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Azide-ways manoeuver: Oxysulfonyl azide is developed for the formation of *N*-oxysulfonyl amidines. Three kinds of Cu¹ catalysts are tested, which include Cul, Cu₂l₂(PDIN) without micropores, and Cu₂l₂(BTTP4) with micropores (PDIN = 1,4-phenylene diisonicotinate, BTTP4 = benzene-1,3,5-triyltriisonicotinate). Both homogeneous Cul and heterogeneous Cu₂l₂(BTTP4) are catalytically efficient and provide *N*-oxysulfonyl amidines in good yields.



Homogeoneous without micropores with micropores

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From Homogeneous to Heterogeneous Catalysis of the Three-Component Coupling of Oxysulfonyl Azides, Alkynes, and Amines DOI: 10.1002/cctc.201300241

From Homogeneous to Heterogeneous Catalysis of the Three-Component Coupling of Oxysulfonyl Azides, Alkynes, and Amines

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A reliable procedure for the synthesis of oxysulfonyl azides has been developed and applied to the three-component coupling reactions of azides, alkynes, and amines catalyzed homogeneously by Cul, which led to the formation of *N*-oxysulfonyl amidines with good yields. To fully evaluate the catalytic activity towards this coupling reaction, two coordination frameworks, namely, Cu₂I₂(PDIN) without micropores and Cu₂I₂(BTTP4) with micropores (PDIN = 1,4-phenylene diisonicotinate, BTTP4 = benzene-1,3,5-triyltriisonicotinate), were prepared by a facile one-pot reaction as heterogeneous catalysts. Catalytic results showed that nonporous Cu₂I₂(PDIN) was almost inactive for the three-component coupling reaction, whereas microporous

Cu₂I₂(BTTP4) was an efficient heterogeneous catalyst for the synthesis of *N*-oxysulfonyl amidines. Furthermore, porous Cu₂I₂-(BTTP4) displayed a shape-selective performance with respect to the alkyne substrates, and aromatic alkynes were preferable to aliphatic alkynes. The location of the catalytically active sites in the Cu₂I₂(BTTP4) framework has been studied by a series physical techniques, which includes powder XRD, CO₂ gas adsorption, IR spectroscopy, energy dispersive X-ray analysis, and X-ray photoelectron spectroscopy, which suggests that the catalytic sites are not only on the external surface but also inside the micropores.

Introduction

Over the past decade, metal–organic frameworks (MOFs), also called porous coordination polymers (PCPs), have attracted considerable interest because of their designable structures, tunable channels, high internal surface area, and micro/meso-porosity. Since the 1990s, a large number of MOFs have been examined as heterogeneous catalysts, which were first based on their intrinsic catalytic properties such as Lewis acid catalysis and redox catalysis of the metal components.^[1–6] To construct catalytic MOFs capable of more valuable reactions, scientists have developed three important strategies, (i) direct incorporation of homogeneous catalysts into a linker ligand,^[7–16] (ii) grafting an organocatalyst onto a metal node,^[17–19] and (iii) adsorption of transition-metal complexes into the cavities followed by reduction to lead to the formation of catalytic nano-

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sized metal particles.^[20-26] In these strategies, the metal nodes usually act as building units rather than catalytic sites.^[27-30]

We are interested and engaged in the development of catalytic MOFs in which the metal nodes themselves can act as catalytic sites and promote reactions that lead to the formation of valuable products.^[31-34] Since 2000, a variety of Cul-based frameworks have been constructed from bi- or tritopic ligands as a result of the rich coordination chemistry of Cu^I as well as the strong coordination nature of I⁻.^[35-38] Interestingly, Cul can promote a number of organic reactions, especially the remarkable click reactions^[39,40] and multicomponent coupling reactions.^[41-44] Therefore, the construction of porous Cul MOFs may provide a feasible and convenient approach to self-supported, heterogeneous catalysts with Cu^I ions that act as both metal nodes and potential catalytic sites.^[45-48] Furthermore, careful investigations into the catalytic activity as well as detailed mechanistic studies show that N-containing ligands, such as benzimidazole, triazole, and pyridine, can accelerate Cul-catalyzed reactions,^[49,50] which arouses our interest to study the applications of porous pyridine-based Cul MOFs in heterogeneous catalysis.

Herein, we reveal that Cul and a porous MOF of Cu₂I₂(BTTP4) (BTTP4 = benzene-1,3,5-triyltriisonicotinate) can catalyze the synthesis of *N*-oxysulfonyl amidines in a three-component coupling reaction with oxysulfonyl azide as an efficient one-Natom source homo- and heterogeneously, respectively. Cu₂I₂-(BTTP4) has a large free volume of 1776.9 Å³ per unit cell, as well as 1D channels (9×12 Å²), which provide a platform to perform reactions in the framework channels and display shape-selective catalytic capability (Figure 1).^[45]

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Figure 1. Illustration of the catalytic behavior of Cu₂I₂(BTTP4).

