

Supplementary information

Highly efficient Lithium adsorption and stable isotopes separation by metal-organic frameworks

Bo Tong,^{ab} Guijie Guo,^{ab} Xiangyunxiu Meng,^{ab} Peng Bai,^{ab} Jiafei Lyu,^{*ab} and Xianghai Guo^{*cd}

^a Dept. of Pharmaceutical Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, P. R. China

^b Key Laboratory of Systems Bioengineering (Ministry of Education), Tianjin University, Tianjin, 300072, P. R. China

^c School of Marine Science and Technology, Tianjin University, Tianjin 300072, P. R. China

^d Key Laboratory of Ocean Observation Technology of Ministry of Natural Resources, School of Marine Science and Technology, Tianjin University, Tianjin 300072, P. R. China

* Corresponding author

Xianghai Guo, email: guoxh@tju.edu.cn

Jiafei Lyu, email: jflv@tju.edu.cn

Contents

1. Experiments

2. Figures

3. Tables

References

1. Experiments

1.1. Chemicals

All chemicals and solvents were purchased from commercial suppliers and used without further purification including zinc(II) nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%, Aladdin, Shanghai, China), zirconium(IV) chloride (ZrCl_4 , 98%, Aladdin, Shanghai, China), chromic(III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99.95%, Aladdin, Shanghai, China), aluminum(III) nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99.9%, Aladdin, Shanghai, China), copper(II) chloride dihydrate (CuCl_2 , 98%, Aladdin, Shanghai, China), scandium(III) nitrate ($\text{Sc}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, 99.9%, Aladdin, Shanghai), iron powder (Fe, 99%, Bailingwei, Beijing, China), chromium powder (Cr, 99.9%, Aladdin, Shanghai, China), terephthalic acid ($\text{C}_8\text{H}_6\text{O}_4$, 99%, TCI, Shanghai, China), benzene-1,3,5-tricarboxylic acid ($\text{C}_9\text{H}_6\text{O}_6$, 98%, Aladdin, Shanghai, China), 2-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, 98%, Aladdin, Shanghai, China), hydrofluoric acid ($\geq 40\%$, Fengchuan, Tianjin, China), hydrochloric acid (36~38%, Yuanli, Tianjin, China), nitric acid (65~68%, Huaweiruike, Beijing, China), methanol (99.5%, Aladdin, Shanghai, China), ethanol (95%, Macklin, Shanghai, China) and lithium chloride anhydrous ($\geq 95\%$, Kermel, Tianjin, China), N,N-dimethylformamide (DMF) (99%, Eney, Shanghai, China), acetone ($\geq 99.5\%$, Aladdin, Shanghai, China), methylene chloride ($\geq 99.9\%$, Aladdin, Shanghai, China). Deionized water was used as water source throughout the experiments.

1.2. Preparation of ten kinds of MOFs

1.2.1. Synthesis of ZIF-8

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (258 mg) was dissolved into methanol (20 mL) to form a solution. 2-methylimidazole (263 mg) was dissolved in methanol (20 mL) to generate another clear solution. Then, all of them were mixed together, and stirred for 5 min. The solution was aged at room temperature for 24 hours. After that, white powders were precipitated. The powders were washed carefully with methanol and dried. The product was dried at 80 °C overnight under vacuum.¹

1.2.2. Synthesis of UiO-66

ZrCl_4 (250 mg), DMF (10 mL) and concentrated hydrochloric acid (2 mL) were added to a Teflon lined vessel (50 mL). The mixture was ultrasonic for 20 min until it was completely dissolved. Terephthalic acid (246 mg) and the remaining DMF (20 mL) were added to the lining and the mixture was ultrasonic again for 20 min. Finally, the mixture was sealed and heated to 80 °C in an

oven for 16h. The resulting product was centrifuged and washed with DMF and ethanol, followed by vacuum drying at 100 °C overnight.²

