Post-Synthetic Coordination Modification of Robust Pillared-Rod Metal-Azolate Frameworks for Diversified Applications

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Post-synthetic coordination modification has proven to be a general and powerful approach for the functionalization of porous coordination polymers or metal-organic frameworks (MOFs). Metal-azolate frameworks (MAFs) are an important subclass of MOFs. In this account, the progress in the coordination post-synthetic modifications of an exceptionally robust pillared-rod MAF, featuring mixed μ -chloride and μ_3 -triazolate bridges as the rods and linear bistriazolates as the pillars, and its structural analogues with different transition metal ions and/or expanded organic bridging ligands are summarized and discussed. Through removal of the terminal coordinated solvent molecules, redox of the metal ions, and exchange of the anionic inorganic bridging ligands in the rods, significantly enhanced performances can be realized in carbon dioxide capture, photocatalytic carbon dioxide reduction, photocatalytic hydrogen generation, electrolytic water oxidation and oxidation of ethylbenzene.

1. Introduction

In the past three decades, porous coordination polymers (PCPs),¹ also more well known as metal-organic frameworks (MOFs),² have been very extensively investigated for the interesting structures and properties, especially relevant with their porous structures. Porous metal-azolate frameworks (MAFs) are an important subclass of PCPs or MOFs based on azolates (deprotonated poly-nitrogen-containing five-membered heterocycles), such as imidazolates, pyrazolates, triazolates and tetrazolates, as well as their derivatives as bridging ligands.³ Azolate ligands have strong coordination ability for transition metal ions. Besides, they could combine the negative charge of carboxylate ligands and the predictable coordination behavior of pyridine ligands. These characteristics are not only helpful to predict and control the local coordination geometries and overall network topologies of MOFs, but also help to construct functional materials with high thermal and chemical stabilities.^{4–7}

Post-synthetic modification (PSM) is the subsequent chemical modification of a synthesized framework in a

heterogeneous manner after the formation of solid lattices rather than a direct generation from functionalized ligands or metal ions.^{8–11} This very useful and powerful method has become quite popular, and has led to the generations of many MOFs with improved gas adsorption, catalysis and other performances.^{8,12–16} PSM can be restricted to modifications on the organic ligands of the frameworks without significant perturbation of the coordination spheres. For instance, the bridging btm^{2–} (H₂btm = bis(5-methyl-1*H*-1,2,4-triazol-3-yl)methane) ligands in the frameworks of some MAFs can be oxidized into btk^{2–} (H₂btk = bis(5-methyl-1,2,4-triazol-3-yl)methanone) to alter the framework flexibilities and pore surface properties for drastic enhancement of carbon dioxide/methane or propylene/propane adsorption selectivity.^{12,17} Such kind of PSM is only limited to a few MOFs (including MAFs) with easily modifiable organic ligands. Coordination modifications are another sort of PSM, which were more frequently reported, because metal-ligand coordination bonds are usually labile and changeable under relatively mild conditions. Such modifications usually refer to capture/release of metal ions and ligands, exchange of metal ions, changes of the valence state of metal ions and inorganic/organic bridging ligands on the coordination frameworks.¹¹ In this account, we will review the investigations on the coordination modifications of a MAF, namely [Mn₂Cl₂(bbta)(H₂O)₂] (MAF-X25-Cl, H₂bbta = 1*H*,5*H*-benzo(1,2-*d*:4,5-*d'*)bistriazole, see Fig. 1a),¹⁸ and its structural analogues ([Fe₂Cl₂(bbta)(H₂O)₂]

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Fig. 1 (a) Structures of the bistriazole ligands. (b) The 3D network of guest-free MAF-X25-Cl. (c) The helical chain fragment in MAF-X25-Cl. PSMs of the helical chains in MAF-X25-Cl and its analogous MAFs, including (d) removal of terminal coordinated solvent molecule, (e) exchange of the bridging chloride ligands with hydroxide ligands, and (f–g) oxidation/reduction of metal(II) ions into metal(III)/metal(I) ions (C, gray; H, light gray; Cl, green; N, blue; O, red; M(II), purple; M(III), orange; M(I), pink).

