

Transmetalations in two metal–organic frameworks with different framework flexibilities: Kinetics and core–shell heterostructure†

Xiaokai Song,^{ab} Seok Jeong,^a Dongwook Kim^a and Myoung Soo Lah^{*a}

Received 23rd June 2012, Accepted 16th July 2012

DOI: 10.1039/c2ce26115d

While only a partially transmetalated network was observed in a rigid metal–organic framework (MOF), not only a completely transmetalated isostructural network but also a partially transmetalated core–shell heterostructural network could be obtained in a flexible MOF by controlling the reaction conditions.

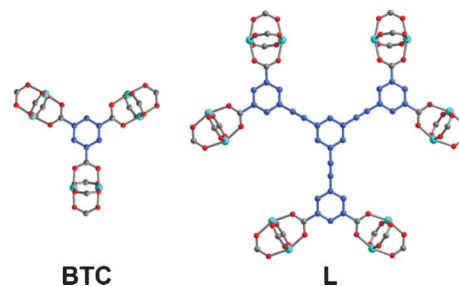
Covalent and dative postsynthetic modifications (PSMs) of metal–organic frameworks (MOFs) have been well developed and have proved to be a general and facile synthetic strategy toward new functionalized MOFs.^{1–3} Recently, the exchange of framework metal ions (*i.e.*, transmetalation)^{4,5} or the replacement of structural organic linkers⁶ have been reported as new types of dative PSMs. The transmetalation of framework metal ions or the exchange of structural organic ligands can proceed *via* even a single-crystal to single-crystal transformation. Although the replacement of framework metal ions has been reported several times, most reports are of incomplete transmetalation.⁴ Recently, Kim and co-workers reported a complete and reversible exchange of the framework metal ion in a water-stable tricarboxylate MOF system.^{5a} The exchange reaction was completed within a week at ambient temperature. Zou and co-workers also reported a complete but irreversible exchange of the framework metal ion in a 3-D MOF system based on a paddle-wheel secondary building unit (SBU).^{5b} However, the exchange reaction was much slower than that in the MOF system reported by Kim's group, and the complete transmetalation took three months. Postsynthetic transmetalation could be utilized as a new approach toward heterometallic MOFs with multifunctional properties in addition to being a general approach for the preparation of isostructural MOFs that are difficult to obtain or unattainable by a direct synthetic strategy. However, it is not well investigated how quickly the transmetalation takes place, which factors control the reaction kinetics, whether the transmetalation will be partial or complete, and

whether the transmetalation process in a single MOF crystal is occurring homogeneously with no site selectivity or heterogeneously with site selectivity in the single crystalline particle.

Two Zn-based 3-D MOFs have been chosen as model systems with the same $Zn_2(COO)_4$ paddle-wheel SBUs but which are interlinked *via* different organic ligands of different flexibilities to study the reaction characteristics related to the transmetalation.

Zn-HKUST-1 ($[Zn_3(BTC)_2(H_2O)_3]$, where BTC = 1,3,5-benzenetricarboxylate), which is a Zn analogue of Cu-HKUST-1 with a (3,4)-connected **tbo** net topology,⁷ was chosen as a model MOF made with the small and rigid tricarboxylate, BTC, as an organic component. As reported, Zn-HKUST-1 based on a $Zn_2(COO)_4$ paddle-wheel cluster as a 4-connected SBU is unstable when the lattice solvent molecules in the pore are removed from the pore of the MOF, although the framework with the lattice solvent in the pore is structurally rigid in anhydrous solvents. For the best comparison, an isoreticular Zn–MOF of the same net topology but with a larger tricarboxylate as a ligand might be appropriate as another model. However, no such isoreticular Zn–MOF has been reported yet. Therefore, Zn-PMOF-2 ($[Zn_2L_8(H_2O)_{12}]$, where L = 1,3,5-tris(3,5-dicarboxylphenylethynyl)benzene) was chosen as a model MOF having the same $Zn_2(COO)_4$ cluster with the same 4-connected SBU, but the clusters were connected *via* hexacarboxylate ligand L, which is larger than BTC, as shown in Scheme 1.⁸ In the framework structure, the isophthalate moiety in L is linked through the Zn(II) paddle-wheel SBU to form a more flexible MOF with a (3,24)-connected **rht** net topology.

