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Synthesis Cu(I)–CN-based MOF with in-situ generated cyanogroup by cleavage of acetonitrile: Highly efficient for catalytic cyclization of propargylic alcohols with CO₂

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ARTICLE INFO	A B S T R A C T		
Keywords: Metal–organic framework C–C cleavage Carboxylic cyclization Heterogenous catalysis	Developing a highly effective process for synthesis a cyano-bridged compound to avoid toxic organic or inorganic cyanides is very significant method for alleviating cyanides pollution. Here, a CN-based MOF catalyst (Cu(I)–CN–BPY) was synthesized by using copper ions coupled with Na ₄ $W_{10}O_{32}$ in CH ₃ CN under solvothermal conditions. The cyano-groups are generated in situ from the cleavage of C(sp ³)–C(sp) in CH ₃ CN. Because Cu(I) sites have ability to activate π -activate internal alkynes of carbon–carbon triple bonds for carboxylic cyclization reactions, which was applied in the cyclization of propargylic alcohols with CO ₂ and exhibited high efficiency with >95 % yields. For seeking out the active sites of MOF structure in carboxylic cyclization, we also synthesized two		

MOFs of Cu(I)-Cl-BPY and Cu(I)-I-BPY, and investigated for this reaction.

1. Introduction

Cyanides are widely applied in common life such as metal cleaning, electroplating, precious metal extraction, biological probes and pharmaceuticals synthesis [1]. Among all kinds of cyanides, the cyano-bridged coordination polymers have attracted great interest from chemists and governments due to their potential properties in molecule magnetism, luminescence, heterogeneous catalysis and so on [2-4]. In the conventional approaches for preparation cyano-bridged coordination polymers, inorganic cyanides and HCN have generally been used as the nitrile sources, however, which are high toxicity and threatens humans and the environment [5-14]. Compared with HCN and metal cyanides, it would be a safer, greener and more economical strategy by direct utilizing acetonitrile as a cyanogroup source through in situ formed cyano-bridged bonds to generate cyano-based metal-organic frameworks (MOFs) [15–18]. However, acetonitrile serving as a cyanide source is quite a challenge. Thermodynamically, the C-CN bond cleavage of acetonitrile needs a strong bond dissociation energy of 133 kcal mol^{-1} [19]. Generally, a number of metals have been mediated for splitting the C–CN bond of acetonitrile, occur with the assist of d¹⁰ metal complexes with a Pt, Zn or Ag centrals [20-22]. In spite of such difficulties, copper as one of the most inexpensive metals comparing above metals, the exploration of copper promoted C-CN cleavage was never stopped and many reports confirmed that copper ions can be applied to cleave C–CN bonds under hydrothermal reactions [23–27].

For minimizing the emissions of carbon dioxide as a renewable C1 resource, considerable approaches have been proposed to transform it to value chemicals [28-31[32]]. Among these strategies to fix and catalysis for CO₂, the cycloaddition with CO₂ into cyclic carbonates demonstrates the advantages of high selectivity and low cost and has been widely applied [33-36]. Recently, reports have shown that transition metal-based or ionic liquids (ILs) systems, such as some Ag@ILs or Cu@ILs have high activity for promoting the resultant α-alkylidene cyclic carbonates in carboxylic cyclization reaction [37-39]. In particular, Cu(I) sites have ability to activate π -activate internal alkynes of carbon-carbon triple bonds for carboxylic cyclization reactions [40,41]. Most of the catalysts containment copper ions are homogeneous catalysts that are tough to recycle, the like copper salts or complexes catalyst systems. However, the leaching of active species in heterogeneous catalysis may be reduced catalytic efficiency with copper complexes. Therefore, to improve catalytic activity and reduce the cost, the explorations on efficient catalysts of heterogeneous catalysis without noble metals for this conversion are necessary and still quite a challenge. Among various heterogeneous porous materials, MOFs are appealing catalysts for heterogeneous catalysis because of their distinctive specialty with periodic, open structures and controllable pores, modifiable

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Fig. 1. (a) The coordination environment of Cu(I)–CN–BPY. (A: 1-x, 1-y, 2-z; Color code: Cu1, teal spheres; Cu2, sky blue spheres; C, gray spheres; N, blue spheres; all hydrogen atoms are omitted for clarity). (b) The 1D chain-like of Cu(I)–CN–BPY. (c) The connection scheme of two kinds of Cu(I) with –CN bonds in the 2D layers of frame. (d) The 3D network frame of Cu(I)–CN–BPY. (For interpretation of the references to colour in the figure legend, the reader is referred to the web version of this article.)

catalytic sites [42–48]. Cu(I)-based MOFs have efficient ability to catalyze cycloaddition of CO₂ with terminal alkynes to produce α -alkylidene cyclic carbonates under mild conditions, for example, Zhao's group reported an effective MOF catalyst with [Cu₄I₄] clusters to catalyze the cyclization of propargylic alcohols with CO₂ under mild conditions, and the turnover number (TON) could reach up to 14400 [49].

Inspired by the excellent work, we optimized the synthesis of a Cu (I)–CN-based MOF, [Cu₂(CN)₂(BPY)] (Cu(I)–CN–BPY, compound 1), by incorporating simple CuCl₂, 4,4'-bipyridine (BPY) organic bridged ligand and Na₄W₁₀O₃₂ in mixable solvent of H₂O and CH₃CN under a solvothermal reaction. In the process, CN⁻ was in situ obtained from the cleavage of the C–CN bond of acetonitrile by the synergistic effect Cu²⁺ ions and W₁₀O⁴/₃₂ under hydrothermal reaction. Despite the structure of Cu(I)–CN–BPY has been synthesised by Zhou and co-workers in 2011, we improved the synthesis process of green cyanide source by replacement K₄Fe(CN)₆·3H₂O with acetonitrile [50].