(MAF-X26-Cl), $[\text{Co}_2\text{Cl}_2(\text{bbta})(\text{H}_2\text{O})_2]$ (MAF-X27-Cl), $[\text{Ni}_2\text{Cl}_2(\text{bbta})(\text{H}_2\text{O})_2]$ (MAF-X28-Cl) and $[\text{Cu}_2\text{Cl}_2(\text{bbta})(\text{H}_2\text{O})_2]$ (MAF-X29-Cl) as examples to illustrate the important roles of PSMs for enhanced performances of MOFs in absorption and catalysis.

Thanks to the exceptionally robust and stable characters, many MAFs can be chemically modified by coordination PSM on the metal ions and/or the ligands. Particularly, MAF-X25-Cl is a very robust MAF, which features a pillared-rod three-dimensional (3D) structure with a honeycomb network along the *c* direction (Fig. 1b).¹⁸ Each bbta^{2-} ligand coordinates to six Mn(II) ions, and each Mn(II) is coordinated in a distorted octahedral fashion by three nitrogen atoms from three $\mu_3\text{-bbta}^{2-}$ ligands, two $\mu\text{-Cl}^-$ anions and one terminal H_2O molecule. Each pair of Mn(II) ions are bridged by two triazolate groups and a $\mu\text{-Cl}^-$ (Mn...Mn 3.6885(7) Å) to form a helical rod (Fig. 1c), which are further pillared by the organic bbta^{2-} ligands into a 3D network. Microcrystalline Fe(II), Co(II), Ni(II), and Cu(II) analogues of MAF-X25-Cl can be also synthesized under similar reaction conditions. By virtue of coordination PSM methods, we and other groups achieved significantly improved performances of the MAF-X25-Cl and its structural analogues with different transition metal ions and organic ligands in gas adsorption and catalysis. The PSMs include removal of the terminal coordinated solvent molecules, oxidation/reduction of metal(II) into metal(III)/metal(I), exchange of the bridging chloride ligands with hydroxide and bromide ligands in the rods (Fig. 1d–g). Such PSMs led to very significant enhancements on the catalysis and gas separation performances of the MAFs, which will be briefly summarized and discussed in the following sections.

2. Removal of the terminal coordinated solvent molecules

When water and small organic solvent molecules act as terminal ligands, they are usually labile. The removal of such coordinated solvent molecules in MOFs is actually the simplest PSM approach,⁸ which provides open metal sites (OMSs) as strong binding sites for absorption of CO_2 and other polar and even non-polar gas molecules. Taking our MAF-X25-Cl as an example, after heating at 180 °C under vacuum, the terminal H_2O molecules in this MAF can be easily removed. The guest-free MAF-X25-Cl can retain its pillared-rod structure and single-crystallinity for X-ray diffraction due the exceptional robustness of the framework, and has large effective 1D channels ($d = 1.1$ nm) parallel to the helical chains. On the pore surface of the 1D channel, there is a high density of open coordination sites in square-pyramidal coordination fashion (Fig. 1d). Owing to such strong binding sites, MAF-X25-Cl has a CO_2 uptake of 5.36 mmol g^{-1} at 298 K and 1 bar, which is a relatively high value in the previous study.¹⁹

Similarly, upon removal of the terminal water ligands, MAF-X26-Cl, an analogous material of MAF-X25-Cl, has open Fe(II) sites, which can undergo a cooperative spin transition above a threshold CO pressure and give stepwise adsorption isotherms at elevated temperatures.²⁰ *In-situ* powder X-ray diffraction (PXRD) study revealed the Fe–C_{CO} bond length of 1.76(4) Å and a nearly linear Fe–C–O bond angle, demonstrating low-spin Fe(II) ions in $[\text{Fe}_2\text{Cl}_2(\text{bbta})(\text{CO})_2]$. Such a strong binding for CO leads to a high adsorption enthalpy of -66 kJ mol^{-1} . In fact, MAFs with such OMSs can also be used to bind other molecules with coordinative ability. For instance, as analogous materials of