Zn-HKUST-1^{7a} was prepared using a procedure that was slightly modified from the reported procedure.† The framework metal ions of Zn-HKUST-1 were replaced by Cu(II) ions in 0.3 M



Scheme 1 Ligand BTC interlinking three Zn(II) paddle-wheel SBUs (left) and ligand L interlinking six Zn(II) paddle-wheel SBUs (right).

^aInterdisciplinary School of Green Energy, Ulsan National Institute of Science & Technology, Ulsan, 689-798, Korea

^bDepartment of Chemistry and Applied Chemistry, Hanyang University, Ansan, Kyunggi-do, 426-791, Korea. E-mail: mslah@unist.ac.kr; Fax: +82 52 217 2019; Tel: +82 52 217 2931

† Electronic supplementary information (ESI) available: Experimental procedure, crystallographic details, a table of sorption properties of the MOFs, and PXRD patterns of the MOFs. CCDC reference number 888257. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce26115d

$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ methanol solution at ambient temperature. Optical microscopic photographs of a single crystal soaked in the Cu(II) methanol solution indicate the replacement of the framework metal ion, *i.e.*, transmetalation (Fig. S1†). The crystal in the Cu(II) methanol solution changes from colorless to blue during the soaking. The powder X-ray diffraction (PXRD) study also supports the structural integrity and the crystallinity during the transmetalation (Fig. S2†). However, the metal ion contents analyzed using an inductively coupled plasma-atomic emission spectrometer (ICP-AES) showed that the transmetalation was incomplete for the sample soaked for a month (Fig. S3a†). The transmetalation to Cu-HKUST-1 could not be completed even for the sample soaked for three months in a 0.5 M Cu(II) methanol solution. The amount of the replaced framework metal ions varied depending on the concentration of the soaking solution and the soaking time, so the extent of the transmetalation could be controlled by adjusting the concentration and the soaking time. However, the ultimate contents of the framework metal ions of the sample soaked for an extended period are not dependent on the concentration. Up to $\approx 56\%$ of the framework metal ions were replaced by Cu(II) ions in methanol solution. The choice of the soaking solvent is also important. In *N,N'*-dimethylformamide (DMF), the exchange rate was too slow to observe meaningful transmetalation. The transmetalation in DMF at an elevated temperature (70°C) was complicated because of the formation of blue powder as a side product during the transmetalation process.

The reverse transmetalation, from Cu-HKUST-1 to Zn-HKUST-1, is not possible. The soaking of as-synthesized Cu-HKUST-1 or transmetalated $\text{Cu}_{0.56}\text{Zn}_{0.44}$ -HKUST-1 in a Zn(II) methanol solution did not indicate any reverse transmetalation no matter how long the sample was kept in the solution.‡ Cu-HKUST-1 is thermodynamically more stable than Zn-HKUST-1 in methanol solution.

The framework metal ions of Zn-PMOF-2 could also be transmetalated by Cu(II) ions in 0.1 M $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ methanol solution at ambient temperature. The optical microscopic photographs of a single crystal soaked in the Cu(II) methanol solution (Fig. 1) and the PXRD pattern of the sample soaked in the solution for 3 d (Fig. S4†) support the structural integrity and the crystallinity of the sample during and after the transmetalation. Unlike Zn-HKUST-1, the ICP-AES analysis showed that the transmetalation was complete within 3 d even in

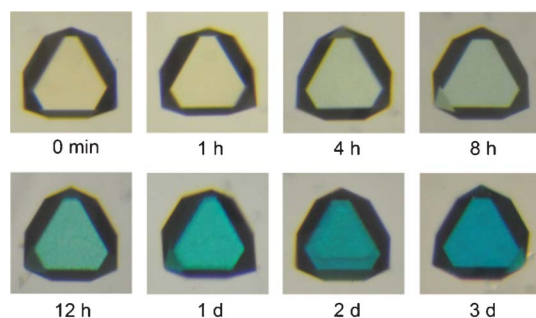


Fig. 1 Optical microscopic photographs of a single crystal of Zn-PMOF-2 ($0.36 \times 0.36 \times 0.20$ mm in size) soaked in 0.1 M $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ methanol solution at ambient temperature. The photographs are for a single crystal in the Cu(II) methanol solution after different periods of time.

