*Supporting Information*

**Characterization of Gas Permeation in the Pores of Zn(II)-Based Metal Organic Framework (MOF) Membranes**

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**Single gas permeation system.**

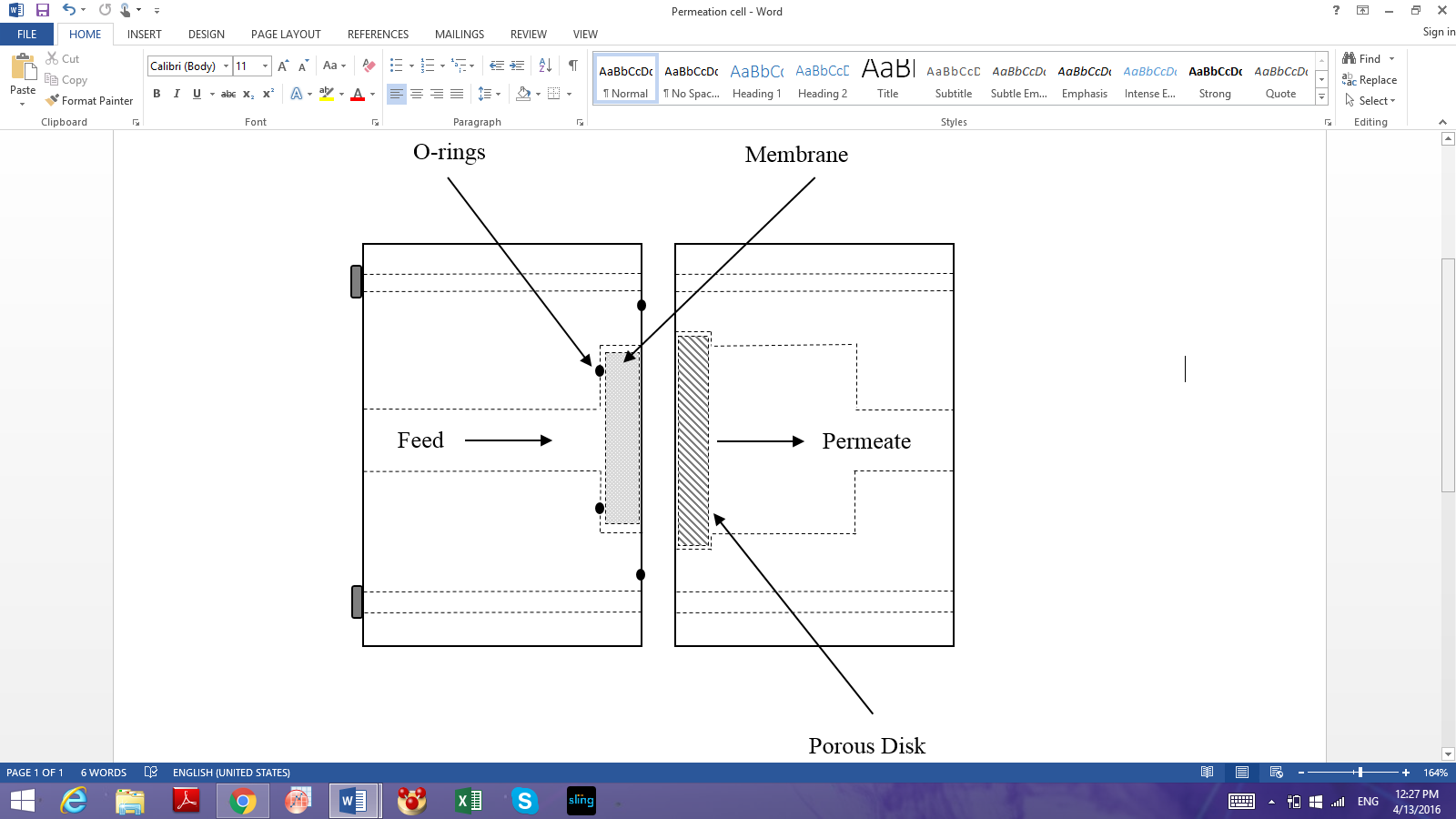
A schematic of the gas permeation apparatus used for gas permeability experiments is detailed in figure S1.



**Figure S1.** Permeation apparatus for single gas transport experiments.

A lab built, removable convection oven can be placed around the permeation cell, feed pipe, and permeate pipe to control the temperature of the system. A thermocouple and temperature controller is used to control the temperature inside the oven. The system is connected to a PC and the permeation apparatus is controlled using LabView. The membrane permeation cell is shown in figures S2. The cell was designed specifically to contain the thick (2mm) 25mm diameter porous alumina substrates used in this work.



**Figure S-2. (**Top) Images of the feed (left) and permeate (right) halves of the membrane permeation cell. (Bottom) Schematic side-view of the membrane permeation cell.

