Alkali Metal Ion-exchange in a Metal–Organic Framework Based on Lanthanum and 1,4-Phenylenebis(methyldiyne)tetrakis(phosphonic acid)

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Abstract

The ion-exchange selectivity of four metal–organic frameworks (denoted as MLaL), formed by alkali metal ions (M^+), La^{3+} , and 1,4-phenylenebis(methyldiyne)tetrakis(phosphonic acid) (L), was examined. Unusual selectivity for the alkali metal ions was observed, which did not follow the previously proposed mechanism that was explained based on the ion-size similarity in the framework. The changes in crystal structures after the ion-exchange reaction were observed by powder X-ray diffraction analysis. The change in the lattice energy in a mixed-metal framework is likely to be one of the significant parameters to affect ion-exchange selectivity.

Metal–organic frameworks (MOFs) have attracted considerable attention in the field of material science because of their unique features such as high tunability, well-defined porous structure, and good functional designability. The post-synthetic ion-exchange reaction of MOFs is one of the most strategic ways to fabricate useful complex materials,^{1–3} and in some cases, it is the only route to obtain a particular material.^{4,5} The ion-exchange reactions of MOFs have also been applied to various methods for the removal, separation,^{6,7} and detection of metal ions.^{8–10}

Although in most cases, selectivity of the metal exchange reactions in MOFs exhibits a common trend as often observed in conventional ion-exchange systems,^{11,12} unusual selectivity has been observed in ion-exchangeable MOFs. For example, Plabst et al.¹³ reported an exceptional selectivity for the ion-exchange reaction between alkali metal ions in an MOF comprising of 1,4-phenylenebis(methyldiyne)tetrakis(phosphonic acid) (**L**; Fig. S1), lanthanum ions (La^{3+}), and sodium ions (Na^+); this MOF is denoted as NaLaL. They concluded that the similarity in the size of the incoming ions with that of the parent Na^+ in the framework of NaLaL was important to generate the exceptional selectivity order ($\text{Li}^+ \approx \text{K}^+ \gg \text{Cs}^+$), which was very different from the well-known order (i.e., $\text{Cs}^+ \geq \text{K}^+ \geq \text{Na}^+ \geq \text{Li}^+$) obtained through the use of common cation exchange resins. However, they only performed experiments on the ion-exchange reactions for the MOF consisting of Na^+ in contact with saturated aqueous solutions of other metal ions. Therefore, the factors controlling the selectivity of NaLaL are still obscure. The unusual ion-exchange selectivity of NaLaL is intriguing and warrants a detailed investigation of the ion-exchange process, including the structural changes caused by ion inclusion, which would significantly affect the ion-exchange selectivity.^{14,15} Using other types of MLaL MOFs instead of NaLaL with different alkali metal ions (M^+) would be helpful to reveal the mechanism.

This study aims to elucidate the factors that strongly affect the unusual ion-exchange selectivity toward alkali metal ions using four types of parent MLaL MOFs ($M = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{and Cs}^+$) by investigating their resulting structural changes. In a previous study, we succeeded in synthesizing LiLaL and CsLaL for the first time,¹⁶ which allowed us to afford four types of MLaL MOFs, including NaLaL (KLaL was synthesized by Plabst et al.,¹³ but it was not used for the study on ion-exchange selectivity).

The ion-exchange reaction of M^+ in MLaL with different alkali metal ions (M'^{+}), hereinafter represented as M'^{+}/M^+ , was studied by performing batch-wise experiments (using H^+ -type MOF is impractical in this system due to the dissolution of MOFs). Optimization of the experimental conditions, including solubility of the MOFs, temperature, concentration of M'^{+} , and reaction time, is described in the Supporting Information (Figs. S2–S5). MLaL (30 mg; $M^+ = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{or Cs}^+$) was added to a 1–25 mM $M'\text{NO}_3$ aqueous solution (10 mL; $M'^{+} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{or Cs}^+$; $M'^{+} \neq M^+$), and the resulting mixture was reacted at 70°C for 35 h using a Thermoshaker system (TAITEC BR-22FH, Aichi, Japan) to attain a state close to equilibrium. MNO_3 was added to adjust the total cation concentration ($C^0(M^+) + C^0(M'^{+})$) to 25 mM, where C^0 represents the initial concentration. The initial molar amount of M'^{+} in the solution was five times that of M^+ in the parent MLaL when $C^0(M'^{+})$ was 25 mM. The concentrations of M^+ and M'^{+} in the supernatant after the reaction, i.e., $C(M^+)$ and $C(M'^{+})$, respectively, were measured using an ion chromatography system (DIONEX ICS1600, Sunnyvale, California, USA). The selectivity coefficient, K_c , was calculated according to the following equation:

$$K_c = \frac{Y(1 - X)}{(1 - Y)X}, \quad (1)$$

where X and Y represent the molar fractions of M'^{+} in the liquid and solid phases, respectively. K_c cannot be regarded as a thermodynamic coefficient because the activity

coefficients, particularly in the solid phases, are not unity and are likely to significantly vary depending on Y , as described later. The powder X-ray diffraction (PXRD) patterns of the as-synthesized MLaL and the ion-exchanged $M'_Y M_{(1-Y)} \text{LaL}$ were recorded by a Bruker D2PHASER diffractometer (Billerica, Massachusetts, USA) with Cu-K α radiation ($\lambda = 0.15418 \text{ nm}$).

Figure 1 summarizes the $\log K_c$ values for M'^+/M^+ reactions, where the vertical dotted lines indicate the alkali metal ions comprising the parent MOFs. Most $\log K_c$ have small values because X values are always large due to an excess amount of M^+ in the initial solutions compared to that of M^+ in the parent MLaL MOFs: for instance, $\log K_c$ is -0.96 , even at $Y = 0.5$. If the ionic size similarity governs the selectivity, $\log K_c$ for M'^+ , which has an ionic radius closest to that of M^+ , should be the largest. In fact, this is true for M'^+/Na^+ , as shown in Fig. 1(B). The selectivity of NaLaL was observed to be $K^+ > Li^+ > Rb^+ > Cs^+$, which seems to follow the order of the deviation in the ionic size from Na^+ , as previously reported.¹³ It should be noted, however, that the order, $K^+ > Na^+ > Li^+ > Rb^+ > Cs^+$, can be applied for all MLaL MOFs. This indicates that the orders of $\log K_c$ in M'^+/Li^+ , M'^+/K^+ , and M'^+/Cs^+ (Figs. 1(A), 1(C), and 1(D), respectively) cannot be solely determined on the basis of the difference in the ionic size between incoming M'^+ and outgoing M^+ .

We found that the order of $\log K_c$ is the same as that of solubility product (K_{sp}) of MLaL, i.e., $(1.5 \pm 0.3) \times 10^{-10} \text{ M}^{-3}$ for KLaL $>$ $(7.7 \pm 2.4) \times 10^{-11} \text{ M}^{-3}$ for NaLaL $>$ $(1.5 \pm 1.2) \times 10^{-12} \text{ M}^{-3}$ for LiLaL $>$ $(6.5 \pm 7.4) \times 10^{-14} \text{ M}^{-3}$ for CsLaL (see Supporting Information). The findings indicate that the order of K_c is opposite to the thermodynamic stability of M'LaL MOFs; $\log K_c$ values for Cs^+/M^+ are small and those for K^+/M^+ are large despite the fact that CsLaL is the most thermodynamically stable and KLaL is the most unstable. This implies that the daughter MOFs are in the metastable state under

individual solution conditions. Although the details are unclear at the present stage, we deduce that the lattice energy (structural stability) of the MLaL frameworks that are related to K_{sp} could be one of the important factors to determine K_c .

Figure 2 shows the PXRD patterns of various $M'_Y M_{(1-Y)}LaL$ species. There are no peaks attributed to MLaL and M'LaL, and the positions of the peaks are shifted from that of the parent MLaL when Y is varied between 0 and 1 for all ion-exchange systems. This indicates that $M'_Y M_{(1-Y)}LaL$ comprises a mixed metal instead of containing both MLaL and M'LaL and the lattices of the daughter $M'_Y M_{(1-Y)}LaL$ are distorted from the parent MLaL, as observed in metal alloys (Vegard's law). Moreover, in Figs. 2(B), 2(C) and 2(E), split peaks are observed in addition to the peak shifts, which may possibly result from the coexistence of two mixed-metal systems, i.e., MLaL-rich and M'LaL-rich $M'_Y M_{(1-Y)}LaL$ phases. The peak splitting could be attributed to the phase separation triggered by local structural strain in a mixed-metal system, which was also observed in metal alloys.^{17,18} Thus, the lattice distortion resulting in a change in the lattice energy of the framework could affect the ion-exchange selectivity.

The lattice energy should play an important role in the ion-exchange reaction because the ion-exchange reaction of MLaL MOFs with an incoming M'^+ requires the cleavage of four M^+-O coordination bonds, followed by the reformation of four new bonds with M'^+ . M^+ in MLaL exhibits six-fold coordination, wherein four coordination sites belong to M^+-OP or $M^+-(OH)P$ (individual four ligand molecules).¹³ The change in the lattice energy of MLaL could affect the bond cleavability, resulting in the unusual ion-exchange selectivity.

