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The Preparation of An Ultrastable Mesoporous Cr(III)-MOF via Reductive Labilization

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Thermodynamic and kinetic labilization of the robust Fe(III)-O coordination bond in a mesoporous metal-organic framework, PCN-333-Fe(III), is realized by the reduction of Fe(III) by Cr(II). The Fe(II)-Cr(II) metathesis is thus completely achieved followed by this reductive labilization process which generates PCN-333-Cr(III). The kinetic inertness of Cr(III) provides PCN-333-Cr(III) with enhanced chemical stability as well as a broader range of applications compare to that of PCN-333-Fe(III). For instance, an alkylamine incorporated PCN-333-Cr(III) demonstrated significant carbon dioxide uptake while PCN-333-Fe(III) lost its crystallinity after alkylamine treatment.

Introduction

Bearing the high surface area, large pore size and volume as well as the tunability of pore environments and functionalities, metal-organic frameworks (MOFs) have demonstrated promising applications in storage, separation, catalysis, guest moiety immobilization, drug delivery and sensing.¹⁻⁵ Many of these applications include the use of metal nodes, or secondary building units (SBUs), as active sites. SBUs are always explored as Lewis acid species, while their redox properties have been studied in only a few reports.^{6,7} One of experimental demonstrations is the reduction of high valence Fe(III) to generate low valence Fe(II) in MIL-100-Fe(III) by carbon monoxide, indicating the possibility of tuning the chemical robustness of the framework by redox reaction.⁷ Based on the Hard and Soft Acid and Base (HSAB) Theory,²⁸ chemically robust MOFs can be constructed with carboxylate ligand, defined as a hard Lewis base, and high valence metal ions, such as Fe(III), Cr(III) or Zr(IV), categorized as hard Lewis acids. Compared with MOFs composed of divalent species, many of these high valence metal containing MOFs can survive in water, or even acid or base solutions. This phenomenon has been exclusively demonstrated in MIL series, UiO series and PCN-22X series.^{9-15,26} A recent example is an iron based mesoporous MOF, PCN-333-Fe(III), which is stable in both acidic and basic aqueous solutions despite its ultrahigh porosity (Figure 1).⁸ However, MOFs constructed with high

valence metal ions may suffer from structure breakdown in some specific environments, for instance, PCN-333-Fe(III) totally loses its crystallinity and porosity in alkylamine solution. Incorporation of kinetically inert metal ions, for example, Cr(III), into the framework backbone could generate MOFs with exceptional stability.^{16,26}

Nevertheless, obtaining crystalline Cr(III)-MOFs with carboxylate ligands are extremely difficult due to the inertness of Cr(III). Hydrothermal conditions are exclusive adopted in the synthesis of crystalline Cr(III)-MOFs, but these conditions might be unfeasible for larger organic ligands as they are extremely hydrophobic. Synthetic attempts of PCN-333-Cr(III) by either hydrothermal or solvothermal conditions with temperature as high as 220°C failed to generate any crystalline products. An alternative synthetic pathway is post synthetic metathesis of metal clusters from a template MOF with a known structure. Fe(III)-MOFs can serve as practical structural templates because iron resembles chromium in both coordination geometry and valence. Disappointingly, metathesis of PCN-333-Fe(III) with CrCl₃ for 24 hours only yielded partially metathesized MOF. The incompleteness of the above metathesis is not surprising since in several reports demonstrating the feasibility of metal metathesis for thermodynamically inert MOFs, complete metal metathesis has never been achieved.²⁴ This is mainly contribute to two reasons: (a) the dissociation of high valence metal ions from framework is thermodynamically unfavorable; (b) the dissociation rate of high valence ions is much slower than that of the divalent species due to the much higher activation energy.²⁵ Therefore, long reaction time or elevated reaction temperature is required in order to achieve complete metathesis. However, under these scenarios, framework decomposition is usually inevitable due to the acidic environments generated by high valence species.^{17,25}

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Herein, we report a reductive labilization-metathesis route for the synthesis of PCN-333-Cr(III) with PCN-333-Fe(III) as the template, wherein redox chemistry has contributed to the generation of labile metathesis intermediates. PCN-333-Cr(III) demonstrated broader range of applications than PCN-333-Fe(III) in consequence of its improved chemical sustainability. The alkylamine incorporated PCN-333-Cr(III) demonstrated significant CO₂ adsorption capacity under low pressure whereas PCN-333-Fe(III) barely shows any CO₂ adsorption capacity due to structural decomposition in alkylamine solution.

