

Supporting information

A Type III porous liquid with high separation performance for linear/branched C₄ olefin mixtures

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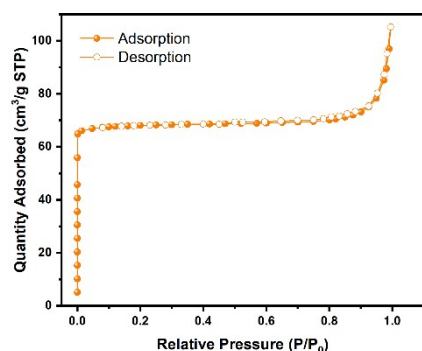


Figure S1. N₂ adsorption-desorption isotherm on CALF-20M at 77 K.

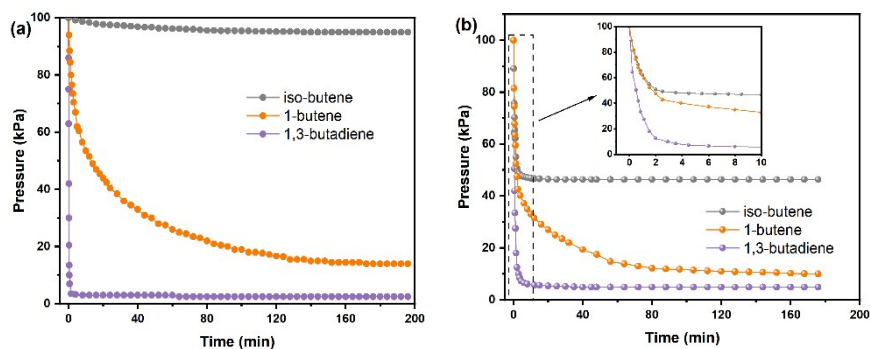


Figure S2. (a) Pressure drop profiles for C₄ olefin adsorption on CALF-20M nanoparticles at 293.2 K with an initial pressure of 100 kPa (initial gas-solid ratio is 49.7). (b) Pressure drop profiles for C₄ olefin sorption by 30 wt% CALF-20M/DMI PLs at 293.2 K with an initial pressure of 100 kPa (initial gas-liquid ratio is 10.4) and a stirring rate of 55 rpm.

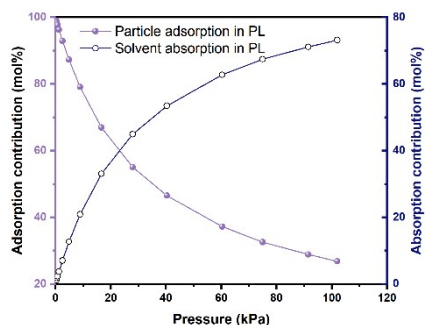


Figure S3. Contributions from adsorption and absorption sides to 1,3-butadiene uptake of the PLs at 293.2 K.

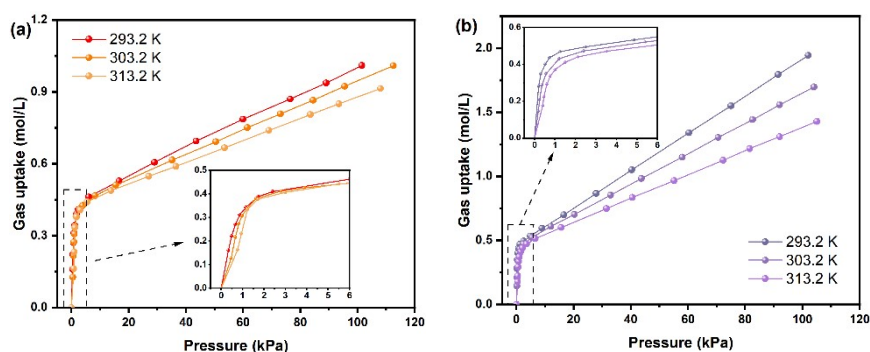


Figure S4. Sorption isotherms of 30 wt% CALF-20M/DMI PLs at different temperatures for (a) 1-butene and (b) 1,3-butadiene.

Table S1. Effect of sorption time on mixed gas separation using CALF-20M/DMI PLs at 303.2 K, a gas-liquid ratio of 15.2, and a stirring rate of 55 rpm.

Gas mixtures	Time min	P_E kPa	S_{C1} mol/L/kPa	S_{C2} mol/L kPa	y_1 mol%	x_1 mol%	R_1 %	β
1-butene(1) /iso-butene(2)	3.5	61.2	0.0098	0.0045	38.8	57.8	68.8	2.2
	7	54.5	0.0156	0.0046	31.1	60.6	77.8	3.4
	15	47.0	0.0316	0.0046	20.1	63.4	87.7	6.9
	28	43.9	0.0582	0.0046	12.6	64.7	92.9	12.7
	45	39.4	0.1839	0.0047	4.6	65.6	97.7	39.0
	58*	38.0	0.2555	0.0049	3.5	65.3	98.3	52.5
1,3-butadiene(1) /iso-butene(2)	118	37.9	0.2606	0.0049	3.4	65.3	98.3	53.4
	1.2	63.2	0.0323	0.0028	11.8	60.5	87.9	11.4
	1.8	56.4	0.0752	0.0033	6.1	60.2	94.4	23.1
	2.7	51.1	0.1293	0.0038	4.0	58.6	96.7	33.8
	5	47.4	0.2959	0.0043	1.9	57.4	98.5	68.1

15	43.5	0.5749	0.0049	1.1	55.9	99.2	115.6
23*	40.3	0.7963	0.0058	0.8	54.3	99.5	137.9
83	40.3	0.7977	0.0058	0.8	54.3	99.4	138.4

* Reaching the thermodynamic equilibrium state

Table S2. The reported membrane separation technology's selectivity for C₄ olefins.