MAF-X25-Cl, MAF-X27-Cl, MAF-X28-Cl, and MAF-X29-Cl can capture large amounts of NH_3 , i.e. 17.95, 14.68, and 19.79 mmol g^{-1} at 1 bar and 298 K, respectively,^{21–22} being attributed to their strong Lewis acidity and high density of the OMSs. Notably, the NH_3 adsorption capacity of MAF-X29-Cl was the highest among those reported for MOF-based NH_3 adsorbents.

■ 3. Changing the valence state of metal ions

3.1. Oxidation of Mn(II) into Mn(III)

When the valence state of metal ions in a MOF is variable, it may possibly be tuned *via* PSM reduction or oxidation. Such PSM modification is usually much more drastic and difficult to retain the framework structure compared with the removal of terminal solvent ligands in a MOF. Therefore, only very robust MOFs with variable valence metal ions can be modified in this way. We found that, with a very robust pillared-rod framework, the exposed Mn(II) ions of MAF-X25-Cl can be partially oxidized by H_2O_2 to form an oxidized MAF, namely $[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}(\text{OH})\text{Cl}_2(\text{bbta})]$ (MAF-X25ox-Cl), under alkaline condition (Fig. 1e),¹⁸ which was the first example of a MOF with Mn(III) ions. Rietveld refinement of the PXRD pattern shows that the Mn(III) is coordinated by three nitrogen atoms from three bbta^{2-} ligands, two $\mu\text{-Cl}^-$ anions and one monodentate hydroxide (Fig. 1f). In contrast, the analogous material $[\text{Mn}_2(\text{dobdc})(\text{H}_2\text{O})_2]$ constructed by the carboxylate ligands becomes amorphous under the similar oxidation condition. These observations imply that, the nitrogen-rich and more stable bistriazolate ligand may play an critical role in stabilizing the Mn(III) ions in MAF-X25ox-Cl. Also notably, without protection of macrocyclic or polydentate chelating ligands, such as a porphyrinate, the Mn(III) ion is usually unstable in solution, thus it is actually not feasible to directly synthesize a MOF with Mn(III) active sites in the absence of protecting macrocyclic or polydentate chelating ligand. Therefore, post-oxidation of Mn(II) ions within the frameworks represents a crucial and effective method to obtain Mn(III) ion-containing MOFs.

The coordination environment of each Mn(III) ion in MAF-X25ox-Cl is similar to those of the well-known Mn^{III} –porphyrinate species. Therefore, we studied the catalytic oxidation performance of this MAF for oxidation of ethylbenzene (EB) into acetophenone by using *tert*-butyl hydroperoxide (TBHP) as the oxidant. MAF-X25ox-Cl exhibits high catalytic activity with the selectivity of >99% and turnover frequency (TOF) of 118 h^{-1} (Fig. 2), which is a much higher catalytic performance than those of Mn(II)-

based MAF-X25-Cl and the excellent homogeneous catalyst $[\text{Mn}(\text{TPP})\text{Cl}]$ (H_2TPP = 5,10,15,20-tetraphenylporphyrin). These results indicate that the high catalytic performance should be ascribed to the Mn(III) ions. Meanwhile, oxygen gas, as the greenest oxidant, can be used to replace the strong organic oxidant TBHP, though the catalytic performance is worse in terms of selectivity and conversion rate (Fig. 2). Furthermore, when diphenylmethane as a larger substrate was used, the catalytic oxidation activity became very poor, implying that it cannot access the internal pores and the catalytic reactions mainly occur on the outer crystal surfaces.

Fig. 2 Comparison of the activities of MAF-X25-Cl and MAF-X25ox-Cl for catalytic oxidation of ethylbenzene. Adapted from Ref. 18.

