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Amino-Induced 2D Cu-Based Metal–Organic Framework as an Efficient Heterogeneous Catalyst for Aerobic Oxidation of Olefins

Jia Tang,^[abc] Mengke Cai,^[c] Guanqun Xie,^[a] Shixiong Bao,^[c] Shujiang Ding,^[b] Xiaoxia Wang,^{*[a]} Jinzhang Tao,^[d] and Guangqin Li^{*[a]}

Dedication

Abstract: With the assistance of hydrogen bonds of the o-amino group, we have successfully tuned the coordination structure from metal-organic polyhedron (MOP) to two-dimensional (2D) metalorganic framework (MOF). The amino group forms hydrogen bonds with the two vicinal carboxylic groups, and induces the ligand to coordinate with copper ion to form 2D structure. The obtained 2D Cu-based MOF (Cu-AIA) has been applied as an efficient heterogeneous catalyst in the aerobic epoxidation of olefins using air as the oxygen source. Without the aggregation problem of active sites in MOPs, Cu-AIA possesses much higher reactivity than MOP-1. Furthermore, the amino group of the framwork has been used as a modifiable site via post-synthetic metallation (PSMet) to prepare 2D MOF supported Pd single-site heterogeneous catalyst, which shows excellent catalytic performance for Suzuki reaction. It indicates that Cu-AIA can also work as a good 2D MOF carrier for the derivation of other heterogeneous catalysts.

Introduction

Metal-organic polyhedra (MOPs) as crystalline coordination materials are constituted by metal ions and organic ligands.^[1-3] Owing to their unique features such as permanent porosity and unsaturated metal centers, MOPs have showed great potential for applications in drug delivery,^[4] gas adsorption and storage,^[5] chemical sensors^[6] and catalysis.^[7-10] As a common ligand isophthalic acid and its corresponding derivatized ligands have been widely used to prepare MOP materials.^[11-13] For example, Zhou et al prepared the stimuli-responsive MOP via the coordination the ligand 5-((2,4of dimethylphenyl)diazenyl)isophthalic acid with copper ion, and used in the capture and release of guest molecules.^[14] However, the disadvantages of poor stability and easy aggregation limit the application of MOPs, especially the removal of the guest molecules would inevitably result in the aggregation of MOP

[a]	Dr. J. Tang, Dr. G. Xie, Prof. X. Wang
	School of Environment and Civil Engineering, Dongguan University
	of Technology, Dongguan 523808, P. R. China
	E-mail: wangxx@dgut.edu.cn
[b]	Dr. J. Tang, Prof. S. Ding
	Department of Applied Chemistry, School of Science, Xi'an Jiaotong
	University, Xi'an 710049, P. R. China
[c]	Dr. J. Tang, M. Cai, Dr. S. Bao, Prof. G. Li
	MOE Laboratory of Bioinorganic and Synthetic Chemistry, Lehn
	Institute of Functional Materials, School of Chemistry, Sun Yat-Sen
	University, Guangzhou 510275, P. R. China
	E-mail: liguangqin@mail.sysu.edu.cn
[d]	Dr. J. Tao
	Guangdong Research Institute of Rare Metals, Guangzhou 510651,
	P. R. China
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molecules and the inaccessibility of active sites.^[15] So far a few strategies have been applied to solve the above problem.^[16-20] One strategy is to introduce MOPs into nanoporous silica and confine MOPs in its channels or cavities, [21,22] and the other is to use MOPs as porous monomers to further convert into framewoks (MOFs) metal-organic or supramolecular polymers.[23-26] Although significant progresses that have been made, the exploration of new strategies is still a hot research topic. Recently, two-dimensional (2D) MOFs have attracted much attention.^[27-29] Compared with three-dimensional (3D) MOFs, active sites that exposed on the surfaces of 2D MOFs are much easier to approach, which favors the interaction between substrate molecules and active sites, and facilitates the mass-transfer of solvent, substrates and products.^[30,31] Due to the interconnected channels and cavities of MOFs,[32-35] active sites can be accessible after activation, thus it may be a good strategy to achieve 2D MOF instead of MOP structure by regulating the inherent binding of ligands with metal ions via the introduction of specific functional groups. As far as we know, such a strategy has not yet been reported.

