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**Supplementary Information to**

# Metal Organic Framework based Mixed Matrix Membranes: a solution for highly efficient $CO_2$ capture?

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## List of acronyms and abbreviations

| | |
|---|---|
| μ-BPA | 1,2-Bis(4-pyridyl)ethane |
| μ-BPP | 1,3-Bis(4-pyridyl)propane |
| 1,4-BDC (or BDC) | 1,4-Benzenedicarboxylate |
| 2,6-NDC | 2,6-Napthalenedicarboxylate |
| 2-amBzIM | 2-Aminobenzimidazole |
| 2MI | 2-Methylimidazole |
| 4,4' BPDC | 4,4'-Biphenyl dicarboxylate |
| 4,4'-BPY | 4,4'-Bipyridine |
| 4,4'-SDA | Bis(4-aminophenyl) sulphide |
| 4MPD | 2,3,5,6-Tetramethyl-1,4-phenylenediamine |
| 6FDA | 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride |
| 6F-PBI | Hexafluoroisopropylidene-containing polybenzimidazole |
| APTMDS | Bis(3-aminopropyl)tetramethyldisiloxane |
| B | Bulk crystals |
| BTC | 1,3,5-Benzenetricarboxylate |
| BuI | 5-Tert-butylisophthalic acid |
| BzIM | Benzimidazole |
| CCS | Carbon Capture and Storage |
| CLC | Chemical looping combustion |
| CMS | Carbon molecular sieves |
| DABA | 3,5-Diaminobenzoic acid |
| DABCO | 1,4-Diazabicyclo[2.2.2]octane |
| DAM (or TMPDA) | 2,4,6-Trimethyl-*m*-phenylenediamine |
| DBzPBI | PBI after N-substitution reaction with 4-tert-butylbenzyl bromide |
| DEA | Diethanolamine |
| DMF | Dimethylformamide |
| DMPBI | PBI after N substitution reaction with methyl iodide |
| DSDA | 3,3',4,4'-Diphenylsulfone tetracarboxylic dianydride |
| ETS | Emissions Trading System |
| Glu | Glutarate |
| GPU | Gas permeance units |
| $H_2$hfipbb | 4,4'-Hexafluoroisopropylidene bis(benzoic acid) |
| HFb | Hollow fiber |
| HFS | Hexafluorosilicate |
| HHV | Higher heating value |
| HSP | Hansen solubility parameters |
| IAST | Ideal adsorbed solution theory |
| IGCC | Integrated gasification combined cycle |
| IPA | Isopropanol |
| IPCC | Intergovernmental Panel on Climate Change |
| LANL | Los Alamos National Laboratory |

| | |
|---|---|
| LB | Langmuir-Blodgett |
| LCOE | Levelized Cost of Energy |
| $M^4$ | MOF-based mixed matrix membrane |
| $M^4$-HFb | MOF-based mixed matrix membrane in asymmetric hollow fiber geometry |
| MEA | Monoethanolamine |
| MM-HFbM | Mixed matrix membranes in asymmetric hollow fiber geometry |
| MMM | Mixed-matrix membrane |
| MOF | Metal organic framework |
| MS | Maxwell-Stefan |
| MSS | Mesoporous silica spheres |
| MTR | Membrane Technology and Research, Inc. |
| Nc | Nanoparticle crystals |
| $NH_2$-BDC | 2-Aminoterephthalate |
| Ns | Nanosheets |
| ODA | 4,4'-Oxydianiline |
| ODPA | 4,4'-Oxydiphthalicanhydride |
| PA | Polyamide |
| PAET | Poly(3-acetoxyethylthiophene) |
| PAI | Polyamide-imide |
| PBI | Polybenzimidazole |
| PC | Pulverized coal |
| PDMS | Polydimethylsiloxane |
| PEI | Polyethylenimine |
| PES | Polyethersulfone |
| PI | Polyimide |
| PIM | Polymer of intrinsic microporosity |
| PLLA | Poly(L-lactic acid) |
| PMDA | Pyromellitic dianhydride |
| PMMA | Poly(methyl methacrylate) |
| PMP | Poly (4-methyl-1-pentyne) |
| PMPS | Polymethylphenylsiloxane |
| POZ | Polyoxazoline |
| PPEES | Poly-(1,4-phenylene ether-ether-sulfone) |
| PPO | Poly(2,6-dimethyl-1,4-phenylene oxide) |
| PSF | Polysulfone |
| PTMSP | Poly[1-(trimethylsilyl)-1-propyne] |
| PVAc | Poly(vinyl acetate) |
| SET-plan | European Strategic Energy Technology Plan |
| TED | Triethylenediamine |
| TPX | Polymethylpentene |
| XLPEO | Cross-linked polyethylene oxide |
| ZEP | Zero Emission Fossil Fuel Power Plants |