1.2.3. Synthesis of MIL-53(Cr)

Cr(NO₃)₃·9H₂O (800 mg) and terephthalic acid (332 mg) were added to 10 mL deionized water. Hydrofluoric acid (0.1 mL) was added to maintain the acidity of the reaction system. The mixture was stirred evenly and sealed in a Teflon lined vessel, then heated to 220 °C in the oven for 3 days. The resulting product was centrifuged and then washed with DMF and ethanol. The product was dried at room temperature and calcined in a muffle furnace at 300 °C for 12 h to remove the unreacted terephthalic acid, followed by vacuum drying at 200 °C overnight.³

1.2.4. Synthesis of MIL-101(Cr)

Cr(NO₃)₃·9H₂O (800 mg), hydrofluoric acid (0.1 mL), terephthalic acid (332 mg) were added in 9.6 mL H₂O. The mixture is introduced in a hydrothermal bomb which is put during 8 h in a Teflon lined vessel held at 220 °C. After natural cooling, the resulting product was centrifuged and washed with DMF and ethanol, followed by vacuum drying at 150 °C overnight.⁴

1.2.5. Synthesis of MIL-96(Al)

Al(NO₃)₃·9H₂O (2628 mg), benzene-1,3,5-tricarboxylic acid (210 mg) and H₂O (5 mL) were placed in a Teflon lined vessel (25 mL) at 210 °C for 24 h. The pH of synthesis was 1. After the hydrothermal treatment, a powdered product was obtained, which was filtered off, washed with deionized water and ethanol. The product was dried at 100 °C overnight under vacuum.⁵

1.2.6. Synthesis of MIL-100(Fe)

MIL-100(Fe) was prepared by adding Iron powder (111.69 mg) and benzene-1,3,5-tricarboxylic acid (281.58 mg) to 10.0 mL deionized water, hydrofluoric acid (0.2 mL) and nitric acid (0.116 mL) were then added to keep the system in an acidic environment throughout the reaction. The reaction mixture and further purified in boiling water for 5 h and ethanol at 60 °C for 3 h. The product was dried at 80 °C overnight under vacuum.^{6,7}

1.2.7. Synthesis of HKUST-1

A mixture consisting of DMF, ethanol and H₂O with a volume ratio of 1:1:1 was prepared. CuCl₂·2H₂O (1720 mg) were dissolved in 24 mL of the above mixture solvent, to which was added benzene-1,3,5-tricarboxylic acid (1000 mg) in 24 mL of the same mixture solvent. The reaction system was reacted at room temperature for 17 d. The precipitate was separated by vacuum filtration

and washed with DMF. Afterwards, the solid was dispersed in 100 mL of CH_2Cl_2 overnight, then separated by vacuum filtration and washed with CH_2Cl_2 . The product was dried at 170 °C overnight under vacuum.⁸

1.2.8. Synthesis of MIL-100(Al)

MIL-100(Al) was synthesized by a mixture consisting of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, benzene-1,3,5-tricarboxylic acid, 4M nitric acid and deionized water with a volume ratio of 1:0.667:2.0:300 at 160 °C for 12 h. The as-synthesized MIL-100(Al) was further purified by two-step processes using hot water and ethanol. After purification, the product was dried at 120 °C overnight under vacuum.⁹

1.2.9. Synthesis of MIL-100(Sc)

MIL-100(Sc) was prepared by dissolving $\text{Sc}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (204 mg) and benzene-1,3,5-tricarboxylic acid (84 mg) in 15 mL DMF. The reaction mixture was stirred at room-temperature for 30 min. Then, the mixture solution was transferred into a Teflon lined vessel (25 mL) and heated at 150 °C for 36 h. After cooling to room temperature, the white powdered product was collected by filtration, washed with DMF, and dried at room temperature. In order to remove the DMF resided in the pores of MIL-100(Sc), the as-synthesized sample was solvothermally treated in ethanol at 60 °C for 16 h and then collected by filtration, then dried at 120 °C overnight under vacuum.¹⁰

