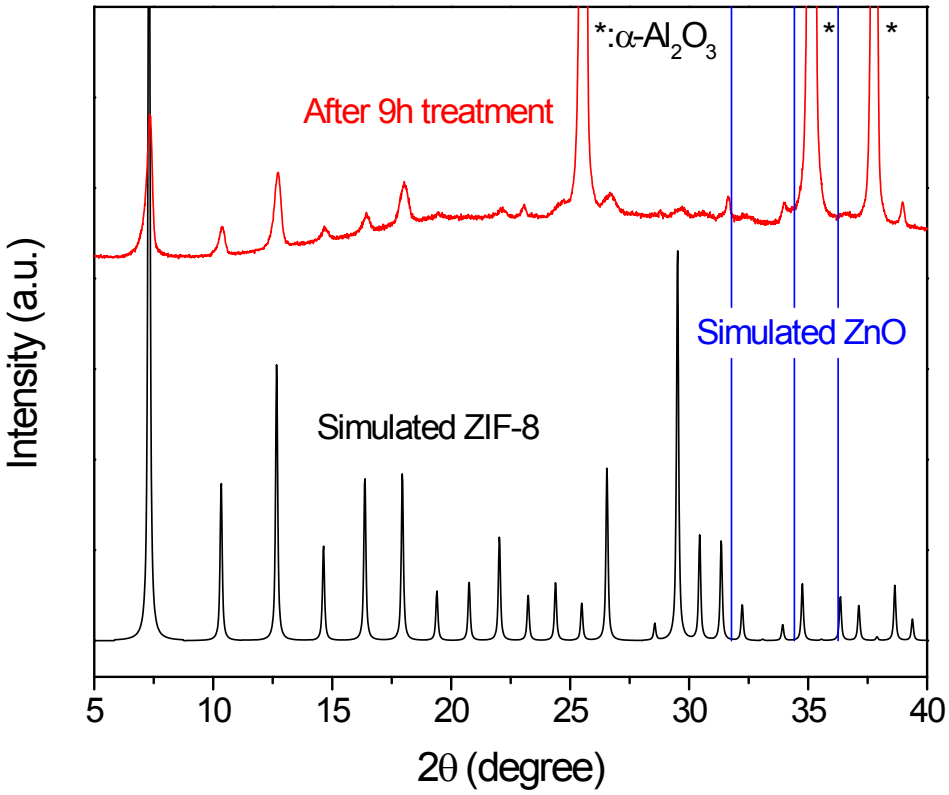

Fig. S2 A magnified X-ray diffraction pattern of a supported ZIF-8 seed crystal layer after the ripening process in comparision with simulated ZIF-8 and ZnO patterns. The ZIF-8 layer was prepared by the microwave-assisted seeding and exposed to a mixture of ligand and water vapors at 145 ^{o}C for 9 h.