| | |
|---|---|
| ZIF | Zeolitic imidazolate framework |

## List of symbols

| | | |
|---|---|---|
| A | Membrane area | $m^2$ |
| $b_i$ | Affinity constant of specie i | $Pa^{-1}$ |
| $C_i$ | Concentration of component i | $mol/m^3$ |
| $C_i^{sat}$ | Langmuir capacity constant of specie i | $mol/m^3$ |
| $D_f$ | Diffusivity of specie i in the filler | $m^2/s$ |
| $D_i$ | Diffusion coefficient of component i | $m^2/s$ |
| $Đ_i$ | Maxwell-Stefan diffusivity of component i | $m^2/s$ |
| $D_i^{eff}$ | 'Effective' diffusion coefficient of component i | $m^2/s$ |
| $D_i^H$ | Diffusivity of specie i in the Henry environment | $m^2/s$ |
| $D_i^L$ | Diffusivity of specie i in the Langmuir environment | $m^2/s$ |
| $D_{Kn,i}$ | Knudsen diffusion coefficient of component i | $m^2/s$ |
| $D_m$ | Diffusivity of specie i in the matrix | $m^2/s$ |
| $d_o$ | Pore diameter | m |
| $D_{self,i}$ | Self-diffusivity of component i | $m^2/s$ |
| F | Correction factor | - |
| $f_i$ | Fugacity of component i | Pa |
| K | Interfacial equilibrium constant or partition coefficient | - |
| $K_i$ | Langmuir isotherm adsorption constant | $Pa^{-1}$ |
| $K_i^H$ | Henry adsorption coefficient of specie i | $mol/(Pa \cdot m^3)$ |
| L | Membrane thickness | m |
| $M_i$ | Molecular weight of component i | kg/mol |
| $N_c$ | Molar flux of a gas species in the continuous phase of a MMM | $mol/(m^2 \cdot s)$ |
| $N_d$ | Molar flux of a gas species in the dispersed phase of a MMM | $mol/(m^2 \cdot s)$ |
| $N_{eff}$ | Effective molar flux of a gas species in a MMM | $mol/(m^2 \cdot s)$ |
| $N_i$ | Molar flux of component i | $mol/(m^2 \cdot s)$ |
| $P_f$ | Permeability of specie i in the filler | $(mol \cdot m)/(m^2 \cdot s \cdot Pa)$ |
| $P_i$ | Permeability coefficient of component i | $(mol \cdot m)/(m^2 \cdot s \cdot Pa)$ |
| $p_i$ | Partial pressure of component i | Pa |
| $P_m$ | Permeability of specie i in the matrix | $(mol \cdot m)/(m^2 \cdot s \cdot Pa)$ |
| $q_i$ | Adsorbed amount or loading of component i in a porous material | mol/kg |
| $q_i^{sat}$ | Maxim adsorbed amount or loading of component i in a porous solid at saturation | mol/kg |
| R | Gas constant | $J/(mol \cdot K)$ |
| $R_a$ | Distance between Hansen parameters | $Pa^{0.5}$ |
| $S_{ij}$ | Ideal selectivity | - |
| T | Temperature | K |
| $X_i$ | Mole fractions of component i | - |
| $\alpha_{ij}$ | Separation factor | - |
| $\Gamma_{ii}$ | Thermodynamic correction factor | - |

| | | |
|---|---|---|
| $\delta_D$ | Hansen solubility parameter to quantitatively describe the dispersion or London interaction between two phases | $Pa^{0.5}$ |
| $\delta_H$ | Hansen solubility parameter to quantitatively describe the hydrogen bonds between two phases | $Pa^{0.5}$ |
| $\delta_P$ | Hansen solubility parameter to quantitatively describe the polar interaction between two phases | $Pa^{0.5}$ |
| Δpi | Partial pressure difference for component i across the membrane | Pa |
| E | Porosity | - |
| $\theta_i$ | Fractional coverage of the surface in a porous material | - |
| P | Density | $kg/m^3$ |
| T | Tortuosity | - |
| $\phi_d$ | Volume fraction of the dispersed phase in a MMM | - |

**Table 2:** Overview of the reported MOF-containing MMMs for gas separation in chronological order

| M[4] | | wt.% loading (best MMM performance) | Example (best performance) | | | | | | Type of analysis | Operation conditions (optimal value) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| MOF | Polymer | | *P $CO_2$* (Barrer) | *$CO_2/CH_4$ selectivity* (-) | *P $CO_2$* (Barrer) | *$CO_2/N_2$ selectivity* (-) | *P $H_2$* (Barrer) | *$H_2/CO_2$ selectivity* (-) | | *T* (°C) | *ΔP* (bar) |