This is a unique process that does not occur in common ion-exchange systems. Although the origin of the difference of structural strain in mixed-metal systems remains unclear, the lattice energy that varies depending on the structural strain is more likely to

be an important factor that governs the ion-exchange selectivity in MLaL. We believe that the findings in this study will be useful for designing novel highly-functionalized materials for the removal, separation, and detection of metal ions in the future, as well as new synthetic routes.

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References

1. S. Abednatanzi, P. Gohari Derakhshandeh, H. Depauw, F.-X. Coudert, H. Vrielinck, P. Van Der Voort, and K. Leus, *Chem. Soc. Rev.*, **2019**, 48, 2535.
2. M. Yadollahi, H. Hamadi, and V. Nobakht, *Appl. Organomet. Chem.*, **2019**, 33, e4819.
3. J. Lee, J. S. Choi, N. C. Jeong, and W. Choe, *Chem. Sci.*, **2019**, 10, 6157.
4. P. Deria, J. E. Mondloch, O. Karagiari, W. Bury, J. T. Hupp, and O. K. Farha, *Chem. Soc. Rev.*, **2014**, 43, 5896.
5. C. K. Brozek and M. Dincă, *Chem. Sci.*, **2012**, 3, 2110.
6. Z. Shao, C. Huang, Q. Wu, Y. Zhao, W. Xu, Y. Liu, J. Dang, and H. Hou, *J. Hazard. Mater.*, **2019**, 378, 120719.
7. S. Sharma, A. V. Desai, B. Joarder, and S. K. Ghosh, *Angew. Chem. Int. Ed.*, **2020**, 59, 7788.
8. H. Wang, X. Wang, M. Liang, G. Chen, R.-M. Kong, L. Xia, and F. Qu, *Anal. Chem.*, **2020**, 92, 3366.
9. K. S. Asha, R. Bhattacharjee, and S. Mandal, *Angew. Chem. Int. Ed.*, **2016**, 55, 11528.
10. Y. Zhou, H.-H. Chen, and B. Yan, *J. Mater. Chem. A*, **2014**, 2, 13691.
11. Q. Yao, J. Sun, K. Li, J. Su, M. V. Peskov, and X. Zou, *Dalton Trans.*, **2012**, 41, 3953.
12. A. Deák, T. Tunyogi, and G. Pálincás, *J. Am. Chem. Soc.*, **2009**, 131, 2815.
13. M. Plabst, L. B. McCusker, and T. Bein, *J. Am. Chem. Soc.*, **2009**, 131, 18112.
14. Y. Tasaki-Handa, Y. Abe, K. Ooi, M. Tanaka, and A. Wakisaka, *Dalton Trans.*, **2014**, 43, 1791.
15. M. Tsuji, H. Kaneko, and Y. Tamaura, *J. Chem. Soc., Faraday Trans.*, **1993**, 89, 851.
16. Y. Tasaki-Handa, M. Shibukawa, and S. Saito, *Inorg. Chem. Commun.*, **2021**, 128,

108560.

17. A. J. Celestian, J. D. Kubicki, J. Hanson, A. Clearfield, J. B. Parise, *J. Am. Chem. Soc.*, **2008**, 130, 11689.
18. A. Clearfield, *Solid State Sci.*, **2001**, 3, 103.

Figure Captions

Fig. 1 Log K_c values of M^{+}/M^+ for (A) LiLaL, (B) NaLaL, (C) KLaL, and (D) CsLaL.

The error bars are based on the calculations of Y using the changes in concentration of the solution and solid phases.

Fig. 2 PXRD patterns of $M'_Y M_{(1-Y)}\text{LaL}$. (A) $\text{Li}_Y \text{Na}_{(1-Y)}\text{LaL}$, (B) $\text{K}_Y \text{Na}_{(1-Y)}\text{LaL}$, (C) $\text{Li}_Y \text{K}_{(1-Y)}\text{LaL}$, (D) $\text{Na}_Y \text{K}_{(1-Y)}\text{LaL}$, and (E) $\text{Cs}_Y \text{K}_{(1-Y)}\text{LaL}$ Top: $M'\text{LaL}$ and bottom: parent $M\text{LaL}$. For the difference in lattice spacing between four $M\text{LaL}$ MOFs, see ref. 16.

Fig. 1

Fig. 2

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