Results and Discussion

Amidine synthesis from oxysulfonyl azide

As a broad class of compounds that are widely available or can be prepared by straight synthesis, azides have the potential to serve as a general type of N source in a variety of reactions. Sulfonyl and phosphoryl azides have drawn much attention as a result of their easy transformation to nitrenes or one-N-atom sources upon the release of molecular N₂ in C-H bond amination^[51,52] and ketenimine-intermediate-based multicomponent reactions,^[41-44] respectively. Oxysulfonyl azides (also called azidosulfates), another class of reactive azides, have been much less exploited in organic transformations, which might be because of a lack of appropriate methods for their synthesis. It has been demonstrated by Zhang et al. that trichloroethoxysulfonyl azide (TcesN₃) can be easily transformed to nitrenes with the loss of N2. [53] This remarkable finding has encouraged us to explore the reactivity of oxysulfonyl azides in the Cul-catalyzed, three-component coupling of azides, alkynes, and amines, which was originally developed by Chang et al.^[41] We discovered that a range of oxysulfonyl azides can be obtained simply in moderate yields by the following procedure: a 1:1.1 mixture of phenol and SO₂Cl₂ in the presence of one equivalent of pyridine was stirred in dry CH_2CI_2 at -78 °C followed by the addition of 1.5 equivalents of NaN₃ [Eq. (1)].

$$R \xrightarrow{OH} CI \xrightarrow{O}_{II} CI \xrightarrow{I}_{I} CI \xrightarrow{I}_{I} Pyridine, CH_2CI_2, -78 °C}{2) \text{ NaN}_3, CH_3CN, 0 °C} R \xrightarrow{O}_{II} O \xrightarrow{S}_{I} O \xrightarrow{O}_{II} O \xrightarrow{I}_{I} O \xrightarrow{I$$

To explore the reactivity of oxysulfonyl azides, we performed comparison tests on the reactions between phenylacetylene (PhCCH), diisopropylamine ((*i*/Pr)₂NH), and different azides, such as *p*-tosyloxysulfonyl azide (TsOxy-N₃), *p*-tosylsulfonyl azide (Ts-N₃), and diphenylphosphoryl azide (DPPA), in the presence of 10 mol% Cul in acetonitrile. To our delight, under the optimized conditions (alkyne/azide/amine = 1:1.2:1.2), the reaction with TsOxy-N₃ was accomplished within 10 min with 100% conversion to form *N*-oxysulfonyl amidine **1** (Table 1, entry 1). In comparison, the reaction with Ts-N₃ yielded the corresponding *N*-sulfonyl amidine **2** with a conversion of 62% in 10 min (entry 2). After 1 h, the reaction with Ts-N₃ achieved 100% conversion. However, the reaction with DPPA was rather poor and achieved only 24% conversion after 4 h. The molecular structure of **1** was determined by single-crystal X-ray crystallograph

ic analysis, which discloses the *E* form of the generated C=N double bond (Figure S22). Next, we examined the scope of the reaction with respect to the azide component. As illustrated by the examples shown in Table 1, a range of oxysulfonyl azides participated efficiently in the three-component coupling reaction. For example, aryl (entries 1, 4–7) and alkyl azides (entry 8) were competent reactants and provided *N*-oxysulfonyl amidines with good yields. Both electron-deficient and -rich oxysulfonyl azides were reactive in this coupling reaction (entries 6 and 7).

Based on these results, oxysulfonyl azides appear to be promising one-N-atom sources, in addition to sulfonyl and phosphoryl azides, and may be further applied in more metal-catalyzed transformations to yield a variety of valuable compounds. To further evaluate the reactivity of oxysulfonyl azides in the three-component coupling of azides, alkynes, and amines, we extended the catalyst from homogeneous Cul to heterogeneous Cul-containing coordination frameworks.

Synthesis and characterization of $\mathsf{Cu}_2\mathsf{I}_2(\mathsf{PDIN})$ and $\mathsf{Cu}_2\mathsf{I}_2(\mathsf{BTTP4})$

It has been established by Finn et al. that flexible N-containing tripodal ligands, which are based on a central tertiary amine surrounded by three *N*-heterocycles such as triazoles, benzimidazoles, and pyridines, can display a dramatic enhancement in the reactivity in reactions catalyzed homogeneously by Cu^{1,[49,50]} Chang et al. discovered that tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA) exhibited a significant rate enhancement in the synthesis of amidines.^[44] Their remarkable results prompted us to examine the effect of N-based ligands on the catalytic activity in three-component coupling reactions with oxysulfonyl azides. Other than flexible ligands for homogeneous catalysis, we are interested to explore whether rigid di- or tritopic ligands, which are typically composed of a benzene core surrounded by two or three *N*-heterocycles (e.g., 3-/

> 4-pyridine), could be exploited as accelerating ligands in heterogeneous transition-metal catalysis because these rigid ligands have been widely applied in the construction of porous MOFs. With the robustness of MOFs, the rigid N-based ligands could not only stabi-

lize the oxidation state of the catalytically active metal center Cu^{l} in the solid state but also maintained its potential reactivity and dynamics.^[45–48]