| Cu 4,4'-BPDC-TED | PAET | 10-30 (30) | 1.4-(0.7) | 18.0-(3.2) | - | - | - | - | Single gas $CO_2$, $O_2$, $N_2$, $CH_4$ | 25 | 2 |
| | | | - | - | - | - | - | - | Gas mixture $CH_4/CO_2$ (10:90) | | |
| $[Cu_2(PF_6)(NO_3)(4,4'\text{-bpy})_4]2PF_6\cdot 2H_2O$ | PSF | 2.5-5 (5) | - | - | - | - | - | - | Single gas He, $H_2$, $O_2$, $N_2$, $CH_4$ | 35 | 1 |
| $[Zn_2(1,4\text{-bdc})_2(dabco)]\cdot 4DMF\cdot 0.5H_2O$ | PAI | 30 | 46.7-(109) | 49.7-(40.4) | 46.7-(109) | 28.3-(24.6) | 79.2-(191) | 1.7-(1.8) | Single gas | - | - |
| | 6FDA-4MPD | | 1000-(3330) | 23.0-(19.6) | 1000-(3330) | 21.4-(19.1) | 743-(1890) | 0.7-(0.6) | | | |
| | PDMS | | 2830-(4010) | 3.4-(3.7) | 2830-(4010) | 10.5-(10.0) | 673-(955) | 0.2-(0.2) | | | |
| HKUST-1 | PDMS | 10-40(30, 10, 40) | 2500-(2900)* | 3.1-(3.6)* | 2500-(3050)* | 7.0-(8.9)* | 550-(900)* | 0.2-(0.4)* | Single gas $H_2$, $CO_2$, $O_2$, $N_2$, $CH_4$ | - | - |
| | PSF | 5-10 (5, 10) | 6.5-(7.5)* | 18-0-(21.5)* | 6.5-(7.5)* | 20.0-(25.0)* | 9.8-(15.0)* | 1.5-(1.9)* | | | |
| $Mn(HCOO)_2$ | PSF | 5-10 (10, 5) | 6.5-(7.0)* | 18.0-(9.5)* | 6.5-(7.0)* | 20.0-(25.5)* | 9.5-(10.5)* | 1.5-(1.6)* | | | |
| Cu-4,4'-BPY-HFS | Matrimid® | 10-40 (20, 30) | 7.3-(9.9) | 34.7-(27.6) | 7.3-(9.9) | 33.1-(31.9) | 17.5-(20.3) | 2.4-(2.0) | Single gas $H_2$, $CO_2$, $O_2$, $N_2$, $CH_4$ | 35 | 2 |
| | | 20 | - | 36.3-(20.5) | - | - | - | 2.6-(2.6) | Gas mixture $H_2/CO_2$ (50:50, 75:25) $CO_2/CH_4$ (50:50, 10:90) $CH_4/N_2$ (94:6, 50:50) | | |
| IRMOF-1 | Matrimid® | 20 | 10.0-(38.8) | 28.2-(29.2) | - | - | 33.1-(114.9) | 3.3-(3.0) | Single gas $H_2$, $CO_2$, $CH_4$ | 50 | 7 |
| | Ultem® | 10, 20 (20) | 2.0-(3.0) | 30.3-(26.3) | - | - | 11.2-(16.9) | 5.7-(5.7) | | | |
| HKUST-1 | Matrimid® | 30 | 10.0-(22.1) | 28.2-(29.8) | - | - | 33.1-(66.9) | 3.3-(3.0) | | | |
| MOF-5 | Matrimid® | 10-30 (30) | 9.0-(20.2) | 41.7-(44.7) | 9.0-(20.2) | 36.0-(38.8) | 24.4-(53.8) | 2.7-(2.7) | Single gas $H_2$, $CO_2$, $O_2$, $N_2$, $CH_4$ | 35 | 2 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 30 | - | 38.0-(29.0) | - | - | - | 2.3-(2.3) | Gas mixture $H_2/CO_2$ (75:25, 50:50, 25:75) $CH_4/N_2$ (94:6, 50:50, 25:75) $CO_2/CH_4$ (10:90, 50:50, 25:75) | | |
| ZIF-8 | PPEES | 10-30 (30) | 6-(25) | - | 6-(25) | - | - | - | - | 30 | 1, 2, 3, 5, 7, 10 |
| Cu 1,4-BDC | PVAc | 15 | 2.4-(3.3) | 34.9-(40.4) | 2.4-(3.3) | 32.1-(35.4) | - | - | Single gas He, $CO_2$, $O_2$, $N_2$, $CH_4$ | 35 | 4.5 (0.1 for $CO_2$) |
| ZIF-8 | Matrimid® | 20-60 (50) | 9.5-(4.7) | 39.7-(124.9) | 9.5-(4.7) | 30.6-(26.2) | 28.9-(18.1) | 3.0-(3.8) | Single gas $H_2$, $CO_2$, $O_2$, $N_2$, $CH_4$, $C_3H_8$ | 25 | 2.7 |
| | | 50-60 (50, 60) | - | 42.1-(89.2) | - | - | - | 2.6-(7.0) | Gas mixture $H_2/CO_2$ (50:50) $CO_2/CH_4$ (10:90) | | |
| HKUST-1 | Matrimid® | 10-30 (30) | 10.0-(17.5)* (GPU) | 18.0-(24.0)* | 11.0-(18.5)* (GPU) | 23.5-(24.5)* | - | - | Gas mixture $CO_2/CH_4$ (10:90, 35:65, 75:25) $CO_2/N_2$ (10:90, 35:65, 75:25) | 35 | 10 |
| HKUST-1 | PMDA-ODA | 3-6 (3, 6) | 306.6-(227.2) | 12.0-(7.0)* | 306.6-(227.2) | 8.0-(5.5)* | 3066-(4445) | 10.0-(27.8) | Single gas $H_2$, $CO_2$, $O_2$, $N_2$, $CH_4$ | 25 | 10 |
| ZIF-90 | Ultem® | 15 | 1.4-(2.9)* | 38-(39)* | - | - | - | - | Single gas $CO_2$, $CH_4$ | 35 | 4.5 |
| | Matrimid® | | 7.5-(10.5)* | 34-(35)* | - | - | - | - | | | |