For seeking out the active sites of MOF structure in carboxylic cyclization of propargylic alcohols, we also constructed two MOFs with Cu-X (X = Cl, I) cluster, $[Cu_2Cl_2(BPY)_2]$ (Cu(I)–Cl–BPY, compound **2**) and $[Cu_2I_2(BPY)_2]$ (Cu(I)–I–BPY, compound **3**), both of them have high density of Cu(I) cores in their structure for this reaction and easily synthesized by simple methods with low-cost materials [51]. Besides, above three unique three-dimensional frameworks were synthesized by 4, 4'-bipyridine as the linker, thus all MOFs cound catalyze cyclization of propargylic alcohols in heterogeneous manner. For convenience, we called collectively of above three MOFs as Cu(I)–BPYs.

2. Experimental

2.1. Synthesis of Cu(I)-CN-BPY

Cu(NO₃)₂·3H₂O (60 mg, 0.25 mmol), [(n-C₄H₉)₄N] [W₁₀O₃₂] (50 mg, 0.019 mmol) and 4, 4'-bipyridine (24 mg, 0.15 mmol) were added in a 100 mL beaker and dissolved by 6.0 mL mixed solution (distilled water: acetonitrile = 2: 1). The resulting was stirred over 10 h. Then adjusted the above turbid solution to pH = 2.3 by the solution of 1 mol·L⁻¹ dilute HCl. Then the mixture was moved into a 25 mL Teflon-lined autoclave, and heated at 130 °C. After the three days, yellow rhombic single crystals were obtained with a yield of 52.49 %, based Cu element. Elemental analyses (EA) and ICP calcd (%) For Cu₂C₁₂H₈N₄: C, 42.95; H,

2.39; N, 16.73; Cu, 37.93; Found: C, 42.98; H, 2.41; N, 16.71; Cu, 37.90.

2.2. Catalysis

Carboxylic cyclization of propargylic alcohols: before the catalysis experiments, compound 1, 2 and 3 as catalysts were solvent exchanged by CH₃CN for three days, and dried in a vacuum at 100 °C to remove the solvent molecules. The typical experiments were studied heterogeneously with 20 μ L TEA, 84 mg (1 mmol, about 100 μ L) 2-methyl-3butyn-2-ol in 1 mL CH₃CN as solvent, 0.05 mmol of Cu(1)–BPYs (about 15, 25 and 35 mg for Cu(1)–CN–BPY, Cu(1)–Cl–BPY and Cu(1)–I–BPY) in autoclave with 0.5 MPa CO₂ at appropriate temperatures and predetermined time. The pressure of CO₂ was staid stable throughout reaction. After the reaction, remains were purified by column chromatography, and then performed by ¹H NMR analysis for yield.

3. Results and discussion

3.1. Structural description

Solvothermal reaction of Cu(NO₃)₂·3H₂O, $[(n-C_4H_9)N]_4[W_{10}O_{32}]$ and 4, 4'-bipyridine gave compound 1 in a yield of 52.5 %. As we known, polyoxometalates (POMs) are class of discrete anionic metal oxide clusters, which commonly used as oxidation catalysts and photocatalysts [52–54]. Especially, decatungstate anion $W_{10}O_{32}^{4-}$ has been especially considered for its very important photocatalytic properties [55,56]. In this synthesis process of synthesizing the Cu(I)–CN–BPY, we found the $W_{10}O_{32}^{4-}$ has an assistant function in prompting the cleavage of C–C bonds of acetonitrile in the process. When in absence of $W_{10}O_{32}^{4-}$, Cu (I)–CN–BPY cannot be obtained.

Cu(I)–CN–BPY crystallizes in the monoclinic system with P2(1)/n space group. The asymmetric Cu(I)–CN–BPY unit consists of two crystallographically distinct copper ions, one BPY ligand and two –CN bonds. The crystallographic data structure refinement for compounds 1, 2 and 3 are listed in Table S1. The relevant bond lengths and bond angles are listed in Tables S2, S3 and S4. As shown in Fig. 1a, Cu1 ion is three-coordinated in a slightly plane triangle environment, and the Cu1 center is coordinated by one N(2) atom from the benzene ring of the BPY ligand, two nitrogen atoms, N(3) and N(4), from the –CN bonds. Cu(2) ion adopts tetrahedral coordination geometry with four nitrogen atoms, one of the N(3) atoms from –CN bond is bound to the other Cu(1) center,



Fig. 2. (a) The 2D sheet of Cu(I)–CN–BPY. (b) The 3D network frame of Cu(I)–CN–BPY showed two kinds of pores. (c) Two kinds of channels interspersed by cylindrical rods simulation in the 3D frame of Cu(I)–CN–BPY.