Results and discussion

MOFs constructed with divalent metal ions have been demonstrated to be good templates for complete metal metathesis due to the thermodynamic and kinetic lability of their coordination bonds.^{17-23,29} The reduction of high valence metal in SBUs can labilize the robust MOF, which will provide possibility for complete metathesis with a robust MOF template. There are several prerequisite for this process to take place: (1) the metal ions of the framework are in their high oxidation state and can be readily reduced under mild condition; (2) the reductant will not cause harsh conditions after oxidation (for example, very low/high pH values); (3) the oxidation potential of the oxidant is much higher than the reduction potential of the reductant, resulting in an irreversible redox reaction. In the practical case, PCN-333-Fe(III) is composed of oxidative Fe(III) species while CrCl₂ matches the prerequisites to be a suitable reductant. The M³⁺/M²⁺ redox potentials for Fe and Cr in aqueous solutions are: 0.77V (Fe), -0.42V (Cr).²⁵ The large potential difference indicates that redox reaction can irreversibly take place between Fe(III) and Cr(II) as indicated in eq. (1):



Driven by the concentration gradient, the metal metathesis between Fe(II) in the intermediate framework and Cr(II) in the solution is thermodynamically and kinetically favorable.

Freshly prepared PCN-333-Fe(III) was dispersed in a solution of CrCl₂ in dry N,N-dimethylformamide (DMF) at 85°C under the protection of N₂. The color of the solid turned gradually from reddish brown to deep green (Figure 2B). The complete metathesis of Fe by Cr was obtained after 30 minutes as confirmed by inductive coupled plasma mass spectroscopy (ICP-MS) and energy-dispersive X-ray spectroscopy (EDS) (Figure 2A, Table S1). The SEM-EDS mapping with 4,000,000 counts results indicated that Cr, C, O and Cl were uniformly distributed on the crystal surface (Figure 2D-F, Figure S2). After that, the solids were washed with DMF three times in the air exposure to guarantee that all of the Cr(II) ions in the framework were oxidized to Cr(III), which was verified by X-ray photoelectron spectroscopy (XPS) (Figure S12). The crystallinity of the metathesized product was maintained and recognized to be isostructural with PCN-333-Fe(III) as shown in

the powder X-ray diffraction patterns (Figure 3, bottom). The surface area and porosity of the metathesized product was also preserved based on the isotherms of N₂ adsorption measurements (Figure 3, top). This reaction condition is optimum since higher or lower temperature with longer or shorter reaction time will either yield partially metathesized material or cause structure decomposition and porosity loss.

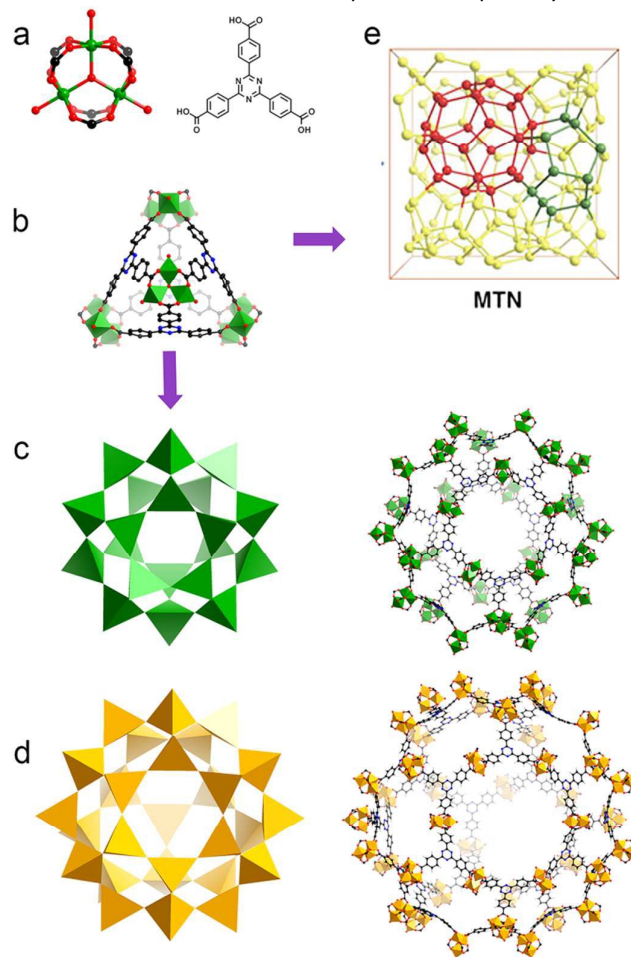


Figure 1 (a) PCN-333 is composed of trimeric clusters and TATB ligands with (b) supertetrahedron as supermolecular building blocks. (c) The small cage with diameter of 4.2 nm and (d) the large cage with diameter of 5.5 nm in the construction of (e) the network with MTN topology.⁸