| | 6FDA-DAM | | 390-(720) | 24-(37) | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | 25 | 2 |
| ZIF-20 | PSF | 8 | - | - | - | - | - | - | Gas mixture $O_2/N_2$ (50:50) | 35 | 2 |
| $NH_2$-MIL-53(Al) | PSF | 8, 16, 25, 40 (25) | 2.0-(2.4) | 45-(117) | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | -10, 35 | 1, 3, 5, 7, 10, 13 |
| ZIF-7 | PBI | 10, 25, 50 (50) | - | - | - | - | 3.7-(26.2) | 8.7-(14.9) | Single gas $H_2$, $CO_2$ | 35 | 3.5 |
| | | | | | | | 75-(440)* | 8.5-(7.2)* | Gas mixture $H_2/CO_2$ (50:50) | 35, 60, 80, 120, 150, 180 | 7 |
| ZIF-8 + S1C | PSF | 16+0, 8+8 (16+0) | 4.6-(12.1) | 24.3-(19.8) | 5.9-(12.3) | 24.6-(19.5) | - | - | Gas mixture $CO_2/CH_4$ (50:50) $CO_2/N_2$ (50:50) | 35 | 2 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| HKUST-1 + S1C | | 16+0, 8+8 (8+8) | 4.6-(4.9) | 24.3-(22.4) | 5.9-(8.4) | 24.6-(38.0) | - | - | $O_2/N_2$ (50:50) $H_2/CH_4$ (50:50) | | |
| HKUST-1 | Matrimid® | 10, 20, 30 (30) | 10.0-(17.5)$^*$ (GPU) | 18.5-(23.0)$^*$ | 11.5-(19.5)$^*$ (GPU) | 18.0-(23.5)$^*$ | - | - | Gas mixture $CO_2/CH_4$ (10:90, 35:65, 75:25) $CO_2/N_2$ (10:90, 35:65, 75:25) | 35 | 10 |
| ZIF-8 | | | 10.0-(22.5)$^*$ (GPU) | 18.5-(19.5)$^*$ | 11.5-(20.0)$^*$ (GPU) | 18.0-(19.5)$^*$ | - | - | | | |
| MIL-53(Al) | | | 10.0-(20.0)$^*$ (GPU) | 18.5-(22.5)$^*$ | 11.5-(20.0)$^*$ (GPU) | 18.0-(23.0)$^*$ | - | - | | | |
| ZIF-8 | PPEEs | 10, 20, 30 (30) | 5.4-(50.0) | 22.9-(20.8) | 5.4-(50.0) | 30.1-(24.5) | 6.7-(92.3) | 1.3-(1.8) | Single gas $H_2$, $CO_2$, $O_2$, $N_2$, $CH_4$, $C_2H_4$, $C_2H_6$ | 10, 20, 30, 40 | 1 |
| ZIF-8 | 6FDA-DAM | 16.4, 28.7, 48 (48) | - | - | - | - | - | - | Single gas $C_3H_6$, $C_3H_8$ | 35 | 2 |
| | | | | | | | | | Gas mixture $C_3H_6/C_3H_8$ (50:50) | | 1.4, 2.8, 4.1, 5.5 |
| MIL-101(Cr) | PSF | 8, 16, 24 | - | - | - | - | - | - | Single gas $O_2$, $N_2$ | 30 | 3 |
| MOF-508a(Zn) | | 8 | - | - | - | - | - | - | | | |
| MIL-53(Al) | | | - | - | - | - | - | - | | | |
| MIL-100(Fe) | | | - | - | - | - | - | - | | | |
| MIL-53(Al) | 6FDA-ODA | 25 | 14.5-(21.0)$^*$ | 48.0-(44.0)$^*$ | - | - | - | - | Single gas $CO_2$, $CH_4$ | 35 | 10 |
| | | | 14.5-(21.0)$^*$ | 42.0-(42.5)$^*$ | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | | |
| $NH_2$-MIL-53(Al) | | 10, 15, 20, 25, 30, 32, 35 (32) | 14.5-(14.7)$^*$ | 48.0-(76.0)$^*$ | - | - | - | - | Single gas $CO_2$, $CH_4$ | | |
| | | | 14.5-(14.7)$^*$ | 42.0-(53.0)$^*$ | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | | |
| ZIF-8 | Ultem® | 10, 13 (13) | - | - | 14.0-(26.0) (GPU) | 30.0-(36.0) | - | - | Single gas $CO_2$, $N_2$ | 25, 30, 35, 45 | 6.7 |
| | | | - | - | (26.0)$^*$ (GPU) | (32.0) | - | - | Gas mixture $CO_2/N_2$ (20:80) | 25, 35, 45 | 2.1, 2.8, 3.4 |
| MIL-53(Al) | PMDA-ODA | 5 | 0.30-(0.21) (GPU) | 72.1-(50.5) | 0.30-(0.21) (GPU) | 34.8-(27.5) | 0.35-(0.42) (GPU) | 1.1-(2.0) | Single gas He, $H_2$, $CO_2$, $N_2$, $CH_4$ | 25 | 6 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| MOF-5 | | | 0.30-(0.27) (GPU) | 72.1-(56.8) | 0.30-(0.27) (GPU) | 34.8-(14.1) | 0.35-(0.24) (GPU) | 1.1-(0.9) | | | |
| HKUST-1 | | | 0.30-(0.32) (GPU) | 72.1-(73.6) | 0.30-(0.32) (GPU) | 34.8-(38.1) | 0.35-(0.44) (GPU) | 1.1-(1.3) | | | |
| ZIF-8 | Matrimid® | 10, 25 (25) | 10.7-(23.2) | 34-(39) | - | - | - | - | Single gas $CO_2$, $CH_4$ | 35 | 4.5 |
| ZIF-8 | Matrimid® | 5, 10, 20, 30, 40 (20, 30) | 8.1-(16.6) | 35.2-(35.8) | 8.1-(16.6) | 22.4-(19.0) | 32.7-(112.1) | 4.0-(3.9) | Single gas $H_2$, $CO_2$, $O_2$, $N_2$, $CH_4$ | 22 | 4 |