Fig. 3. (a) The coordination environment of Cu(I)–Cl–BPY. (A: 1-x, 0.5-y, z; Color code: Cu, sky blue spheres; C, gray spheres; N, blue spheres; all hydrogen atoms are omitted for clarity). (b) The 2D sheet of Cu(I)–Cl–BPY. (c) The interpenetrated simulation of two 2D layers of frame. (d) The 3D network frame of Cu(I)–Cl–BPY. (For interpretation of the references to colour in the figure legend, the reader is referred to the web version of this article.)

two of the N(4) atoms as nodes connect with Cu(2) ions and form rhombus-like plane of a dimeric $[Cu_2(CN)_2]$ secondary building unit with the approximate cross sectional area of 2.49 \times 3.66 Å, the remaining one N(1) atom from the benzene ring of the BPY ligand. Each $[Cu_2(CN)_2]$ is connected by two Cu1 cations and two linear –CN bonds, generating a 2D layer (Fig. 1c). Meanwhile, BPY ligands linked by copper ions arranged alternately on the Cu–CN chain and like bridges connect with $[Cu_2(CN)_2]$ and Cu–CN chains forming a long channel, which spiraled up and looks like a string of similar parallelogram shape (Fig. 1b). The channels are then linked by N atoms to form a 3D network frame, between the two benzene rings of BPY ligands with a considerable distance of 11.67 Å, which provided enough space for next catalysis (Fig. 1d).

Cu(I)–CN–BPY has two types of pores which arranged on the cross sections of dumbbell-shaped, the approximate size is 4.84×11.67 Å for pore A and 3.55×15.45 for B (Fig. 2b, c). Both pores are architectures of amphoteric channels, hydrophobic organic BPY ligands and –CN bonds with alkaline sites could facilitate the capture of CO₂. And the hydrophilous copper ions can activate carbon–carbon triple bonds of

propargylic alcohols species, which making the cyclization reaction more smoothly.

Solvothermal reaction of CuX (X = Cl, I) and 4, 4'-bipyridine gave Cu (I)-Cl-BPY and Cu(I)-I-BPY in a yield of 81.42 % and 57.70 %, respectively. Cu(I)-Cl-BPY crystallizes in the tetragonal system with I4 (1)/acd space group crystallize, and Cu(I)-I-BPY crystallizes in the Orthorhombic system with *Fddds*pace group crystallize. Compound 2 and 3 are isostructural, therefore, Cu(I)-Cl-BPY is described as an example below. An asymmetric unit of 2 consists of two crystallographically uniform copper atoms, two chlorine atoms, and four BPY ligands. Copper atoms are connected to each other forming a copper bridge bond, the Cu1 and Cu1A atoms are linked by a pair of chlorine atoms form a dimeric [Cu2Cl2] SBU (Fig. 3a). Each [Cu2Cl2] SBU is connected by four linear BPY groups, generating a 2D layer (Fig. 3b). Compound 2 has two kinds of one-dimensional open channels with approximate dimensions of 2.75×10.98 Å of A and 17.32×26.48 Å of B. A high density of [Cu₂Cl₂] clusters are dispersed along the channels, the specific structure of $\mathbf{2}$ improved capacity of absorbing CO₂, which vastly improve the selectivity in cyclization catalysis. All 2D sheets are



Fig. 4. SEM images of compounds 1, 2 and 3 display the morphology of Cu(I)-CN-BPY (a, b), Cu(I)-Cl-BPY (c, d) and Cu(I)-I-BPY (e, f).

vertical interpenetrated with each other and form to a 3D braided structure could significantly enhance the stability of framework (Fig. 3c, d). All the copper ions in compound **1**, **2** and **3** are +1, calculated by the BVS (bond valence sum) and consistent with results the X-ray structure determination. TGA revealed all catalysts have high thermal stability (Fig. S1).

3.2. Characterizations of catalysts

3.2.1. Morphology characterization

Fig. 4 shows the morphology of the compounds 1, 2 and 3. It can be seen that the samples of Cu(I)–CN–BPY are the prism-like solid blocks with well-defined diamond shapes with smooth surfaces (Fig. 4a, b). Compared to compound 1, the Cu(I)–Cl–BPY has a cube-like morphology, and almost ten times volume of compound 1 (Fig. 4c), but some of samples were weathered with uneven surfaces (Fig. 4d). The samples of Cu(I)–Cl–BPY are regularly hexagonal prisms shaped blocks, but these samples were more weathered than compound 2.

3.2.2. IR spectra and PXRD pattern

The IR spectra of compounds 1, 2 and 3 are collected and shown in Fig. 5a. Three compounds have similar characteristic bands at 1600 and 1411 cm⁻¹, which assigned to the C–N and C–H bonds stretching vibrations of BPY groups, respectively. In addition, differing from compounds 2 and 3, Cu(I)–CN–BPY has characteristic resonances of –CN bond in the ranges of 2123 and 2097 cm⁻¹. These characteristic vibration resonances confirm the existence of –CN bond, which forming in situ at the solution of acetonitrile. The PXRD patterns of compounds 1, 2 and 3 are measured to verify purity of synthesized catalysts, shown in Fig. 5(b–d). The bottom lines represent simulated pattern, which calculated pattern based on the single-crystals prepared for catalysis. The top lines represent experimental pattern, which collected after synthesized catalysts. Its showing that almost strong peaks were well matched between the simulated and experimental.

3.2.3. BET and CO₂-adsorption analysis

The N₂ adsorption-desorption isotherms (Fig. 6a) of Cu(I)-I-BPY



Fig. 5. (a) The IR spectra of compounds 1, 2 and 3; correspond the black line to Cu(I)–CN–BPY, blue line to Cu(I)–Cl–BPY and red line to Cu(I)–I–BPY, respectively. (b) The PXRD patterns of Cu(I)–CN–BPY. (c) PXRD patterns of Cu(I)–Cl–BPY. (d) PXRD patterns of Cu(I)–I–BPY. (For interpretation of the references to colour in the figure legend, the reader is referred to the web version of this article.)