Fig. S3

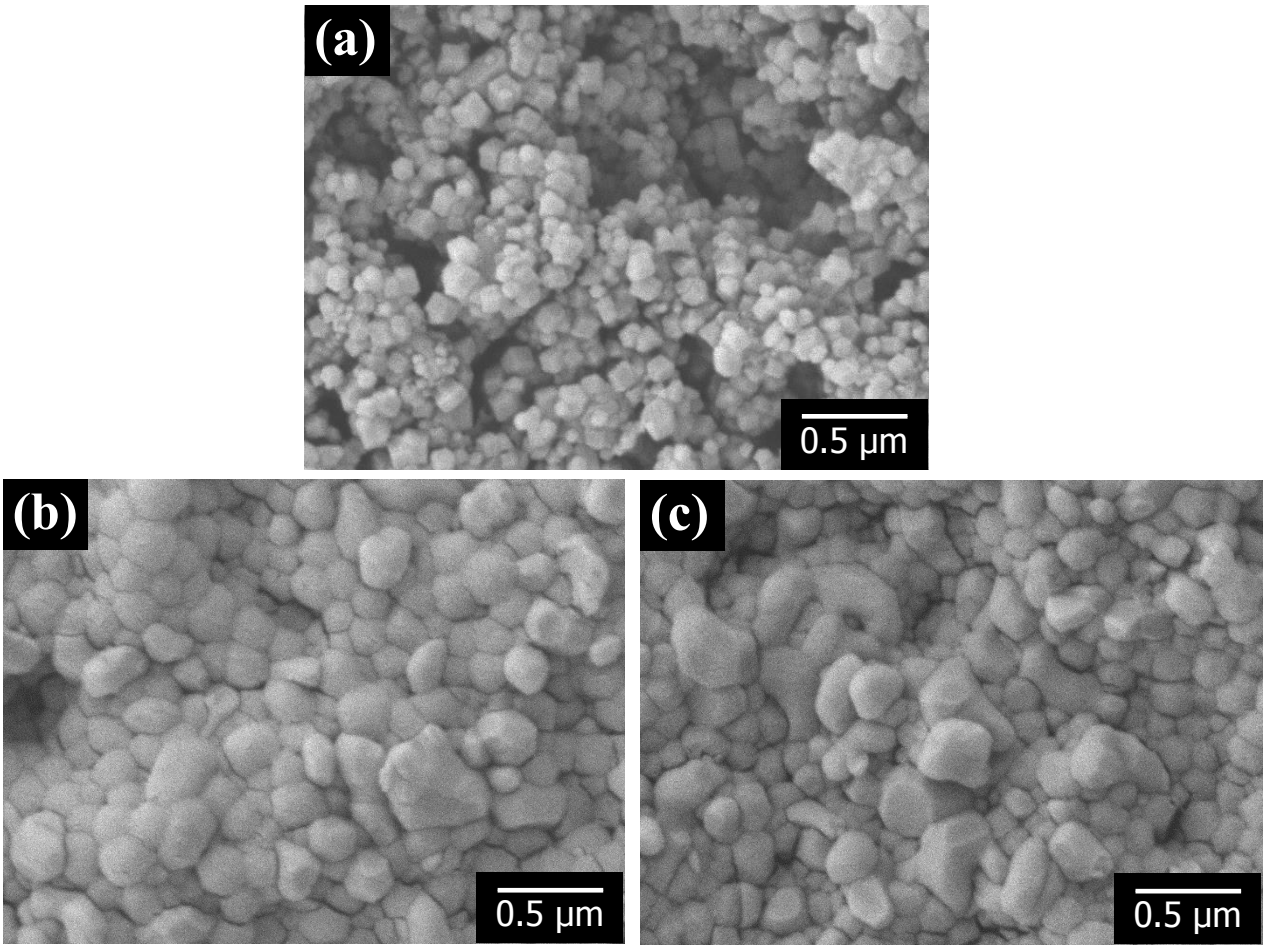

Fig. S3 Electron micrographs of supported ZIF-8 seed crystal layers that were exposed to a mixture of ligand and water vapors at 145 ^{o}C for (a) 1 h, (b) 18h, and (c) 24 h.

Fig. S4

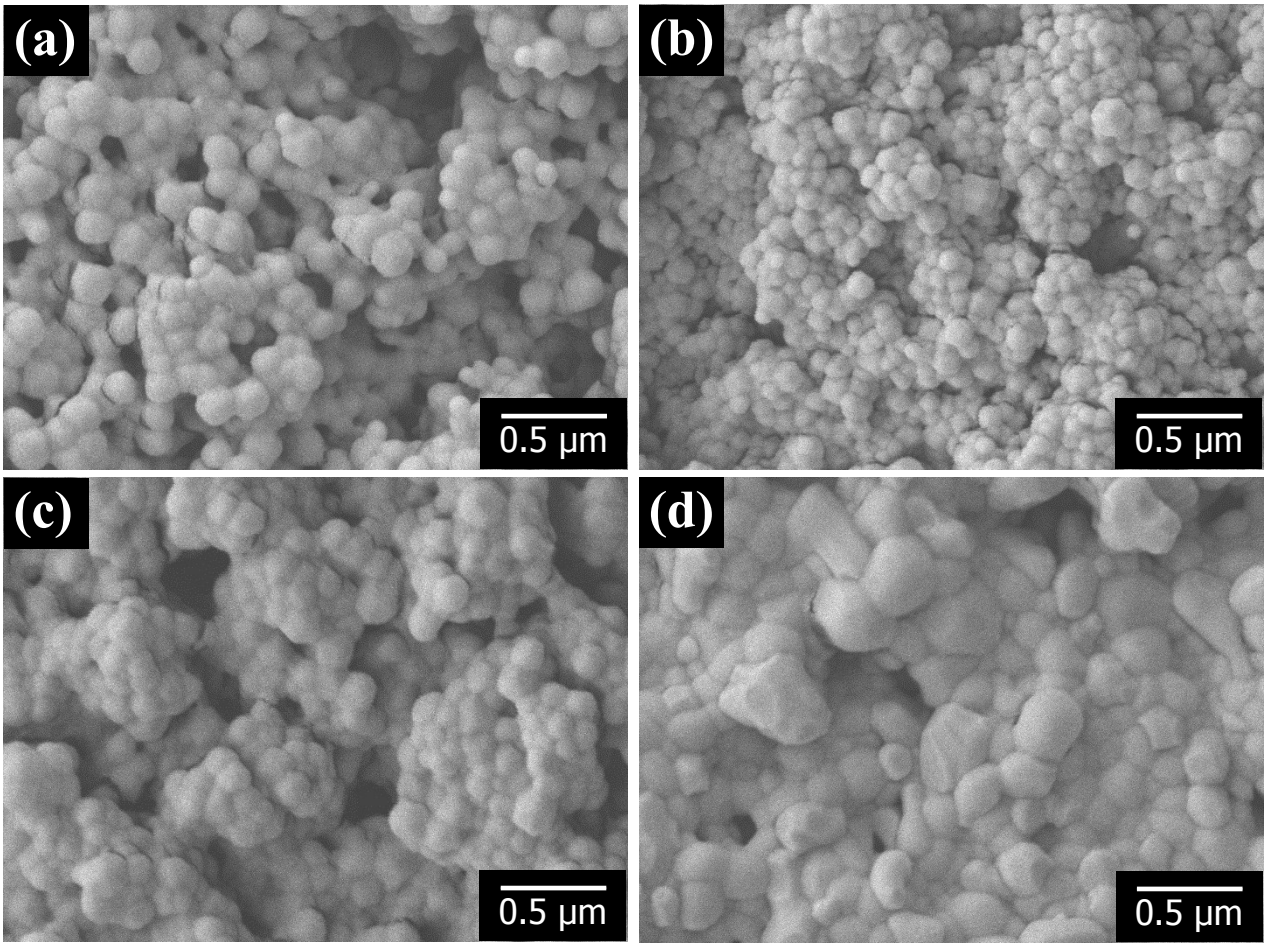

Fig. S4 Electron micrographs of supported ZIF-8 seed crystal layers that were exposed to (a) neither water nor ligand, (b) water only, (b) ligand only, and (d) both water and ligand vapors at 145 ^{o}C for 9h, respectively.