1.2.10. Synthesis of MIL-100(Cr)

MIL-100(Cr) was prepared by adding chromium powder (104 mg) to hydrofluoric acid (0.2 mL), followed by 1,3,5-tricarboxylic acid (300 mg) and deionized water (9.6 mL). The reactants were mixed evenly and placed in a hydrothermal synthesis reactor, then heated to 220 °C for 4 days. After the reactor is cooled to room temperature, the product is filtered, then washed with deionized water and ethanol. The resulting green solid was dried at 100 °C overnight under vacuum.¹¹

1.3. Characterization

1.3.1. X-ray diffraction analyses

Powder X-ray diffraction (PXRD) patterns of the samples were measured by a Rigaku X-ray diffractometer model Smart lab equipped with a 9 kW $\text{Cu-K}\alpha 1$ X-ray radiation ($\lambda = 0.154056$ nm) rotating anode with 2θ angle ranging from 5° to 50° with a step size of 0.02°.

1.3.2. Scanning electron microscopy

Scanning electron microscopy (SEM) images were acquired from Apreo S LoVac operated at 5.0 kV.

1.3.3. ICP-OES

Lithium concentration in the aqueous solutions was tested by inductively coupled plasma optical emission spectroscopy Agilent 5180.

1.3.4. ICP-MS

Isotopic abundance ratio of lithium in the aqueous solutions was tested by inductively coupled plasma mass spectroscopy Agilent 7700x.

1.3.5. X-ray photoelectron spectroscopy

Before and after lithium adsorption, MIL-100(Fe) was analyzed by an X-ray photoelectron spectroscopy (XPS) conducted on Axis Supra with Al K α X-ray source (0.48 eV).

1.4. Adsorption experiment

1.4.1. Lithium adsorption

About 10 mg of activated MOFs and 2 mL lithium salt solution were added in a 10 mL centrifuge tube which was shaken in a thermostatic shaker at 25 °C for 24 h. The liquid was separated by using a 0.22 μm micro-pore filter. The concentration of initial and residual Li(I) in aqueous solution was measured by ICP-OES. Adsorption capacity (q) was defined as follows,

$$q = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where q is the adsorption capacity for lithium, $\text{mg} \cdot \text{g}^{-1}$; C_0 and C_e are the initial and equilibrium Li(I) concentrations in aqueous phases respectively, $\text{mg} \cdot \text{L}^{-1}$; V is the volume of the solution, mL; m is the mass of the adsorbent, mg.

Lithium isotopes separation was evaluated by the measurement of the lithium isotopes using ICP-MS. The single-stage separation factor (α) for ${}^6\text{Li}/{}^7\text{Li}$ was defined by Eq. (2). The subscripts 's' and 'l' represent the concentrations of lithium isotopes in solid phase and liquid phase, respectively.

$$\alpha = \frac{\left(\frac{[{}^7\text{Li}]_s}{[{}^6\text{Li}]_s} \right)}{\left(\frac{[{}^7\text{Li}]_l}{[{}^6\text{Li}]_l} \right)} \quad (2)$$

1.4.2. Competitive adsorption experiments

0.1 mol of LiNO_3 , NaNO_3 , KNO_3 , CsNO_3 were successively added to deionized water for dissolution, respectively. After complete dissolution, the solution was added to a 1 L volumetric flask for constant volume. About 10 mg of activated MOFs and 2 mL nitrate solution were added in a 10 mL centrifuge tube which was shaken in a thermostatic shaker at 25 °C for 24 h.

1.4.3. Reusability

The exhausted material was obtained after 24 h of adsorption in $10 \text{ mg}\cdot\text{L}^{-1}$ lithium nitrate solution. The exhausted material was regenerated by soaking in 0.1 M hydrochloric acid solution, and then washed with water for 3 times after soaking overnight. The adsorbent was activated at 120 °C under vacuum overnight before each regeneration adsorption.