Fig. 6. (a) N_2 adsorption-desorption isotherms and BJH pore distribution of Cu(I)–I–BPY. (b) CO_2 adsorption isotherms of Cu(I)–BPYs at 273 K, the black line to Cu(I)–CN–BPY, blue line to Cu(I)–I–BPY and red line to Cu(I)–CN–BPY, respectively. (For interpretation of the references to colour in the figure legend, the reader is referred to the web version of this article.)

displayed that the BET surface area was determined to be 18.93 m² g⁻¹ and BJH pore distribution determined the average pore diameter of Cu (I)–I–BPY was 4.87 nm. The above results revealed that Cu(I)–I–BPY was mesoporous structure with the BJH pore volume of 0.023 cm³ g⁻¹. To demonstrate the potential of three catalysts in CO₂ gas absorption, we measured the adsorption isotherm of CO₂ at 278 K with a de-solvated samples of Cu(I)–BPYs (Fig. 6b). The uptake value of CO₂ was 7.3478 m² g⁻¹ for Cu(I)–CN–BPY, 1.2404 m² g⁻¹ and 1.1827 m²/g for Cu(I)–I–BPY and Cu(I)–Cl–BPY, respectively. Cu(I)–I–BPY and Cu(I)–Cl–BPY have similar and lower uptake values of CO₂, compared with them, the CO₂ adsorption capacity of Cu(I)–CN–BPY is about 6 times higher. The main reason for the higher gas uptake is presumably the presence of –CN bonds in channels of Cu(I)–CN–BPY, which increased the containing of nitrogen-atoms in framework and thus enhanced CO₂ adsorption

Table 1

Cyclization of propargylic alcohols in Cu	1(I)–BPYs/TEA/CO ₂ system. ^a
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Entry	Substrate	Product	Yield (%) ^b	TON ^c	TOF/ h ^{-1d}
1	/	ц [°]	1a, 96 1b, 95	19.2 19.0	0.80 0.79
1	≡		1c, 94	18.8	0.78
		~ F	2a, 94	18.8	0.78
2	=	⁰	2b, 93	18.6	0.77
		j c	2c, 96	19.2	0.80
	/	<i>۳</i> ٦	3a, 59	11.8	0.49
3	————————————————————————————————————	⁰	3b, 56	11.2	0.47
			3c, 53	10.6	0.44
			4a, <1	<0.2	< 0.01
4			4b, <1	<0.2	< 0.01
		L'	4c, <1	< 0.2	< 0.01

^a Reaction conditions: 0.05 mmol catalysts, Cu(I)–CN–BPY(a), Cu(I)–Cl–BPY (b), Cu(I)–I–BPY(c); 1 mmol substrates of propargylic alcohols, 1 mL CH₃CN, 0.5 MPa CO₂, 50 °C, 24 h.

^b The yields were determined by ¹H NMR.

^c Turnover number was calculated by the ratio of moles of product/mol of catalyst.

 $^{\rm d}$ Turnover frequency was calculated by the ratio of TON/hour of catalytic time.

capacity.

3.3. Carboxylic cyclization of propargylic alcohols in Cu(1)–BPYs/TEA/ CO₂ system

For the carboxylic cyclization of 2-methyl-3-butyn-2-ol as a model to optimize reaction system under various reaction conditions are presented in Fig. S2. Initially, the influence of temperature carboxylic cyclization of 2-methyl-3-butyn-2-ol was examined; reaction conditions: triethylamine (TEA, 20 μ L), Cu(I)–CN–BPY (0.05 mmol, 15 mg); 2-methyl-3-butyn-2-ol (1 mmol, 84 mg), 24 h, 0.5 MPa CO₂, and CH₃CN (1 mL). We found that the yield was increased with temperature in the low temperature range of 30 °C to 50 °C, but it had a decrease with further elevated the temperature to 60 °C, which possibly due to a slight azeotrope of TEA and CH₃CN during the temperature rise and partial TEA overflow from solution. Therefore, the suitable reaction temperature, when the CO₂ pressure was lifted from atmospheric pressure to 0.5 MPa,

reaching to highest yield.

The effect of various amounts of catalyst was also explored. After adding 0.05 mmol of catalyst, the substrate was obviously activated and the yield rose to 96 %. However, the increased reaction rate was gradually turned slow with the amount of catalyst increasing. With time increasing, the reaction yield reached to ~96 % at 24 h and declined gradually despite of continued extension of reaction time. Hence, the optimized reaction conditions of the carboxylic cyclization was found that this reaction was carried out in an autoclave reactor with 2-methyl-3-butyn-2-ol (0.5 mmol, 84 mg), 0.5 MPa CO2 in 1 mL of CH3CN and stirring about 24 h at 50 °C. Control experiments indicated that the individual catalysts and raw materials of MOFs were hardly catalyze this reaction under the same condition, which proved that assembly of the metal centers with organic ligands into one framework and combining with TEA can greatly improve catalytic efficiency (Table S5). The existing TEA provided a yield of 33%, which proved TEA and catalysts are also indispensable for the reaction. Finally, several typical propargylic alcohols were further examined under identical reaction conditions, and the yields of the target products are summarized in Table 1. According to the model experiment, reactions were proceed with various propargylic alcohols (1 mmol), catalyzed by pure crystals of Cu (I)-BPYs (0.05 mmol), where a, b, and c represented by Cu(I)-CN-BPY, Cu(I)-Cl-BPY, Cu(I)-I-BPY, respectively, and 0.5 MPa CO2 in 1 mL of CH₃CN at 50 °C. Notably, Cu(I)-BPYs showed the excellent catalytic activity substrates of substituted R1 groups, providing a high yield from 93% to 96% of corresponding cyclic carbonates after 24 h reaction (Entries 1, 2).