Based on the above concept, two MOFs, namely, $Cu_2I_2(PDIN)$ (PDIN = 1,4-phenylene diisonicotinate) and $Cu_2I_2(BTTP4)$, have been synthesized based on the pyridine-containing ligands PDIN and BTTP4, respectively. The orange-yellow $Cu_2I_2(PDIN)$ crystallites were obtained from the direct mixing of a CH₃CN solution of CuI and a CHCI₃ solution of PDIN followed by stirring at room temperature for 30 min. Single crystals suitable for XRD analysis were obtained one week after layering a CH₃CN solution of CuI onto a CHCI₃ solution of PDIN. The crystal structure displays a closely packed 2D network in which Cu_2I_2 ribbons are connected by the bridging PDIN ligand (Figure S2). The phase purity of the crystalline precipitates ob-

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Table 1. Cul-catalyzed three-component coupling reactions of oxysulfonyl azides, alkynes, and amines. ^[a]							
RN ₃ + Ph-=== +	. (<i>i</i> Pr) ₂ NH	→ Ph ↓	२				
1.2 equiv. 1.0 equiv.	CH ₃ CN, RT 1.2 equiv.		`N(<i>i</i> Pr) ₂				
Entry RN_3	Product	Conversion [%] (t [min])	lsolated yield [%]				
1	O [°] ^S N Ph N(<i>i</i> Pr) ₂	100 (10)	87				
2 - SO ₂ N ₃	$\begin{array}{c} 1 \\ & \bigcirc \\ O^{<}S \\ Ph \\ & \bigvee \\ N(iPr)_2 \end{array}$	62 (10) 83 (20) 90 (30) 100 (60)	n.d. ^[b]				
3 O=P-N ₃	2 0.0 0.0 0.0 0.0 0.0 N N(<i>i</i> /Pr) ₂	12 (30) 15 (60) 24 (4 h)	n.d. ^[b]				
4	3 ↓ O ² S.N Ph N(<i>i</i> Pr) ₂	95 (10) 100 (30)	87				
5 tBu— OSO ₂ N ₃	tBu Ph N(iPr)2	100 (30)	89				
6 F	$F \xrightarrow{O_{i}} (O_{i}) = (O_$	100 (30)	67				
7 MeO-COSO ₂ N	MeO MeO N(<i>i</i> Pr)	100 (30) 2	81				
8 CI-CI-CI	CI = 0 CI = 0 $O^{S} N$ $Ph = N(iPr)_2$	100 (30)	90				
8 [a] Reaction conditions: oxysulfonyl azide (0.3 mmol), phenylacetylene (0.25 mmol), (<i>i</i> Pr) ₂ NH (0.3 mmol), Cul (0.025 mmol), CH ₃ CN (0.5 mL); [b] Not determined.							

tained by the direct mixing of Cul and PDIN solutions was determined by powder XRD (PXRD) analysis (Figure 2a). Particlesize analysis shows that the average edge length is approximately 0.4 μ m (Figure 2b). SEM images of Cu₂l₂(PDIN) reveal a flaky crystal with particle sizes in the range 0.1–1 μ m (Figure 2c), which agrees with the particle-size analysis.

Cu₂I₂(BTTP4) has been prepared previously by our group.^[45] Its crystal structure features a polycatenated 3D framework consisting of 2D (6,3) networks through inclined catenation, and contains large 1D channels (9×12 Å², after considering the



Figure 2. Characterization of Cu₂l₂(PDIN) (left) and Cu₂l₂(BTTP4) (right): a, d) PXRD patterns; b, e) particle-size analyses; c, f) SEM images; scale bars = 1.0 and 5.0 μ m, respectively.

van der Waals radii). The solvent-accessible voids amount to 43% of the unit-cell volume. In this work, we simplified the synthetic procedure and prepared orange-yellow $Cu_2I_2(BTTP4)$ crystallites by the direct mixing of a CH₃CN solution of Cul and a CHCI₃ solution of BTTP4. The PXRD patterns of the bulky samples prepared in this way matched those of pure crystals of $Cu_2I_2(BTTP4)$ (Figure 2d). Particle-size analysis showed that the average edge length is about 7.2 µm (Figure 2e). A typical SEM image of $Cu_2I_2(BTTP4)$ revealed block-like crystals with particle sizes in the range 1–10 µm, which agrees with the particle-size analysis (Figure 2 f).

Quantitative amounts of Cu_2l_2 (PDIN) and Cu_2l_2 (BTTP4) crystalline products could be obtained by a simple and convenient synthetic method in a one-pot reaction, which promotes their applications in catalytic reactions.

