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Supplementary Information

Mixed-Matrix Membranes for CO_2 Separation: Role of the Third Component

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Table S1. Summary of the reported MMMs containing small molecules as the third component for CO_2 separation. The literatures are ordered chronologically in each category (ILs, Organic silanes, Metal ions, and other small molecules).

Filler	Polymer	The third component	Loading of filler	Loading of the third component	Feed gas	Operation conditions	CO_2 permeability (Barrer)	CO_2/CH_4 selectivity	CO_2/N_2 selectivity	CO_2/H_2 selectivity	Methodology	Role of the third component	Published year and ref.
SAPO-34	poly(vinyl-IL)	[emim][TF$_2$N]	10 wt%	0	CO_2, CH_4, N_2	23 °C, 0.1 MPa	13.9	35	35	-	Direct physical blending	Eliminating interfacial voids	2010[58]
			10 wt%	18 wt%			72	30	44	-			
ZSM-5	6FDA-Durene	[bmim][TF$_2$N]	15 wt%	0	CO_2, CH_4, N_2	35 °C, 0.1 MPa	1492	7.4	9.1	-	Direct physical blending	Eliminating interfacial voids	2014[59]
			15 wt%	9 wt%			441	21.1	18.5	-			
EST-10	Chitosan	[emim][Ac]	5 wt%	0	CO_2, N_2	25 °C, 0.5 MPa	~120	-	~4	-	Direct physical blending	1. Eliminating interfacial voids; 2. Increasing CO_2 solubility	2014[60]
			5 wt%	5 wt%			~220	-	~12	-			
SAPO-34	PES	[emim][TF$_2$N]	20 wt%	0	CO_2, CH_4	RT, 3.0 MPa	85.7 (GPU)	20.7	-	-	Direct physical blending	1. Eliminating interfacial voids; 2. Increasing CO_2 solubility	2014[61]
			20 wt%	20 wt%			300 (GPU)	62.6	-	-			
ZIF-8	PSF	[bmim][Tf$_2$N]	6 vol%	0	CO_2/CH_4 (50/50), CO_2/N_2 (50/50)	30 °C, 0.6 MPa	420 (CO_2/CH_4) 464 (CO_2/N_2)	19.1	29.7	-	Encapsulation	1. Reducing effective cage size; 2. Increasing CO_2 solubility	2015[64]
			6 vol% (composite)	1.4 ILs per SOD cage			311 (CO_2/CH_4) 350 (CO_2/N_2)	38.3	116	-			
ZIF-8	Pebax 1657	[bmim][Tf$_2$N]	15 wt%	0	CO_2, CH_4, N_2, H_2	25 °C, 0.1 MPa	128	19.5	39.5	8.3	Encapsulation	1. Eliminating interfacial voids; 2. Reducing effective pore size; 3. Improving mechanical properties	2016[65]
			15 wt% (composite)	~16.5 wt% of composite			104.9	34.8	83.9	9.8			
NH_2-MIL-101(Cr)	PIM-1	[C$_3$NH$_2$bim][Tf$_2$N]	5 wt%	0	CO_2, N_2	25 °C, 0.3 MPa	3200	-	17.5	-	Encapsulation	1. Increasing CO_2 solubility; 2. Increasing CO_2 diffusion selectivity	2016[66]
			5 wt% (composite)	NA			2979	-	37.2	-			
HKUST-1	6FDA-Durene	[emim][TF$_2$N]	10 wt%	0	CO_2, CH_4, N_2	25 °C, 0.2 MPa	1310	19	17.5	-	Filler surface modification	Eliminating interfacial voids	2016[67]
			10 wt% (composite)	13.8 wt% of HKUST-1			1100	28.5	27	-			
ZIF-8	Pebax 1657	[bmim][NTf$_2$]	15 wt%	0	CO_2, CH_4, N_2	23 °C, 0.1 MPa	~107	16.5	35	-	Direct physical blending	1. Eliminating interfacial voids; 2. Increase fractional free volume	2017[62]
			15 wt%	10 wt%			~120	17	42.1	-			
Ag NPs	Pebax 1657	[bmim][BF$_4$]	0.5 wt%	0	CO_2, CH_4, N_2	35 °C, 1.0 MPa	220	36.7	118.9	-	Direct physical blending	1. Eliminating interfacial voids; 2. Increasing CO_2 solubility	2017[63]
			0.5 wt%	50 wt%			180	61	187.5	-			
SAPO-34	PSF	[emim][TF$_2$N]	5 wt%	0	CO_2, CH_4, N_2	25 °C, 0.375 MPa	6.53 (GPU)	3.47	5.67	-	Filler surface modification	1. Eliminating interfacial voids; 2. Increasing CO_2 solubility	2017[68]
			5 wt% (composite)	0.361 wt% of composite			7.24 (GPU)	20.35	18.82	-			
ZIF-8	Pebax 1657	[DnBM][Cl]	8 wt%	0	CO_2, CH_4, N_2	30 °C, 0.2 MPa	288	21	41	7	Polymer modification with IL	Eliminating interfacial voids	2017[71]
			8 wt%	NA			261	36	71	10			

Table S1. (*continued*)