| UiO-66 | 6FDA-ODA | 25 | 14.4-(50.4) | 44.1-(46.1) | - | - | - | - | Single gas $CO_2$, $CH_4$ | 35 | 10 |
| | | | - | 41.7-(42.3) | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | | |
| $NH_2$-UiO-66 | | | 14.4-(13.7) | 44.1-(51.6) | - | - | - | - | Single gas $CO_2$, $CH_4$ | | |
| | | | - | 41.7-(44.7) | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | | |
| HKUST-1 | | | 14.4-(21.8) | 44.1-(51.2) | - | - | - | - | Single gas $CO_2$, $CH_4$ | | |
| | | | - | 41.7-(50.7) | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | | |
| $NH_2$-HKUST-1 | | | 14.4-(26.6) | 44.1-(59.6) | - | - | - | - | Single gas $CO_2$, $CH_4$ | | |
| | | | - | 41.7-(52.4) | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | | |
| UiO-67 | | | 14.4-(20.8) | 44.1-(15.0) | - | - | - | - | Single gas $CO_2$, $CH_4$ | | |
| | | | - | 41.7-(15.0) | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | | |
| ZIF-8 | PBI | 18, 20, 29, 34, 59 (29) | - | - | - | - | 3.7-(105.4) | 8.6-(12.3) | Single gas $H_2$, $CO_2$ | 25 | 3.5 |
| | PBI/ Matrimid® | 10, 20, 33 (10) | - | - | - | - | 2.1-(8.9) (GPU) | 6.2-(9.5) (GPU) | | | |
| | | 10, 20, 33 (10) | - | - | - | - | (65.4) (GPU) | (12.3) (GPU) | Gas mixture $H_2/CO_2$ (50:50) | 25, 80, 120, 150, 180 | 7 |
| ZIF-8 | 6FDA-DAM:DABA 4:1 | 20 | - | - | 211.4-(553) | 21.3-(19.3) | - | - | Single gas $CO_2$, $N_2$ | 30 | 1.4 |
| ZIF-8 | PBI | 30, 60 (30) | - | - | - | - | 4.1-(82.5) | 8.9-(12.0) | Single gas $H_2$, $CO_2$ | 35 | 3.5 |
| | | | - | - | - | - | (470) | (26.3) | Gas mixture $H_2/CO_2$ (50:50) | 35, 60, 120, 180, | 2 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | $H_2/CO_2/CO$ (49.5:49.5:1) | 230 | |
| ZIF-7 | Pebax® | 8, 22, 34 (22) | 72-(111) | 14-(30) | 72-(111) | 34-(97) | - | - | Single gas $CO_2$, $N_2$, $CH_4$ | 20 | 6.5 (2.75 for $CO_2$) |
| ZIF-8 | PIM-1 | 13.8, 24.2, 32.4, 39.0 (39.0) | 4390-(6300) | 14.2-(14.7) | 4390-(6300) | 24.4-(18.0) | 1630-(6680) | 0.4-(1.1) | Single gas He, $H_2$, $CO_2$, $O_2$, $N_2$, $CH_4$ | 20-22 | 1 |
| HKUST-1 | P84 | 20 | - | - | - | - | - | - | Gas mixture $C_2H_4$/ $C_2H_6$ (80:20) | - | 5, 10, 15 |
| FeBTC | | | - | - | - | - | - | - | | | |
| MIL-53(Al) | | | - | - | - | - | - | - | | | |
| HKUST-1 | P84 | 10, 20, 40 (20) | - | - | - | - | - | - | Gas mixture $C_2H_4$/ $C_2H_6$ (80:20) | - | 5, 10, 15 |
| ZIF-90 | PBI | 10, 25, 45 (45) | - | - | - | - | 4.1-(24.5) | 8.9-(25) | Single gas $H_2$, $CO_2$ | 35 | 3.5 |
| | | 45 | - | - | - | - | (226.9) | (13.3) | Gas mixture $H_2/CO_2$ (50:50) | 35, 60, 80, 120, 180 | 7 |
| HKUST-1 | PPO | 10, 20, 30, 40, 50 (40) | 68.7-(115)* | 16.4-(34)* | 68.7-(115)* | 16.0-(26)* | 75.0-(119)* | 1.1-(1.0)* | Single gas $H_2$, $CO_2$, $N_2$, $CH_4$ | 30 | - |
| ZIF-8 | 6FDA-durene | 33.3 | 468.5-(1552.9) | 15.6-(11.0) | 468.5-(1552.9) | 13.4-(11.3) | 518.5-(2136.6) | 1.1-(1.4) | Single gas $H_2$, $CO_2$, $O_2$, $N_2$, $CH_4$ | 35 | 3.5 |
| | 6FDA-durene (cross-linked) | | 0.4-(23.7) | (16.9) | 0.4-(23.7) | (11.9) | 52.1-(283.5) | 130.3-(12.0) | | | |
| $NH_2$-MIL-53(Al) | 6FDA:DSDA-4MPD:4,4’-SDA 1:1 | 0, 5, 10, 15 (15) | 57.9-(66.5) | 35.1-(36.9) | - | - | 90.1-(100) | 1.6-(1.8) | Single gas $H_2$, $CO_2$, $CH_4$ | 35 | 3 |
| | 6FDA-4MPD:4,4’-SDA 1:1 | 10 | 134-(137) | 30.2-(27.2) | - | - | 169-(175) | 1.3-(1.3) | | | |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $NH_2$-MIL-101(Al) | 6FDA:DSDA-4MPD:4,4'-SDA 1:1 | 0, 5, 10 (10) | 57.9-(70.9) | 35.1-(41.6) | - | - | 90.1-(114) | 1.6-(1.6) | | | |
| | 6FDA-4MPD:4,4'-SDA 1:1 | 10 | 134-(151) | 30.2-(29.6) | - | - | 169-(191) | 1.3-(1.3) | | | |
