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Solvent-Free Heterogeneous Catalysis for Cyanosilylation in a Modified Sodalite-typed Cu(II)-MOF†

Cite this: DOI: 10.1039/x0xx00000x

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DOI: 10.1039/x0xx00000x

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Solvothermal reaction of $\text{Cu}(\text{OAc})_2$ and $\text{H}_3\text{BTT}\cdot 2\text{HCl}$ generated a sodalite-type metal-organic framework $[(\text{Cu}_4\text{O}_{0.27}\text{Cl}_{0.73})_3(\text{H}_{0.5}\text{BTT})_8(\text{H}_2\text{O})_{12}]\cdot 3\text{MeOH}\cdot 9\text{DMF}$ (**1**) (BTT³⁻ = 1,3,5-benzene tristetrazolate), which features a porous 3D (3,8)-connected framework constructed by square $[\text{Cu}_4(\mu_4\text{-O}/\text{Cl})]$ units and triangular BTT ligands and can be subjected to dehydrate to form $[(\text{Cu}_4\text{O}_{0.27}\text{Cl}_{0.73})_3(\text{H}_{0.5}\text{BTT})_8]$ (**1'**) with coordinatively unsaturated Cu^{2+} centers. Compared with related M-BTT MOFs, partial replacement $\mu_4\text{-Cl}$ with $\mu_4\text{-O}$ at the square Cu_4 cluster and the absence of irremovable guest $[\text{M}(\text{DMF})_6]^{2+}$ cations in **1'** enhance Lewis acidity of coordinatively unsaturated metal centers and the effective pore volume. Open Cu(II) sites with stronger Lewis acidity give rise to **1'** being an active, stable and reusable solvent-free heterogeneous catalyst for C-C bond-forming reaction by cyanosilylation of carbonyl compounds. The loading of 1 mol% of catalyst **1'** is as low as one eleventh of that used in related Mn-BTT but lead as high as 96% conversion of benzaldehyde, indicating catalytic activity of M-BTT MOFs was significantly improved via post-modification. In addition, larger pore volume makes **1'** selectively adsorb N_2 and O_2 gases with hysteresis loops over CO_2 and H_2 gases without hysteresis loops, which did not appear in related M-BTT MOFs.

Introduction

As an important C-C bond-forming method in organic synthesis, the cyanosilylation of carbonyl compounds have recently attracted great concern, due to providing a convenient route to cyanohydrins, which are key derivatives in the synthesis of fine chemicals and pharmaceuticals.¹ Various catalytic systems, including homogeneous² and heterogeneous³ systems, have been developed for the cyanosilylation of carbonyl compounds. However, from the point of view of green chemistry, a pressing challenge facing organic catalysis is to advance new processes that are efficient, selective, high yielding and environmentally friendly. Therefore, the ideal strategy to reduce their impact on the environment is to conduct reaction with heterogenous catalyst under solvent-free conditions.⁴ One of the latest developments in organic catalysis involved heterogeneous catalysis based on MOFs whose features of high level of porosity, functionalized pore walls and relatively easy separation has aroused intense interest of chemists.^{5,6} But so far, there are few reports about the cyanosilylation with MOFs as heterogeneous catalyst under solvent-free conditions.⁷ Consequently, the development of a new strategy for the construction of MOFs with high heterogeneous catalytic activity for the cyanosilylation is highly desirable.

Nowadays, increasing interest in metal-organic frameworks (MOFs) is mainly due to the well-known porosity⁸ and high surface area as well as potential applications in adsorption,⁹ clean energy, sensors¹⁰ and heterogeneous catalysis.^{5,6} Numerous studies have shown that the selection and design of organic ligands have significant influences on structures and properties of MOFs.