Comparison of the catalytic activity of Cul, $\text{Cu}_2\text{I}_2(\text{PDIN}),$ and $\text{Cu}_2\text{I}_2(\text{BTTP4})$

To study the potential of $Cu_2I_2(PDIN)$ and $Cu_2I_2(BTTP4)$ as heterogeneous catalysts in the three-component coupling reaction, we compared their activities with the naked homogeneous Cul by keeping Cu content the same (10 mol%). As the azide only acts as a N source and variation of the alkyne component can lead to the formation of various amidine compounds, we selected three alkynes that contained different substituents for comparison, namely, PhCCH, cyclohexyl acetylene (CyCCH), and *tert*-butyl acetylene (tBuCCH). The optimized reactant ratio under heterogeneous conditions is alkyne/azide/amine = 1:1:1, which is different to that of the homogeneous reaction with

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Cul but apparently more economic. Before the catalytic reactions, the Cu₂I₂(PDIN) and Cu₂I₂(BTTP4) crystallites were dried completely under vacuum until no further solvent loss was observed from thermogravimetric analysis (Figures S1 and S4). The results are summarized in Figure 3 and provide the following important information about their catalysis: (i) Cu₂I₂(PDIN) is relatively ineffective for *N*-oxysulfonyl amidine, and the con-



Figure 3. Comparison of the catalytic behavior of Cul, Cu_2l_2 (PDIN), and $Cu_2l_2^-$ (BTTP4). The selectivities towards PhCCH (\blacksquare), CyCCH (\blacksquare), and *t*BuCCH (\blacksquare).

version of the reactions with all of the alkynes was around 10%; (ii) Cul showed a similar activity for all of the alkynes, and the conversion was in the range of 70–80%; (iii) Cu₂I₂(BTTP4) performed differently with respect to the alkyne substrates. For example, the conversion of the reactions of PhCCH, CyCCH, and *t*BuCCH after 10 min was 96, 55, and 24%, respectively.

Notably, negligible loss of the orange-yellow crystallites of Cu₂I₂(PDIN) and Cu₂I₂(BTTP4) was detected, which testifies their competence as heterogeneous catalysts. Thus, we employed various physicochemical techniques to characterize the catalysts before and after the reactions in an attempt to illustrate the origin of their catalytic differences. For Cu₂l₂(PDIN) crystallites, the PXRD patterns measured after catalytic reactions disclosed that the crystallinity was retained (Figure S7). Additionally, particle-size analysis showed that the average edge length of the Cu₂l₂(PDIN) crystallites was enlarged to approximately 1.2 µm after catalytic reactions. Such a phenomenon could also be seen from the SEM images (Figure S9), which suggested that the flaky crystals might undergo aggregation during the catalytic reactions. From the single-crystal structural analysis we know that Cu₂I₂(PDIN) is nonporous (Figure S2). Therefore, the catalytic sites could only exist on the outer surface. The fact that the catalytic reaction can only take place on the outer surface accounts for the low activity of the Cu₂I₂(PDIN) crystallites as a heterogeneous catalyst compared with homogeneous catalyst Cul, which contains the same amount of Cu. Furthermore, aggregation of crystallites during the reaction makes catalysis ineffective. The surface catalytic reaction was proved by IR and energy-dispersive X-ray spectroscopic (EDS) examination of the Cu₂I₂(PDIN) crystallites after catalytic reactions, which confirmed that no *N*-oxysulfonyl amidine products could be detected inside the recycled catalyst either by the observation of S in the EDS spectra or by the presence of C=N vibrations in the IR spectrum (Figures S11, S12, and S19).

On the contrary, the single-crystal structural analysis of Cu₂I₂-(BTTP4) revealed that there are 1D open channels of an effective size of 9×12 Å² inside the coordination framework, which provide a platform for the catalytic reactions within the channels.^[45] The PXRD patterns of the Cu₂I₂(BTTP4) crystallites after catalytic reactions closely matched those of Cu₂I₂(BTTP4) single crystals, which indicates the unchanged framework (Figure S8). The average edge length of the Cu₂I₂(BTTP4) crystallites was reduced to approximately 3.2 µm, which may be explained by the SEM observation that some of the Cu₂I₂(BTTP4) crystallites fell apart into smaller particles (Figure S10). As the reactions go on inside the crystal channels, it is understandable that the Cu₂I₂(BTTP4) crystallites are smashed on exclusion of N₂ from TsOxy-N₃.

With the development of MOFs as promising heterogeneous catalysts, there is always a debate as to whether the catalytic reactions proceed within the crystal voids.^[1–8] To investigate whether the catalytic transformation can proceed inside the crystal pores or only on the external crystal surface of Cu₂I₂-(BTTP4), we firstly performed selective accommodation experiments of the alkyne substrates by ¹H NMR spectroscopy. After Cu₂I₂(BTTP4) was immersed in a 1:1 mixture of PhCCH and CyCCH in CD₃CN for 10 min, the molar ratio of these two alkynes changed to 0.73:1 (Figure 4), indicative of the selective inclusion of aromatic alkyne PhCCH over the aliphatic alkyne CyCCH, which is consistent with the selective vapor adsorption of benzene over cyclohexane by the Cu₂I₂(BTTP4) framework observed previously.^[45] Similar results were obtained from an immersion experiment of Cu₂I₂(BTTP4) in a 1:1 mixture of



Figure 4. Selective adsorption behavior of Cu₂I₂(BTTP4) determined by ¹H NMR spectroscopy of a 1:1 mixture of PhCCH and CyCCH in CD₃CN a) before and b) after the immersion of Cu₂I₂(BTTP4).