| $NH_2$-CAU-1 | PMMA | 5, 10, 15, 20, 25 (15) | - | - | - | - | 5000-(11000) | 3-(13) | Single gas $H_2$, $CO_2$ | RT | 3 |
| | | | - | - | - | - | - | 2-(10)* | Gas mixture $H_2$, $CO_2$ (-) | | |
| MIL-68(Al) | PSF | 4, 8 (8) | 5.4-(4.7) | 31.1-(36.5) | - | - | - | - | Gas mixture $CO_2$/$CH_4$ (50:50) | 35 | 2 |
| HKUST-1 | PLLA | 5 | - | - | - | - | - | - | - $CO_2$, $O_2$ | 23 | - |
| ZIF-8 | 6FDA-durene (400 °C) | 20 | 541-(1090) | 13.1-(13.0) | - | - | - | - | Single gas $CO_2$, $CH_4$, $C_3H_6$, $C_3H_8$ | 35 | 10 (3.5 for $C_3H_6$ and $C_3H_8$) |
| | 6FDA-durene:DABA 9:1 (200 °C) | 5, 10, 15, 20, 30, 40 (40) | 256-(779) | 19.5-(20.9) | - | - | - | - | | | |
| | 6FDA-durene:DABA 7:3 (400 °C) | 20 | 429-(698) | 26.0-(25.8) | - | - | - | - | | | |
| | 6FDA-durene:DABA 9:1 (400 °C) | 20, 40 (20) | 305-(728) | 13.8-(19.6) | - | - | - | - | Gas mixture $CO_2$/$CH_4$ (50:50) | 35 | 20 |
| $NH_2$-MIL-53(Al) | Matrimid® | 15 | 6.2-(9.2) | 31.0-(2.1) | - | - | - | - | Single gas $CO_2$, $CH_4$ | 35 | 10 |
| | | | - | 28.5-(2.1) | - | - | - | - | Gas mixture $CO_2$/$CH_4$ (50:50) | | |
| | Ultem® | 15 | 1.5-(3.0) | 39.5-(36.2) | - | - | - | - | Single gas $CO_2$, $CH_4$ | | |
| | | | - | 31.6-(36.1) | - | - | - | - | Gas mixture $CO_2$/$CH_4$ (50:50) | | |
| | 6FDA-ODA:DAM 1:1 | 15, 20, 22 (10) | 54.1-(51.2) | 23.5-(34.1) | - | - | - | - | Single gas $CO_2$, $CH_4$ | | |
| | | | - | 23.6-(31.8) | - | - | - | - | Gas mixture $CO_2$/$CH_4$ (50:50) | | |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| | 6FDA-ODA:DAM 1:4 | 10, 15, 20 (15) | 130.0-(113) | 23.2-(28.2) | - | - | - | - | Single gas $CO_2$, $CH_4$ | | |
| | | | - | 23.6-(28.5) | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | | |
| | 6FDA-ODA:DAM 1:1 (APTMDS) | 15, 20, 25, 30, 32, 35 (30) | 32.2-(58.5) | 18.9-(36.6) | - | - | - | - | Single gas $CO_2$, $CH_4$ | | |
| | | | - | 20.2-(33.9) | - | - | - | - | Gas mixture $CO_2/CH_4$ (10:90) $CO_2/CH_4$ (35:65) $CO_2/CH_4$ (50:50) $CO_2/CH_4$ (60:40) $CO_2/CH_4$ (80:20) $CO_2/CH_4$ (85:15) | 30, 35, 45, 60, 75 | 3.4-41 (10) |
| MIL-53 | Matrimid® | 15 | 6.2-(6.7) | 31.0-(9.4) | - | - | - | - | Single gas $CO_2$, $CH_4$ | 35 | 10 |
| | | | - | 28.5-(8.5) | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | | |
| | Ultem® | 15 | 1.5-(1.8) | 39.5-(43.1) | - | - | - | - | Single gas $CO_2$, $CH_4$ | | |
| | | | - | 31.6-(42.8) | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | | |
| | 6FDA-ODA:DAM 1:1 | 20 | 54.1-(61.5) | 23.5-(12.5) | - | - | - | - | Single gas $CO_2$, $CH_4$ | | |
| | | | - | 23.6-(13.0) | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | | |
| | 6FDA-ODA:DAM 1:4 | 25 | 130.0-(123) | 23.2-(18.1) | - | - | - | - | Single gas $CO_2$, $CH_4$ | | |
| | | | - | 23.6-(19.1) | | | | | Gas mixture $CO_2/CH_4$ (50:50) | | |
| | 6FDA-ODA:DAM 1:1 (APTMDS) | 25 | 32.2-(76.4) | 18.9-(8.9) | | | | | Single gas $CO_2$, $CH_4$ | | |
| | | | - | 20.2-(8.8) | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | | |
| TKL-107 | Matrimid® | 5, 10, 20, 30 (20) | 7-(17)* | 36-(64.6) | - | - | - | - | Single gas $CO_2$, $CH_4$ | 25 | 2 |
| | | | 6-(15)* | 24-(50.3) | - | - | - | - | Gas mixture $CO_2/CH_4$ (20:80) | | |
| CPO-27(Mg) | XLPEO | 10 | - | - | 380-(250) | 22-(25) | - | - | Single gas $CO_2$, $N_2$ | 25 | 2 |
| | 6FDA-TMPDA | 10 | - | - | 650-(850) | 14-(23) | - | - | | | |
| | PDMS | 20 | - | - | 3100-(2100) | 9.5-(12) | - | - | | | |