2. Figures

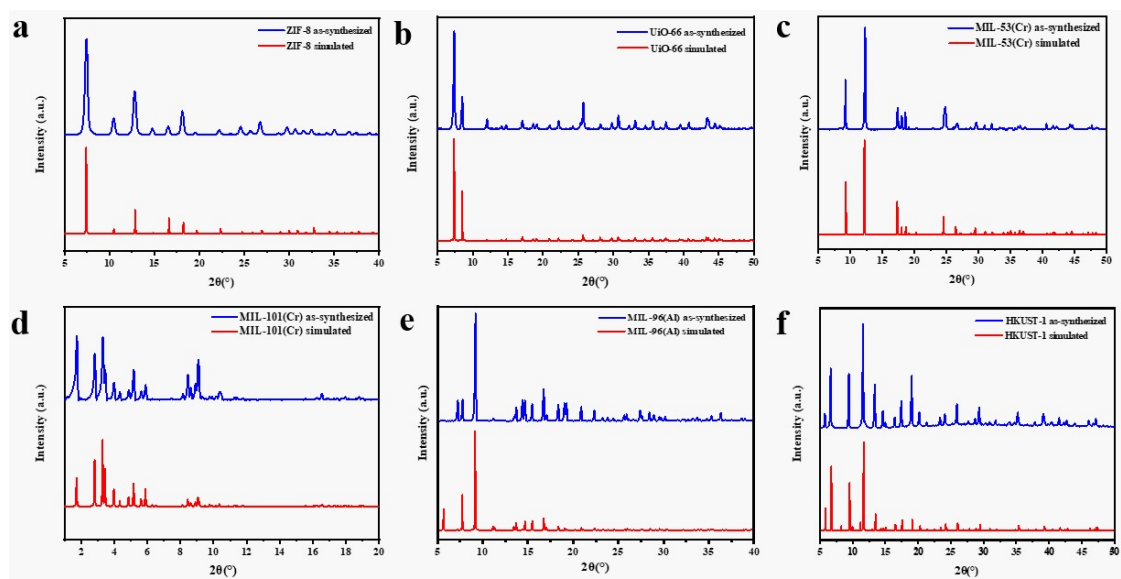


Fig. S1 PXRD patterns of six kinds of MOFs

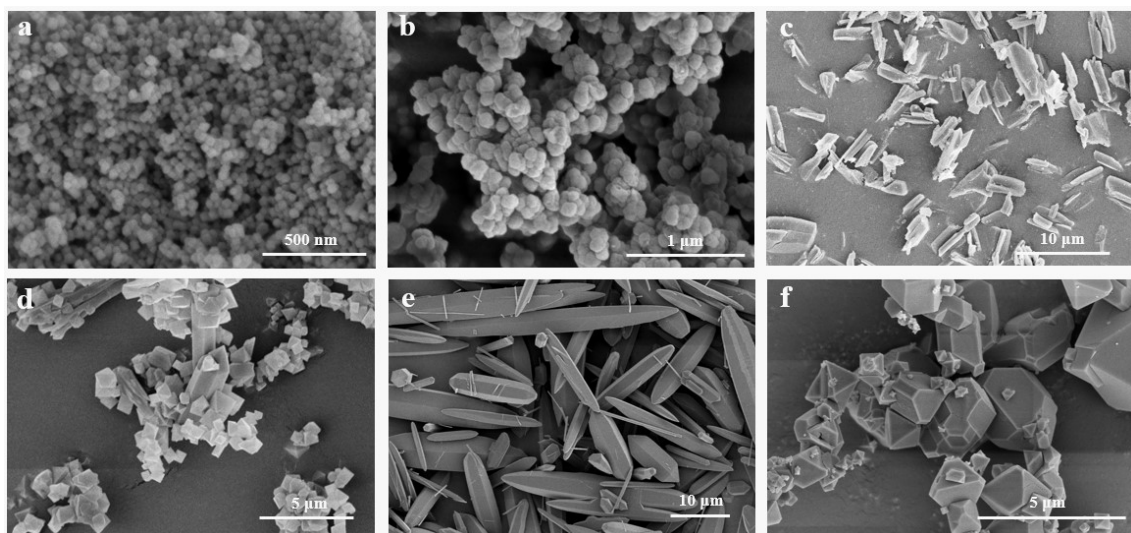


Fig. S2 SEM images of six kinds of MOFs: (a). ZIF-8 (b). UiO-66 (c). MIL-53(Cr) (d). MIL-101(Cr) (e). MIL-96(Al) (f). HKUST-1.