However, comparing to 2-methyl-3-butyn-2-ol, when increasing the bulk of substituted R2 groups to phenyl propargylic alcohols caused the yield decrease about 40 % (Entry 3). This result indicated that substrates with benzene groups can not be adsorbed into the channels of Cu(I)–BPYs, in turn, it suggested that substrates with smaller size were enter into the pores of catalysts during the catalytic processes. In addition, only trace of products (<1 %) were detected, when employed the secondary propargylic alcohols with benzene groups (Entry 4). From another perspective, observe individual entries carefully, although changed the substituent R_1 , R_2 in the skeleton of propargylic alcohols, the catalytic properties of the three kinds of catalysts are almost identical. All three catalysts have the common characteristic of high density of Cu(I) sties fasten on channels, thus, the catalytic activity in carboxylic cyclization of propargylic alcohols should be ascribed to Cu(I) sties.

As expected, the all above results revealed that three kinds of catalysts all have effective heterogeneous catalysis for the cyclization with propargylic alcohols of substituted R1 groups without benzene groups in the presence of TEA and afforded nearly complete conversion with a



Fig. 7. (a) Recyclability tests of compounds 1, 2 and 3; correspond the blue bar to Cu(I)–CN–BPY, orange bar to Cu(I)–Cl–BPY and yellow bar to Cu(I)–I–BPY, respectively. (b) The PXRD patterns of Cu(I)–CN–BPY after recycled three times. (For interpretation of the references to colour in the figure legend, the reader is referred to the web version of this article.)



Scheme 1. Possible mechanism of carboxylic cyclization the catalytic process.

highest yield up to 96 % within 24 h. Tertiary propargylic alcohols with a phenyl group at the acetylenic terminus have lower reactivity, but it suggests that carboxylic cyclization indeed occurred in the channels of the MOFs, not on the external surface. It is noticeable, however, that this reaction did not proceed when using secondary terminal propargylic alcohol as substrate.

3.4. Heterogeneity and recyclability of Cu(I)-BPYs catalysts

To examine heterogeneity of the typical carboxylic cyclization system with Cu(I)-CN-BPY catalyst in model catalysis system, after reacting 12 h, the catalyst was removed from carboxylic cyclization system. Then the remaining mixture was keep reacting for another 12 h. Finally, it is proved that the conversion has hardly no addition after removing catalysts. The recyclability of catalyst was performed with the model catalysis and expressed that Cu(I)-CN-BPY can be reused at least three times. Although a little of catalyst was inevitably lost, the yields of cyclic carbonates had almost no influence when added reaction cycles (Fig. 7a), the loss of small amounts of the catalyst is unavoidable. ICP analysis of the filtrate after reaction revealed that almost negligible detection of metal ions at the end of reaction. The patterns of Cu(I)-BPYs after three reaction cycles showed in Fig. 7b and Fig. S3. The PXRD patterns of the initial and recovered of catalysts were good similar, which indicated that Cu(I)-BPYs were keeping the original structure after several times of reaction. These results above suggested that all three catalysts have high stability and capacity to heterogeneous catalysis process.

3.5. Mechanism of the carboxylic cyclization of propargylic alcohols process

Based on the above results and literature reports, Cu(I)–Cl–BPY is described as an example, a possible catalytic mechanism is proposed (Scheme 1). Initially, Cu(I) sites of $[Cu_2Cl_2]$ clusters can activate the hydroxy of propargylic alcohols to form the intermediate state (A) with TEA. Subsequently, after synergistically activated by Cu(I) sites and TEA, the activated oxygen atom in hydroxyl group of propargylic

alcohols is more favorable to the electrophilic attack of the C atom in CO_2 , at the same time, terminal alkyne was activated by Cu(I) sites and forming the Cu(I)...C=C bonds, then the propargylic carbonate intermediate (**B**) was resulted. Finally, the oxygen atom attacks the carbon atom of terminal alkyne which has been activated by Cu(I) sites, and the intramolecular ring was closed with the C–O bond formation and generated propargylic carbonate intermediate (**C**). Simultaneously, carboxylic cyclization products are obtained process of protodemetallation and the regeneration of catalyst [39].

4. Conclusion

We presented a green process to synthesize cyano-bridged MOF by cleavage of the C–C bond of acetonitrile using transition metal ions coupled with decatungstate anion $W_{10}O_{32}^{4-}$ under hydrothermal reaction. Cu(I)–CN–BPY was investigated as catalyst for carboxylic cyclization reactions with CO₂. For seeking out the active sites of MOF structure in carboxylic cyclization of propargylic alcohols, we also synthesized two MOFs with Cu-X (X = Cl, I) cluster, $[Cu_2Cl_2(BPY)_2]$ and $[Cu_2I_2(BPY)_2]$, and investigated for this reaction. Cu-nodes in three MOFs serve as efficient active catalytic centers for cyclization of various tertiary propargylic alcohols with CO₂ under mild conditions, and the highest yield reached to 96 %. Three MOFs all exhibit significant stability and proved as excellent heterogeneous catalysts. Together with the conventional approaches for preparation cyano-bridged coordination polymers, this approach may lead to the generation of MOFs containing cyano-bridged ligands by using less toxic acetonitrile solvent.

CRediT author statement

Zhuolin Shi: Synthesis, Methodology, Software, Investigation, Writing - Original Draft. Jiachen Jiao: Experiments on CV and Electrochemical Impedance Spectroscopy, Formal Analysis. Qiuxia Han: Resources, Writing - Review & Editing, Supervision, Data Curation. Yang Xiao: Catalytic Experiments and Results Analysis. Laikuang Huang: Experiments on IR and PXRD. Mingxue Li: Review & Editing.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.111190.