**Reported properties of Zn4(pdc)4(DMF)2•3DMF.**

Table S-1 summarizes the structural characteristics, thermodynamic and kinetic parameters previously reported by our research groups. Additional details and parameters may be find in these references. [1], [2]

**Table S-1.** Structural characteristics, thermodynamic and kinetic parameters of MOF.

|  |  |
| --- | --- |
| Formula mass [1] | 1287.38 |
| Crystal system [1] | Monoclinic |
| Density (g/cm3) [1] | 1.778 |
| BET Surface Area (m2/g, determined from CO2 sorption at 273 K) [1] | 196 |
| Langmuir Surface Area (m2/g, determined from CO2 sorption at 273 K) [1] | 390 |
| Pore width (Å) [1] | 7.17 |
| *Kads* • 10-6(bar-1, CO2 at 308 K) [2] | 1.04 |
| *Qeq* (mol/Kg, CO2 at 308 K) [2] | 3.24 |
| *ΔHads* (KJ/mol, CO2) [2] | -23.73 |
| Mass transfer coefficient, *kt* (sec-1, CO2 at 308 K and 1 bar) [2] | 0.0119 |
| Adsorption activation energy, *EA* (KJ/mol, CO2 at 1 bar) [2] | 3.52 |
| Diffusion coefficient, *Ds/rp2* • 10-4(1/sec, CO2 at 308 K and 1 bar) [2] | 7.92 |
| Desorption transport coefficient, *Kdes* (sec-1, CO2 at 308 K and 1 bar) [2] | 0.011 |
| Gas residence time, *τ* (sec, CO2 at 308 K and 1 bar) [2] | 89.97 |
| Desorption activation energy, *EA* (KJ/mol, CO2 at 1 bar) [2] | 10.35 |

**Permeability data for the different stages of membrane formation.**

The gas permeability of pure polysulfone (UDEL P-3500, Solvay) used in our experiments has been previously reported by our research group under equal conditions[3]. Other values of permeability for PSF (Ultrason 6010) have been previously reported in the literature[4]. Values for the permeability of the pure polysulfone membrane, the PSF-covered MOF-seed-crystal film and the PSF-covered MOF membrane are shown in table S-1. Data for the permeability of the PSF-covered MOF membrane is presented for an average 100 μm membrane thickness, however the membrane surface is asymmetric and its thickness may vary within this range. Gas permeation experiments using a bare alumina support, a PEI coated support, and a MOF membrane after secondary growth (without PSF coat) were conducted; nonetheless, all these experiments showed extremely fast permeation following convective flow transport and are not presented in this study. Nonetheless, they confirm that none of the initial stages of membrane formation affect the transport mechanisms or act as a barrier to permeation.

**Table S-2.** Gas permeability of CO2, N2, CH4 and H2 at 296 K on the PSF-covered MOF-seed-crystal film, the MOF membrane, and control data for the permeability of a pure polysulfone membrane.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Membrane | Permeability  CO2 (Barrer) | Permeability  N2 (Barrer) | Permeability  CH4 (Barrer) | Permeability  H2 (Barrer) |
| Polysulfone[3] | 3.9 | 0.17 | 0.17 | N/A |
| Polysulfone[4] | 6.5 | 1.5 | 1.4 | 13.2 |
| PSF-coated sparse non-continuous film | 1724.08 | 2166.40 | 2955.80 | 6678.44 |
| PSF-coated MOF Membrane | 2.92E+06 | 3.36E+06 | 4.64E+06 | 8.56E+06 |

**Knudsen diffusion, pore width and mean free path.**

The transport of gases through a porous membrane can be described by three main mechanisms: viscous flow, Knudsen Diffusion, and surface flow[5]. Each transport regime is a function of the size of the crystalline pores of the material, the kinetic diameter of the molecules flowing, the driving force for transport and the molecular/superficial interactions that govern the transport. The Knudsen number () can be used to estimate the preferential mechanism of diffusion trough the pores of a crystalline material (equation 1) [3], [5],

**Equation 1**

This number relates the mean free path () to the pore diameter of the material () (7.17 Å [1]). values greater than 10 indicate that Knudsen diffusion and viscous flow will be the main diffusion mechanisms in the absence of other interactions between molecules and with the pore walls. Viscous flow, which is the bulk flow of the gas, occurs mainly due to pressure differences inside pinholes and cracks on the membrane surface, this mechanism can be neglected if the membrane obeys Knudsen diffusion behavior or if the transport of a non-adsorbable gas is independent of pressure [3], [6], [7]. Knudsen diffusion occurs as the number of collisions between the gas molecules and the pore walls is greater than the effective number of collisions between molecules. Values of below 10 suggest the presence of a greater number of interactions among gas molecules and between active surfaces and gas molecules [3], [5]. Table 1 lists values of mean free path and Knudsen number for the diffusion of different gases through the MOF in study.

**Table S-3.** Mean free path and Knudsen number at 296 K and 1 atm of different gases.

|  |  |  |  |
| --- | --- | --- | --- |
| **Gas** | **Kinetic diameter (Å)** | **Mean free path (nm)** | **Knudsen number** |
| CO2 | 3.30 | 83.65 | 116.67 |
| N2 | 3.64 | 68.75 | 95.89 |
| CH4 | 3.76 | 64.44 | 89.87 |
| H2 | 2.80 | 116.19 | 162.05 |

The Knudsen number values in Table S-3 are all greater than 10 suggesting that diffusion will be mainly due to Knudsen type transport inside the MOF pores given the analysis presented in the results section of the manuscript.

**References.**

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