Fig. S5

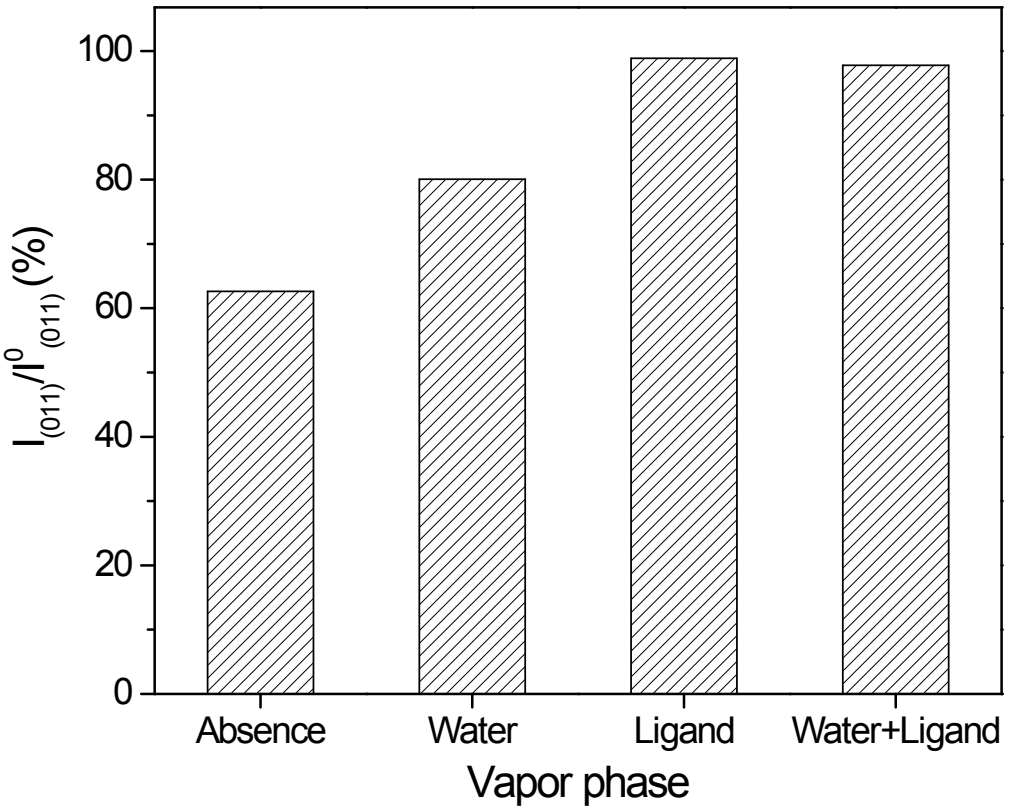

Fig. S5 Normalized (011) XRD peak intensities of suppored ZIF-8 seed crystal layers that were exposed to different vapor environments at 145 ^{o}C for 9 h, respectively. Full X-ray diffraction patterns are presented in Fig. S5.

Fig. S6

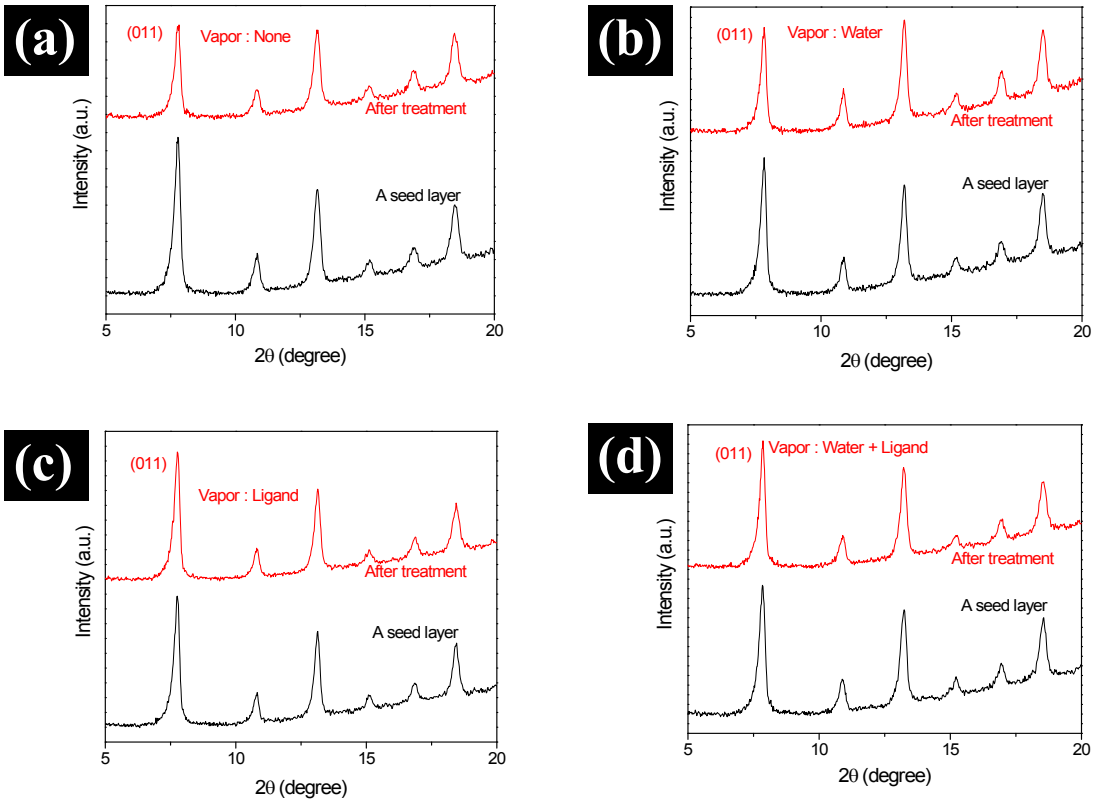

Fig. S6 X-ray diffraction patterns of supported ZIF-8 seed crystal layers that were exposed to (a) neither water nor ligand, (b) water only, (c) ligand only, and (d) both water and ligand vapors at 145°C for 9 h, respectively.