References

- S.H. Zou, R.H. Li, K. Hisayoshi, J.J. Liu, J. Fan, Photo-assisted cyanation of transition metal nitrates coupled with room temperature C–C bond cleavage of acetonitrile, Chem. Commun. 49 (2013) 1906–1908, https://doi.org/10.1039/ C2CC37277K.
- [2] J. Yang, Y.F. Deng, X.Y. Zhang, X.Y. Chang, Z.P. Zheng, Y.Z. Zhang, An azidocyanide mixed-bridged [Fe₄Ni₄] single-molecule magnet, Inorg. Chem. 58 (2019) 7127–7130, https://doi.org/10.1021/acs.inorgchem.8b03559.
- [3] H.Y. Kuo, T.S. Lee, A.T. Chu, S.E. Tignor, G.D. Scholes, A.B. Bocarsly, A cyanidebridged di-manganese carbonyl complex that photochemically reduces CO₂ to CO, Dalton Trans. 48 (2019) 1226, https://doi.org/10.1039/C8DT03358G.
- [4] P. Ghosh, M. Quiroz, R. Pulukkody, N. Bhuvanesha, M.Y. Darensbourg, Bridging cyanides from cyanoiron metalloligands to redox-active dinitrosyl iron units, Dalton Trans. 47 (2018) 11812, https://doi.org/10.1039/C8DT01761A.
- [5] Y.Y. Wu, Y.F. Zhao, R.P. Li, B. Yu, Y. Chen, X.W. Liu, C. Wu, X.Y. Luo, Z. Liu, Tetrabutylphosphonium-based ionic liquid catalyzed CO₂ transformation at ambient conditions: a case of synthesis of α -alkylidene cyclic carbonates, ACS Catal. 7 (2017) 6251–6255, https://doi.org/10.1021/acscatal.7b01422.
- [6] Q. Zhang, M.H. Chen, L.J. Zhong, Q. Ye, S.S. Jiang, Z.J. Huang, Highly effective removal of metal cyanide complexes and recovery of palladium using quaternaryammonium-functionalized MOFs, Molecules 23 (2018) 2086, https://doi.org/ 10.3390/molecules23082086.
- [7] Z. Zhou, C. He, L. Yang, Y.F. Wang, T. Liu, C.Y. Duan, Alkyne activation by a porous silver coordination polymer for heterogeneous catalysis of carbon dioxide cycloaddition, ACS Catal. 7 (2017) 2248–2256, https://doi.org/10.1021/ acscatal.6b03404.
- [8] Z.W. Hou, Z.Y. Mao, Y.Y. Melcamu, X. Lu, H.C. Xu, Electrochemical synthesis of imidazo-fused N-heteroaromatic compounds through a C@N bond-forming radical cascade, Angew. Chem. Int. Ed. 57 (2018) 1–6, https://doi.org/10.1002/ anie.201712460.
- [9] L.O. Yang, X.D. Tang, H.T. He, C.R. Qi, W.F. Xiong, Y.W. Ren, H.F. Jiang, Copperpromoted coupling of carbon dioxide and propargylic alcohols: expansion of substrate scope and trapping of vinyl copper intermediate, Adv. Synth. Catal. 357 (2015) 2556–2565, https://doi.org/10.1002/adsc.201500088.
- [10] Q.W. Song, W.Q. Chen, R. Ma, A. Yu, Q.Y. Li, Y. Chang, L.N. He, Bifunctional silver (I) complex-catalyzed CO₂ conversion at ambient conditions: synthesis of α-methylene cyclic carbonates and derivatives, ChemSusChem 8 (2015) 821–827, https://doi.org/10.1002/cssc.201402921.
- [11] Y. Yuan, Y. Xie, C. Zeng, D.D. Song, S. Chaemchuen, C. Chen, F. Verpoort, A recyclable AgI/OAc⁻ catalytic system for the efficient synthesis of α-alkylidene cyclic carbonates: carbon dioxide conversion at atmospheric pressure, Green Chem. 19 (2017) 2936–2940, https://doi.org/10.1039/C7GC00276A.
- [12] Y. Hu, J.L. Song, C. Xie, H.R. Wu, T. Jiang, G.Y. Yang, B.X. Han, Transformation of CO_2 into α -alkylidene cyclic carbonates at room temperature cocatalyzed by CuI and ionic liquid with biomass-derived levulinate anion, ACS Sustain. Chem. Eng. 7 (2019) 5614–5619, https://doi.org/10.1021/acssuschemeng.8b05851.
- [13] B. Grignard, C. Ngassamtounzoua, S. Gennen, B. Gilbert, R. Méreau, C. Jerome, T. Tassaing, C. Detrembleur, Boosting the catalytic performance of organic salts for the fast and selective synthesis of α-alkylidene cyclic carbonates from carbon dioxide and propargylic alcohols, ChemCatChem 10 (2018) 2584–2592, https:// doi.org/10.1002/cctc.201800063.
- [14] J. Liu, H.X. Zheng, C.Z. Yao, B.F. Sun, Y.B. Kang, Pharmaceutical-oriented selective synthesis of mononitriles and dinitriles directly from methyl(hetero)arenes: access to chiral nitriles and citalopram, J. Am. Chem. Soc. 138 (2016) 3294–3297, https://doi.org/10.1021/jacs.6b00180.
- [15] L.L. Li, L.L. Liu, Z.G. Ren, H.X. Li, Y. Zhang, J.P. Lang, Solvothermal assembly of a mixed-valence Cu (I,II) cyanide coordination polymer [Cu(II)Cu(I)₂(μ-Br)₂(μ-CN)₂(bdmpp)]_n by C-C bond cleavage of acetonitrile, CrystEngComm 11 (2009) 2751–2756, https://doi.org/10.1039/B903972D.
- [16] K.S. Kisel, A.S. Melnikov, E.V. Grachova, A.J. Karttunen, A.D. Carbo, K. Yu, Monakhov, V.G. Semenov, S.P. Tunik, I.O. Koshevoy, Supramolecular construction