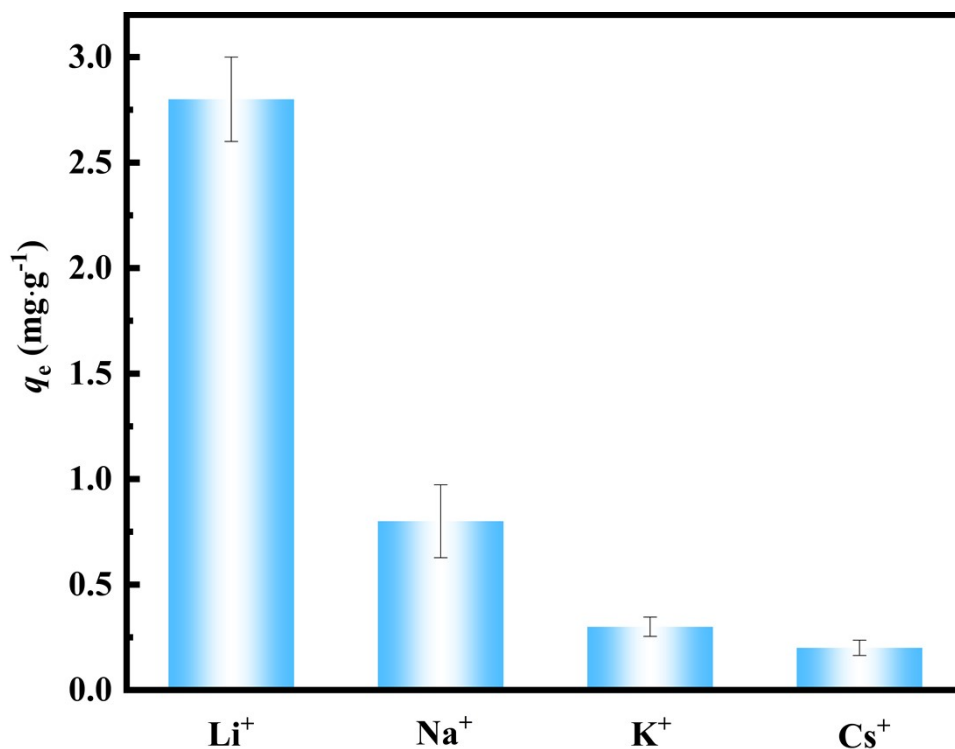


Fig. S3 Competitive adsorption characteristics between lithium and other metals of MIL-100(Fe)