Filler	Polymer	The third component	Loading of filler	Loading of the third component	Feed gas	Operation conditions	CO_2 permeability (Barrer)	CO_2/CH_4 selectivity	CO_2/N_2 selectivity	CO_2/H_2 selectivity	Methodology	Role of the third component	Published year and ref.
GO	Pebax 1657	1-(3-aminopropyl)-3-methylimidazolium bromide	0.2 wt%	0	CO_2, CH_4, N_2, H_2 CO_2/H_2 CO_2/N_2 (30/70)	25 °C, 0.4 MPa	88 (single gas)	-	44 (single gas)	8.0 (single gas)	Filler surface modification	1. Eliminating interfacial voids; 2. Facilitating CO_2 transport	2018[69]
			0.2 wt% (composite)	NA			143 (single gas) 118.6 (gas mixture)	-	79.4 (single gas) 71 (gas mixture)	13.8 (single gas) 9.5 (gas mixture)			
Zeolite 4A	PSF	[APTMS][Ac]	30 wt%	0	CO_2/CH_4, CO_2/N_2	25 °C, 1.0 MPa	~16.5 (CO_2/CH_4) ~17.5 (CO_2/N_2)	~18.5	~19.5	-	Filler surface modification	1. Eliminating interfacial voids; 2. Increasing CO_2 solubility	2018[70]
			30 wt%	NA			~14.5 (CO_2/CH_4) ~15 (CO_2/N_2)	~30	~34	-			
SAPO-34	PSF	[bmim][Ac]	5 wt%	0	CO_2, N_2	30 °C, 0.35 MPa	13 (GPU)	-	~4.3	-	MMMs post-impregnated in IL solution	Eliminating interfacial voids	2018[72]
			5 wt%	3.95 wt%			2 (GPU)	-	39.6	-			
Zeolite 4A	PES	APDEMS	20 wt%	0	CO_2, CH_4	35 °C, 1.0 MPa	~1.45	28	-	-	Filler surface modification	Reducing pore blockage	2006[33]
			20 wt%	NA			~1.75	30.5	-	-			
MIL-53(Al)	Ultem® 1000	APTMS	10 wt%	0	CO_2, N_2	25 °C, 0.5 MPa	22.5 (GPU)	-	24.5	-	Filler modification	1. Improving filler distribution; 2. Eliminating interfacial voids; 3. Increasing CO_2 solubility	2016[73]
			10 wt%	NA			24.1 (GPU)	-	41.1	-			
Montmorillonite	Polyvinylamineacid	APTES	~57 wt%	~38 wt%	CO_2/N_2 (15/85), CO_2/CH_4 (10/90), CO_2/H_2 (40/60)	50 °C, 0.11-3.0 MPa	~820 (GPU)	140	125	80	Filler modification	Collaboratively control filler orientation	2016[74]
TiO_2	Pebax 1657	APDEMS	3 wt%	0	CO_2, N_2	25 °C, 2.0 MPa	~148	-	~74	-	Filler surface modification	1. Eliminating interfacial voids; 2. Increasing CO_2 solubility	2017[75]
			3 wt%	~5.6 wt% of filler			188.6	-	84.9	-			
ZIF-8	Pebax 1657	APTES	40 wt%	0	CO_2, CH_4	35 °C, 0.5 MPa	~950	10.6	-	-	Filler surface modification	Eliminating interfacial voids	2017[76]
			40 wt%	NA			~910	16	-	-			
GO	Pebax 1657	APTES	0.9 wt%	0	CO_2/CH_4 (30/70), CO_2/N_2 (20/80)	35 °C, 0.2 MPa, humid condition	630	20.5	43.5	-	Filler surface modification	1. Eliminating interfacial voids; 2. Facilitating CO_2 transport	2019[77]
			0.9 wt%	NA			934.3	40.9	71.1	-			
POSS® Octa Amic Acid	Matrimid® 5218	Zn^{2+}	20 wt%	0	CO_2, CH_4, N_2	35 °C, 1.0 MPa	5.3	37.2	27.9	-	Membrane ion binding	1. Reducing effective pore size; 2. Facilitating CO_2 transport	2010[78]
			20 wt%	NA			3.4	62.8	30.9	-			
ZIF-108	PSF	Co^{2+}	0.5 wt%	0	CO_2/CH_4 (50/50), CO_2/N_2 (50/50)	25 °C, 0.5 MPa	~26	~8	~5.5	-	Partial ion substitution	Increasing CO_2 solubility	2014[80]
			0.5 wt%	Co/Zn = 0.06/0.94			~170	~13	~11.4	-			

Table S1. (*continued*)