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PhCCH and tBuCCH in CD₃CN (Figure S6). We ascribed such selective adsorption to the preferential host–guest interactions between the pyridyl rings of the BTTP4 ligands and the phenyl rings of the aromatic alkynes. This selective inclusion of alkyne substrates by the porous Cu_2l_2 (BTTP4) MOF not only confirmed that the substrates could enter the pores of the MOF catalyst but also explained the much faster rate of reaction with PhCCH than that with CyCCH or tBuCCH.

Secondly, we measured CO₂ gas adsorption-desorption isotherms for the Cu₂l₂(BTTP4) crystallites before and after catalytic reactions (Figure S21). At 195 K, the amount of CO₂ uptake at 1 atm was 23.7 and 13.7 wt% before and after catalytic reaction. The decrease of the adsorption capability of CO₂ by the Cu₂I₂(BTTP4) framework after catalysis might be caused by Noxysulfonyl amidine products that remain in the channels, which might partially block the framework pores. Additionally, we characterized Cu₂I₂(BTTP4) after catalytic reactions by IR, EDS, and X-ray photoelectron spectroscopy (XPS). The IR spectrum disclosed the presence of C=N bonds of the amidine products (Figure S20), and both EDS (Figure 5) and XPS (Figure 6) confirmed the presence of S in the recycled catalyst sample. XPS also verified that the valence (+1) of Cu₂I₂(BTTP4) remained unchanged after the catalytic reactions, which was ascertained by observation of the same two intense peaks at 932.5 ± 0.2 and 952.5 ± 0.2 eV assigned to $Cu 2p_{3/2}$ and $Cu 2p_{1/2}$ components for the Cu₂I₂(BTTP4) crystallites before and after



Figure 5. Elemental distribution of Cu_2l_2(BTTP4) after catalytic reactions (2.12 keV, AuM_{\alpha}; 2.30 keV, SK_a).



Figure 6. XPS spectra of $Cu_{2l_2}(BTTP4)$ before (top) and after (bottom) catalytic reactions. MNN=initial vacancy in the M shell and final double vacancy in the N shell; LMM=initial vacancy in the L shell and final double vacancy in the M shell.

catalytic reactions. This XPS result suggested that the recycled Cu_2l_2 (BTTP4) catalyst is still active for further reaction.

From the comparison of the catalytic results of the homogeneous catalyst Cul, nonporous, heterogeneous catalyst Cu₂I₂-(PDIN), and porous, heterogeneous catalyst Cu₂I₂(BTTP4), we may conclude that the porous Cu₂I₂(BTTP4) framework stands out as a shape-selective catalyst because of the presence of catalytic sites on the inner micropore surfaces and its heterogeneous catalytic activity is comparable with that of homogeneous Cul for aromatic alkyne substrates.

Catalytic performance of Cu₂I₂(BTTP4)

To explore the substrate scope of Cu₂I₂(BTTP4) as a heterogeneous catalyst, three-component reactions of TsOxy-N₃, (*i*Pr)₂NH, and different alkynes have been studied. To our delight, a series of aromatic alkynes can take part in the catalytic reactions, and the reactions could be finished in 30 min with good yields (Table 2, entries 1–7). In all cases, N-oxysulfonyl amidines were formed as the sole products, except in the reaction with p-fluorophenylacetylene, in which a minor amount of oxysulfonyl triazole was obtained (entry 4). In contrast, N-oxysulfonyl amidines were obtained with modest yields from the reactions with alkyl alkynes (entries 8-13). In particular, the reaction with the bulky alkyne tBuCCH gave amidine 10 in only 38% yield (entry 9). With respect to functional group compatibility, a range of functional groups, which includes halide, alcohol, ether, and silyl groups, are tolerated in Cu₂I₂(BTTP4)-catalyzed reactions. It is interesting that hydroxyl groups in the alkyne substrates could even promote the reaction (entries 11 and 12),^[54] which is in agreement with our previous observation that the inclusion of polar alcohols by the Cu₂I₂(BTTP4) framework is superior to the inclusion of cyclohexane.^[45] Amines other than (iPr)₂NH, such as N-methylaniline (Ph(Me)NH) and diphenylamine (Ph₂NH), have also been tested, and the results show that the reactivity is in the order of (iPr)₂NH> $Ph(Me)NH > Ph_2NH$ (entries 1 and 14). Only a trace amount of amidine product could be detected from the reaction with Ph₂NH, which indicates that the basicity of the amine affects the coupling significantly.