The reductive labilization-metathesis process was facilitated in the PCN-333 system for several structural characteristics. First, the microcrystalline and mesoporous nature of PCN-333 allows the metal ions to diffuse efficiently into the inner cavity of the framework. Besides, the trimeric clusters in PCN-333 are able to accommodate both di- and trivalent metal ions by varying charges of the terminal ligands, the bridging oxygen atoms, and/or the number of counterions.²⁴ Furthermore, the usage of the anhydrous reaction solvent decelerated the hydrolysis of Cr(III) species. The absence of acidic condition contributes to the structural intactness of the intermediate MOF composed of fragile Cr(II)-O bond.

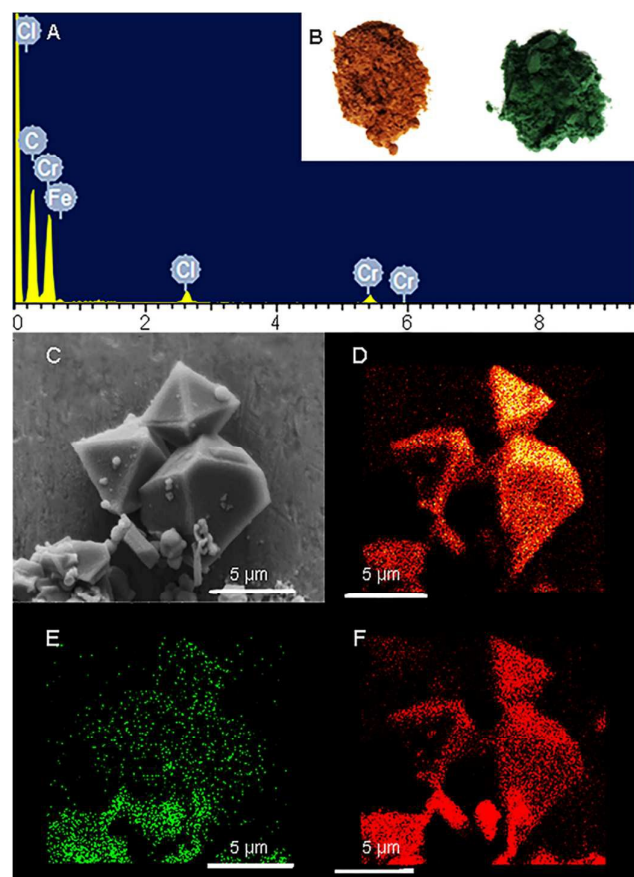


Figure 2 (A) The EDS spectrum of PCN-333-Cr(III); (B) PCN-333-Fe(III) on the left and PCN-333-Cr(III) on the right; (C) SEM images of PCN-333-Cr(III); elemental mappings of (D) C, (E) Cr, and (F) O from EDS analysis on PCN-333-Cr(III).

In order to exclude the possibility that the metathesis of PCN-333-Fe(III) with CrCl_2 circumvented the reductive labilization mechanism, a redox inert isostructural framework PCN-333-Sc was synthesized as a template to metathesize with CrCl_2 . If the Cr(II) species were hypothesized to metathesize with Fe(III) ions in the framework directly without undergoing redox reaction, complete metal metathesis should also be observed in the system of PCN-333-Sc and Cr(II) since the Sc(III)-O coordination bond is not as robust as the Fe(III)-O bond.²⁵ The mixture of PCN-333-Sc and CrCl_2 in dry DMF was heated at 85°C for 30 minutes. The EDS results showed that only one fifth of the scandium in the framework was exchanged with chromium (Table S2). This observation suggests that the metathesis between PCN-333-Fe(III) and CrCl_2 should undergo reductive labilization-metathesis manner since a thermodynamically more labile framework failed to generate complete metathesized product without reductive labilization. According to Marcus Theory and some calculation results, the electron transfer between Fe(III) and Cr(II) in this case should undergo outer-sphere mechanism²⁷ although the experimental evidence of this mechanism is still pursuing in our group. First of all, inner-sphere mechanism requires the dissociation of axial ligands from Fe(III) whereas outer-sphere mechanism

does not include coordination bond dissociation. Since the dissociation of Fe(III)-ligand bond is thermodynamically and kinetically unfavorable, outer-sphere electron transfer mechanism is more reasonable. Moreover, based on calculations, the rate constant of the cross redox reaction between Fe(III) and Cr(II) in aqueous solution is nearly $3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, which is close to the rate constant of the well-known outer-sphere redox couples, for example, $[\text{Fe}(\text{phen})_3]^{2/3+}$ ($1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$),²⁷ and much larger than the well-known inner-sphere redox couples, for example, $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} + [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ ($1.46 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$). The metal ions are still in high-spin electronic configurations and their coordination field splittings in the framework or in the DMF solutions are similar to those in aqueous solutions which indicates that outer-sphere electron transfer is expected between these two metal ions.