Filler	Polymer	The third component	Loading of filler	Loading of the third component	Feed gas	Operation conditions	CO_2 permeability (Barrer)	CO_2/CH_4 selectivity	CO_2/N_2 selectivity	CO_2/H_2 selectivity	Methodology	Role of the third component	Published year and ref.
PDA NPs	Pebax 1657	Ag^+	10 wt%	0	CO_2, CH_4	30 °C, 0.2 MPa	94.6	17.6	-	-	Ion chelating	Facilitating CO_2 transport	2015[79]
			10 wt%	18.5 wt% of filler			150	25.9	-	-			
UiO-66	PIM-1	Ti^{4+}	5 wt%	0	CO_2, N_2	25 °C, 0.2 MPa	5340	-	20.2	-	Partial ion substitution	Increasing CO_2 solubility	2015[81]
			5 wt%	NA			13540	-	20.5	-			
PVI@CNT	Matrimid® 5218	Zn^{2+}	7 wt%	0	CO_2/CH_4 (30/70)	30 °C, 0.2 MPa	~5.5	~41.5	-	-	Ion chelating	Facilitating CO_2 transport	2016[82]
			7 wt%	NA			~11.6	~70	-	-			
PVI@CNT	Matrimid® 5218	Cu^{2+}	7 wt%	0	CO_2/CH_4 (30/70)	30 °C, 0.2 MPa	~5.5	~41.5	-	-	Ion chelating	Facilitating CO_2 transport	2016[83]
			7 wt%	NA			~10.4	~46.8	-	-			
PDA-GO	Pebax 1657	Zn^{2+}	1 wt%	0	CO_2/CH_4 (30/70)	30 °C, 0.2 MPa	~93	~23	-	-	Ion chelating	Facilitating CO_2 transport	2017[84]
			1 wt%	34.2 wt% of filler			137.9	28.8	-	-			
ZIF-8	Pebax 2533	Ni^{2+}	10 wt%	0	CO_2/N_2 (20/80)	25 °C, 0.2 MPa	266	-	33.8	-	*In-situ* synthesize Ni-Zn-ZIF-8	Increasing CO_2 solubility	2018[85]
			10 wt%	Ni/Zn=1/12			321	-	42.8	-			
SAPO-34	PES	2-Hydroxy 5-Methyl Aniline	20 wt%	0	H_2, CO_2, CH_4	35 °C, 0.3 MPa	5.77	37.0	-	2.24 (H_2/CO_2)	Direct physical blending	1. Eliminating interfacial voids; 2. Stiffening polymer matrix	2012[86]
			20 wt%	10 wt%			1.34	44.7	-	3.96 (H_2/CO_2)			
ZSM-5	6FDA-Durene	Liquid Sulfolane	15 wt%	0	CO_2, CH_4, N_2, H_2	35 °C, 0.2 MPa	1492	7.3	9.1	1.3	Direct physical blending	Eliminating interfacial voids	2013[87]
			15 wt%	31 wt%			101	18.0	27.2	2.1			
GO	Ultem® 1000	Ethylenediamine	0.75 wt%	0	CO_2, CH_4	25 °C, 1.0 MPa	1.926	58.4	-	-	Filler surface modification	1. Eliminating interfacial voids; 2. Increasing CO_2 solubility; 3. Facilitating CO_2 transport	2014[92]
			0.75 wt%	NA			1.570	142.7	-	-			
CMS	PES	Diethanolamine	30 wt%	0	CO_2, CH_4	25 °C, 1.0 MPa	44.69 (GPU)	11.1	-	-	Direct physical blending	1. Increasing CO_2 solubility 2. Facilitating CO_2 transport	2015[88]
			30 wt%	15 wt%			106.65 (GPU)	51.39	-	-			
ZIF-90	Matrimid® 5218	Ethylenediamine	21 wt%	0	H_2/CO_2 (50/50)	25 °C, 0.2 MPa	6	-	-	5.0 (H_2/CO_2)	Blending and covalently bonding	1. Reducing effective pore size; 2. Stiffening polymer matrix	2015[89]
			21 wt%	0.05625 wt% of filler			2	-	-	9.5 (H_2/CO_2)			
UiO-66-NH_2	Matrimid® 5218	Phenyl acetyl	23 wt%	0	CO_2, N_2	RT, 0.24 MPa	~24	-	~36.3	-	Filler surface modification	Eliminating interfacial voids	2015[93]
			23 wt%	2-6% of filler			~29	-	~37	-			
MWCNTs-NH_2	Pebax 1657	Glycerol triacetate	1 wt%	0	H_2, CO_2, CH_4, N_2	35 °C, 0.7 MPa	202	~16.5	~51.8	~10	Direct physical blending	1. Improve filler distribution; 2. Increasing fractional free volume	2017[90]
			1 wt%	25 wt%			1408	~14	~39	~13			
Zeolite Y	Matrimid® 5218	Co^{2+}-diamine-diketone complex	15 wt%	0	CO_2, CH_4	35 °C, 0.2 MPa	17.52	43.3	-	-	Encapsulation	1. Reducing effective pore size; 2. Increasing CO_2 diffusion selectivity	2018[91]
			15 wt%	NA			18.96	111.7	-	-			

Table S1. (*continued*)

Filler	**Polymer**	**The third component**	**Loading of filler**	**Loading of the third component**	**Feed gas**	**Operation conditions**	**CO_2 permeability (Barrer)**	**CO_2/CH_4 selectivity**	**CO_2/N_2 selectivity**	**CO_2/H_2 selectivity**	**Methodology**	**Role of the third component**	**Published year and ref.**
UiO-66-NH_2	Polynorborne ne	Norbornene	0	0	CO_2, H_2, N_2	30 °C, 0.3 MPa	16.4	-	-	3.3 (H_2/CO_2)	Filler surface modification	1. Eliminating interfacial voids; 2. Improving mechanical properties	2018[94]
			50 wt%	NA			31.2	-	-	6.8 (H_2/CO_2)			
UiO-66-NH_2	PIM-1	4-cyanobenzoyl chloride	20 wt%	0	CO_2, N_2 CO_2/N_2 (50/50)	25 °C, 0.14 MPa	8619.5 (Single gas)	-	18.0 (Single gas)	-	Filler modification	Reducing pore blockage	2019[95]
			20 wt%	NA			16121.3 (Single gas) 12063.3 (CO_2/N_2)	-	27.0 (Single gas) 53.5 (CO_2/N_2)	-			

Table S2. Summary of the reported MMMs containing macromolecules as the third component for CO_2 separation. The literatures are ordered chronologically in each category (PEG, PDA, PEI, and other macromolecules).