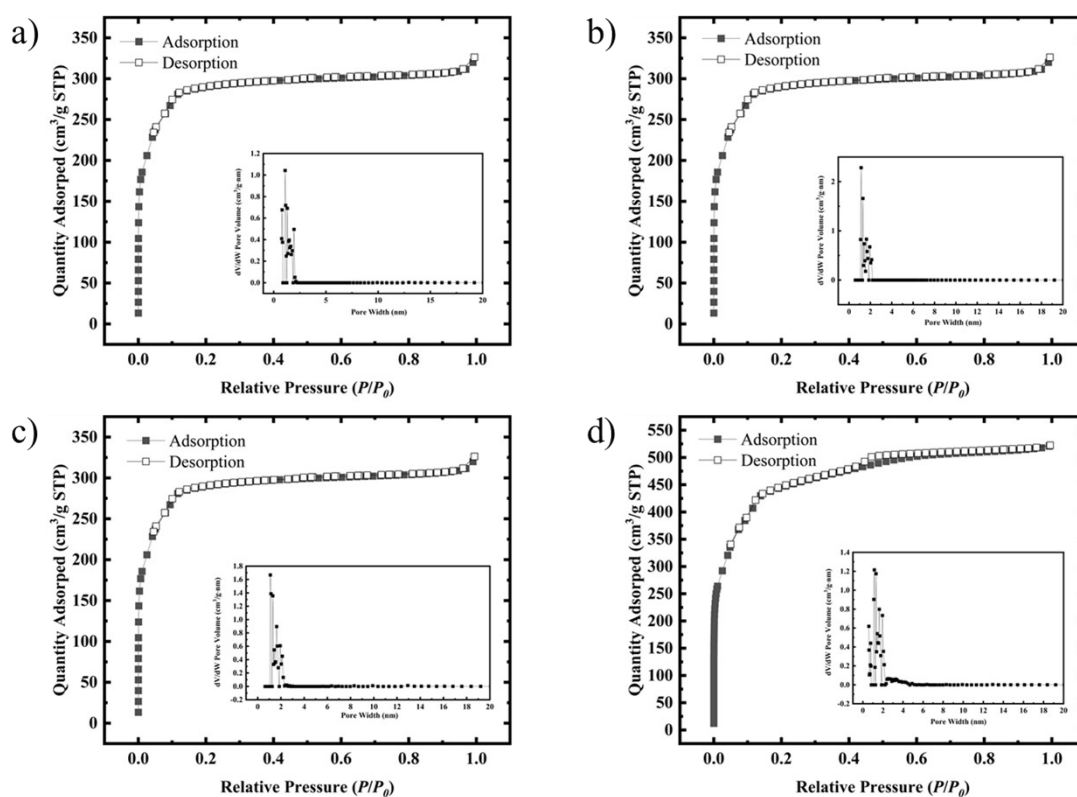


Fig. S4 N_2 adsorption-desorption isotherms of (a). MIL-100(Al), (b). MIL-100(Sc), (c). MIL-100(Cr), and (d). MIL-100(Cr) and corresponding pore size distribution

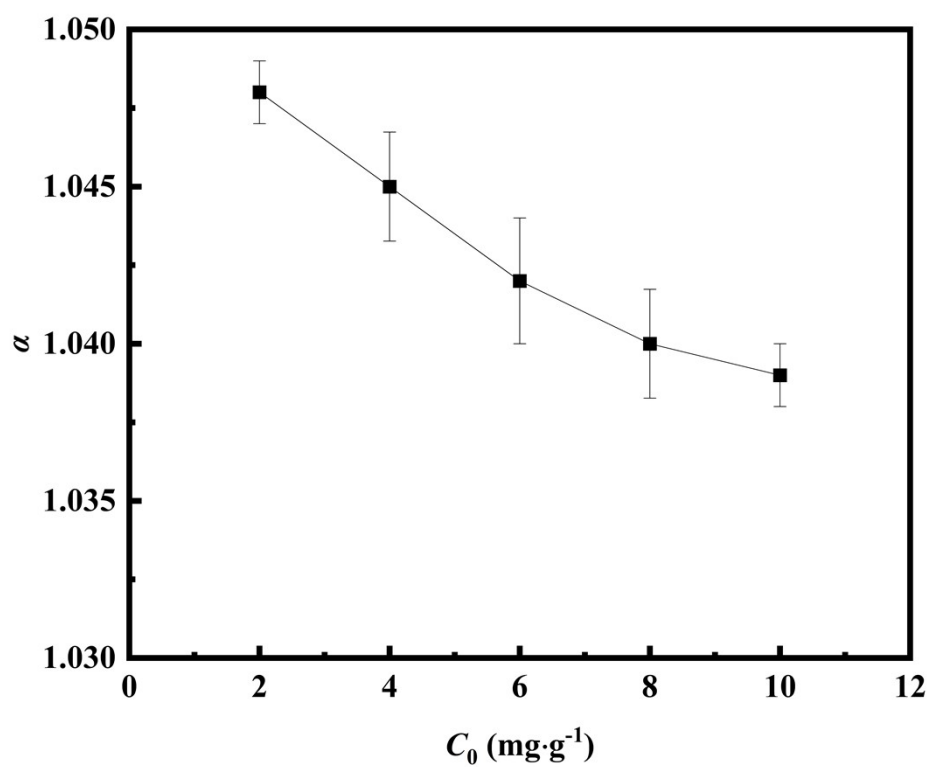


Fig. S5 Isotopes separation performance under different concentrations of lithium salts