the lower concentration of Cu(II) methanol solution (Fig. S3b†). As in Zn-HKUST-1, the soaking of Zn-PMOF-2 in DMF solution did not show any indication of transmetalation, and soaking at elevated temperature (70°C) also generated blue powder as a side product during the transmetalation process. As expected, the reverse transmetalation from Cu-PMOF-2 to Zn-PMOF-2 did not occur, which again indicates that Cu-PMOF-2 is thermodynamically more stable than its Zn(II) analogue.

Optical microscopic photographs of a Cu_1Zn_0 -PMOF-2 crystal and its face-cut fragments also support the complete transmetalation in the methanol solution (Fig. 2a,b). In contrast, the optical microscopic photographs of a partially transmetalated $\text{Cu}_{0.22}\text{Zn}_{0.78}$ -PMOF-2 crystal and its face-cut fragments clearly show that the cyan color is localized only at the external shell region of the crystal, while the internal core remained colorless (Fig. 2c,d).§ The exchange of the framework metal ions has occurred selectively at the external shell, which led to a core-shell heterostructure. The exchange occurs heterogeneously with site selectivity in a single crystalline particle.

The sorption behaviors of the transmetalated MOFs were investigated to study the effects of the modification. The as-synthesized Zn-HKUST-1 activated *via* the conventional vacuum drying (CVD) process is not stable, losing its crystallinity during the activation, and does not show any significant N_2 sorption at 77 K, as reported (Fig. 3a and Table S2†).^{7a} However, the transmetalated core-shell MOF prepared by soaking Zn-HKUST-1 for one month, $\text{Cu}_{0.56}\text{Zn}_{0.44}$ -HKUST-1, keeps its crystallinity and shows type I sorption isotherms with $259\text{ cm}^3\text{ g}^{-1}$ N_2 uptake amount and $980\text{ m}^2\text{ g}^{-1}$ BET specific surface area, which are ≈ 65 and $\approx 67\%$ of those of the as-synthesized Cu-HKUST-1, respectively. In addition, the sorption capacity could be adjusted simply by controlling the metal content in the transmetalated MOF. The transmetalated MOF prepared by soaking Zn-HKUST-1 for 15 d, $\text{Cu}_{0.46}\text{Zn}_{0.54}$ -HKUST-1, shows a $208\text{ cm}^3\text{ g}^{-1}$ N_2 uptake amount and $770\text{ m}^2\text{ g}^{-1}$ BET specific surface area, which are ≈ 52 and $\approx 53\%$ of those of the as-synthesized Cu-HKUST-1, respectively. The recovery of the sorption capacity is approximately proportional to the extent of the framework metal replacement.

As-synthesized Zn-PMOF-2 activated *via* the CVD process also did not show any significant N_2 sorption, as in the case of Zn-HKUST-1. However, the complete transmetalation led to full

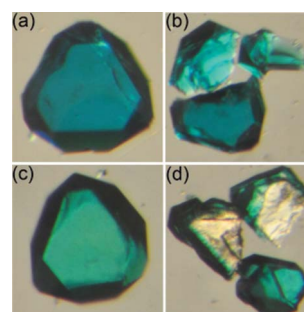


Fig. 2 Optical microscopic photographs of (a) a single crystal of Zn-PMOF-2 soaked in 0.1 M $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ methanol solution for 3 d at ambient temperature and (b) its face-cut fragments. Optical microscopic photographs of (c) a single crystal of Zn-PMOF-2 soaked in the same solution for 12 h and (d) its face-cut fragments.