Compared with polycarboxylate ligands, azoles have the advantage of rigid and directional coordination ability to bridge metal ions.¹¹ Actually, azoles-based MOFs have emerged as a new kind of crystalline porous materials recently.¹² For example, imidazoles and polypyrazolates have been utilized to generate novel coordination frameworks that have not been observed for polycarboxylates. A variety of imidazolate-based MOFs have been prepared, which were named zeolitic imidazolate frameworks (ZIFs) by Yaghi due to realization of similarity between imidazolate in ZIFs and oxo in zeolites.^{13,14} In contrast to the weak acidity of imidazole, pyrazole and triazole, tetrazole with the highest number of *N*-donors has higher acidity while tetrazolate has lower basicity. As a consequence, tetrazolates have unique electronic properties and flexible coordination behaviors. A large variety of tetrazolate-based frameworks with novel structures have been constructed. For instance, Long and co-workers have reported a number of anti-van't Hoff planar M_4Cl clusters based sodalite-type metal-organic frameworks $\text{Fe}_3[(\text{Fe}_4\text{Cl})_3(\text{BTT})_8(\text{MeOH})_4]_2$,^{15a} $[\text{Mn}(\text{DMF})_6]_3[(\text{Mn}_4\text{Cl})_3(\text{BTT})_8(\text{H}_2\text{O})_{12}]_2$,^{15b} and $[\text{H}[\text{Cu}(\text{DMF})_6][(\text{Cu}_4\text{Cl})_3(\text{BTT})_8(\text{H}_2\text{O})_{12}]$ (BTT = 1,3,5-benzenetrisetetrazolate),^{15c} which exhibited high surface areas, gas uptake, open metal sites and catalytic behaviors depending on metal ions and encapsulated guest cations.¹⁵

In situ and post-synthesized modifications of sodalite-type M-BTT MOFs are very interesting to understand in depth the relationship between structure and property and to find better functional materials. It is generally recognized that nature of metal ion, space distribution of charge, and uncoordinated atom or group could have influence on whole properties of MOFs. As far as M-

BTTs are concerned, due to the existence of different guest M^{n+} or $[M(\text{DMF})_6]^{n+}$ cations in channels,¹⁵ the porosity of these MOFs was decreased to some extent, which affected the amount of gas uptake and selectivity. To be noted, the framework M ions show octahedral geometry with one terminal water or solvent molecule, whose nature and coordination preference may result in different catalytic reactions of these M-BTT MOFs. The d^9 configuration of Cu(II) ion is subject to dynamic Jahn–Teller distortion, offering unique characteristics of “4 + 1” coordination geometry with one long and weak bond. As expected and observed, sodalite-type Cu-BTT and isostructural $H_3[(Cu_4Cl)_3(BT\text{Tri})_8(\text{DMF})_{12}]$ (Cu-BTTri, $H_3BT\text{Tri} = 1,3,5\text{-tris}(1\text{H-}1,2,3\text{-triazol-}5\text{-yl})\text{benzene}$) MOFs are easy to generate proton acid and open Cu(II) site for catalysis and grafting reaction.¹⁵ Besides porosity related properties, existence of van't Hoff planar tetracoordinate Cl atom is very interesting in the M-BTT MOFs. Recently, we found that the interesting planar tetracoordinate oxygen atom in a related tetracopper cluster-based copper-tetrazolate framework, which encourage us to explore the possibility of replacement planar tetracoordinate Cl atom with oxygen atom in Cu-BTT MOF.¹⁶ This kind of exploration is very important to search for van't Hoff planar tetracoordinate oxygen^{17,18} and modify of porosity-related properties of MOF because replacement of larger Cl atom of minus one with smaller O atom of minus two will change Lewis acidity of open Cu site and whole charge distribution of framework. These changes will further induce Cu-MOF porosity and properties related unsaturated coordination such as gas adsorption and organic catalysis.

Considering the aforementioned factors, the development of efficient methods for increasing the pore sizes of tetrazolate-based coordination polymers to improve the sorption property and the heterogeneous catalytic activity have been highly desired. One feasible strategy for addressing the challenge is through the replacement of $M^{n+}/[M(\text{DMF})_6]^{n+}$ guest cations with proton to balance the anionic charge of the tetrazolate-based framework. We have been devoted on the assembly of new polymers with heterogeneous catalytic activity toward C-C bond-forming reactions. During the course of these studies, surprisingly, it was found that the sodalite-type MOF $[(Cu_4O_{0.27}Cl_{0.73})_3(H_{0.5}BTT)_8(H_2O)_{12}] \cdot 3MeOH \cdot 9DMF$ (**1**) could be synthesized, which adopts a square-planar $Cu_4(\mu_4-O_{0.27}Cl_{0.73})$ SBU with $\mu_4\text{-oxo}$ (27%) or $\mu_4\text{-chloride}$ (73%) residing at the center of Cu_4 square.