Filler	Polymer	The third component	Loading of filler	Loading of the third component	Feed gas	Operation conditions	CO_2 permeability (Barrer)	CO_2/CH_4 selectivity	CO_2/N_2 selectivity	CO_2/H_2 selectivity	Methodology	Role of the third component	Published year and ref.
MWCNT	PIM-1	PEG 200	1 wt%	0	CO_2, CH_4, N_2	27 °C, 0.2 MPa	6130	8.1	16.3	-	Filler surface modification	1. Improving filler distribution; 2. Eliminating interfacial voids; 3. Increasing CO_2 solubility	2012[99]
			1 wt%	~2 wt% of filler			7090	10.4	33.0	-			
MWCNT	PIM-1	PEG 200	1 wt%	0	CO_2, CH_4, N_2	30 °C, 0.2 MPa	6219	8.2	17.2	-	Filler surface modification	1. Improving filler distribution; 2. Increasing CO_2 solubility	2013[100]
			1 wt%	NA			7813	9.9	18.7	-			
GO	Ultem® 1000	PEG 400	0.75 wt%	0	CO_2, CH_4	25 °C, 1.0 MPa	1.926	58.4	-	-	Filler surface modification	1. Eliminating interfacial voids; 2. Increasing CO_2 solubility	2014[92]
			0.75 wt%	NA			1.197	74.8	-	-			
Mesoporous TiO_2	PVC-*g*-POEM	Amino silane-PEGDE	20 wt%	0	CO_2, N_2	35 °C, ~0.1 MPa	127.35	-	17.7	-	Filler surface modification	1. Increasing CO_2 solubility; 2. Eliminating interfacial voids	2014[101]
			20 wt%	15 wt% of filler			79.33	-	41.1	-			
ZSM-5	Matrimid® 5218	PEG 200	5 wt%	0	CO_2, CH_4	35 °C, 1.0 MPa	8.63	53.9	-	-	Direct physical blending	1. Eliminating interfacial voids; 2. Increasing CO_2 solubility	2015[96]
			5 wt%	5 wt%			11.53	60.1	-	-			
NaX	Pebax 1657	PEG 200	10 wt%	0	CO_2, CH_4	25 °C, 0.8 MPa	57	27	-	-	Direct physical blending	1. Increasing fractional free volume; 2. Increasing CO_2 solubility	2015[98]
			10 wt%	30 wt%			95	45	-	-			
GO	Pebax 1657	PEGME 5000	10 wt%	0	CO_2, CH_4, N_2	30 °C, 0.2 MPa, humid condition	~255	~25	~59	-	Filler surface modification	Increasing CO_2 solubility	2015[102]
			10 wt%	NA			~720	~27	~64	-			
UiO-66-NH_2	Polyactive	PEGMA Mw=475	20 wt%	0	CO_2, N_2	35 °C, 0.3 MPa	5870	-	2.1	-	Filler surface modification	1. Improving filler distribution; 2. Eliminating interfacial voids; 3. Increasing CO_2 diffusion selectivity	2017[103]
			20 wt%	46.5 wt% of filler			329	-	47	-			
ZIF-8	Matrimid® 5218	PEG 200	30 wt%	0	CO_2/CH_4 (50/50)	25 °C, 0.8 MPa	31.5	10.7	-	-	Direct physical blending	Increasing CO_2 solubility	2019[97]
			30 wt%	4 wt%			33.1	15.4	-	-			
UiO-66-NH_2	PVAm	PEGDE	28.5 wt%	0	CO_2/N_2 (15/85)	25 °C, 0.3 MPa, humid condition	989 (GPU)	-	81	-	Filler surface modification	Eliminating interfacial voids	2019[104]
			28.5 wt%	NA			1295 (GPU)	-	91	-			
ZIF-8	TBDA2-6FDA-PI	PDA	30 wt%	0	CO_2, H_2, CH_4, N_2	35 °C, 0.1 MPa	1437	16	12	1.8 (H_2/CO_2)	Filler surface coating modification	Eliminating interfacial voids	2016[109]
			30 wt%	1-2 nm thick coating			1056	20	14	1.8 (H_2/CO_2)			
ZIF-8	Pebax 4033	PDA	15 wt%	0	CO_2, N_2	25 °C, 0.1 MPa	170	-	44.9	-	Filler surface coating modification	1. Eliminating interfacial voids; 2. Facilitating CO_2 transport	2016[110]
			15 wt%	~8.3 wt% of filler			220	-	56.1	-			

Table S2. (*continued*)