One remarkable feature of this catalysis is that Cu₂I₂(BTTP4) crystallites can be easily isolated from the reaction suspension by simple filtration alone and can be reused at least three times without any loss in yield or chemoselectivity (Figure 7). The PXRD patterns recorded for the recovered catalyst after the three runs show no signs of framework collapse or decomposition (Figure S8). Moreover, inductively coupled plasma optical emission spectroscopic (ICP-OES) analysis of the reaction filtrate indicates that the amount of Cu leached into the reaction mixture is only 6.0% of the total Cu content in Cu_2I_2 -(BTTP4), which corresponds to 3.879 ppm. To eliminate the possibility that the catalysis might be a result of the leached Cu in the solution, a new batch of starting materials, TsOxy-N₃ (0.25 mmol), PhCCH (0.25 mmol), and (*i*Pr)₂NH (0.25 mmol), was added to the filtrate. After 1 h, a negligible amount of amidine was detected by in situ ¹H NMR spectroscopic monitoring,

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Table 2. Three-component coupling reactions of oxysulfonyl azides, al- kynes, and amines catalyzed by $Cu_{2l_2}(BTTP4)$. ^[a]						
TsO: 1.0 e	xyN ₃ + R───── + quiv. 1.0 equiv.	(<i>i</i> Pr) ₂ NH 1.0 equiv. CH ₃ CN, RT, 30	min R	NTsOxy ↓ N(<i>i</i> Pr)₂		
Entry	Alkyne	Product	Conversion [%]	lsolated yield [%]		
1		NTsOxy N(<i>i</i> Pr) ₂	96	92		
2	Me-	1 Me NTsOxy N(/Pr) ₂	93	74		
3	tBu-√	11 tBu NTsOxy N(iPr) ₂	93	89		
4	F-	12 F NTsOxy N(<i>i</i> Pr) ₂	93 ^[b]	82		
5	Br-	13 Br NTsOxy N(<i>i</i> Pr) ₂	75 ^[c]	66		
6	MeO-	14 MeO NTsOxy N(<i>i</i> Pr) ₂	92	87		
7		15 NTsOxy N(/Pr) ₂	77	66		
8		16 NTsOxy N(<i>i</i> Pr) ₂	58	48		
9	$\rightarrow =$	9 NTsOxy N(<i>i</i> Pr) ₂	44	38		
10		10 NTsOxy N(<i>i</i> Pr) ₂	75	60		
11	\rightarrow =	HO NTsOxy N(<i>i</i> Pr) ₂	81	68		
12	Ph Ph }─ ━ HO	18 Ph NTsOxy HO N(<i>i</i> Pr) ₂	63	53		
13	-jsi-=	$NTsOxy \\ Si \\ N(iPr)_2$	88	64		
14 ^[d]		20 NTsOxy N(Me)Ph 21	63 ^(e)	40		
[a] Reaction conditions: $TsOXy-N_3$ (0.25 mmol), alkyne (0.25 mmol), (<i>iPr</i>) ₂ NH (0.25 mmol), Cu_2l_2 (BTTP4) (0.0125 mmol), CH_3CN (0.5 mL); [b] Conversion in 60 min, and 7% triazole was found; [c] Conversion in 60 min; [d] PhNHMe was used instead of (<i>iPr</i>) ₂ NH, and Et ₃ N (1 equiv.) was added: [e] Conversion in 6 h						



Figure 7. Recycling experiments for Cu₂I₂(BTTP4).

which confirms that heterogeneous $Cu_2l_2(BTTP4)$ was responsible for the catalytic performance.

Conclusions

We have developed a new protocol for the synthesis of N-oxysulfonyl amidines with satisfactory yields from the three-component coupling reactions of oxysulfonyl azides, alkynes, and amines in the presence of the homogeneous Cul or heterogeneous Cu₂I₂(BTTP4) catalysts. As a result of the presence of large, open channels in the Cu₂I₂(BTTP4) framework, the reactants could enter the pores and undergo reactions in the inner cavities, which endowed porous Cu₂I₂(BTTP4) with shape-selective catalytic activity. This hypothesis has been proved directly and indirectly by the substrate adsorption of aromatic alkynes in solution and the observation of N-oxysulfonyl amidine products in the catalyst sample after catalytic reactions. As an efficient heterogeneous catalyst, the porous Cu₂I₂(BTTP4) crystallites could be recycled and used in three runs without significant loss of activity. Further investigations on the catalytic applications of Cu₂I₂(BTTP4) towards more organic reactions are in progress.