Compound **1** show efficient heterogeneous catalytic activity for cyanosilylation of carbonyl compounds under solvent-free conditions. The loading of 1 mol % of catalyst **1'** is as low as one eleventh of that used in related Mn-BTT but lead as high as 96% conversion of benzaldehyde, indicating catalytic activity of M-BTT MOFs was significantly improved via post-modification. Interestingly, **1** also shows adsorption-desorption hysteresis loops for nitrogen and oxygen gases, different from related sodalite-MOFs. Compared with related M-BTT and Cu-BTTri MOFs.¹⁵ The efficient solvent-free heterogeneous catalytic activity and adsorption-desorption hysteresis loop for **1** possibly is due to charge difference between O^{2-} and Cl^- ions as well as electron-withdrawing ability difference between tetrazolate and triazolate, which affect the whole electronic property of skeleton. Coordinatively unsaturated Cu(II) centers¹⁵ and proton acid property of **1** also contribute to efficient heterogeneous catalytic activity.

EXPERIMENTAL SECTION

Materials and physical measurements

All chemicals were analytically pure from commercial sources and used without further purification. Elemental analyses were

performed on a Vario EL-II analyzer. FTIR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Perkin Elmer Spectrum BX FT-IR spectrometer. Powder X-ray diffraction (PXRD) data were collected in a Rigaku Ultima IV diffractometer.

Synthesis of $[(Cu_4O_{0.27}Cl_{0.73})_3(H_{0.5}BTT)_8(H_2O)_{12}] \cdot 3MeOH \cdot 9DMF$ (**1**)

A solution of $Cu(\text{CH}_3\text{COO})_2 \cdot 4H_2O$ (40 mg, 0.2 mmol) in 4 mL of methanol and nitric acid (0.2 mL) were added to a solution of $H_3BTT \cdot 2HCl \cdot H_2O \cdot CH_3OH$ (45 mg, 0.11 mmol) in 4 mL of DMF. The resulting mixture was stirred in air for 20 min and then heated to 85°C for 48 h in a 25 mL Teflon-lined stainless container. After it had been cooled to RT and filtered, green crystals of compound **1** were recovered in 80% yield. IR (KBr, cm^{-1}): 3434s, 2924w, 1652s, 1417m, 1253w, 1103w, 792w, 665w.

Structure Analysis

Data collection were performed with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker Apex CCD diffractometer at 298(2) K for 1. The SAINT program was used for integration of the diffraction profiles, and the SADABS program was used for X absorption correction. All the structures were solved by direct methods using the SHELXS program and refined by full-matrix least-squares methods with SHELXL. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms of organic ligands were generated theoretically onto the specific carbon and nitrogen atoms, and refined isotropically with fixed thermal factors. The contribution of the solvent to the diffraction pattern was subtracted from the observed data by the SQUEEZE method implemented in PLATON. Further details for structural analysis, selected bond lengths and bond angles are summarized in Table S1-3.

The heterogeneous Catalytic Cyanosilylation with Cu-MOF **1'**

Dried copper-MOF catalyst (0.014 mg, 0.005 mmol) was added to a mixture of the corresponding carbonyl compound (0.5 mmol) and trimethylsilyl cyanide (0.133 mL, 1.0 mmol) under nitrogen atmosphere. Then, the mixture was stirred at 40°C. The reaction was monitored by GC (FID from AGILENT 7820) using a cross-linked (95%)-dimethyl-(5%)-diphenylpolysiloxane column (HP-5, 30 m * 0.32 mm * 0.25 μm), helium, injector temperature 250°C, detector temperature 300°C, and oven temperature program 45°C (3 min)-20°C/min-280°C (2 min). The reaction conversions were determined by gas chromatography (GC) analysis. For filtration test, catalyst was separated after a reaction time of 2 h with 50% conversion. The reaction was allowed to proceed in the filtrate, with no additional conversion after 17 h.

Recycling Experiments

A reuse experiment was carried out for the cyanosilylation of furaldehyde. The reaction was carried out under the standard conditions. After the reaction was completed, the catalyst was recovered by filtration, washed with methanol, and dried under vacuum for 12 h prior to reuse. The PXRD pattern of the retrieved catalyst was identical to that of the fresh catalyst (Supporting Information Fig. S1). The catalytic recyclability was checked five times with the same batch of catalyst, and no obvious decrease in activity was observed.