| Silica-(ZIF-8) core-shell | PSF | 8, 12, 16, 20, 32 (32) | 11.8-(73.1)* | 10.2-(5.5)* | - | - | 35.0-(224.1)* | 3.4-(3.9)* | Gas mixture $H_2/CO_2$ (50:50) $CO_2/CH_4$ (10:90, 50:50, 90:10) | 35, 60, 90,120, 150 | 2 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | 35, 60, 90, 120 | |
| ZIF-8 | Pebax® | 5, 10, 15, 20, 25, 30, 35 (35) | 351-(1287) | 8.3-(9.0) | 351-(1287) | 33.8-(32.3) | - | - | Single gas $CO_2$, $O_2$, $N_2$, $CH_4$ | RT | 2, 6 |
| | | 5, 10, 15, 20, 25, 30, 35, 40, 50 (25) | - | - | 200-(900)* | 66-(53)* | - | - | Gas mixture $CO_2/N_2$ (10:90) | 25 | 1.5 |
| MIL-53 | Matrimid® | 5, 10, 15, 20 (15) | 6.4-(12.4) | 28.2-(51.8) | - | - | - | - | Single gas $CO_2$, $CH_4$ | 35 | 3 |
| ZIF-8 | PSF | 8 | - | - | - | - | - | - | Gas mixture $H_2/CH_4$ (50:50) $O_2$/ $N_2$ (50:50) | 35 | 2 |
| $NH_2$-MIL-53(Al) | | | - | - | - | - | - | - | | | |
| [$Cd_2$6FDA($H_2O$)]$_2$5 $H_2O$ | 6FDA-ODA | 10 | 20.6-(37.8) | 33.1-(44.8) | 20.6-(37.8) | 26.4-(35.1) | - | - | Single gas $CO_2$, $N_2$, $CH_4$ | 25 | 2 |
| MIL-53(Al) | PMP | 5, 10, 15, 20, 25, 30, 35, 40 (30) | - | - | - | - | 100-(365)* | 0.11-(0.04) | Single gas $H_2$, $CO_2$ | 30 | 2, 4, 6, 8 |
| ZIF-8 | 6FDA-Durene | 3, 5, 7, 10, 15, 20, 30 (30) | 1468.3-(2185.5) | 22.6-(17.1) | 1468.3-(2185.5) | 25.4-(17.0) | - | - | Single gas $CO_2$, $O_2$, $N_2$, $CH_4$ | RT | 2, 6 |
| | | | - | - | - | - | - | - | Gas mixture $CO_2/N_2$ (10:90) | 25 | 1.5 |
| $NH_2$-MIL-53(Al) + MSSs | PSF | 16+0, 12+4, 8+8, 4+12 (4+12) | - | - | - | - | - | - | Gas mixture $O_2/N_2$ (50:50) $H_2/CH_4$ (50:50) | 35 | 2 |
| $NH_2$-MIL-53(Al) + MSSs | Matrimid® | 8+8, 4+12 (4+12) | - | - | - | - | - | - | | | |
| $NH_2$-MIL-53(Al) | Matrimid® | 15, 20, 25 (25) | 4.8-(3.9) | 100-(107) | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | 0, 25, 35 | 3, 5, 9, 12 |
| | PSF | 15, 20, 25 (25) | 5.2-(5.4) | 23.0-(27.5) | - | - | - | - | | 35 | 3 |
| $NH_2$-MIL-101(Al) | Matrimid® | 8, 15, 25 (25) | 4.8-(3.0) | 100-(98) | - | - | - | - | | 0, 25, 35 | 3, 5, 9, 12 |
| | PSF | 8, 15, 25 (25) | 5.2-(8.4) | 23.0-(28.5) | - | - | - | - | | 35 | 3 |
| ZIF-8 | 6FDA-DAM | 17, 30 (17) | - | - | - | - | - | - | Single gas $O_2$, $N_2$ | 35 | 2 |
| | | | | | | | | | Gas mixture $C_3H_6$, $C_3H_8$ (50:50) | | 1.4 |
| ZIF-8 | Matrimid® | 15 | 9-(26)* | 34.5-(35)* | - | - | - | - | Single gas $CO_2$, $CH_4$ | 35 | 3.45 |
| ZIF-7-8-(20) | | | 9-(20)* | 34.5-(35.5)* | - | - | - | - | | | |
| ZIF-8-ambz-(15) | | | 9-(12)* | 34.5-(36)* | - | - | - | - | | | |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ZIF-8-ambz-(30) | | | 9-(11)* | 34.5-(38.5)* | - | - | - | - | | | |
| ZIF-7-8-(20) | | | 8-(19)* | 43-(41)* | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | - | 6.9, 13.8, 27.6, 41.4 |
| ZIF-8-ambz-(15) | | | 8-(14)* | 43-(40)* | - | - | - | - | | | |
| ZIF-8-ambz-(30) | | | 8-(11)* | 43-(42.5)* | - | - | - | - | | | |
| FeBTC | Matrimid® | 10, 20, 30 | 14-(14)* | 55-(35)* | - | - | - | - | Single gas $CO_2$, $CH_4$ | 35 | 2-40 (40) |
| | | | 14-(8.2)* | 22-(28)* | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | - | 5 |
| ZIF-8 | PBI-BuI | 10, 20, 30 (30) | 2.3-(5.2) | 57.0-(43.6) | 2.3-(5.2) | 26.8-(16.0) | 6.2-(22.1) | 2.7-(4.2) | Single gas He, $H_2$, $CO_2$, $N_2$, $CH_4$ | 35 | 20 |
| | DMPBI-BuI | 10, 20, 30 (30) | 3.8-(53.9) | 47.2-(15.7) | 3.8-(53.9) | 21.7-(11.3) | 12.8-(127.5) | 3.4-(2.4) | | | |
| | DBzPBI-BuI | 10, 20 (20) | 25.8-(89.8) | 15.9-(11.6) | 25.8-(89.8) | 12.9-(14.3) | 61.4-(180.3) | 2.4-(2.0) | | | |
| $NH_2$-MIL-53(Al) | PMP | 5, 10, 15, 20, 25, 30, 35, 40 (30) | 96.5-(358.2) | 8.8-(24.4) | - | - | - | - | Single gas $CO_2$, $CH_4$ | 30 | 2, 4, 6, 8 |