Experimental Section

General

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded by using Varian/Mercury-Plus (300 MHz) or Bruker AVANCE III (400 MHz) spectrometers. IR spectra were recorded by using a Nicolet Nexus-670 FTIR spectrometer with KBr pellets in range 4000-400 cm⁻¹. PXRD patterns were recorded by using a Bruker D8 Advance diffractometer at 40 kV and 40 mA with a Cutarget tube and a graphite monochromator. X-ray intensity data were collected by using an Oxford Diffraction Xcalibur Onyx Nova diffractometer using CuK_{$\alpha1$} radiation ($\lambda = 1.54184$). ICP-OES was conducted by using a Spectro Ciros Vision ICP-OES spectrometer equipped with vacuum optics that cover the spectral range from 175–777 nm, plasma power, 1300 W; coolant flow, 15.00 Lmin⁻¹; auxiliary flow, 0.80 Lmin⁻¹; nebulizer 0.70 Lmin⁻¹. ESI-MS was performed by using a AccuTOF CS JMS-T100CS spectrometer. HRMS were recorded by using a MAT95XP instrument by using the EI method or a maxis 4G ESI-Q-TOF instrument by using the ESI method. The sorption isotherms of Cu₂I₂(BTTP4) for CO₂ (195 K) were performed by using a Micromeritics ASAP 2020 instrument.

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Prior to the sorption examination, the samples were prepared under vacuum at 35 °C for 16 h. Thermogravimetric (TG) analyses were performed under an N₂ atmosphere at a heating rate of 10 °C min⁻¹ by using a NETZSCH TG 209 system. XPS spectra were measured by using a Thermo-VG Scientific ESCALAB 250 spectrometer under a pressure of $\approx 2 \times 10^{-9}$ mbar with X-ray monochromatized AlK_{α} radiation (15 kV, 150 W, spot size = 500 mm). SEM images and the elemental distribution of Cu₂l₂(PDIN) and Cu₂l₂(BTTP4) were obtained by using a JSM-6330F field emission scanning electron microscope combined with EDS. Prior to examination, the compounds were coated with a thin layer of Au. The particle sizes were measured by using a MasterSizer 2000 Analyzer.

Synthesis of oxysulfonyl azides

The synthesis of oxysulfonyl azides was achieved by using a similar procedure to that of TsOxy-N₃ as follows: A solution of p-cresol (p- $CH_{3}C_{6}H_{4}OH$; 1.08 g, 10 mmol) and pyridine (0.81 mL, 10 mmol) in dry CH₂Cl₂ (11 mL) was added dropwise to a solution of SO₂Cl₂ (0.89 mL, 11 mmol) in dry CH_2Cl_2 (10 mL) at $-78\,^\circ C$ under $N_2.$ The mixture was allowed to warm to RT and stirred overnight. After the reaction was complete, all of the solvent was removed by rotary evaporation. The residue was dissolved in CH₃CN (10 mL), and the solution was stirred at 0°C for 15-20 min. Sodium azide (0.975 g, 15 mmol) was added to the mixture in six portions, and the reaction mixture was allowed to warm to RT and stirred overnight. After the reaction was complete, the crude product was filtered through Celite and washed with EtOAc (ethyl acetate) until all the product was washed out. The filtrate was collected and concentrated by rotary evaporation. The crude product was dissolved in ether and washed with aqueous NaOH solution (0.1 M) and brine, dried over sodium sulfate, and concentrated by rotary evaporation. The resulting oil was then purified by flash chromatography (silica gel). Yield = 0.92 g, 43 %; R_f = 0.48 (EtOAc/PE = 1/20); ¹H NMR (300 MHz, CDCl₃): $\delta = 7.24$ (d, J = 0.8 Hz, 4 H), 2.40 ppm (s, 3 H); ^{13}C NMR (75 MHz, CDCl₃): $\delta\!=\!147.51,\ 138.26,\ 130.53,\ 121.07,\ 20.93,$ 20.88 ppm; IR (KBr): v = 2923, 2852, 2147, 1501, 1416, 1179, 1142, 1018, 883, 804, 765, 641, 623, 581, 552 cm⁻¹.

Synthesis of Cu₂I₂(PDIN)

A solution of Cul (68.4 mg, 0.36 mmol) in CH₃CN (8 mL) was added dropwise over 15 min to a solution of PDIN (57.6 mg, 0.18 mmol) in CHCl₃ (8 mL).The mixture was stirred for 30 min at RT. The precipitates were collected by filtration through Celite (P4), washed with CHCl₃/CH₃CN (1:1, 2 mL×3), and dried under vacuum. The product was obtained as a yellow precipitate. Yield = 111 mg, 88%; elemental analysis calcd (%) for Cu₂l₂Cl₈H₁₂N₂O₄ (Cu₂l₂(PDIN): C 30.83, H 1.72, N 4.00; found: C 30.60, H 1.88, N 3.90; IR (KBr): $\tilde{\nu}$ = 3084, 3049, 1742, 1503, 1414, 1323, 1272, 1173, 1101, 1093, 1062, 1017, 896, 854, 810, 755, 698, 677, 524 cm⁻¹. Phase purity was verified by powder XRD.