Fig. S7

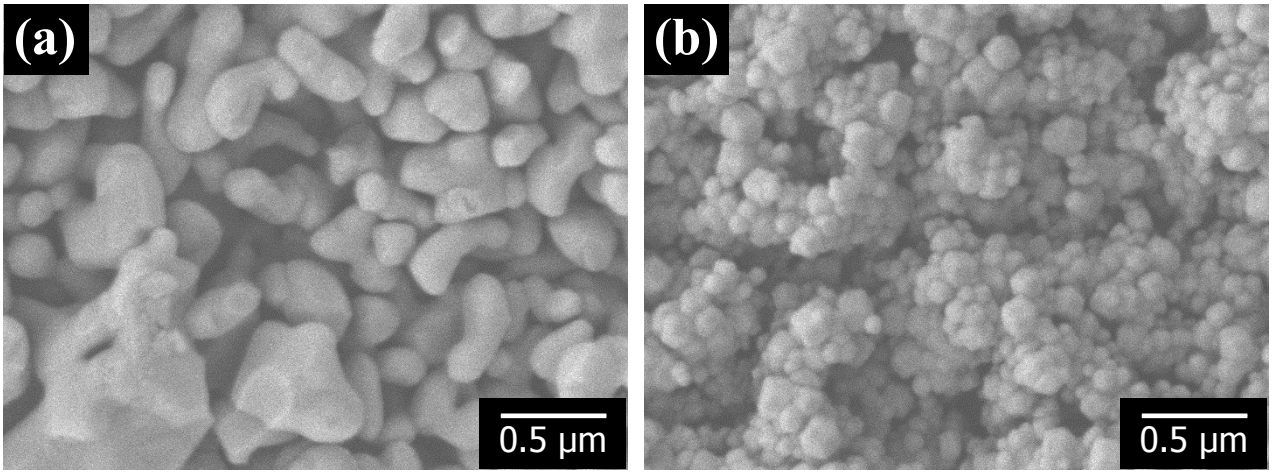

Fig. S7 Electron micrographs of supported ZIF-8 seed crystal layers that were exposed to (a) 1M HNO_3 and (b) 1M KOH vapors for 9 h at 145 ^{o}C. ZIF-8 crystals were completely dissolved upon the exposure to the acid vapor. In contrast, ZIF-8 crystals remained intact upon the exposure to the base vapor.

Fig. S8

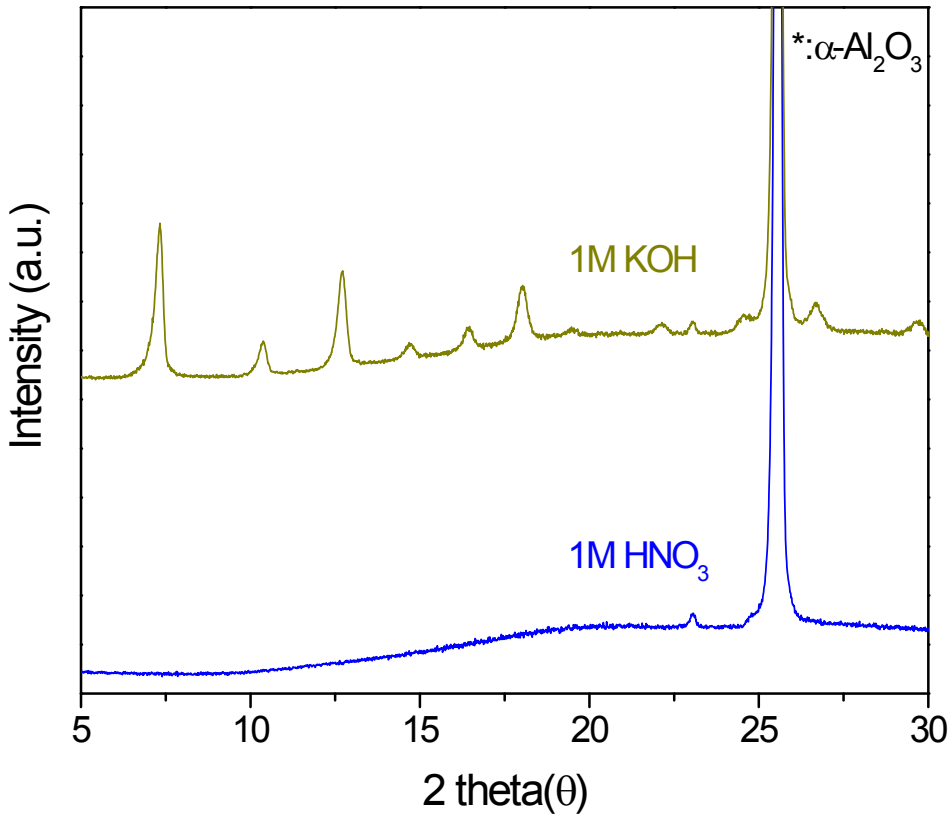

Fig. S8 X-ray diffraction patterns of supported ZIF-8 seed crystal layers that were exposed to (a) 1M HNO_3 and (b) 1M KOH vapors for 9 h at 145 ^{o}C.