The epoxidation of olefins is one of the most important oxidative reactions due to the wide range of applications of the resulting epoxides both in industry and academia. $^{\left[36,37\right] }$ So far, a variety of new catalysts have been developed in the past decades to achieve the efficient transformation from alkenes into expoxides including both homogeneous catalysts (Ruthenium porphyrin,^[38,39] Manganese complexes,^[40,41] Iron complexes,^[42-44] etc^[45-48]) and heterogeneous catalysts (silica-supported titanium catalysts,^[49] Mn(III)-polymer catalyst,^[50] MOFs,^[51-53] etc^[54-57]). A number of oxidants such as alkyl hydroperoxides, H₂O₂, O₂ and air have been utilized for the epoxidation. With respect to the environmental and economic consideration, the inexpensive and eco-friendly O₂ and air as the oxidants are no doubt the most attractive.^[58,59] Despite the progress that have been achieved, development of novel green and efficient catalytic systems for air-mediated epoxidation is still desirable.

In this paper, by inserting an amino group at both of the ortho position of the two carboxylic groups of isophthalic acid, we have successfully regulated the coordination of the ligand with copper ion and constructed a 2D MOF structure rather than MOP structure under the same synthetic condition. The amino group forms hydrogen bonds with the two vicinal carboxylic groups, which induces the ligand to coordinate with copper ion to form 2D structure (Figure 1a). The obtained new Cu-based 2D MOF (Cu-AIA) as an efficient heterogeneous catalyst has been applied in catalyzing the aerobic epoxidation of olefins using air as the oxygen source. Moreover, by the post-synthetic metallation method (PSMet) Cu-AIA can also be used as a carrier to support metal active site using the amino group as a modifiable site. The good catalytic activity of the obtained Cu-AIA-PC-Pd catalyst for Suzuki–Miyaura coupling confirms the

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feasibility of Cu-AIA as a good 2D MOF carrier for supported heterogeneous catalysts.

Results and Discussion



Figure 1. (a) Schematic illustration for the preparation of MOP-1 and Cu-AIA. (b) The photograph of the Cu-AIA crystal sample. (c) X-Ray crystal structure of Cu-AIA (view down from *a*-axis). (d) Side view of the 2D sheets. (e) The simulated and measured XRPD patterns of Cu-AIA.

Cu-AIA was prepared by the solvothermal reaction of the AIA ligand and Cu(NO₃)₂·3H₂O. The reaction was run in a mixed solvent of DMF and ethanol at 80 °C for 24 h to give deep green rectangular block-shaped crystals (Figure 1b). Single crystal X-ray diffraction shows that Cu-AIA is formulated as $Cu_2(AIA)_2$ ·2(H₂O), and it crystallizes in the orthorhombic space group Pnma (Figure 1c, d) (see CIF, CCDC 1874182). The

carboxylates of the AIA ligand bridge two copper (II) ions forming a paddle-wheel type dinuclear secondary building unit (SBU) $Cu_2(CO_2)_4$ (Figure 1c). The amino group in the ortho position forms hydrogen bonds with the carboxylic groups (Figure 1a), which interestingly induces the ligand and copper ion to coordinate into a 2D MOF rather than MOP-1 structure (Figure S1, S2). Each copper (II) ion also coordinates with one