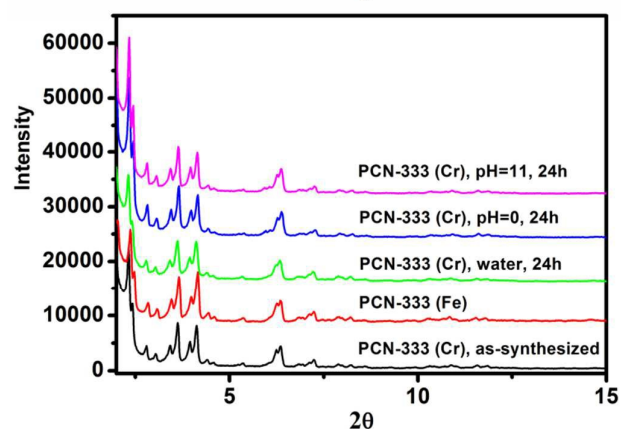
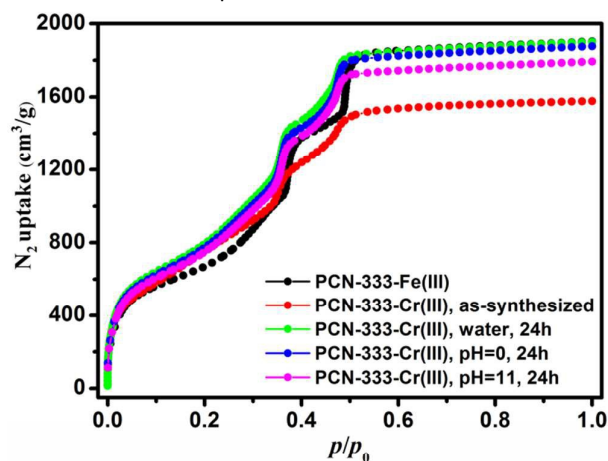


Figure 3 N_2 isotherms (top) and PXRD patterns (bottom) of PCN-333-Fe(III), PCN-333-Cr(III), PCN-333-Cr(III) treated with water, pH=0 and pH=11.0 aqueous solutions for 24 hours.

As expected, the chemical stability of PCN-333-Cr(III) was much enhanced compared with PCN-333-Fe(III). Suspended in water, HCl aqueous solution (pH=0) and NaOH aqueous solution (pH=11.0) at room temperature for 24 hours, PCN-333-Cr(III) maintained structural integrity without appreciable loss of crystallinity as confirmed by PXRD measurements (Figure 3, bottom). In contrast, PCN-333-Fe(III) was only stable in aqueous solutions at pH ranging from 3.0 to 9.0. To

demonstrate the intactness of porosity, N_2 isotherms were conducted before and after each treatment. The results indicated that the void volume accessibility, the characteristic mesoporous adsorption patterns and the pore size distributions of PCN-333-Cr(III) after each treatment was unequivocally preserved (Table S4, Figure S3-S7). Remarkably the samples after each treatment even showed higher total adsorption amount than the as-prepared PCN-333-Cr(III). That is probably because some insoluble Cr(III) compounds, generated during metal metathesis and trapped in the pores, were removed upon the above mentioned treatments.

Table 1 Ligand exchange rate of water molecules in trivalent aqua complexes.²⁷

	Inert complexes		Labile complexes		
M(OH ₂) ₆ ³⁺	Cr(OH ₂) ₆ ³⁺	Ir(OH ₂) ₆ ³⁺	V(OH ₂) ₆ ³⁺	Fe(OH ₂) ₆ ³⁺	Ti(OH ₂) ₆ ³⁺
<i>k</i> (s ⁻¹)	2.4×10 ⁻⁶	1.1×10 ⁻¹⁰	8.7×10 ¹	1.6×10 ²	1.8×10 ⁵