Fig. S9

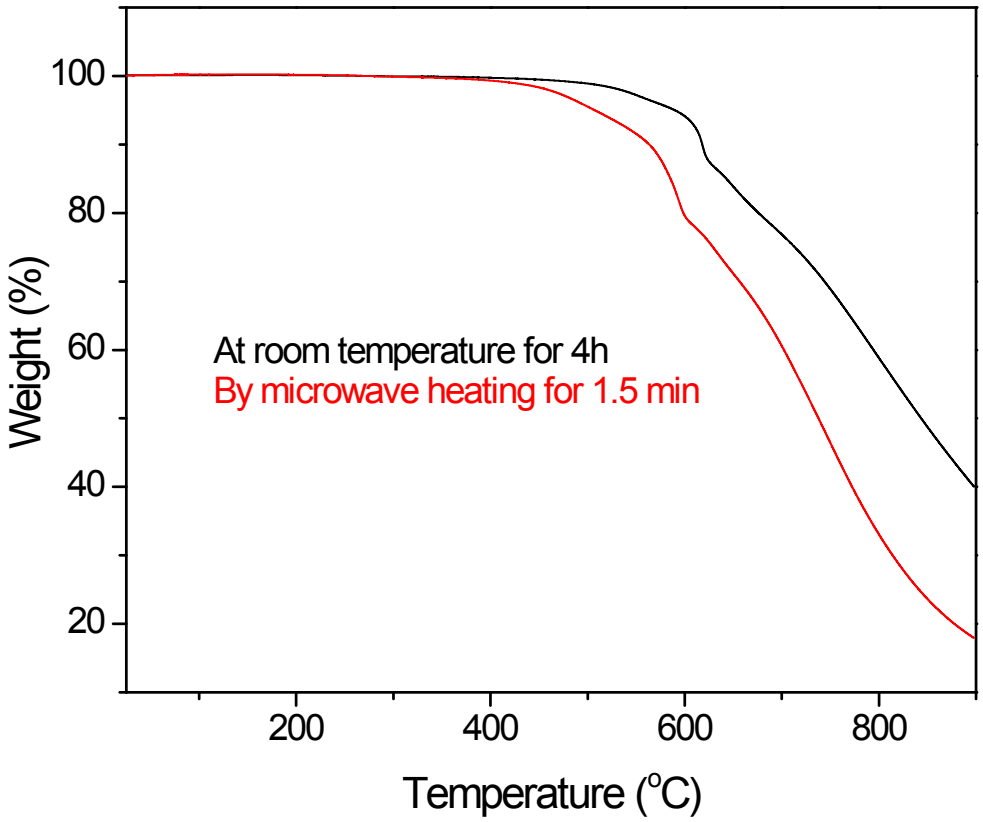

Fig. S9 TGA data of two ZIF-8 power samples: one synthesized at RT for 4h and the other under microwave heating for 1.5min

Fig. S10

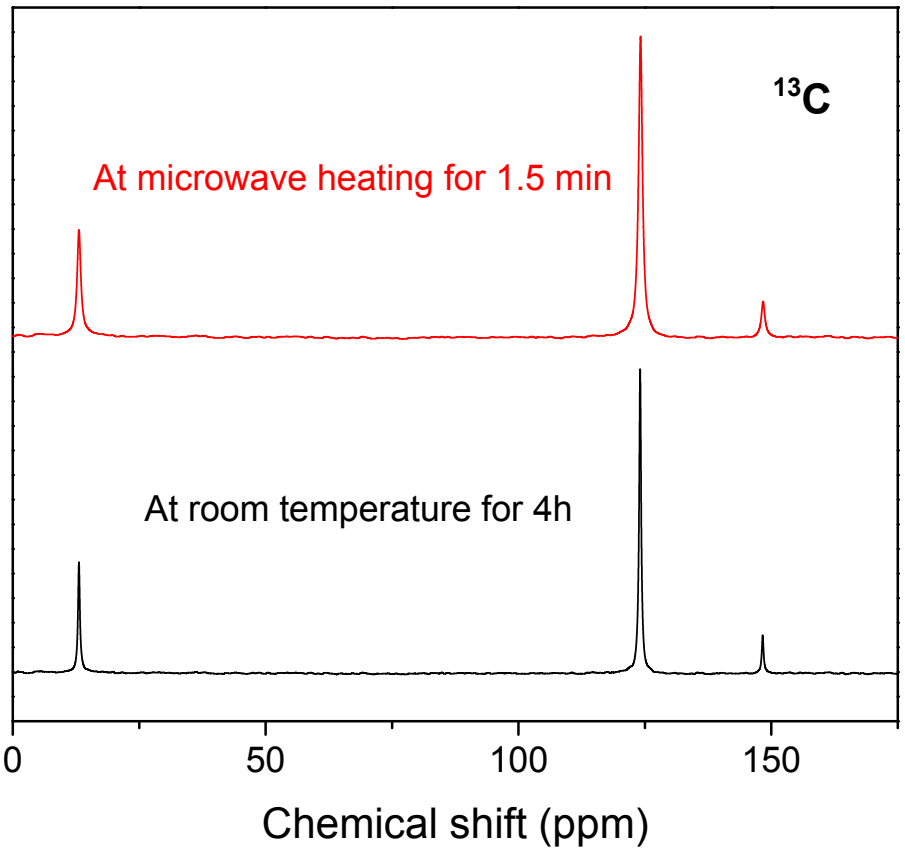

Fig. S10 ^{13}C NMR spectra of the ZIF-8 crystals that were prepared in different time scales. The ^{13}C NMR peaks of the MW sample are notably broader than those of the RT sample.

Fig. S11

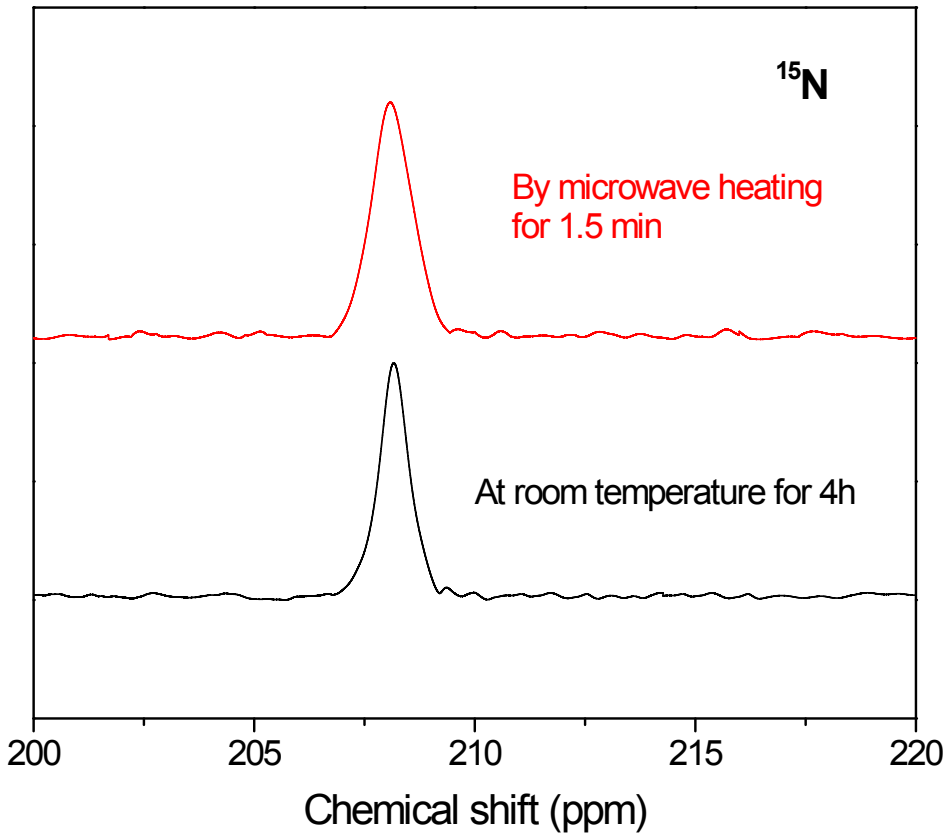

Fig. S11 ^{15}N NMR spectra of the ZIF-8 crystals that were prepared in different time scales. The ^{15}N NMR peaks of the MW sample are notably broader than those of the RT sample.