3.2. Oxidation of Co(II) into Co(III)

Capturing CO_2 under humid conditions is a great challenge. Although many porous materials can capture large amounts of CO_2 under dry conditions, the capture capacity is significantly reduced in the presence of water, since water molecules strongly compete for binding sites or destroy the skeleton. The monodentate hydroxide is the key active site of carbonic anhydrase, which can greatly accelerate the conversion between CO_2 and HCO_3^- in an aqueous environment. Thus, a porous material with monodentate hydroxides may be a very good candidate for capturing CO_2 under humid conditions.

As being mentioned in Section 3.1, the post-synthetic oxidized MAF, MAF-X25ox-Cl, has monodentate hydroxide groups on the pore surface, we then studied the CO_2 capture performances of MAF-X25ox-Cl and its cobalt analogue $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\text{OH})\text{Cl}_2(\text{bbta})]$ (MAF-X27ox-Cl) under humid conditions, in which the cobalt MAF was synthesized by using the similar post-oxidation treatment for MAF-X25ox-Cl (Fig. 1f). With the presence of the monodentate hydroxide groups on the pore surfaces, the CO_2 capture performances of both MAF-X25ox-Cl and MAF-X27ox-Cl are much higher than those of MAF-X25-Cl and MAF-X27-Cl, and even higher than most porous materials.¹⁹ Specifically, MAF-X27ox-Cl showed

the highest CO₂ adsorption enthalpy (124 kJ mol⁻¹) and uptake (9.1 mmol cm⁻³ 298 K and 1 bar), CO₂/N₂ selectivity (262 at 298 K), as well as very good recycling stability and fast CO₂ adsorption/desorption kinetics. *In-situ* infrared (IR) spectra demonstrated that the reaction of OH⁻ + CO₂ = HCO₃⁻ is reversible during the CO₂ adsorption/desorption, which is very similar to the CO₂ binding mechanism of carbonic anhydrase mentioned in the previous section (Fig. 3) for capturing and transportation of CO₂ in biological systems. Similar phenomena were latter observed in other MOFs systems.²³⁻²⁴ Through the gas breakthrough experiments, we demonstrated that MAF-X27ox-Cl has a very fast sorption kinetics and an ultrahigh working capacity for capturing CO₂

from flue gas at 313 K, even in the presence of high relative humidity (83%), highlighting the suitability of MAF-X27ox-Cl as a promising CO₂ capture adsorbent. It should be noted that it is difficult to introduce the monodentate hydroxide into the porous materials, because the hydroxide ligands strongly tend to form bidentate or tridentate coordination in their metal compounds, indicating the importance of this PSM approach. In fact, MAF-X25ox-Cl and MAF-X27ox-Cl represented the first examples of monodentate hydroxide-containing MOFs and showed exceptionally high CO₂ capture performances and stabilities under high humid conditions.

3.3. *In-situ* reduction of Cu(II) into Cu(I)