The above results have clearly demonstrated that employing kinetically inert metal ions is an efficient strategy for constructing ultrastable MOFs with high porosity. Since the association-dissociation equilibrium of metal-ligand coordination bond always exists, coordination bonds in a MOF also undergo association-dissociation process. In the aqueous solution, carboxylate ligand substitution around metal ions with other ligands from the solution, for example, water or hydroxyl group, may take place, which could lead to the breakdown of MOF structure. For two metal ions with the same valence, ligand substitution rate of the kinetically inert species is far slower than that of the labile counterpart.²⁵ As shown in **Table 1**, the ligand exchange rate of Cr(III) in aqueous solutions is more than 10¹⁰ times slower than that of Fe(III) species, which is believed to be the key factor that contribute to the superior chemical stability of Cr(III)-MOFs compared with other MOFs based on trivalent species. Meanwhile, the slow Cr-ligand dissociation rate also decreases the hydrolysis rate of the carboxylate ligand which also contributes to the improvement of MOF stability.

By taking advantage of the superior chemical stability of PCN-333-Cr(III), alkylamine was incorporated in PCN-333-Cr(III) aiming to improve the CO₂ adsorption capacity. Branched polyethylenimine (PEI, M_w=800) was selected for the high density of amine groups on each molecule. After PEI treatment the solid maintained its crystallinity with CO₂ adsorption capacity of 8.4 wt% at 1 bar (Figure S8). In contrast, PCN-333-Fe(III) completely lost its crystallinity and porosity after PEI treatment according to the PXRD pattern and N₂ adsorption measurement (Figure S9, S10).

Conclusions

In conclusion, we reported a reductive labilization-metathesis route for the construction of an ultrastable mesoporous Cr(III)-MOF from a robust iron based MOF template. The involvement of redox chemistry has switched a thermodynamically and kinetically forbidden process into a

feasible one. The whole process includes (1) reduction of Fe(III) on the framework backbone to Fe(II); (2) metal metathesis between Fe(II) and Cr(II); (3) oxidation of Cr(II) in the framework to Cr(III). The presence of Fe(II) intermediate was proved by incomplete metathesis of PCN-333-Sc exchanged with CrCl₂. After metathesis, PCN-333-Cr(III) has demonstrated unprecedented chemical stability in aqueous solutions at pH 0 to 11.0 whereas PCN-333-Fe(III) can only survive in solution at pH 3.0 to 9.0. Significantly, PCN-333-Cr(III) is robust enough to bear the harsh condition of alkylamine solution, displaying high CO₂ adsorption capacity after PEI incorporation. Overall, the method we represent here demonstrated a new platform to synthesize ultrastable MOFs with high porosity for practical applications.

Experimental

Materials and Instruments.

Iron(III) chloride anhydrous (FeCl₃), chromium(II) chloride anhydrous (CrCl₂), N,N-dimethylformamide (DMF), N,N-diethylformamide (DEF), trifluoroacetic acid (TFA) were purchased from Alfa Aesor. 4, 4', 4''-s-Triazine-2, 4, 6-triyltribenzoic acid (H₃TATB) were synthesized following the reported procedure.⁸ All commercial chemicals were used without further purification.

Powder X-ray diffraction (PXRD) was carried out with a BRUKER D8-Focus Bragg-Brentano X-ray powder diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178\text{\AA}$) at 40 kV and 40 mA. Thermogravimetric analyses (TGA) were conducted on a TGA-50 (SHIMADZU) thermogravimetric analyzer. Gas sorption measurements were conducted using a Micromeritics ASAP 2420 system at various temperatures. Inductively Coupled Plasma Emission - Mass Spectrometry (Laser Ablation) was carried out by Perkin Elmer DRCII ICP-MS with both solution and laser ablation capabilities.

Synthesis and activation of PCN-333-Cr(III)

FeCl₃ (60 mg), H₃TATB (60 mg), DEF (10 mL) and TFA (0.5 mL) were mixed in a 20 mL vial. The solids were supersonically dissolved and the vial was heated at 150°C for 12 hours. The resulting solid was centrifuged and washed with anhydrous DMF for several times. 10 mL of anhydrous DMF was added into the vial and the mixture was degassed with nitrogen for 2 hours. 120 mg CrCl₂ was added into the vial in a glove box. Then the vial was heated at 85°C for about 30 minutes until all of the solids turned green. Then the vial was centrifuged and transferred into the glove box to discard the mother liquor followed by rinsing with anhydrous DMF for three times. The vial was taken out of the glove box and rinsed with DMF twice in the air. For sample activation, the sample was rinsed with acetone twice, dried in a 85°C oven, activated at 150°C for 5 hours.

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