of cyanide-bridged ReI diimine multichromophores, Inorg. Chem. 58 (2019) 1988–2000, https://doi.org/10.1021/acs.inorgchem.8b02974.

- [17] Y. Yamada, K. Oyama, R. Gates, S. Fukuzumi, High catalytic activity of heteropolynuclear cyanide complexes containing cobalt and platinum ions: visiblelight driven water oxidation, Angew. Chem. Int. Ed. 54 (2015) 5613–5617, https:// doi.org/10.1002/anie.201501116.
- [18] Y. Gao, R. Broersen, W. Hageman, N. Yan, M.C.M. Hazeleger, G. Rothenberg, S. Tanase, High proton conductivity in cyanide-bridged metal-organic frameworks: understanding the role of water, J. Mater. Chem. A 3 (2015) 22347, https://doi. org/10.1039/C5TA05280G.
- [19] L. Li, C. Hai, W.X. Li, Z.X. Liu, A fivefold interpenetrating dmd Topological copper (I) cyanide complex formed by C–C bond cleavage of acetonitrile, Eur. J. Inorg. Chem. 5 (2015) 859–863, https://doi.org/10.1002/ejic.201403037.
- [20] L. Munjanja, C.T. Lopez, W.W. Brennessel, W.D. Jones, C–CN bond cleavage using palladium supported by a Dippe ligand, Organometallics 35 (2016) 2010–2013, https://doi.org/10.1021/acs.organomet.6b00304.
- [21] Li-Rong Guo, Song-Song Bao, Yi-Zhi Li, Li-Min Zheng, Ag(I)-mediated formation of pyrophosphonate coupled with C-C bond cleavage of acetonitrile, Chem. Commun. 20 (2009) 2893–2895, https://doi.org/10.1039/B902162K.
- [22] K. Zhou, C. Qin, X.L. Wang, L.K. Yan, K.Z. Shaoa, Z.M. Su, Ag(i)-mediated formation of a 2D cyano-bridged multinuclear silver(i) alkynyl network coupled with the C-C bond cleavage of acetonitrile, CrystEngComm 16 (2014), 10376, https://doi.org/10.1039/C4CE01707B.
- [23] D.S. Marlin, M.M. Olmstead, P.K. Mascharak, Heterolytic cleavage of the C-C bond of acetonitrile with simple monomeric Cu^{II} complexes: melding old copper chemistry with new reactivity, Angew. Chem. 113 (2001) 4888–4890, https://doi. org/10.1002/1521-3757(20011217)113:24<4888::AID-ANGE4888>3.0.CO;2-M.
- [24] T.B. Lu, X.M. Zhuang, Y.W. Li, S. Chen, C-C bond cleavage of acetonitrile by a dinuclear copper(II) cryptate, J. Am. Chem. Soc. 126 (2004) 4760–4761, https:// doi.org/10.1021/ja031874z.
- [25] X.Z. Kou, M.D. Zhao, X.X. Qiao, Y.M. Zhu, X.F. Tong, Z.M. Shen, Copper-catalyzed aromatic C-H bond cyanation by C–CN Bond cleavage of inert acetonitrile, Chem. Eur. J. 19 (2013) 16880–16886, https://doi.org/10.1002/chem.201303637.
- [26] F. Xu, W. Huang, X.Z. You, Novel cyano-bridged mixed-valent copper complexes formed by completely in situ synthetic method via the cleavage of C–C bond in acetonitrile, Dalton Trans. 39 (2010) 10652–10658, https://doi.org/10.1039/ C0DT00345J.
- [27] F. Xu, T. Tao, K. Zhang, X.X. Wang, W. Huang, X.Z. You, C-C bond cleavage in acetonitrile by copper(ii)-bipyridine complexes and in situ formation of cyanobridged mixed-valent copper complexes, Dalton Trans. 42 (2013) 3631–3645, https://doi.org/10.1039/C2DT32281A.
- [28] M.S. Maru, S. Ram, R.S. Shukla, N.H. Khan, Ruthenium-hydrotalcite (Ru-HT) as an effective heterogeneous catalyst for the selective hydrogenation of CO₂ to formic acid, Mol. Catal. 446 (2018) 23–30, https://doi.org/10.1016/j.mcat.2017.12.005.
- [29] K. Feng, S. Wang, D. Zhang, L. Wang, Y. Yu, K. Feng, Z. Li, Z. Zhu, C. Li, M. Cai, Z. Wu, N. Kong, B. Yan, J. Zhong, X. Zhang, G.A. Ozin, L. He, Cobalt plasmonic superstructures enable almost 100% broadband photon efficient CO₂ photocatalysis, Adv. Mater. (2020), https://doi.org/10.1002/adma.202000014, 2000014.
- [30] N.W.J. Ang, J.C.A. Oliveira, L. Ackermann, Electroreductive cobalt-catalyzed carboxylation: cross-electrophile electrocoupling with atmospheric CO₂, Angew. Chem. Int. Ed. 59 (2020) 1–7, https://doi.org/10.1002/anie.202003218.
- [31] T.P. Nguyen, D.M.T. Nguyenc, D.L. Trand, H. K.Led, D.N. Vof, S.S. Lamg, R. S. Varmah, M. Shokouhimehri, C.C. Nguyenj, Q.V. Le, MXenes: applications in electrocatalytic, photocatalytic hydrogen evolution reaction and CO₂ reduction, Mol. Catal. 486 (2020), 110850, https://doi.org/10.1016/j.mcat.2020.110850.
- [32] X. Li, J. Xiong, X. Gao, J. Huang, et al., Recent advances in 3D g-C3N4 composite photocatalysts forphotocatalytic water splitting, degradation of pollutants and CO2reduction, J. Alloys Compd. 802 (2019) 169–209, https://doi.org/10.1016/j. jallcom.2019.06.185.
- [33] M. Liu, P. Zhao, Y. Gu, R. Ping, J. Gao, F. Liu, Squaramide functionalized ionic liquids with well-designed structures: highly-active and recyclable catalyst platform for promoting cycloaddition of CO₂ to epoxides, J. CO₂ Util. 37 (2020) 39–44, https://doi.org/10.1016/j.jcou.2019.11.028.
- [34] J. Zhang, X. Zhu, B. Fan, J. Guo, P. Ning, T. Ren, Li Wang, J. Zhang, Combination of experimental and theoretical methods to explore the aminofunctionalized pyrazolium ionic liquids: an efficient single-component catalyst for chemical fixation of CO₂ under mild conditions, Mol. Catal. 466 (2019) 37–45, https://doi. org/10.1016/j.mcat.2019.01.001.
- [35] J. Xu, Y. Gan, J. Pei, B. Xue, Metal-free catalytic conversion of CO₂ into cyclic carbonate by hydroxyl-functionalized graphitic carbon nitride materials, Mol. Catal. 491 (2020), 110979, https://doi.org/10.1016/j.mcat.2020.110979.
- [36] Y. Liu, Y. Song, J. Zhou, X. Zhang, Modified polyether glycols supported ionic liquids for CO₂ adsorption and chemical fixation, Mol. Catal. 492 (2020), 111008, https://doi.org/10.1016/j.mcat.2020.111008.
- [37] Y.Y. Wu, Y.F. Zhao, R.P. Li, B. Yu, Y. Chen, X.W. Liu, C.L. Wu, X.Y. Luo, Z.M. Liu, Tetrabutylphosphonium-based ionic liquid catalyzed CO₂ transformation at ambient conditions: a case of synthesis of α-alkylidene cyclic carbonates, ACS Catal. (7) (2017) 6251–6255, https://doi.org/10.1021/acscatal.7b01422.
- [38] X.D. Lang, L.N. He, Green catalytic process for cyclic carbonate synthesis from carbon dioxide under mild conditions, Chem. Rec. 16 (2016) 1337–1352, https:// doi.org/10.1002/tcr.201500293.
- [39] S.S. Islama, N. Salamc, R.A. Mollad, S. Riyajuddine, N. Yasminb, D. Dasc, K. Ghoshe, S. Ma. Islam, Zinc(II) incorporated porous organic polymeric material (POPs): A mild and efficient catalyst for synthesis of dicoumarols and carboxylative