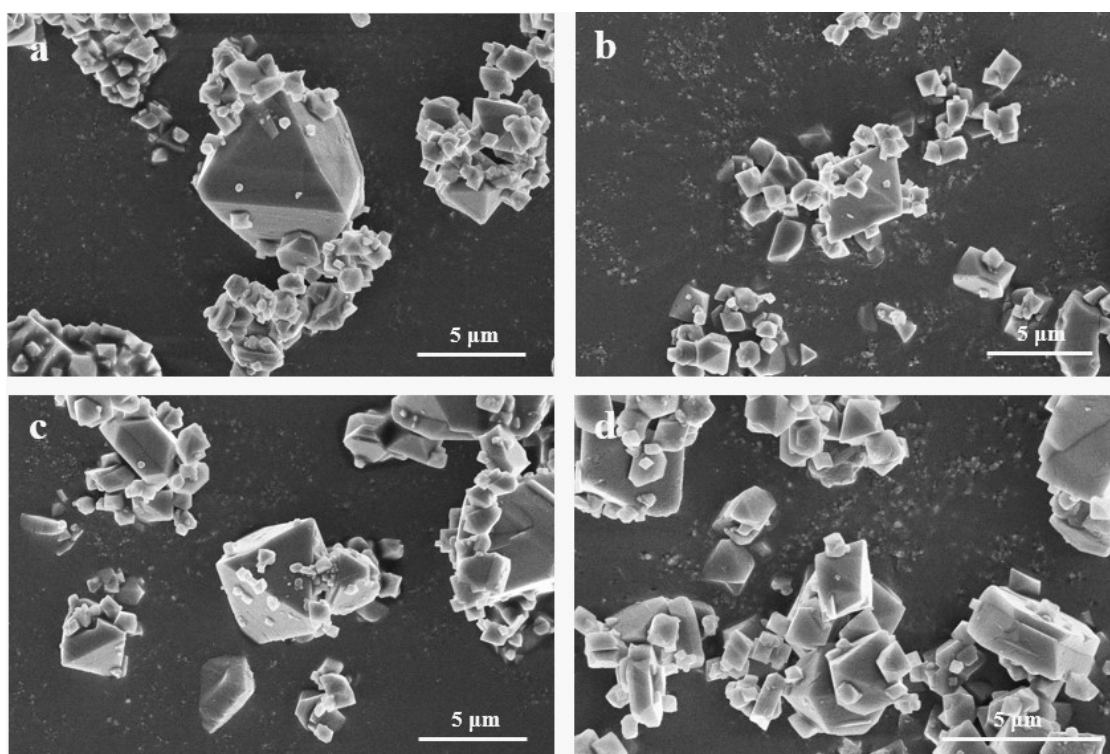


Fig. S6 SEM images of MIL-100(Fe) after fourth recycle of Li adsorption: (a). first (b). second (c). third (d). fourth

3. Tables

Table S1 Li⁺ adsorption and isotope separation performance of different adsorbents

Adsorbent	Adsorption capacity (mg·g ⁻¹)	Separation factor	Reference
PCGFMs-B15C5	6.46	1.037 ± 0.002	12
SBA-NH-B15C5	~3.8	1.049 ± 0.002	13
MCM-g-AB15C5	10.88	1.022 ± 0.002	14
SBA-15@PDA@PGMA-B15C5	~6.6	~1.039	15
TJU-21	41	/	16
MIL-100(Fe)	46.3	1.039 ± 0.002	This work

Table S2 XPS surface characterization of the MIL-100(Fe) samples

	C (atom, %)	O (atom, %)	Fe (atom, %)	Li (atom, %)	C/Fe (atom. / atom.)
MIL-100(Fe)	55.17	39.78	5.05	/	10.92
MIL-100(Fe) after Li adsorption	44.12	47.01	4.08	4.79	10.81