Besides the oxidative PSM discussed above, reductive PSM is also possible for some MOFs. Recently, we found that the Cu(II) ions in MAF-X29-Cl can be *in-situ* reduced into Cu(I) ions during photodriven hydrogen evolution reaction.²⁵ The catalytic activity of MAF-X29-Cl was evaluated under visible light ($\lambda > 420$ nm) in water/acetonitrile (v/v, 25:65) with [Ru(bpy)₃]Cl₂ (bpy = 2,2'-bipyridine) as a photosensitizer and triethanolamine (TEOA) as a sacrificial agent. Interestingly, the H₂ production rate was slow initially and then became fast and fast, and finally reached 101.4 mmol g⁻¹ h⁻¹, which is much higher than that for the as-synthesized sample (4.6 mmol g⁻¹ h⁻¹). The *in-situ* electron paramagnetic resonance (EPR) spectroscopy showed that the EPR signals ($g_{\parallel} = 2.28$ and $g_{\perp} = 2.09$) assigned to Cu(II) species become weakened gradually and disappear eventually, demonstrating the generation of Cu(I) species. After hydrogen evolution experiment, the catalyst was recovered and its PXRD pattern was very similar to that of the as-synthesized sample. Based on the EPR spectroscopy, Raman spectra and PXRD pattern, it can be concluded that during the hydrogen evolution, MAF-X29-Cl had been turned into a Cu(I)-based [Cu₂(bbta)] (MAF-29), which was the actual photocatalyst. As a result of the reduction of Cu(II) ions, the μ -Cl⁻ ligands were free from the rod for the charge compensation of the framework, each Cu(I) ion in MAF-29 is coordinated in a T-shaped fashion by three nitrogen atoms from three bbta²⁻ ligands (Fig. 1g). The photodriven hydrogen evolution experiment for MAF-29 was measured under the same reaction conditions. As expected, the initial production rate for H₂ was 102.8 mmol g⁻¹ h⁻¹, which is very close to that of MAF-X29-Cl after a hydrogen evolution experiment for 3 h (Fig. 4). Importantly, the performance of MAF-29 is not only higher than those of most other catalysts, but also higher than those of most Pt decorated catalysts. The synergistic catalysis of two adjacent Cu(I) ions within MAF-29 for the reduction of H₂O to H₂ was investigated at molecular level by

Fig. 3 Comparison of the local framework structures (a) before and after oxidative PSM (C, gray; H, light gray; Cl, green; N, blue; O, red; M(II), purple; M(III) orange). CO₂ adsorption mechanisms (b) of MAF-X25/MAF-X27 and MAF-X25ox-Cl/MAF-X27ox-Cl. Breakthrough curves for 10:90 CO₂/N₂ (v/v) mixture with 0% (open) and 82(3)% relative humidity (solid) at 313 K and 1 bar passing through a column packed by microcrystalline (c) MAF-X27-Cl or (d) MAF-X27ox-Cl. Lines are drawn to guide eyes. C_i and C₀ are the concentrations of each gas at the inlet and outlet, respectively. Adapted from Ref. 19.

density functional theory (DFT) calculations. Compared to the Cu-based catalysts with single metal catalytic centers, MAF-29 has a very low energy barrier for water dissociation due to the synergistic catalysis of two adjacent Cu(I) ions, that is, one serves as a catalytic center to bind and activate the H₂O molecule while the other acts as an assistant catalytic site to facilitate the HO–H bond breaking.

Fig. 4 (a) The photodriven hydrogen-production rates of MAF-X29-Cl (black) and MAF-29 (red). (b) *in-situ* EPR spectra of MAF-X29-Cl measured before (blue) and after photodriven hydrogen evolution reaction for 30 (green) and 60 (black) min, respectively. Adapted from Ref. 25.

■ ■ 4. Exchange of the anionic inorganic bridging ligand

Considering that the redox property of the Co(II) ions of MAF-X27 is beneficial to the oxygen evolution reaction (OER), and there is a high-concentration (5.88 mmol g⁻¹, 6.69 mmol cm⁻³) of square-pyramidal Co(II) ions, each with an open coordination site exposed on the pore surface, we studied the OER property of MAF-X27-Cl in 1.0 M KOH solution.²⁶ Interestingly, by repeating the linear sweep voltammetry (LSV), the OER performance become better, and finally reached a η_{10} of 387 mV, being 121 mV lower than for the as-synthesized sample (Fig. 5). By virtue of Rietveld refinement of PXRD, Raman spectroscopy and XPS analyses, we found that the μ -Cl⁻ ligands in the rods of MAF-X27-Cl were replaced by μ -OH⁻ ions to form a new MAF [Co₂(μ -OH)₂(bbta)] (MAF-X27-OH) (Fig. 1e). To more accurately evaluate the OER activity of MAF-X27-