Membrane	Testing conditions	Selectivity		Ref
		1,3-butadiene/ Iso-butene	1-butene/ Iso-butene	
P2533	306 K, 50 kPa	2.8	1.2	1
P1500	306 K, 50 kPa	4.2	1.2	
P4000	306 K, 50 kPa	4.5	1.2	
ZSM-5 membrane	403 K, 100 kPa	-	10	2
polyZIF(4:1)membrane	298 K, 100 kPa	28.1	-	3
zeolite CGC membrane-1 a _g (ZIF-62) _{0.7} /(SAPO-34) _{0.3}	298 K, 100 kPa	6.44	-	4
zeolite CGC membrane-2 a _g (ZIF-62) _{0.7} /(SSZ-13) _{0.3}	298 K, 100 kPa	10.31	-	

Table S3. Selectivity comparison of 1-butene/iso-butene and 1,3-butadiene/iso-butene binary mixture with the solid adsorbents.

Adsorption medium	T (K)	Gas uptake at 100 kpa* mmol/g			Uptake ratio		Selectivity**		Ref
		(1)	(2)	(3)	(1)/(3)	(2)/(3)	(1)/(3)	(2)/(3)	
CALF-20M	293.15	1.48	1.38	0.09	17.41	16.23	-	11159.40	This work
CALF-20M/DMI PLs	293.15	1.66	0.86	0.46	3.65	1.85	294.87	122.52	
GeFSIX-2-Cu-i	298.15	3.63	3.26	1.23	2.95	2.65	5.4(H)	1.4(H)	5
SIFSIIX-2-Cu-i	298.15	3.99	2.98	1.53	2.61	1.95	4.6(H)	1.5(H)	
NbFSIX-2-Cu-i	298.15	2.61	2.24	0.45	5.8	4.98	142(H)	138(H)	
GeFSIX-14-Cu-i	298.15	2.59	0.54	0.44	5.89	1.23	111(H)	1.3(H)	
Y-fum-fcu-MOF	303.15	3.41	2.70	0.98	3.48	2.76	5.29	3.57	6

TMOF-1	298.15	1.64	1.09	0.21	7.81	5.19	-	83(I)	7
SOFOUR-DPDS-Ni	298.15	1.68	1.48	0.17	9.88	8.7	2321.8(H)	233.5(H)	8
Mg-gallate	298.15	1.94	1.43	0.145	13.38	9.86	106(H)	29(H)	9
Co-gallate	298.15	1.86	0.88	0.145	12.827	6.06	63(H)	40(H)	
Ni-gallate	298.15	1.38	0.56	0.10	13.8	5.6	148(H)	67(H)	
Zu-36-Co	298.15	-	2.01	0.22	-	9.13	-	2050(I)	10
MET-Fe	298.15	-	1.56	0.558	-	2.795	-	699.30(I)	

*The above table assigns numbers to gases as follows: (1) refers to 1,3-butadiene; (2) refer to 1-butene; (3) refer to iso-butene.

**H stands for Henry's selectivity, and I indicates the IAST selectivity, and the unmarked ones represent the selectivity measured in the experiment.

Reference

1. M. Rahman, *J. Membr. Sci.*, 2023, 666, 121176.
2. C. Chmelik , H. Bux , H. Voss and J. Caro, *Chem. Ing. Tech.*, 2011, 83, 104–112.
3. N. Li , C. Ma , J. Zhang , L. Xu , S. Wang , Z. Wang , S. Zhang , J. Pang , J. Hou , Z. Qiao and C. Zhong, *Angew. Chem. Int. Ed.*, 2025, 64, e202506117.
4. D. Ao , Z. Yang , A. Chen , Y. Sun , M. Ye , L. Tian , X. Cen , Z. Xie , J. Du , Z. Qiao , A. Cheetham , J. Hou and C. Zhong, *Angew. Chem. Int. Ed.*, 2024, 63, e202401118.
5. Z. Zhang , Q. Yang , X. Cui , L. Yang , Z. Bao , Q. Ren and H. Xing, *Angew. Chem. Int. Ed.*, 2017, 56, 16282–16287.
6. A. Assen , T. Viridis , W. De Moor , A. Moussa , M. Eddaoudi , G. Baron , J. Denayer and Y. Belmabkhout, *Chem. Eng. J.*, 2021, 413, 127388.
7. J. Cui , Z. Zhang , J. Hu , L. Yang , Y. Li , L. Chen , X. Cui and H. Xing, *Chem. Eng. J.*, 2021, 425, 130580.
8. J. Liu , H. Xiong , H. Shuai , X. Liu , Y. Peng , L. Wang , P. Wang , Z. Zhao , Z. Deng , Z. Zhou , J. Chen , S. Chen , Z. Zeng , S. Deng and J. Wang, *Nat. Commun.*, 2024, 15, 2222.
9. J. Chen , J. Wang , L. Guo , L. Li , Q. Yang , Z. Zhang , Y. Yang , Z. Bao and Q. Ren, *Appl. Mater. Interfaces*, 2020, 12, 9609–9616.
10. Y. Jiang , C. Deng , C. Liang , X. Peng , Z. Zhang , L. Zhao , X. Wu , J. Zou , Y. Jia , M. Cheng , J. Li , J. Zhang , Y. Peng , M. Gao , G. Chen and M. Zaworotko, *ACS Materials Lett*, 2024, 6, 4972–4979.