H₂O molecule in the first coordination sphere. The twodimensional (2D) layers that bridged SBU through the AIA ligand are extended by hydrogen bonds to build a 3D supramolecular architecture due to the coordinated H₂O molecule. The Cu--Cu distance is 2.6101(1) Å in Cu₂ dinuclear units, and the Cu-O distances are 1.9708(1) and 2.1255(1) Å in the SBU, where the oxygen atoms are derived from the organic ligand and H₂O molecules, respectively. The MOF is stable in air and insoluble in common solvents. The experimental and simulated XRD patterns show the bulk crystals have the same structure as the individual single crystal (Figure 1e). After being dried, the bulk crystal sample displays different XRD results from the original Cu-AIA sample, which indicates the change of the crystalline form and could be caused by the removal of the solvent (TGA anaylsis shows the removal of the solvents at 50~200 °C (Figure S3)). However, the peaks of the dried sample at 9.2 $^{\circ}$, 13 $^{\circ}$ and 18.2 ° retain, which indicates the 2D structure of Cu-AIA remains intact. In FT-IR spectra (Figure S4), two sharp bands at 3450 and 3350 cm⁻¹ are related to the N–H absorption (the asymmetric and symmetric), the peaks at 1631 and 1391 cm⁻¹ are ascribed to the anti-symmetric and symmetric vibrations of the carboxyl groups (C–O), and the C–N vibration appears around 1258 cm⁻¹.

PSMet as one of the most important strategies among the post synthetic modifications (PSM) has been well developed to enhance the application of MOFs in wider fields, including gas storage, sensing and catalysis.^[60,61] Especially PSMet provides an expansive scope for heterogeneous catalysis.^[62] So far, the PSMet strategy mainly focuses on the performance regulation of 3D MOFs.^[63] The PSMet of 2D MOFs has only been reported in rare cases since the organic frameworks of the reported 2D MOFs usually have no extra functional groups that can be modified,^[64,65] thus making it less feasible to anchor metal catalyst by PSMet. Here, we report the preparation of 2D MOF supported Pd single-site heterogeneous catalyst (Cu-AIA-PC-Pd) by employing Cu-AIA as a 2D MOF support.



Figure 2. (a) Schematic illustration for the preparation of Cu-AIA-PC-Pd catalyst. (b) SEM images of Cu-AIA-PC nanosheets (inset: (right) photograph of the Tyndall effect of Cu-AIA-PC nanosheets suspension in acetone and (left) AFM image of Cu-AIA-PC nanosheets). (c) Out-of-plane and (d) in-plane XRD patterns of Cu-AIA-PC nanosheets.

The 2D Cu-AIA crystals prepared as above is reacted with 2pyridinecarboxaldehyde to form the desired framework (Cu-AIA-PC) (Figure 2a) *via* the condensation between the amino group in the former and the carbonyl group in the latter. Scanning electron microscopy (SEM) images show the synthesized Cu-AIA-PC takes on the sheet-like structure with a size of a few micrometers (Figure 2b). Cu-AIA-PC nanosheets display a thickness of about 76 nm as determined by atomic force microscopy (AFM) (inset in Figure 2b). The suspension of Cu-AIA-PC nanosheets in acetone possesses the Tyndall effect when a red laser passes it through (inset in Figure 2b). In order to further examine the crystalline structure of Cu-AIA-PC

nanosheets, out-of-plane and in-plane X-ray diffractions were carried out (Figure 2c, d). As shown in Figure 2c, only (001) diffraction signal is observed for the out-of-plane direction, suggesting the (001) face of Cu-AIA-PC is parallel to the

substrate. Furthermore, the (010) diffraction signal collected from the in-plane direction suggests an obvious angular dependence (Figure 2d). Therefore, the structural information indicates the (001) orientation of Cu-AIA-PC nanosheets.



Figure 3. (a-f) XPS patterns of Cu-AIA-PC-Pd. (g) XRPD patterns of Cu-AIA, Cu-AIA-PC and Cu-AIA-PC-Pd. (h-l) EDS mapping of Cu-AIA-PC-Pd.