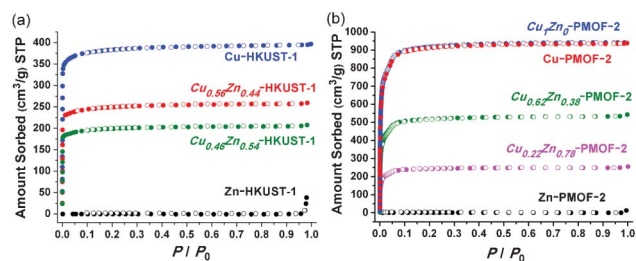


Fig. 3 (a) The N_2 sorption isotherms of Zn-HKUST-1, $Cu_{0.56}Zn_{0.44}$ -HKUST-1, $Cu_{0.46}Zn_{0.54}$ -HKUST-1, and Cu-HKUST-1 at 77 K. (b) The N_2 sorption isotherms of Zn-PMOF-2, $Cu_{0.22}Zn_{0.78}$ -PMOF-2, $Cu_{0.62}Zn_{0.38}$ -PMOF-2, Cu_1Zn_0 -PMOF-2, and Cu-PMOF-2 at 77 K. Solid and open shapes represent adsorption and desorption isotherms, respectively.

recovery of the sorption capacity. The N_2 adsorption amount ($942 \text{ cm}^3 \text{ g}^{-1}$) and the BET specific surface area ($3550 \text{ m}^2 \text{ g}^{-1}$) of Cu_1Zn_0 -PMOF-2 activated *via* the CVD process are comparable to the reported values of as-synthesized Cu-PMOF-2 (Fig. 3b and Table S2†).⁸ The recovery of the sorption capacity in the PMOF-2 system is also approximately proportional to the extent of the framework metal replacement. The partially transmetalated core-shell heterostructures, $Cu_{0.62}Zn_{0.38}$ -PMOF-2 and $Cu_{0.22}Zn_{0.78}$ -PMOF-2, have $2010 \text{ m}^2 \text{ g}^{-1}$ and $950 \text{ m}^2 \text{ g}^{-1}$ BET specific surface areas, respectively, which are ≈ 56 and $\approx 27\%$, respectively, of the BET specific surface area of the fully transmetalated Cu_1Zn_0 -PMOF-2. The replacement of the framework metal ions enhances the overall framework stability and subsequently increases the sorption capacity of the transmetalated MOF system.

The metal centers connected *via* a flexible organic linker are more reactive than those connected *via* a rigid organic linker. The different reactivities of the same metal centers within a single crystalline particle are related to the different rigidities of the metal centers, depending on their locations. It is natural that the metal centers close to the surface of a particle are more flexible than those in the internal core of the particle. Hence, even in the same MOF system, the metal centers close to the surface are more reactive than those in the internal core. The transmetalation starts at the surface of a single crystalline particle and gradually propagates toward the internal core region, which leads to core-shell heterostructures.

Conclusions

Here, we have demonstrated transmetalation using the two MOFs, Zn-HKUST-1 and Zn-PMOF-2, having the same Zn paddle-wheel framework metal centers but linked by ligands of different size and flexibility. The characteristics of the transmetalation are determined by several factors controlling the thermodynamics and the kinetics of the reaction, such as choice of solvent, concentration of soaking solution, and reaction temperature. The thermodynamically unstable Zn-based MOFs could be transmetalated in methanol to the corresponding isostructural Cu-based MOFs, which are thermodynamically more stable. However, no significant reverse transmetalations were observed. A similar attempt in DMF did not show any appreciable indication, probably because of the extremely slow exchange kinetics of the

reaction. The transmetalations in DMF at an elevated temperature led to the formation of a side product together with the transmetalation.

The transmetalation kinetics is influenced not only by the chemical nature but also by the flexibility of the framework metal center. While the complete transmetalation could be accomplished in a flexible Zn-PMOF-2 framework system made with a large organic linker, only the partial transmetalation could be observed in a rigid Zn-HKUST-1 framework system consisting of a small and rigid organic linker. The framework metal centers seemingly in the same chemical environments actually are not in the same environment because the single particle itself behaves like an extended macromolecule. Depending on the locations of the framework metal ions in the particle, they are in different environments and show different reactivities. The metal centers in close vicinity of the surface of the particle are in a more flexible environment; hence, they are more reactive than the metal centers in the internal core region, which are in a more rigid environment. The different site reactivities led to a core-shell heterostructure.