Filler	Polymer	The third component	Loading of filler	Loading of the third component	Feed gas	Operation conditions	CO_2 permeability (Barrer)	CO_2/CH_4 selectivity	CO_2/N_2 selectivity	CO_2/H_2 selectivity	Methodology	Role of the third component	Published year and ref.
MCM-41	Pebax 1657	PEI	20 wt%	0	CO_2, CH_4, N_2	25 °C, 0.2 MPa, humid condition	752	19	52	-	Impregnation	1. Facilitating CO_2 transport; 2. Eliminating interfacial voids	2014[122]
			20 wt%	~50 wt% of filler			1521	41	102	-			
TiO_2	SPEEK	PDA-PEI	15 wt%	0	CO_2, CH_4, N_2	25 °C, 0.1 MPa, humid condition	565	23	38	-	Filler surface modification	1. Facilitating CO_2 transport; 2. Eliminating interfacial voids	2014[114]
			15 wt%	13.23 wt% (PDA) and 4.12 wt% (PEI) of filler			1629	58	64	-			
GO	Pebax 1657	PEI	10 wt%	0	CO_2, CH_4, N_2	30 °C, 0.2 MPa, humid condition	~255	~25	~59	-	Filler surface modification	1. Increasing CO_2 solubility; 2. Facilitating CO_2 transport	2015[102]
			10 wt%	38 wt% of filler			~1090	~32	~104	-			
MIL-101(Cr)	SPEEK	PEI	40 wt%	0	CO_2/CH_4 (30/70), CO_2/N_2 (10/90)	25 °C, 0.1 MPa, humid condition	~1580 (CO_2/CH_4) ~1530 (CO_2/N_2)	29	37.5	-	Impregnation	1. Eliminating interfacial voids; 2. Facilitating CO_2 transport	2015[119]
			40 wt%	22 wt% of filler			~2350 (CO_2/CH_4) ~2450 (CO_2/N_2)	69	78	-			
SiO_2	Cross-linked PEG	PDA-PEI	5 wt%	0	CO_2, N_2	35 °C, 0.35 MPa	~1600 (GPU)	-	15.4	-	Co-deposition on filler surface with PDA	1. Facilitating CO_2 transport; 2. Eliminating interfacial voids	2016[115]
			5 wt%	NA			1290 (GPU)	-	27	-			
CAU-1	XLPEO	PEI	30 wt%	0	CO_2/CH_4 (50/50)	35 °C, 0.3 MPa	7450	9.8	-	-	Filler surface modification	1. Improving filler distribution; 2. Facilitating CO_2 transport	2018[126]
			30 wt%	NA			546	27.8	-	-			
ZIF-8	PVAm	PEI	16.7 wt%	0	CO_2/CH_4 (10/90), CO_2/N_2 (15/85)	25 °C, 0.3 MPa	~1136 (GPU)	28.0	65.0	-	In situ grafting modification during ZIF-8 synthesis	1. Eliminating interfacial voids; 2. Increasing CO_2 solubility	2018[127]
			16.7 wt%	NA			~1890 (GPU)	40.7	79.9	-			
TiO_2	Pebax 1657	PDA-PEI	3 wt%	0	CO_2, N_2	20 °C, 0.3 MPa	126	-	63	-	Co-deposition on filler surface with PDA	1. Facilitating CO_2 transport; 2. Eliminating interfacial voids	2019[116]
			3 wt%	NA			67	-	101	-			
COF-300	6FDA-DAM	PEI	7 wt%	0	CO_2/CH_4 (50/50), CO_2/N_2 (50/50)	25 °C, 0.1 MPa	1185 (CO_2/CH_4) 1205 (CO_2/N_2)	30.3	32.6	-	Filler surface modification	1. Eliminating interfacial voids; 2. Increasing CO_2 solubility	2019[128]
			7 wt%	17 wt% of filler			1023 (CO_2/CH_4) 1088 (CO_2/N_2)	40.5	44.5	-			
COF-300	Pebax 1657	PEI	10 wt%	0	CO_2/CH_4 (50/50), CO_2/N_2 (50/50)	25 °C, 0.1 MPa	107 (CO_2/CH_4) 125 (CO_2/N_2)	25.5	56.6	-	Filler surface modification	1. Eliminating interfacial voids; 2. Increasing CO_2 solubility	2019[128]
			10 wt%	17 wt% of filler			101 (CO_2/CH_4) 112 (CO_2/N_2)	36.2	72.1	-			
Pd NPs	PSF	PVP	0	0	CO_2, H_2	RT, 0.1 MPa	303 (GPU)	-	-	4.4 (H_2/CO_2)	Direct physical blending	Improving filler distribution	2014[129]
			2 wt%	NA			3124 (GPU)	-	-	6.2 (H_2/CO_2)			

Table S2. (*continued*)