With the pyridyl-containing chelating group, the Cu-AIA-PC is coordinated with Pd(II) to afford Cu-AIA-PC-Pd via PSMet method (Figure 2a). XPS was performed to investigate the chemical state of each element in Cu-AIA-PC-Pd and the obtained results were shown in Figure 3. The XPS spectrum shows the presence of C, O, N, Cu and Pd in the sample (Figure 3a). The C 1s spectrogram suggests the presence of C-C (285 eV) and C-O (288 eV) (Figure 3b). The two peaks at 533 and 531 eV in the O 1s spectrogram are assigned to C-O-Cu and C=O, respectively (Figure 3c), and the two peaks at 400 and 395 eV in the deconvolution of the N 1s spectrum can be ascribed to the C-NH₂ and C=N, respectively (Figure 3d).^[66] The Cu 2p binding energy at 935 eV is corresponding to $Cu^{2+} 2p_{1/2}$ and the broad peaks are the satellites (Figure 3e). The Pd 3d binding energies at 343 and 338 eV are attributed to Pd²⁺ 3d_{3/2} and Pd²⁺ 3d_{5/2}, respectively (Figure 3f). The powder XRD patterns of Cu-AIA-PC and Cu-AIA-PC-Pd show the same reflection as that of Cu-AIA, indicating the modification of pyridine-2-aldehyde and the Pd(II) loading on 2D MOF do not change the 2D MOF crystal structure (Figure 3g). The EDX mapping images of Cu-AIA-PC-Pd show the elements of C, O, Cu and Pd are homogeneously dispersed throughout the MOF nanosheets (Figure 3h-I). The quantitative measurement with ICP-MS shows that Cu-AIA-PC- Pd contains 8.3 wt% Pd, which is very close to the EDX result (8.8 wt%) (Figure S5, Table S1 and S2).

Catalytic performance and reaction mechanism analysis

2D Cu-AIA is directly applied in the epoxidation of olefins using air as the oxygen source. Firstly, the conditions for the catalytic epoxidation were optimized using cyclooctene as a model substrate. As shown in Figure S6, various solvents are screened to obtain the most suitable solvent for the epoxidation. When DMF, toluene, ethanol and CH₂Cl₂ are examined respectively as the solvent, almost no epoxidation could be observed. In contrast, 1,4-dioxane and ethyl acetate could afford the epoxide 1 in 25% and 17% yield, respectively. For the solvents of CH₃CN, dioxane, ethyl acetate, CH₂Cl₂ and toluene, it seems the greater the polarity, the better the catalytic efficiency. For DMF and ethanol, they are inclined to coordinate with copper ions, the active sites for the epoxidation, and reduced the catalytic efficiency. Acetonitrile is the most appropriate solvent, giving 1 in 32% yield. Control experiment shows that aldehyde as an essential additive has a significant impact on reaction efficiency, and no reaction occurs without its presence (Figure S7), consisting with the report that aldehyde as a sacrificial coreductant plays an important role in the epoxidation reaction.^[67] Aromatic aldehydes both with electron-withdrawing groups (– NO_2 , –Br) and with electron-donating groups (–H and –CH₃) show a low epoxidation reactivity. Aliphatic aldehydes and cyclic aldehydes (cyclo-hexanecarboxaldehyde) could significantly accelerate the reaction, which suggests the structures of aldehydes are critical to the catalytic efficiency, and the use of isobutyraldehyde gives the best yield.

Chemistry - A European Journal

RESEARCH ARTICLE



Figure 4. Substrate scope for the aerobic epoxidation of olefins using the Cu-AIA as a catalyst (bar: conversion, ball: selectivity). Reaction conditions: 1 mmol of olefin, 3 mmol of isobutyraldehyde and 5 mL of CH_3CN were mixed with 10 mol% catalyst in a 25 mL three-necked round-bottomed flask along with a condensation tube. The mixture was stirred with air bubbling at 80 °C for 24 h.

The effect of the amount of catalyst on the substrate conversion has also been studied. The conversion of cyclooctene is only 2% when the reaction is carried out without Cu-AIA catalyst (Table S3, entry 1), and the conversion increased steadily from 32% to 91% as the amount of catalyst increased from 2 mol% to 10 mol% (Table S3, entries 2-4). For comparison, MOP-1 is also used to catalyze the epoxidation of cyclooctene, and only 15% conversion is obtained (Table S3, entry 5), which are remarkably lower than that of Cu-AIA under the same condition. Thus, it is proposed Cu active sites exposed on surfaces of the 2D MOF are easier to approach for the reactants. For the influence of temperature on the epoxidation of cyclooctene, it is found the conversion of cyclooctene is

significantly improved by increasing the temperature (Figure S8). High yield of the epoxidation product can be obtained when the reaction is conducted in acetonitrile at 80 $^{\circ}$ C for 24 h in the presence of Cu-AIA catalyst.