Fig. S12

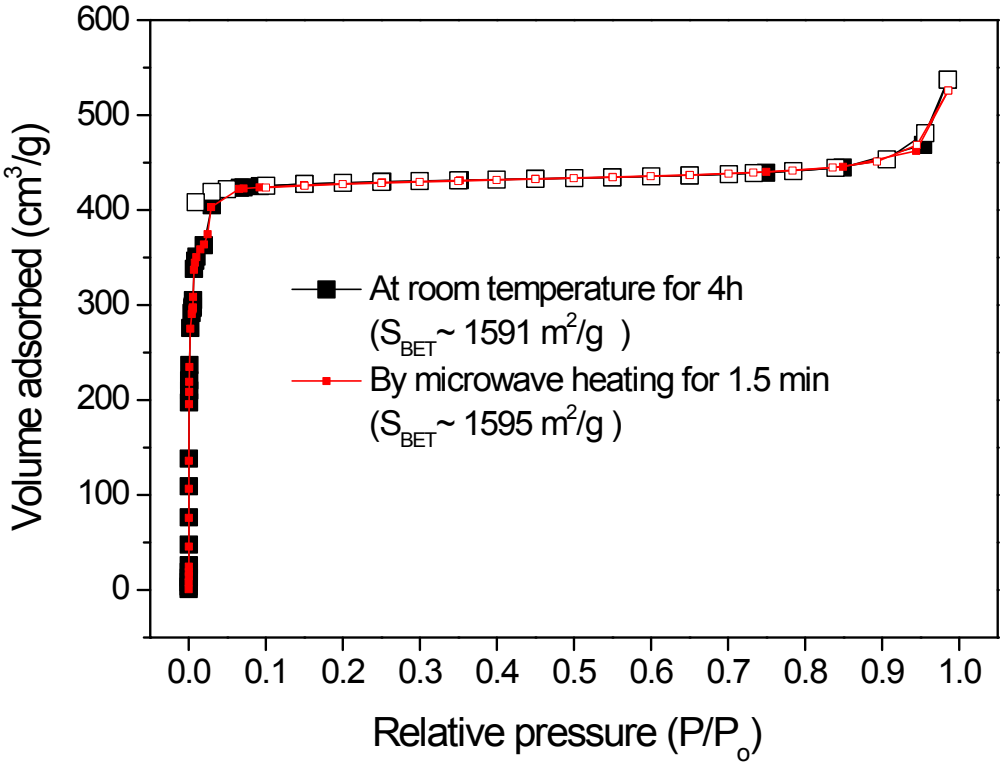

Fig. S12 N_2 adsorption isotherms of the ZIF-8 crystals that were prepared in different time scales; filled square, adsorption and empty square, desorption.

Fig. S13

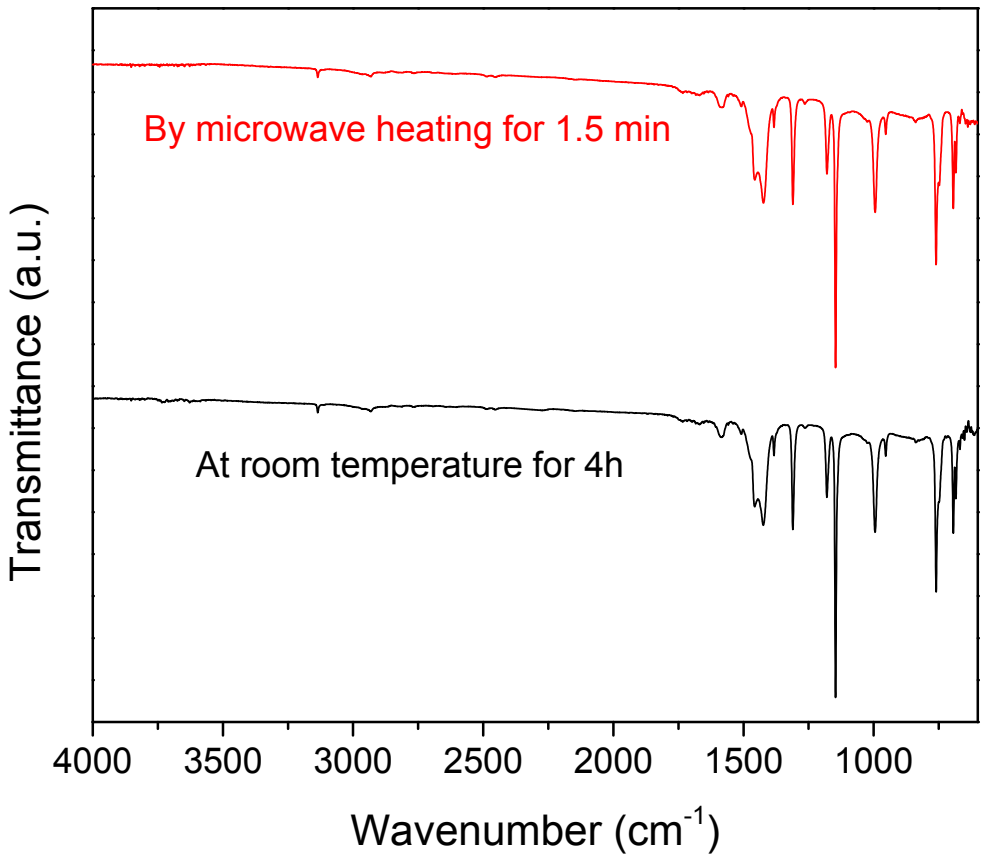

Fig. S13 ATR-FTIR spectra of the ZIF-8 crystals that were prepared in different time scales.