Filler	Polymer	The third component	Loading of filler	Loading of the third component	Feed gas	Operation conditions	CO_2 permeability (Barrer)	CO_2/CH_4 selectivity	CO_2/N_2 selectivity	CO_2/H_2 selectivity	Methodology	Role of the third component	Published year and ref.
CNT	Matrimid® 5218	Polyzwitterion [poly(SBMA)]	0	0	CO_2, CH_4 CO_2/CH_4 (30/70)	30 °C, 0.2 MPa	6.2 (dry, Single gas) 49.8 (humidified, CO_2/CH_4)	42.8 (dry, Single gas) 39.5 (humidified, CO_2/CH_4)	-	-	Filler surface coating via precipitation polymerization	Facilitating CO_2 transport	2014[130]
			5 wt%	NA			4.8 (dry, Single gas) 103 (humidified, CO_2/CH_4)	73.3 (dry, Single gas) 36 (humidified, CO_2/CH_4)	-	-			
CNT	Pebax 1657	N-isopropylacrylamide hydrogel	0	0	CO_2/CH_4 (10/90), CO_2/N_2 (10/90)	25 °C, 0.2 MPa, humid condition	280 (CO_2/CH_4) 310 (CO_2/N_2)	~30	~53	-	Filler surface coating via *in situ* atom transfer radical polymerization	Facilitating CO_2 transport	2016[131]
			5 wt%	NA			530 (CO_2/CH_4) 610 (CO_2/N_2)	~38.7	~75	-			
TiO_2	Pebax 1657	Carboxymethyl chitosan	3 wt%	0	CO_2, N_2	25 °C, 2.0 MPa	~148	-	~74	-	Filler surface modification	1. Eliminating interfacial voids; 2. Increasing CO_2 solubility	2017[75]
			3 wt%	~4.2 wt% of filler			194.6	-	82.4	-			
PMAA submicrocapsules	SPEEK	Poly(1-vinylimidazole)	20 wt%	0	CO_2, CH_4, N_2	25 °C, 0.1 MPa, humid condition	1708	58.5	62.3	-	Filler surface modification	Facilitating CO_2 transport	2017[133]
			20 wt%	NA			2236	73.8	76.3	-			
UiO-66-NH_2	ODPA-DAM	Polyimide	27 wt%	0	CO_2, CH_4, N_2	35 °C, 0.31 MPa	229	19	9	-	Filler surface modification	Eliminating interfacial voids	2018[135]
			27 wt%	NA			142	44	27	-			
Graphene NPs	Chitosan	Silk fibroin	0.5 wt%	0	CO_2/N_2 (20/80), $CO_2/N_2/H_2$ (10/80/10)	90 °C, 0.2 MPa	~47 (GPU, CO_2/N_2)	-	57	-	Direct physical blending	1. Improving mechanical properties; 2. Facilitating CO_2 transport	2018[132]
			0.5 wt%	45 wt%			159 (GPU, CO_2/N_2) 126 (GPU, $CO_2/N_2/H_2$)	-	93 (CO_2/N_2) 104 ($CO_2/N_2/H_2$)	- 52 ($CO_2/N_2/H_2$)			
Halloysite nanotube	SPEEK	Polyaniline	0.9 wt%	0	CO_2, N_2	25 °C, 0.1 MPa, humid condition	~1093	-	74	-	Filler modification	Facilitating CO_2 transport	2019[134]
			0.9 wt%	NA			~1260	-	87	-			
COF	PVAm	Immobilized PVAm	10 wt%	0	CO_2/CH_4 (10/90), CO_2/N_2 (15/85), CO_2/H_2 (40/60)	25 °C, 0.15 MPa	~1810 (GPU)	-	~73	-	Filler modification	1. Eliminating interfacial voids; 2. Facilitating CO_2 transport through pore channels and crowding out N_2	2019[137]
			10 wt%	NA			1678 (GPU, CO_2/CH_4) 1789 (GPU, CO_2/N_2) 1342 (GPU, CO_2/H_2)	60.4	86.01	22.0			
UiO-66-Allyl	PDMS	PDMS	50 wt%	0	CO_2, N_2	RT, 0.4 MPa	~20000	-	~1.0	-	Filler modification	1. Improving filler distribution; 2. Eliminating interfacial voids	2019[138]
			50 wt%	3.8 wt% of filler			~5100	-	~10.4	-			
UiO-66-NH_2	6FDA-Durene	6FDA-Durene oligomer	0	0	CO_2, CH_4, N_2 CO_2/CH_4 (50/50)	35 °C, 0.1 MPa	1280 1180 (CO_2/CH_4)	15.4 17.0 (CO_2/CH_4)	14.8	-	Filler modification	1. Improving filler distribution; 2. Eliminating interfacial voids	2019[136]
			40 wt%	3.8 wt% of filler			1890 1610 (CO_2/CH_4)	17.7 19.3 (CO_2/CH_4)	17.4	-			

Table S3. Summary of the reported MMMs containing porous materials as the third component for CO_2 separation. The literatures are ordered chronologically in each category (MOFs and COFs, Carbon materials, and other porous materials).

Filler	Polymer	The third component	Loading of filler	Loading of the third component	Feed gas	Operation conditions	CO_2 permeability (Barrer)	CO_2/CH_4 selectivity	CO_2/N_2 selectivity	CO_2/H_2 selectivity	Methodology	Role of the third component	Published year and ref.
Silicalite-1	PSF	HKUST-1	16 wt%	0	CO_2/CH_4 (50/50), CO_2/N_2 (50/50)	35 °C, 0.275 MPa	9.6 (CO_2/CH_4) 9.3 (CO_2/N_2)	21.0	22.0	-	Direct physical blending	Increasing CO_2 solubility	2011[144]
			8 wt%	8 wt%			8.9 (CO_2/CH_4) 8.4 (CO_2/N_2)	22.4	38.0	-			
[emim][B(CN)$_4$]	poly(RTIL)	ZIF-8	~31 wt%	0	CO_2, CH_4, N_2	35 °C, 0.35 MPa	365	15.8	29.9	-	Direct physical blending	Providing additional transport paths	2013[147]
			~31 wt%	25.8 wt%			1062	12.3	24.2	-			
Silica	PSF	ZIF-8	0	0	CO_2/CH_4 (50/50)	35 °C, 0.33 MPa	6.1	31	-	-	*In situ* growth ZIF-8 on silica surface	Eliminating interfacial voids	2014[161]
			32 wt%	NA			24.4	31	-	-			
[emim][Ac]	Chitosan	ZIF-8	5 wt%	0	CO_2, N_2	50 °C, 0.2 MPa	~1300	-	4.25	-	Direct physical blending	1. Providing additional transport paths; 2. Increasing CO_2 diffusion selectivity	2015[146]
			5 wt%	10 wt%			5413	-	11.5	-			
		HKUST-1	5 wt%	0			~1300	-	4.25	-			
			5 wt%	5 wt%			4754	-	19.3	-			
CNTs	6FDA-Durene	NH_2-MIL-101(Al)	5 wt%	0	CO_2, CH_4	25 °C, 0.2 MPa	~780	~12	-	-	MOF decorated on CNTs	Increasing CO_2 solubility	2015[162]
			5 wt%	48.3 wt% of filler			818	29.7	-	-			
GO	PSF	ZIF-302	1 wt%	0	CO_2, N_2	25 °C, 0.1 MPa	8.5	-	33	-	Direct physical blending	1. Increasing CO_2 solubility; 2. Providing additional transport paths	2016[153]
			1 wt%	30 wt%			13	-	52	-			
GO	PSF	ZIF-301	1 wt%	0	CO_2, N_2	25 °C, 0.1 MPa	8.5	-	33	-	Direct physical blending	1. Increasing CO_2 solubility; 2. Providing additional transport paths	2016[154]
			1 wt%	30 wt%			25	-	63	-			
CNTs	PSF	ZIF-302	8 wt%	12 wt%	CO_2, N_2	25 °C, 0.2 MPa	18	-	35	-	Direct physical blending	1. Increasing CO_2 solubility 2. Improving filler distribution	2016[156]
ZIF-8	PSF	MIL-101(Cr)	16 wt%	0	CO_2/CH_4 (50/50), CO_2/N_2 (50/50)	35 °C, 0.2 MPa	14	22	-	-	Direct physical blending	Facilitating CO_2 transport	2016[145]
			8 wt%	8 wt%			14	40	-	-			
GO	Pebax 2533	ZIF-8	6 wt%	0	CO_2, N_2	25 °C, 0.1 MPa	120	-	31	-	ZIF-8 grow on GO	1. Providing additional transport paths; 2. Improving filler distribution	2016[167]
			6 wt%	69.8 wt% of filler			249	-	47.6	-			
Porous GO	Pebax 1657	ZIF-8	0.02 wt%	0	CO_2/N_2 (50/50)	35 °C, 0.3 MPa	87	-	50.5	-	ZIF-8 grow on GO	1. Providing additional transport paths; 2. Improving filler distribution	2017[168]
			0.02 wt%	28 wt% of filler			163	-	57	-			