RESULTS AND DISCUSSION

Description of structure

X-ray single-crystal analysis revealed that **1** crystallizes in the cubic $Pm-3m$ space group and the asymmetric unit consists of eight non-hydrogen atoms including one copper, one indistinguishable O(1)/Cl(1), one O_{water} , three C and two N atoms. The crystallographically independent Cu(II) is adopts a Jahn-Teller distorted elongated octahedral geometry, coordinated by four nitrogen atoms from BTT ligands in the equatorial plane and O(2) and O(1)/Cl(1) at the axial positions (Fig. 1a). The O(1) and Cl(1) atoms occupy same position, which is indistinguishable. X-ray refinement reveals O(1) and Cl(1) ratio is close to 27:73. The Cu-N distances are 2.018(3) Å and the Cu- O_{water} distance is 2.396(9) Å. The Cu-O(1)/Cl(1) distance is 2.448 Å (Fig. 1b), which is shorter than 2.546 Å of Cu-Cl distance in square Cu_4Cl cluster^{14c} but close to 2.470(1) Å of Cu-O distance in square Cu_4O cluster.¹⁶

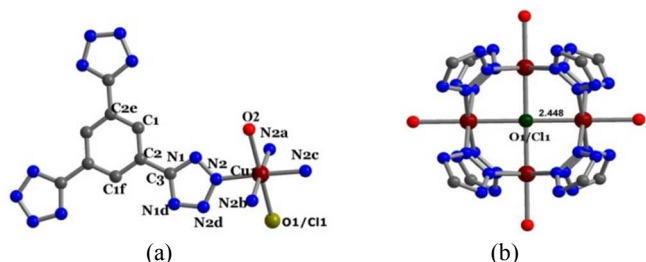


Fig. 1 (a) the coordination environment of Cu(II) ions; (b) the connection modes of tetracopper cluster-based SBU. For clarity, hydrogen atoms have been omitted.

The BTT ligand is coordinated to six Cu atoms, in which each tetrazyl ligates two Cu atoms in μ_2 mode via 3,4-nitrogen atoms. The four Cu centers and the indistinguishable O(1)/Cl(1) form a planar $\text{Cu}_4\text{O}/\text{Cl}$ cluster with adjacent and opposite Cu-Cu distances of 3.463(1) Å and 4.898(2) Å. Each $\text{Cu}_4\text{O}/\text{Cl}$ unit is connected to eight surrounding BTT ligands, and each triangular BTT ligand is connected to three $\text{Cu}_4\text{O}/\text{Cl}$ units to generate a three-dimensional 3,8-connected net (Fig. 2a). The solvent accessible volume calculated by *Platon* software is 4295.6 Å³ per unit cell, namely 66.5% of the total volume. If the coordinate water molecule can be removed, the expected void volume will reach 4526.4 Å³ per unit cell (70.1% of the total volume). The structure of **1** can also be viewed as sodalite framework of interconnected truncated octahedral cages, each of which consists of six $\text{Cu}_4\text{O}/\text{Cl}$ squares and eight BTT ligands (Fig. 2b). One truncated octahedron shares its square faces with

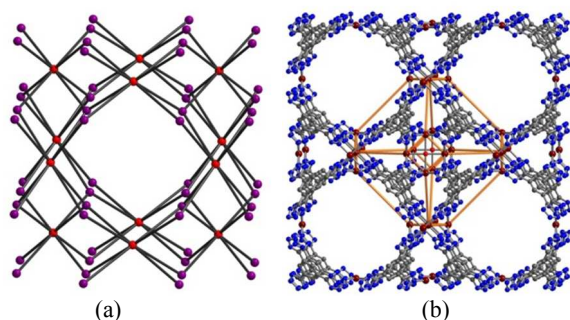


Fig. 2 The schematic view of (3,8)-connected net (a) and 3D sodalite structure (b) in **1**.

six neighboring cages to form the cubic anionic framework structure with 3D channels filled by solvents that could not be located from Fourier map. The solvents and coordinated water molecules could be removed or exchanged with other molecules. Charge balance requires that there are four additional protons per formula, and it is reasonable to assume that the protons are attached to the

uncoordinated N atoms of the tetrazolate rings. Statistically, there is approximately one proton per four BTT ligands.

Thermal Analysis and powder X-ray diffraction

Thermal measurement of polycrystalline as-synthesized **1** was performed in air at a heating rate of 10°C min⁻¹. The analysis showed initial two steps of weight loss about 8.1% (calcd: 7.7%) up to 120°C and 17% (calcd: 16.3%) up to 240°C, which was attributed to the removal of H₂O, MeOH and DMF molecules, respectively (Fig. S2). The further weight loss corresponds to the decomposition of the framework. The temperature varied PXRD patterns also confirmed the stability of **1**. The positions of the major peaks undergo no significant changes and only the intensity of some peaks varies below 250°C, which support the notion that the crystal lattice remains intact after the lattice guest molecules have been removed (Fig. S3). Thermal analysis of methanol exchanged **1** also illustrated the stability about 250°C, and the subsequent decomposition is mainly due to the tetrazole ligand being a high energy explosive substance and occurrence of the spurt of powder in the experiment.