Fig. S14

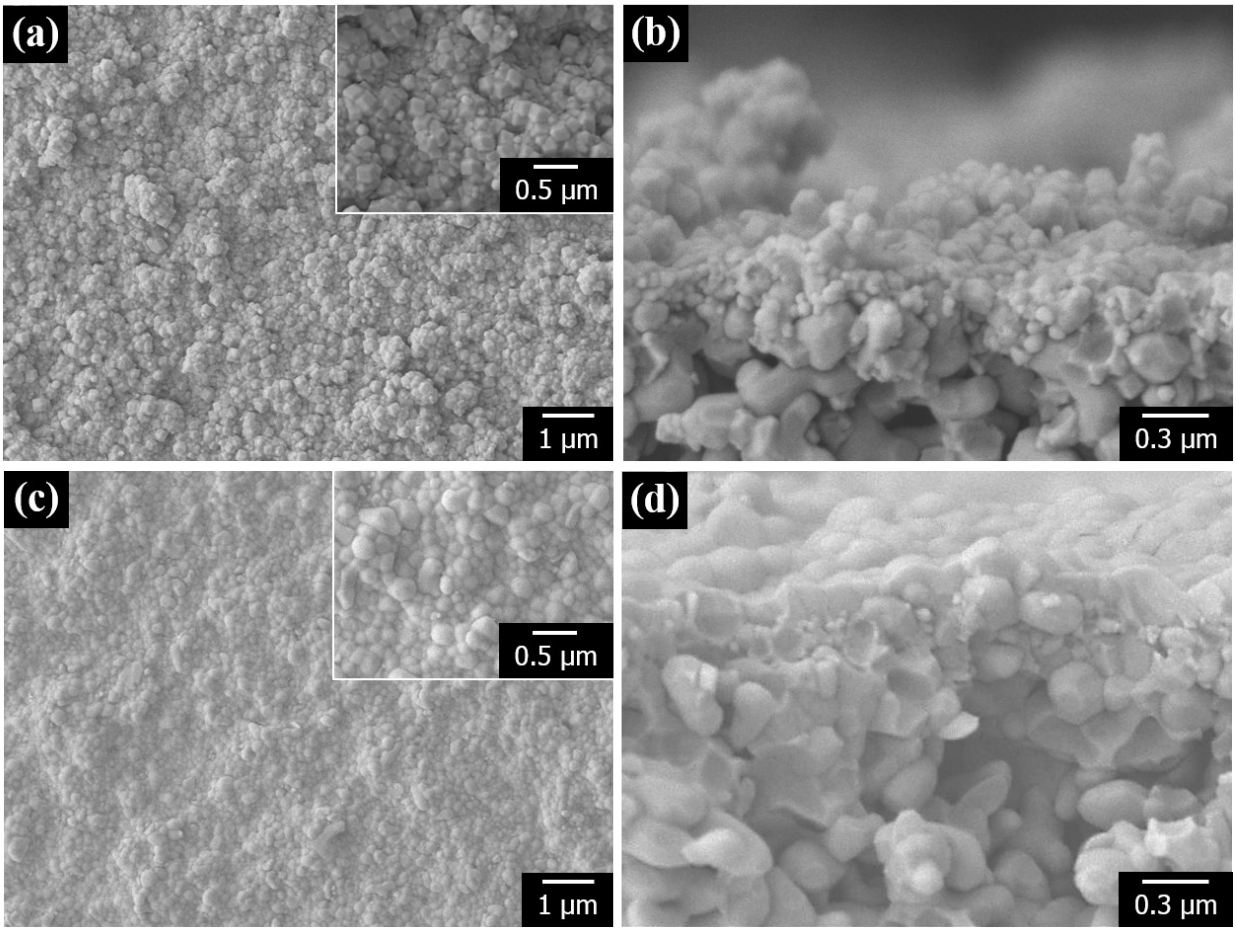

Fig. S14 Electron micrographs of a supported ZIF-8 seed crystal layer on an asymmetric substrate, prepared by the microwave-assisted seeding technique, (a, b) before and (c, d) after being exposed to a mixture of ligand/water vapors at 145^{o}C for 9h.