Table S3. (*continued*)

Filler	Polymer	The third component	Loading of filler	Loading of the third component	Feed gas	Operation conditions	CO_2 permeability (Barrer)	CO_2/CH_4 selectivity	CO_2/N_2 selectivity	CO_2/H_2 selectivity	Methodology	Role of the third component	Published year and ref.
GO	Matrimid® 5218	UiO-66	8 wt%	0	CO_2/CH_4 (50/50)	35 °C, 0.34 MPa	~2.8	~16	-	-	UiO-66 grow on GO	1. Providing additional transport paths; 2. Improving filler distribution	2017[169]
			24 wt%	57 wt% of filler			21	51	-	-			
Fumed silica	PES	Zn-MOF	15 wt%	0	CO_2, CH_4	25 °C, 0.35 MPa	1.24	41.33	-	-	Direct physical blending	1. Providing additional transport paths; 2. Increasing CO_2 solubility	2017[152]
			7.5 wt%	7.5 wt%			30.92	48.31	-	-			
UiO-66-NH_2	PSF	ZIF-8	40 wt%	0	CO_2, N_2	35 °C, 0.3 MPa	48.2	-	25	-	*In situ* growth ZIF-8 on UiO-66-NH_2 surface	Reducing effective pore size	2017[163]
			40 wt%	NA			45.2	-	39	-			
ZIF-8	PBI	ZIF-7	20 wt%	0	H_2/CO_2 (50/50)	180 °C, 0.3 MPa	~27.5	-	-	8.0	Converting the surface of ZIF-8 to ZIF-7	1. Eliminating interfacial voids; 2. Reducing effective pore size	2017[164]
			20 wt%	10% based on ligand			~34.7	-	-	10.1 (H_2/CO_2)			
ZIF-93	PBI	ZIF-11	20 wt%	0	H_2/CO_2 (50/50)	180 °C, 0.3 MPa	~43.1	-	-	5.8 (H_2/CO_2)	Converting the surface of ZIF-93 to ZIF-11	1. Eliminating interfacial voids; 2. Reducing effective pore size	2018[165]
			20 wt%	7% based on ligand			26.88	-	-	7.7 (H_2/CO_2)			
GO	Matrimid® 5218	ZIF-8	20 wt%	0	CO_2, N_2	30 °C, 0.1 MPa, humid condition	134	-	36	-	*In-situ* growth of ZIF-8 on GO	1. Providing additional transport paths; 2. Improving filler distribution	2018[170]
			20 wt%	95 wt% of filler			238	-	65	-			
LDH	Pebax 1657	ZIF-8	2 wt%	0	CO_2/CH_4 (30/70)	30 °C, 0.1 MPa	615	28.2	-	-	*In-situ* growth of ZIF-8 on LDH surface	1. Eliminating interfacial voids; 2. Providing additional transport paths; 3. Improving filler distribution	2018[173]
			2 wt%	40 wt% of filler			1307	31.6	-	-			
p-Nitro aniline	PES	ZIF-8	4 wt%	0	CO_2, CH_4	35 °C, 0.3 MPa	~2.6	~48.3	-	-	Direct physical blending	Providing additional transport paths	2018[148]
			4 wt%	10 wt%			~4.5	~30	-	-			
GO	PSF	ZIF-300	1 wt%	0	CO_2, N_2	25 °C, 0.1 MPa	8.5	-	33	-	Direct physical blending	1. Increasing CO_2 solubility; 2. Providing additional transport paths	2018[155]
			1 wt%	30 wt%			21	-	61	-			
GO	ODPA-TMPDA	ZIF-8	5 wt%	0	CO_2/CH_4 (50/50)	25 °C, 0.1 MPa	97.5	44	-	-	Direct physical blending	Providing additional transport paths	2018[149]
			5 wt%	10 wt%			145	43	-	-			
CNTs	PSF	ZIF-301	6 wt%	18 wt%	CO_2, N_2	25 °C, 0.2 MPa	19	-	48	-	Direct physical blending	1. Increasing CO_2 solubility 2. Improving filler distribution	2018[157]