Synthesis of Cu₂I₂(BTTP4)

A solution of Cul (68.4 mg, 0.36 mmol) in CH₃CN (8 mL) was added dropwise over 15 min to a solution of BTTP4 (79.4 mg, 0.18 mmol) in CHCl₃ (8 mL). The mixture was stirred for 30 min at RT. The precipitates were collected by filtration through Celite (P4) and washed by CHCl₃/CH₃CN (1:1, 2 mL×3). The product was obtained as a yellow powder. Yield = 156 mg, 96%; elemental analysis calcd (%) for Cu₂l₂Cl_{1.5}C_{25.1}H_{16.4}N_{3.3}O₆ ([Cu₂l₂(BTTP4)]·0.5 CHCl₃·0.2 CH₃CN): C

33.60, H 1.82, N 5.04, Cu 14.28; found: C 33.73, H 2.20, N 5.15, Cu 14.00 (ICP-OES).

[Cu₂l₂(BTTP4)]·0.5 CHCl₃·0.2 CH₃CN was dried under high vacuum for 16 h at 35 °C to give the solvent-free complex with an empty framework, Cu₂l₂(BTTP4). IR (KBr): $\tilde{\nu}$ = 3040, 2920, 2850, 1750, 1606, 1561, 1455, 1431, 1323, 1252, 1210, 1132, 1080, 1059, 896, 848, 754, 695, 660, 585 cm⁻¹. Phase purity was verified by powder XRD.

Typical procedure for the three-component coupling reactions catalyzed by Cul

Under a N₂ atmosphere, to a mixture of phenylacetylene (27.5 mg, 0.25 mmol, 1 equiv.), TsOxy-N₃ (63.9 mg, 0.3 mmol, 1.2 equiv.), and Cul (4.75 mg, 0.025 mmol, 10 mol%) in CH3CN (0.5 mL) was slowly added diisopropylamine (42 µL, 0.3 mmol, 1.2 equiv.). The whole reaction mixture was allowed to stand at RT for 30 min. The organic solvent was removed by reduced pressure. The remaining solid mixture was treated by adding CH₂Cl₂ (3 mL) and aqueous NH₄Cl solution (2 mL). The two layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 mL×3). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography with an appropriate eluting solvent system. The pure product of N^1 , N^1 -diisopropyl- N^2 -(4-methylbenzeneoxysulfonyl)-2-phenylacetamidine (1) was obtained as an off-white solid. Yield = 84.7 mg, 87%; R_f = 0.45 (EtOAc/hexane, 1:3); m.p.: 96–97°C; ¹H NMR (300 MHz, CDCl₃): δ = 7.33–7.15 (m, 7 H), 7.10 (d, J = 8.3 Hz, 2H), 4.29 (s, 2H), 4.02 (dt, J=13.2, 6.6 Hz, 1H), 3.47 (brs, 1H), 2.32 (s, 3 H), 1.38 (d, J=6.6 Hz, 6 H), 0.89 ppm (d, J=6.6 Hz, 6 H); ¹³C NMR (75 MHz, CDCl₃): δ = 165.58, 148.86, 135.38, 134.39, 129.65, 128.83, 127.83, 126.88, 121.42, 51.19, 48.72, 38.55, 38.48, 20.94, 19.67 ppm; IR (KBr): v = 3085, 3029, 3011, 2982, 2966, 2932, 2872, 1549, 1521, 1502, 1472, 1457, 1438, 1374, 1317, 1271, 1193, 1159, 1132, 1053, 1018, 950, 857, 830, 817, 787, 754, 718, 691, 639, 618, 577, 548, 519, 479, 462 cm⁻¹; HRMS (EI): *m/z*: calcd for C₂₁H₂₈N₂O₃S: 388.1815 [M⁺]; found: 388.1816.

Typical procedure for the three-component coupling reactions catalyzed by Cu₂I₂(BTTP4)

To CH₃CN (0.5 mL) in a vessel was added Cu₂I₂(BTTP4) (10.2 mg, 0.012 mmol, 10 mol% based on Cu), phenylacetylene (27.5 mg, 0.25 mmol, 1 equiv.), and TsOxy-N₃ (53.3 mg, 0.25 mmol, 1 equiv.) under a N₂ atmosphere. Disopropylamine (35 μ L, 0.25 mmol, 1 equiv.) was added slowly to the vessel. The whole reaction mixture was allowed to stand at RT. After the reaction was complete, the supernatant was filtered through a thin pad of Celite (P4) and washed by CH₃CN (0.5 mL×3). The organic solvent was removed under reduced pressure followed by flash chromatography. Pure 1 was obtained as an off-white solid. Yield = 89.3 mg, 92%.

Crystal structure determination

Diffraction data for Cu₂I₂(PDIN), **1**, **9**, and **10** were collected by using an Oxford Gemini S Ultra diffractometer equipped with CuK_α radiation ($\lambda = 1.54178$ Å) at 150 K by using ϕ and ω scans. Structural solution and refinement against F^2 were performed with SHELXL programs.^[55] Anisotropic thermal factors were assigned to all of the non-hydrogen atoms. The positions of the hydrogen atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their respective patent atoms before the final cycle of least-squares refinement.

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CCDC 919898 (Cu₂l₂(PDIN)), CCDC 919890 (1), CCDC 919897 (9), and CCDC 919891 (10) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

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