OH, we fabricated the electrode consisting of MAF-X27-Cl firmly attached on the metal surface (denoted as MAF-X27-Cl(Cu)) by growing the MAF-X27-Cl crystals directly on Cu foil. After ion exchange treatment of MAF-X27-Cl(Cu), the electrode MAF-X27-OH(Cu) was obtained. In 1.0 M KOH solution, MAF-X27-OH(Cu) gives much improved OER performances with overpotential as low as 292 mV at 10 mA cm⁻² and turnover frequency (TOF) up to 0.019/0.25 s⁻¹ at overpotentials of 300/400 mV. Notably, MAF-X27-OH(Cu) showed a markedly better catalytic activity than those of the conventional OER catalysts Co(OH)₂ (421 mV) and Co₃O₄ (445 mV) directly grown on carbon cloth substrates. Furthermore, cyclic voltammetry curves, LSV curves, PXRD patterns, and SEM images of MAF-X27-OH showed negligible changes after the electrolysis for 24 h. At pH = 7, MAF-X27-Cl can be completely stable in the absence of ion exchange. At pH = 7, MAF-X27-OH exhibited a better OER activity (η_2 of 489 mV) than that of MAF-X27-Cl (a current density of 0.028 mA cm⁻² at a η_{10} of 570 mV), which unambiguously demonstrates the effectiveness of the μ -OH⁻ ligand (Fig. 5). Using an isotope tracing technique, we found the high catalytic performance of MAF-X27-OH is attributed to the directly participation of the coordinated OH⁻ ligands in the formation of O₂, which provides a low-energy intraframework coupling pathway in the OER process (Fig. 5b). MAF-X27-OH was the first example of azolate-based MOFs showing a high OER performance and stability, which demonstrates the suitability of such MOFs as OER catalysts.

More interestingly, the presence of bridging hydroxy ligands in the framework of a MAF not only can enhance the OER through the direct participation, but also can render a stronger binding ability to CO₂ molecule, and hence remarkably promote the photocatalytic CO₂ reduction. By comparing the photocatalytic activities of a series of cobalt-based MOFs possessing different coordination environments, we recently demonstrated that the μ -OH⁻ ligands in MAF-X27-OH can provide a synergistic effect of the microenvironment of open metal centers to remarkably promote the photocatalytic activity for CO₂ reduction.²⁷ For comparison, three isostructural honeycomb-like Co(II)-based MOFs, namely MAF-X27-Cl, MAF-X27-OH and MOF-74-Co), were used for photocatalytic CO₂ reduction. The photocatalytic CO₂ reduction performances of the these Co-based MOFs were studied under visible light in pure CO₂ at 1.0 bar in 4:1 CH₃CN/H₂O mixed solvent for 10 h, using [Ru(bpy)₃]Cl₂ as the photosensitizer. Obviously, the catalytic performance of MAF-X27-OH with the TOF of 28×10^{-3} s⁻¹ and selectivity of 97.2% is much higher than those of

MOF-74-Co (TOF = $13 \times 10^{-3} \text{ s}^{-1}$, selectivity = 63.6%) and MAF-X27-Cl (TOF = $6.3 \times 10^{-3} \text{ s}^{-1}$, selectivity = 58.8%), indicating the importance of the $\mu\text{-OH}$ ligands (Fig. 6a). More attractively, when the CO_2 partial pressure was reduced to 0.1 bar, only MAF-X27-OH exhibited a high CO TOF of $23 \times 10^{-3} \text{ s}^{-1}$ with an unchanged CO selectivity of 97.2%, comparable to the TOF ($28 \times 10^{-3} \text{ s}^{-1}$) under pure CO_2 . Also notably, the performance of MAF-X27-OH under 0.1 bar CO_2 is even better than that of the best homogeneous catalyst (TOF of $19 \times 10^{-3} \text{ s}^{-1}$, selectivity of 92%) working under the same condition. MAF-X27-OH represents the first example of MOFs showing a high performance of the photocatalytic CO_2 reduction under dilute CO_2 atmosphere.

Fig. 5 (a) Framework and pore surface structure of MAF-X27-OH. (b) Solid-liquid coupling pathway for MAF-X27-Cl and intraframework coupling pathway for MAF-X27-OH. (c) LSV curves of MAF-X27-Cl and MAF-X27-OH at pH = 7. (d) LSV curves for electrodes modified by MAF-X27-OH or other related materials at pH = 14. Adapted from Ref. 26.