Acknowledgements

This work was supported by NRF-2009-0084799, NRF-2011-0027950, NRF-2012-003077 and WCU programs (R31-2011-000-20012-0) through the National Research Foundation of Korea.

References

- 1 S. M. Cohen, *Chem. Rev.*, 2012, **112**, 970–1000.
- 2 (a) Z. Wang and S. M. Cohen, *J. Am. Chem. Soc.*, 2007, **129**, 12368–12369; (b) Y.-H. Kiang and G. B. Gardner, *J. Am. Chem. Soc.*, 1999, **121**, 8204–8215; (c) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982–986; (d) T. Haneda, M. Kawano, T. Kawamichi and M. Fujita, *J. Am. Chem. Soc.*, 2008, **130**, 1578–1579; (e) T. Yamada and H. Kitagawa, *J. Am. Chem. Soc.*, 2009, **131**, 6312–6313; (f) S. Han, Z. Ma, R. Hopson, Y. Wei, D. Budil, S. Gulla and B. Moulton, *Inorg. Chem. Commun.*, 2012, **15**, 78–83.
- 3 (a) A. M. Shultz, A. A. Sarjeant, O. K. Farha, J. T. Hupp and S. T. Nguyen, *J. Am. Chem. Soc.*, 2011, **133**, 13252–13255; (b) Z. Zhang, L. Zhang, L. Wojtas, P. Nugent, M. Eddaoudi and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2012, **134**, 924–927; (c) K. L. Mulfort, O. K. Farha, C. L. Stern, A. A. Sarjeant and J. T. Hupp, *J. Am. Chem. Soc.*, 2009, **131**, 3866–3868; (d) E. D. Bloch, D. Britt, C. Lee, C. J. Doonan, F. J. Uribe-Romo, H. Furukawa, J. R. Long and O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, **132**, 14382–14384; (e) K. Oisaki, Q. Li, H. Furukawa, A. U. Czaja and O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, **132**, 9262–9264.
- 4 (a) S. Huang, X. Li, X. Shi, H. Hou and Y. Fan, *J. Mater. Chem.*, 2010, **20**, 5695–5699; (b) T. K. Prasad, D. H. Hong and M. P. Suh, *Chem.–Eur. J.*, 2010, **16**, 14043–14050; (c) M. Dinca and J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 11172–11176; (d) L. Mi, H. Hou, Z. Song, H. Han, H. Xu, Y. Fan and S. W. Ng, *Cryst. Growth Des.*, 2007, **7**, 2553–2561; (e) L. Mi, H. Hou, Z. Song, H. Han and Y. Fan, *Chem.–Eur. J.*, 2008, **14**, 1814–1821.
- 5 (a) S. Das, H. Kim and K. Kim, *J. Am. Chem. Soc.*, 2009, **131**, 3814–3815; (b) G. Mukherjee and K. Biradha, *Chem. Commun.*, 2012, **48**,

-
- 4293–4295; (c) Q. Yao, J. Sun, K. Li, J. Su, M. V. Peskova and X. Zou, *Dalton Trans.*, 2012, **41**, 3953–3955.
- 6 (a) B. J. Burnett, P. M. Barron, C. Hu and W. Choe, *J. Am. Chem. Soc.*, 2011, **133**, 9984–9987; (b) B. J. Burnett and W. Choe, *Dalton Trans.*, 2012, **41**, 3889–3894; (c) M. Kim, J. F. Cahill, Y. Su, K. A. Prather and S. M. Cohen, *Chem. Sci.*, 2012, **3**, 126–130.
- 7 (a) J. I. Feldblyum, M. Liu, D. W. Gidley and A. J. Matzger, *J. Am. Chem. Soc.*, 2011, **133**, 18257–18263; (b) S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148–1150.
- 8 (a) S. Hong, M. Oh, M. Park, J. W. Yoon, J.-S. Chang and M. S. Lah, *Chem. Commun.*, 2009, 5397–5399; (b) D. Zhao, D. Yuan, D. Sun and H.-C. Zhou, *J. Am. Chem. Soc.*, 2009, **131**, 9186–9188.