Fig. S15

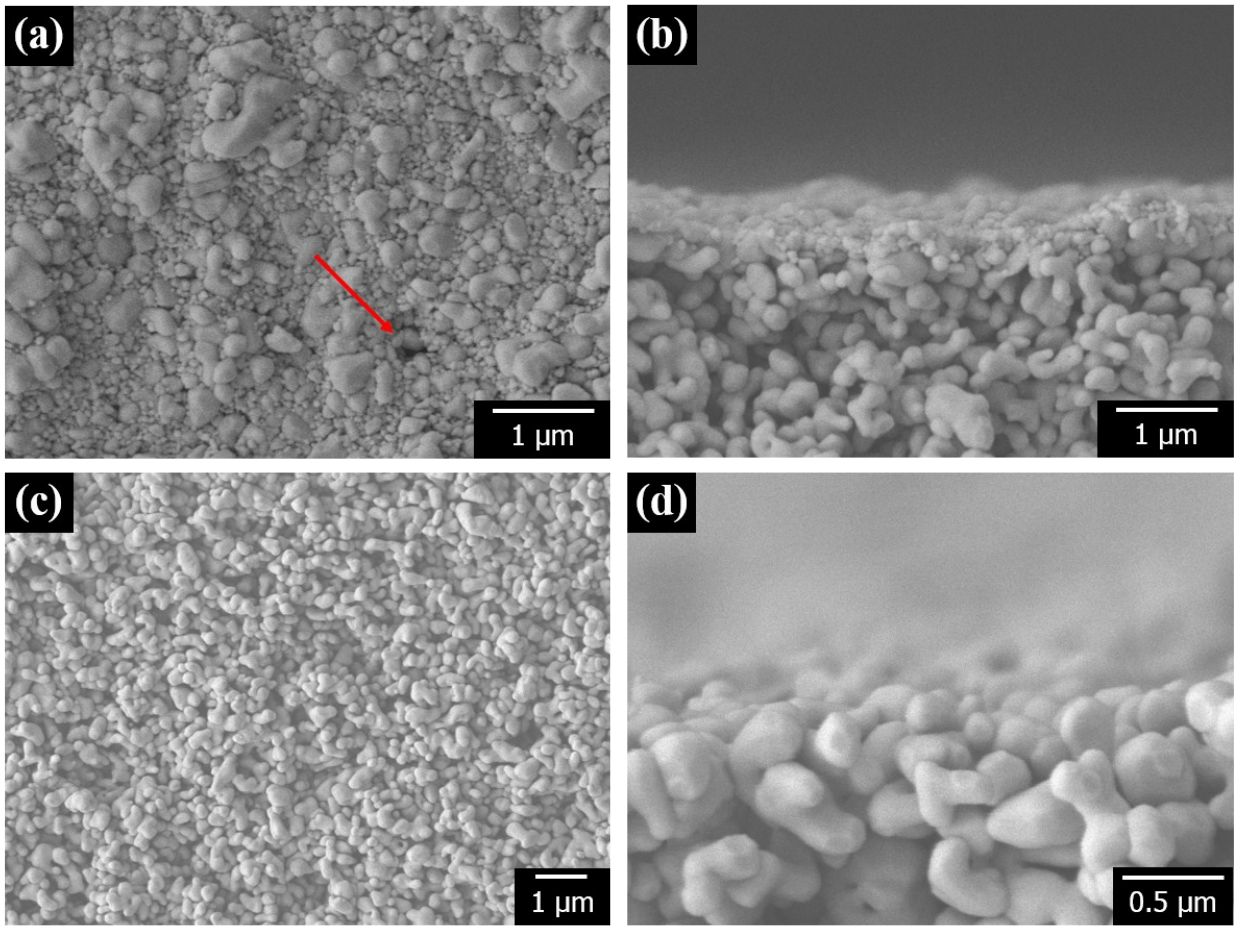

Fig. S15 Electron micrographs of (a, b) an asymmetric and (c, d) a symmetric α-Al_2O_3 supports.

Fig. S16

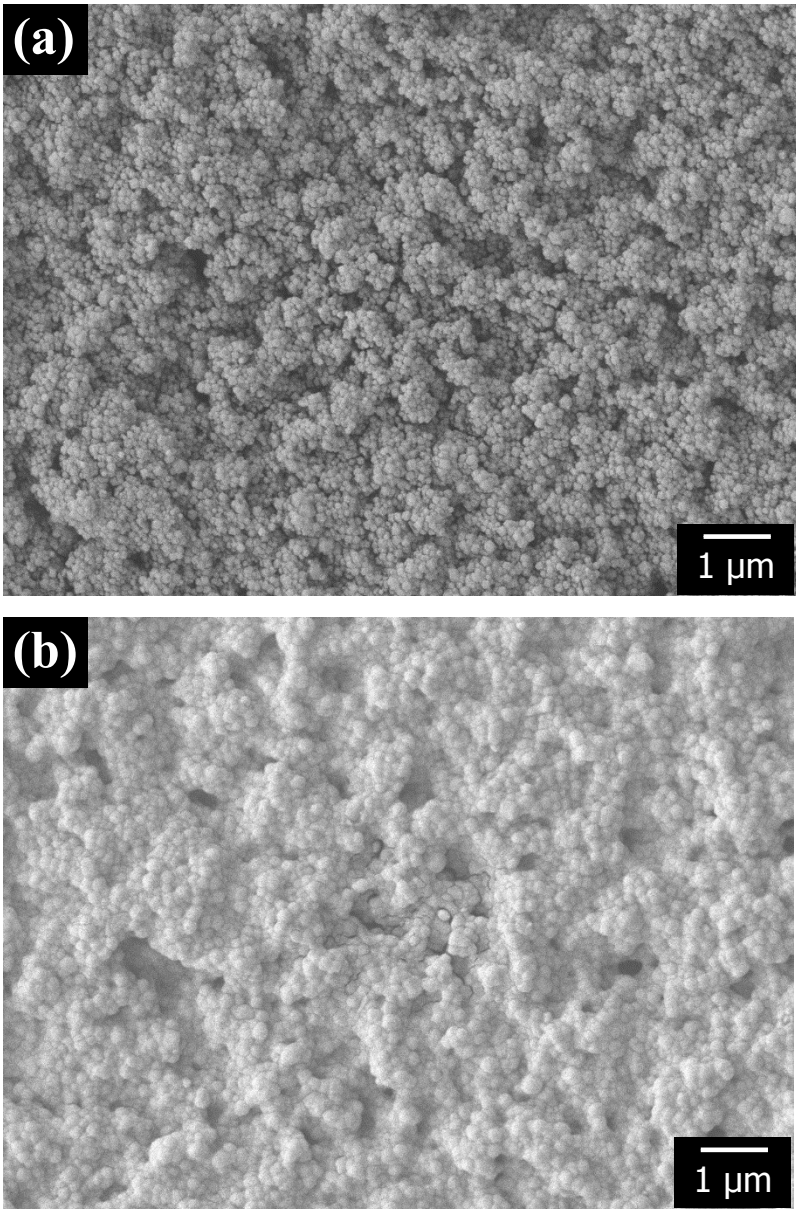

Fig. S16 Electron micrographs of a supported ZIF-8 seed crystal layer on a symmetric support (a) before and (b) after being exposed to a mixture of ligand and water vapors at 145 ^{o}C for 9 h.

Table S1 Room temperature binary propylene/propane separation performances of ZIF-8 membranes prepared on asymmetric supports by the ripening process

Membranes	Permeance of C3= ($\times 10^{-10}$ mol / s·pa·m^2)	Separation factor (C3=/C3-)
1	125.5	122.5
2	266.1	7.2
3	No separation	