We studied the mechanism of this superb catalytic performance through periodic density functional theory (PDFT) calculations and isotope labeling, and revealed that, the $\mu\text{-OH}$ ligands located at the *cis*-positions of the Co active site can form a pair of hydrogen bonds to stabilize the Co- CO_2 adduct and also act as the proton source in the reduction process (Fig. 6b). Thanks to such a pair of hydrogen bonds, the MAF-X27-OH binds CO_2 more strongly than H_2O . The strong CO_2 binding affinity can stabilize the initial Co- CO_2 adduct to promote the CO_2 reduction, and a weak H_2O binding affinity can suppress H_2 (the byproduct) production and ensure a high CO selectivity. A similar phenomenon was latter observed for a Ni-based metal-organic framework.²⁸

Fig. 6 (a) Comparison of the TOF values for the photo-catalytic reductions of CO_2 to CO under 1.0 atm (blue) and 0.1 atm (orange). (b) Comparison of the CO_2 and H_2O binding structures and energies of the reduced forms of MAF-X27-Cl and MAF-X27-OH. Adapted from Ref. 27.

Moreover, the photocatalytic CO_2 reduction performance can be further improved by enlarging the pore size of the MAF. When bis(1*H*-1,2,3-triazolo-[4,5-*b*],[4',5'-*i*]) dibenzo[1,4]dioxin (H_2btdd)²⁹ as an expanded version of the bridging ligand (Fig. 1a) is used to replace H_2bbta , $[\text{Co}_2(\mu\text{-Cl})_2(\text{btdd})]$ (MAF-X27l-Cl) with larger pores can be obtained. Upon ion exchange treatment of MAF-X27l-Cl, $[\text{Co}_2(\mu\text{-OH})_2(\text{btdd})]$ (MAF-X27l-OH) can be generated, which has a larger pore size (*ca.* 2.2 nm) compared to MAF-X27-OH (*ca.* 1.1 nm). Interestingly, in both 1.0 or 0.1 atm CO_2 , the catalytic performances of MAF-X27l-OH are greatly better than those of MAF-X27-OH, as shown in Fig. 6a. Since the catalytic sites including the hydrogen bonding interactions of MAF-X27l-OH and MAF-X27-OH are basically the same, the higher catalytic activities of the expanded version can be ascribed to the larger pore size, which is beneficial for a quicker diffusion of the reactants/products.

Recently, Dincă *et al.* found that the $\mu\text{-Cl}^-$ bridges in $[\text{Ni}_2(\mu\text{-Cl})_2(\text{btdd})]$ (MAF-X28l-Cl), a nickel analogue of MAF-X27l-Cl, can be exchanged by $\mu\text{-Br}^-$ to generate a new material $[\text{Ni}_2(\mu\text{-Br})_2(\text{btdd})]$ (MAF-X28l-Br).³⁰ This PSM results in a slight pore shrinkage of 0.1 nm, which shifts the water pore-filling step from a partial pressure of 0.32 to 0.24. As a result, MAF-X28l-Br achieved a new record with the gravimetric water uptake of 0.64 g g^{-1} below 25% relative humidity, making it as a strong candidate for water harvesting under drought conditions.

5. Conclusion

As shown above, the mixed organic and inorganic bridged helical rods in the robust pillared-rod MAFs are changeable and can be modified through removal of the terminal coordinated solvent molecules, redox reactions on the metal ions and exchanges of the inorganic bridging ligands. Although only a series of examples are known and summarized here, the results clearly demonstrate that, for robust and modifiable MAFs, PSM approaches provide important opportunities to functionalize and promote the performances of MAFs for diverse applications, such as carbon dioxide capture and catalysis, through optimizing the coordination environment of metal ions, the valence state of metal ions, as well as the microenvironment of the active sites.

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Profile

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