Figure 5. (a) Reusability of Cu-AIA catalyst for the aerobic epoxidation of cyclooctene (bar: conversion, ball: selectivity) Reaction conditions: 1 mmol of cyclooctene, 3 mmol of isobutyraldehyde and 5 mL of CH₃CN were mixed with 10 mol% catalyst in a 25 mL three-necked round-bottomed flask along with a condensation tube, and the mixture was stirred with air bubbling from the bottom of the flask at 80 °C for 24 h. After each reaction, Cu-AIA catalyst was isolated from the solution, and recovered by washing with CH₃CN (3×10 mL) for another run in which the conversion and selectivity would be detected by GC-MS. (b) Proposed mechanism for the aerobic epoxidation of cyclooctene in the presence of Cu-AIA using isobutyraldehyde as a sacrificial co-reductant.

Under the optimized conditions, the scope of Cu-AIA was explored (Figure 4). Cyclic olefins such as cyclooctene and norbornene show high conversion with excellent selectivity (>99%) for their corresponding epoxides. Cyclohexene is converted to cyclohexene oxide smoothly in 62% yield, and the byproduct 2-cyclohexen-1-one with 34% selectivity is produced. Substituted styrenes with either electron-withdrawing group (– NO_2) or electron-donating group (– CH_3) are oxidized to the corresponding aldehydes. Styrene is transformed into 1,2-epoxyethylbenzene contaminated with benzaldehyde (36% selectivity) as the main by-product. *Trans*-stilbene is oxidized to the corresponding epoxide in 75% selectivity with the 24%

selectivity for benzaldehyde. Linear terminal alkene such as 1octene gives the corresponding epoxide cleanly. Sterically hindered 9-vinylanthracene only affords the corresponding aldehyde.

To evaluate the stability of Cu-AIA catalyst for the epoxidation reaction, a leaching test was conducted. The Cu-AIA catalyst is removed via centrifugation after 2 h of reaction and the remaining supernatant is allowed to react for another 8 h (Figure S9). The results show that the conversion of cyclooctene increases slightly from 35% to 48% without Cu-AIA catalyst, which should result from the slow oxidation. In addition, no obvious presence of Cu could be observed in the solution as analyzed by ICP-MS. Thanks to its good stability, the Cu-AIA catalyst can catalyze the epoxidation of cyclooctene over six successive cycles with the same selectivity of >99% for 1,2epoxycyclooctane (Figure 5a). The powder XRD results also indicate that the overall structure of the Cu-AIA catalyst remains intact after 2 and 4 cycles (Figure S10). The Cu-AIA catalyzed aerobic epoxidation of cyclooctene is rationalized in Figure 5b. The isobutyraldehyde I coordinates with the Cu²⁺ sites of Cu-AIA II to form the complex III. By losing a hydrogen, an acyl radical IV was produced. Inermediate IV would then combine with dioxygen to form an acylperoxy radical V, which is reported to be the predominant oxidizing species for the expoxidation of olefin IX into epoxide 2.[68] However, V can also transform into a copper-acylperoxy VI, another efficient epoxidation species.^[69] In fact, the formation of Cu(IV) species VII may also work in the expoxidation process.^[70] Although the exact epoxidation species remains to be clarified, the high selectivity of the Cu-AIA catalyst for the epoxidation reaction is impressive.