Table S3 BET surface area, pore volume and specific adsorption capacity of four MIL-100 serial materials

Materials	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Specific adsorption capacity β (mg/m ²)
MIL-100(Al)	1136	0.50	0.0180
MIL-100(Fe)	1656	0.75	0.0280
MIL-100(Sc)	984	0.74	0.0185
MIL-100(Cr)	1606	0.81	0.0189

References:

- 1 N. L. Torad, M. Hu, Y. Kamachi, K. Takai, M. Imura, M. Naito and Y. Yamauchi, *Chemical Communications*, 2013, **49**, 2521-2523.
- 2 M. J. Katz, Z. J. Brown, Y. J. Colon, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chemical Communications*, 2013, **49**, 9449-9451.
- 3 C. Serre, F. Millange, C. Thouvenot, M. Nogues, G. Marsolier, D. Louer and G. Ferey, *Journal of the American Chemical Society*, 2002, **124**, 13519-13526.
- 4 G. Ferey, *Science*, 2005, **310**, 1119-1119.
- 5 T. Loiseau, L. Lecroq, C. Volkringer, J. Marrot, G. Ferey, M. Haouas, F. Taulelle, S. Bourrelly, P. L. Llewellyn and M. Latroche, *Journal of the American Chemical Society*, 2006, **128**, 10223-10230.
- 6 J. W. Yoon, Y. K. Seo, Y. K. Hwang, J. S. Chang, H. Leclerc, S. Wuttke, P. Bazin, A. Vimont, M. Daturi, E. Bloch, P. L. Llewellyn, C. Serre, P. Horcajada, J. M. Greneche, A. E. Rodrigues and G. Ferey, *Angewandte Chemie-International Edition*, 2010, **49**, 5949-5952.
- 7 P. Horcajada, S. Surble, C. Serre, D. Y. Hong, Y. K. Seo, J. S. Chang, J. M. Greneche, I. Margiolaki and G. Ferey, *Chemical Communications*, 2007, DOI: 10.1039/b704325b, 2820-2822.
- 8 Y. F. Liu, B. L. Liu, Q. F. Zhou, T. Y. Zhang and W. B. Wu, *Chemical Research in Chinese Universities*, 2017, **33**, 971-978.
- 9 Y. K. Seo, J. W. Yoon, J. S. Lee, Y. K. Hwang, C. H. Jun, J. S. Chang, S. Wuttke, P. Bazin, A. Vimont, M. Daturi, S. Bourrelly, P. L. Llewellyn, P. Horcajada, C. Serre and G. Ferey, *Advanced Materials*, 2012, **24**, 806-810.
- 10 C. P. Cabello, P. Rumori and G. T. Palomino, *Microporous and Mesoporous Materials*, 2014, **190**, 234-239.
- 11 G. Ferey, C. Serre, C. Mellot-Draznieks, F. Millange, S. Surble, J. Dutour and I. Margiolaki, *Angewandte Chemie-International Edition*, 2004, **43**, 6296-6301.
- 12 W. Q. Wang, P. Julaiti, G. Ye, X. M. Huo and J. Chen, *Chemical Engineering Journal*, 2018, **336**, 669-678.
- 13 Y. K. Liu, F. Liu, G. Ye, N. Pu, F. C. Wu, Z. Wang, X. M. Huo, J. A. Xu and J. Chen, *Dalton Transactions*, 2016, **45**, 16492-16504.
- 14 I. C. Chen, C. X. Xu, J. Peng, D. Han, S. Q. Liu and M. L. Zhai, *Molecules*, 2019, **24**, 2762.
- 15 Y. K. Liu, X. G. Liu, G. Ye, Y. Song, F. Liu, X. M. Huo and J. Chen, *Dalton Transactions*, 2017, **46**, 6117-6127.
- 16 X. Jiang, B. Wu, P. Bai, J. Lyu and X. Guo, *Acs Applied Materials & Interfaces*, 2021, **13**, 47793-47799.