Gas Sorption

To study the porosity of **1**, gas sorption measurements were carried out. The gas physisorption experiments were performed at 77 K for N₂, O₂ and H₂ but 273 K for CO₂. For this purpose, the synthesized sample was immersed in methanol for 24 h to remove the guest solvent molecules, and fresh methanol was added after the extract was decanted, which was operated at least five times. After the removal of methanol by decanting, the sample was dried under a dynamic vacuum at 120°C overnight to obtain the desolvated framework **1'**. The H₂ adsorption data indicate fully reversible uptake of 1.44 wt % at 77K and 1.05 bar, with a Langmuir surface area of 226.58 cm² g⁻¹, which is less than 2.1, 2.3, and 2.3 wt % for related Mn-, Fe-, and Cu-BTTs at 1.0 bar.^{15d,19} Similarly, CO₂ physisorption measurement was also lower than those of M-BTTs (Fig. S4). The results were consistent with the reducing of available open metal sites in **1'** compared to Mn-, Fe-, and Cu-BTT, which resulted from the replacement of Mⁿ⁺/[M(DMF)₆]ⁿ⁺ guest cations by protons. However, the N₂ and O₂ absorptions of complex **1'** were completely different from the adsorption characteristics of Mn- and Cu-BTTri.^{15b,15d} At pressures above 0.2 bar, adsorption-desorption hysteresis loops of isotherm were observed. As shown in Fig. 3, N₂

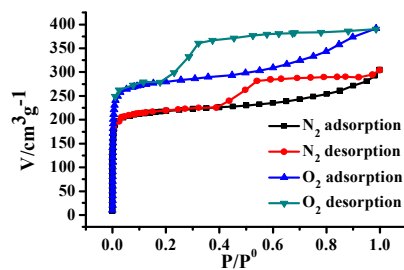


Fig.3 Adsorption isotherms in **1** for the uptake of N₂ and O₂ at 77 K.

and O₂ adsorption measurements at 77 K showed the characteristics of micro-mesoporous material, with BET and Langmuir fits affording surface areas of 736.96 and 1223.04 cm² g⁻¹, respectively. To investigate interactions between N₂ molecules and framework in **1'**, grand canonical Monte Carlo (GCMC) simulations were employed at 77 K. The simulated adsorption isotherm for N₂ is 72 molecules per unit cell above 0.5 bar, which is close to measured 70 molecules per unit cell (Fig. S5). The hysteresis loops of isotherm

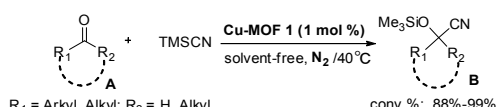
can be explained that both substitution of triazolate by protonated tetrazolate and partial replacement of Cl⁻ with O²⁻ enhance the affinity of ligands and coordinatively unsaturated Cu^{II} sites for N₂/O₂. The foregoing results demonstrate the successful post-synthesized modification of sodalite-type M-BTT MOFs changed the gas adsorption characteristics significantly.

Catalytic Study

To compare the catalytic activity of **1** with that of other MOFs, we probed the cyanosilylation of carbonyl compounds. After removal of coordinative water molecules, unsaturated metal centers which might serve as potent Lewis acids are exposed and the pore sizes of **1** are obviously increased. First, our model experiments were tested with benzaldehyde as the standard molecule and varying the amount of catalyst and temperature in the absence of solvent. To our delight, as shown in **Table S4**, a loading of 1 mol % of **1'** led to a 96% conversion of benzaldehyde at 40°C under a N₂ atmosphere, which only is one eleventh of that used in related Mn-BTT.²⁰ Comparatively, we found that the reactivity of our catalyst was higher than that of some previously reported ones (Sc-MOF and Ln-MOFs) in which the loading of catalysts were 5 mol%.⁷ Importantly, removal of **1'** by filtration after only 2 h completely shut down the reaction, affording only 51% total conversion upon standing for 15 h. This demonstrates that no homogeneous catalyst species exists in the reaction solution and indicates that Cu-MOF **1'** is truly heterogeneous in nature (**Fig. S7**).