In order to expand its application range, Cu-AIA has been used as a carrier to support Pd catalyst via PSMet method using the amino group as modifiable sites, and the catalytic activity of the obtained Cu-AIA-PC-Pd catalyst is firstly evaluated by Suzuki-Miyaura coupling reaction with 4-iodobenzaldehyde and phenylboronic acid as model substrates (Figure S16-S19).^[71,72] As shown in Figure 6, no target product can be found without the catalyst, nor does the reaction proceed in the presence of Cu-AIA. An excellent conversion of 4-iodobenzaldehyde is obtained with 1 mol% Pd in Cu-AIA-PC-Pd in 0.5 h, and 4iodobenzaldehyde is converted almost completely to the corresponding product [1,1'-biphenyl]-4-carbaldehyde in 1 h. The reaction mechanism for the Suzuki-Miyaura reaction has been proposed in Figure S20. Furthermore, other aryl halides also have been explored in the reaction (Table S4). The employed aryl iodides containing electron-withdrawing groups such as 4-CHO, 4-CN, 4-NO₂, 4-CH₂-OH proceed satisfactorily, and good isolated yields (>90%) are obtained (Table S4, entries 1, 3-5). 9lodophenanthrene as a typical macromolecule substrate affords the corresponding product 9-phenylphenanthrene in an excellent yield (92.1%). But the reaction of the aryl iodide containing electron-donating groups (4-CH₃) with phenylboronic acid gives



Figure 6. Suzuki–Miyaura coupling of 4-iodobenzaldehyde and phenylboronic acid catalyzed by Cu-AIA-PC-Pd. Reaction conditions: 1 mmol of 4-iodobenzaldehyde, 1.5 mmol of phenylboronic acid, 1.5 mmol of K₂CO₃ and catalyst (1 mol%) were added into 5 mL of ethanol. The mixture was stirred at room temperature for 6 h.

coupling product in lower yield (Table S4, entry 2). The reactions of substituted aryl bromides with phenylboronic acid also afford the corresponding products in good yields (Table S4, entries 7, 9 and 11) except the aryl bromides with $4-CH_3$ and $4-CH_2OH$ groups (Table S4, entries 8, 10). However, 4chlorobenzaldehyde and 4-fluorobenzaldehyde show much lower activities (Table S4, entries 12, 13). The leaching test shows the heterogeneous catalysis feature of the catalytic system (Figure S21). After six successive cycles, the Cu-AIA-PC-Pd catalyst remains substantially active and no significant decreases in catalytic efficiency (Figure S22). Compared with the catalysts reported in literatures (Table S5), [73-83] the obtained Cu-AIA-PC-Pd also exhibits excellent catalytic activity. The results confirm that Cu-AIA as a 2D carrier to support metal catalysts is feasible.

Conclusion

In this paper, the transformation of coordination structure from MOP to 2D MOF has been achieved using 2-aminoisophthalic acid instead of isophthalic acid. The amino group in the ortho position supplies hydrogen bonds to the carboxylic groups and induces the ligand to coordinate with copper ion to form 2D structure. In the 2D MOF structure, Cu active sites are better exposed on surfaces, much easier to approach and avoid the aggregation problem, which makes the Cu-based 2D MOF (Cu-AIA) behave as an efficient heterogeneous catalyst for the aerobic epoxidation of olefins in an air atmosphere. Furthermore, Cu-AIA has also been used as a carrier to support metal active sites using the amino group as a modifiable site to PSMet. SEM images, AFM images and out-of-plane and in-plane XRD

patterns show that bulk Cu-AIA crystals are exfoliated into nanosheets (\sim 76 nm) with (001) orientation. The obtained 2D MOF supported Pd single-site heterogeneous catalyst exhibits excellent catalytic performance for the Suzuki–Miyaura coupling reaction, which indicates Cu-AIA as a good 2D MOF carrier can be used to prepare other supported heterogeneous catalysts.

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RESEARCH ARTICLE

Entry for the Table of Contents

-NH₂ induced

Self-assembly

2D MOF

RESEARCH ARTICLE

With the assistance of the hydrogen bond of *o*-amino group, we have tuned the coordination structure from MOP to 2D MOF. The amino group forms hydrogen bonds with the two vicinal carboxylic groups and induces the ligand to coordinate with copper ion to form 2D structure. The obtained 2D MOF (Cu-AIA) shows high catalytic activity for the aerobic oxidation of olefins under air atmosphere.

Jia Tang, Mengke Cai, Guanqun Xie, Shixiong Bao, Shujiang Ding, Xiaoxia Wang*, Jinzhang Tao, and Guangqin Li*

Page No. – Page No.

Amino-Induced 2D Cu-Based Metal–Organic Framework as an Efficient Heterogeneous Catalyst for Aerobic Oxidation of Olefins