| | | | 80.1-(339.5) | 8.1-(22.9) | - | - | - | - | Gas mixture $CO_2/CH_4$ (10:90) | | |
| MIL-53(Al)-ht | Matrimid® | 33.3, 37.5 (37.5) | 8.4- (51) | 39.4- (47.0) | 8.4- (51) | 33.6- (28.3) | 25.7-(103) | 3.1- (2.0) | Single gas $H_2$, $CO_2$, $O_2$, $N_2$, $CH_4$ | 35 | 2 |
| MIL-53(Al)-as | | 37.5 | 8.4- (40) | 39.4- (90.1) | 8.4- (40) | 33.6- (95.2) | 25.7-(66.0) | 3.1- (1.7) | | | |
| c-MOF-5 | PEI | 5, 15, 25 (25) | 1.7- (5.4) | 18.7- (23.4) | 1.7- (5.4) | 16.8- (28.4) | 10.1-(28.3) | 6.0- (5.3) | Single gas $H_2$, $CO_2$, $N_2$, $CH_4$ | 25 | 6 |
| HKUST-1 | Ultem® | 10, 20, 30, 35, 40 (35) | 1.1- (4.1) | 36.8- (34.0) | 1.1-(4.1)* | 28.0-(28.0)* | - | - | Single gas $CO_2$, $O_2$, $N_2$, $CH_4$ | 35 | 3.5 |
| HKUST-1 | ODPA-DAM (annealed 200 °C 24 h) | 10, 15, 20, 30, 40, 50 (40) | 47.7-(260.7) | 29-(28)* | - | - | - | - | Single gas $CO_2$, $O_2$, $N_2$, $CH_4$ | 35 | 2 |
| | Matrimid® (annealed 200 °C 24 h) | 20 | 7.6-(24.8) | 37.5-(37.8) | - | - | - | - | | | |
| ZIF-8 | ODPA-DAM (annealed 200 °C 24 h) | | 47.7-(134)* | 29-(26)* | - | - | - | - | | | |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| ZIF-71 | 6FDA-durene | 10, 20, 30 (20) | 959-(4006) | 16.4-(12.8) | 959-(4006) | 14.7-(12.9) | 756-(2310) | 0.8-(0.6) | Single gas $H_2$, $CO_2$, $O_2$, $N_2$, $CH_4$, $C_2H_4$, $C_2H_6$, $C_3H_6$, $C_3H_8$ | 35 | 3.5 (2 for $C_2H_4$, $C_2H_6$, $C_3H_6$ and $C_3H_8$) |
| | | 10, 20, 30 (20) | 917-(3435) | 21.8-(16.0) | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | 35 | 7 |
| [$Cu_2(Glu)_2$(μ-bpa)]·($CH_3CN$) | POZ | 5, 10, 15, 20 (15) | - | - | 28-(11.6)* | 1-(55)* | - | - | Single gas $CO_2$, $N_2$ | - | 3.1 |
| [$Cu_2(Glu)_2$(μ-bpp)]·($C_3H_6O$) | | | - | - | 28-(16.0)* | 1-(7)* | - | - | | | 0.4 |
| MIL-53(Al) | Matrimid® | 10, 20, 30 (30) | 14-(24)* | 55-(66)* | - | - | - | - | Single gas $CO_2$, $CH_4$ | 35 | 2.5, 5, 7.5, 10, 12.5, 15, 20, 25, 30, 40 |
| ZIF-8 | | | 14-(24)* | 55-(72)* | - | - | - | - | | | |
| HKUST-1 | | | 14-(18)* | 55-(52)* | - | - | - | - | | | |
| MIL-53(Al) | | | 9-(18)* | 5-(40)* | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | | 2.5, 5, 7.5, 10, 15, 20 |
| ZIF-8 | | | 9-(20)* | 5-(37)* | - | - | - | - | | | |
| HKUST-1 | | | 9-(14)* | 5-(46)* | - | - | - | - | | | |
| ZIF-11 | PSF | 4.7 | - | - | - | - | - | - | - | - | - |
| | PES | 4.7 | - | - | - | - | - | - | | | |
| | PBI | 16.1, 29.7, 39.5 (39.5) | - | - | - | - | 17.2-(464.7) | 5.0-(3.6) | Single gas $H_2/CO_2$ | RT | - |
| b-Cu 1,4-BDC | Matrimid® | 8 | 5.8-(5.2) | 59.8-(45) | - | - | - | - | Gas mixture $CO_2/CH_4$ (50:50) | 25 | 3, 4.5, 6, 7.5 |
| nc-Cu 1,4-BDC | | 8 | 5.8-(5.0) | 59.8-(49.4) | - | - | - | - | | | |
| ns-Cu 1,4-BDC | | 2, 4, 8 (8) | 5.9-(2.8) | 47.7-(88.2) | - | - | - | - | | | 3, 4.5, 6, 7.5 |
| ns-Cu 2,6-NDC | | 8 | 5.8-(6.3) | 59.8-(43.5) | - | - | - | - | | | 3 |
| ZIF-8 100 nm | PSF | 5 | 25.7-(15.6) (GPU) | 19.4-(28.5) | - | - | - | - | Single gas $CO_2$, $CH_4$ | 27 | 4 |
| ZIF-8 300 nm | | | 25.7-(25.9) (GPU) | 19.4-(5.8) | - | - | - | - | | | |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ZIF-8 500 nm | | | 25.7-(28.1) (GPU) | 19.4-(5.8) | - | - | - | - | | | |
| ZIF-8 | PDMS | 2.5, 5, 10, 15, 20 | - | - | - | - | - | - | Single gas $C_3H_8$, $N_2$ | - | 1.5 |
| | | | - | - | - | - | - | - | Gas mixture $C_3H_8/N_2$ (10:90, 20:80, 30:70, 40:60) | 20, 27, 35, 45, 55 | 0.5, 1.5, 2.5, 3.5, 4.5 |

Results with * are calculated from graphs.