With condition for the efficient and high conversion in hand, we turned our attention to scope investigation for exploring the general utility of Cu-MOF catalyst and the results are summarized in **Table 1**. It was observed that the reaction showed broad tolerance for various substrates. Aryl- (**Table 1**, entries 1-4), heteroaryl- (**Table 1**, entry 7), aliphatic aldehydes (**Table 1**, entry 8) or cyclic ketone (**Table 1**, entry 9) were suitable substrates and gave the corresponding cyanohydrin trimethylsilyl ethers in high to excellent

Table 1. The cyanosilylation of various carbonyl compounds with TMSCN^a



Entry	R ₁	R ₂	Conv. (%) ^b
1	Ph	H	96
2	4-CH ₃ C ₆ H ₄	H	94
3	2-CH ₃ C ₆ H ₄	H	88
4	4-ClC ₆ H ₄	H	99
5	1-naphthyl	H	78
6	9-anthryl	H	0
7	2-furyl	H	99
8	n - Bu	H	99
9	(CH ₂) ₅		99

^a Reaction conditions: Me₃SiCN (1 mmol), aldehyde/ketone (0.5 mmol), **1'** (0.013 mg, 0.005 mmol), 40°C, under N₂ atmosphere. ^b Determined by GC based on the carbonyl substrate.

conversions. As depicted in **Table 1**, either the electronic effect or the position of substituent on aromatic ring, did not show any significant change in the overall conversion. Both excellent conversions and good general utility of cyanosilylation reconfirm that both protonated tetrazolate and partial replacement of Cl⁻ with O²⁻ enhance the Lewis acidity of coordinatively unsaturated metal centers of MOF **1'**.

A significant size-selectivity effect is observed with **1'**, when the substrate was 1-naphthaldehyde, only 78% of product was obtained,

and 9-anthracenecarboxaldehyde was inert to the conversion. These also suggest that the cyanosilylation occurred in the pore of MOF **1'**.

Recycle Experiment.

Reusability of the Cu-MOF **1'** was also studied. At the end of the conversion, the catalyst could be recovered by simple filtration from the reaction medium and, after washing and drying in vacuum, it could be reused five times of the reaction of furfuraldehyde and TMSCN without significant loss of activity (the conversion decreased only for 9%, **Fig. 4**). Comparison of the powder XRD

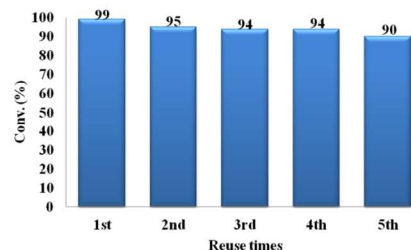


Fig. 4 Reusability of Cu-MOF catalyst experiments.

patterns of the fresh and five times reused MOF were also recorded (**Fig. S1**) which clearly show that the reused catalyst exhibits a similar powder XRD pattern. All results clearly demonstrate the practical recyclability of this catalyst and its remarkable stability.

Conclusions

In conclusion, we have shown herein that the modification of sodalite-type M-BTT MOFs via different atomic substitution of different valence state and removal of guest metal complexes in channels could lead to modified MOF with different charge distribution, pore volume, pore wall, and Lewis acid activity. Compared with related M-BTT MOFs, partial replacement μ₄-Cl⁻ with μ₄-O²⁻ at the square Cu₄ cluster and the absence of guest [M(DMF)₆]²⁺ cations enhanced Lewis acidity of coordinatively unsaturated metal centers and the effective pore volume. Desolvated MOF with open Cu(II) sites and strong Lewis acidity can be an active solvent-free heterogeneous catalyst for C-C bond-forming reaction by cyanosilylation of carbonyl compounds. The loading amount of catalyst is only one eleventh of catalyst in related Mn-BTT but it could lead to as high as 96% conversion of benzaldehyde. This MOF is stable and can be reusable five times without apparent lowering of activity. The excellent conversion, low catalyst loading and no need for solvents make the modified MOF to be ideal green catalyst. Besides, larger pore volume and open metal sites are possible reason for desolvated material selectively adsorption of N₂ and O₂ gases with hysteresis loops, which is a phenomenon not observed in related M-BTT MOFs. Further studies focused on other reactions of the construction of C-C bond are in progress.

Acknowledgements

This work was supported by the 973 Program (2012CB821701), the Ministry of Education of China (Grant IRT1156) and the NSFC (Grant 21402112).

Notes and references

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† Electronic Supplementary Information (ESI) available: Crystal data **1** in CIF format, additional figures, tables for selected bonds and angles, IR spectra, thermal analyses, PXRD patterns and adsorption isotherms for H₂ and CO₂. See DOI: 10.1039/b000000x/

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