Table S3. (*continued*)

Filler	Polymer	The third component	Loading of filler	Loading of the third component	Feed gas	Operation conditions	CO_2 permeability (Barrer)	CO_2/CH_4 selectivity	CO_2/N_2 selectivity	CO_2/H_2 selectivity	Methodology	Role of the third component	Published year and ref.
ZIF-8	ODPA-TMPDA	CuBDC nanosheet	10 wt%	0	CO_2/CH_4 (50/50)	25 °C, 0.1 MPa	144	37	-	-	Direct physical blending	Improving CO_2 diffusion selectivity	2018[158]
			10 wt%	2 wt%			131	47	-	-			
			0	2 wt%			99	43	-	-			
GO	Matrimid® 5218	UiO-66-NH_2	1 wt%	0	CO_2, N_2	25 °C, 0.3 MPa	3.15	-	64.3	-	*In-situ* growth of UiO-66-NH_2 on GO nanosheets	1. Providing additional transport paths; 2. Improving filler distribution	2019[171]
			5 wt%	NA			7.28	-	52	-			
GO	Ethyl cellulose	ZIF-8	1.1 wt%	0	CO_2, N_2	25 °C, 0.2 MPa	75	-	30	-	*In-situ* growth of ZIF-8 on GO surface	1. Providing additional transport paths; 2. Improving filler distribution	2019[172]
			20 wt%	NA			203.3	-	33.4	-			
UiO-66-NH_2	PSF	TpPa-1	5 wt%	0	CO_2/CH_4 (50/50)	25 °C, 0.1 MPa	8.3	22.1	-	-	*In-situ* growth of TpPa-1 on UiO-66-NH_2 surface	Eliminating interfacial voids	2019[166]
			5 wt%	22 wt% of filler			7.1	46.7	-	-			
PEG 200	Matrimid® 5218	ZIF-8	4 wt%	0	CO_2/CH_4 (50/50)	25 °C, 0.8 MPa	27.5	24.3	-	-	Direct physical blending	Providing additional transport paths	2019[150]
			4 wt%	30 wt%			33	15.4	-	-			
Piperazine glycinate	PVA	ZIF-8	30 wt%	0	CO_2/N_2 (20/80)	95 °C, 0.25 MPa	180	-	210	-	Direct physical blending	Providing additional transport paths	2019[151]
			30 wt%	5 wt%			328	-	370	-			
MCM-41	PDMS	Carbon	30 wt%	0	CO_2/H_2 (50/50)	25 °C, 1.0 MPa	59	-	-	2.4	Encapsulation	Increasing CO_2 solubility	2013[174]
			30 wt%	18.7 wt% of filler			42	-	-	6.0			
MCM-41	Matrimid® 9725	Carbon	30 wt%	0	CO_2/N_2 (50/50), CO_2/CH_4 (50/50)	35 °C, 0.9 MPa	~22	~29	~29.5	-	Encapsulation	Increasing CO_2 solubility	2015[175]
			30 wt%	23.3 wt% of filler			~26	38.1	37.6	-			
CNT	Matrimid® 5218	GO	10 wt%	0	CO_2, CH_4, N_2	30 °C, 0.2 MPa	10.29	27.8	26.4	-	Direct physical blending	CNT: providing additional transport paths; GO: increasing CO_2 diffusion selectivity; Improving filler distribution	2015[176]
			5 wt%	5 wt%			38.07	84.6	81.0	-			
			0	10 wt%			6.46	70.3	64.6	-			
Halloysite nanotubes	Pebax 1657	Porous reduced GO	0.15 wt%	0	CO_2, N_2	30 °C, 0.3 MPa	71	-	42	-	Direct physical blending	Increasing CO_2 diffusion selectivity	2018[177]
			0.15 wt%	0.02 wt%			124	-	118	-			
PEG-MEA	Pebax 1657	GO	50 wt%	0	CO_2, N_2	35 °C, 0.1 MPa	~565	-	~28.5	-	Direct physical blending	Increasing CO_2 diffusion selectivity	2019[178]
			50 wt%	0.3 wt%			~605	-	~56	-			
Porous reduced GO	Pebax 1657	Halloysite nanotubes	0.02 wt%	0	CO_2, N_2	30 °C, 0.3 MPa	~77	-	~78	-	Direct physical blending	1. Improving filler distribution; 2. Providing additional transport paths	2018[177]
			0.02 wt%	0.15 wt%			124	-	118	-			

Table S3. (*continued*)

Filler	Polymer	The third component	Loading of filler	Loading of the third component	Feed gas	Operation conditions	CO_2 permeability (Barrer)	CO_2/CH_4 selectivity	CO_2/N_2 selectivity	CO_2/H_2 selectivity	Methodology	Role of the third component	Published year and ref.
MWCNT	Pebax 1657	mesoporous SiO_2	10 wt%	0	CO_2/CH_4 (10/90), CO_2/N_2 (10/90)	25 °C, 0.2 MPa, humid condition	355	~29	~38	-	SiO_2 grow on CNT	Eliminating interfacial voids	2018[179]
			10 wt%	NA			~370	39	58	-			
[emim][TF$_2$N]	poly(IL)	SAPO-34	20 wt%	0	CO_2, CH_4	21 °C, 0.1 MPa	22.9	26	-	-	Direct physical blending	Increasing CO_2 diffusion selectivity	2019[180]
			16 wt%	20 wt%			47	42	-	-			