cyclization of propargyl alcohols and CO₂ in ambient conditions, Mol. Catal. 477 (2019), 110541, https://doi.org/10.1016/j.mcat.2019.110541.

- [40] Q.W. Song, L.N. He, Robust silver(I) catalyst for the carboxylative cyclization of propargylic alcohols with carbon dioxide under ambient conditions, Adv. Synth. Catal. 358 (2016) 1251–1258, https://doi.org/10.1002/adsc.201500639.
- [41] X.D. Li, Y. Cao, R. Ma, L.N. He, Thermodynamically favorable protocol for the synthesis of 2-oxazolidinones via Cu(I)-catalyzed three-component reaction of propargylic alcohols CO₂ and 2-aminoethanols, J. CO₂ Util. 25 (2018) 338–345, https://doi.org/10.1016/j.jcou.2018.01.022.
- [42] X. Lian, L. Xu, M. Chen, C. Wu, W. Li, B. Huang, Y. Cui, Carbon dioxide captured by metal organic frameworks and its subsequent resource utilization strategy: a review and prospect, J. Nanosci. Nanotechnol. 19 (2019) 3059–3078, https://doi. org/10.1166/jnn.2019.16647.
- [43] Q.X. Han, C. He, M. Zhao, B. Qi, J.Y. Niu, C.Y. Duan, Engineering chiral polyoxometalate hybrid metal-organic frameworks for asymmetric dihydroxylation of olefins, J. Am. Chem. Soc. 135 (2013) 10186–10189, https://doi.org/10.1021/ ja401758c.
- [44] Z.L. Shi, G.Q. Niu, Q.X. Han, X.Y. Shi, M.X. Li, A molybdate-incorporated cooperative catalyst: high efficiency in the assisted tandem catalytic synthesis of cyclic carbonates from CO₂ and olefins, Mol. Catal. 461 (2018) 10–18, https://doi. org/10.1016/j.mcat.2018.10.003.
- [45] S. Hou, J. Dong, X. Jiang, Z. Jiao, B. Zhao, A noble-metal-free metal-organic framework (mof) catalyst for the highly efficient conversion of CO₂ with propargylic alcohols, Angew. Chem. Int. Ed. 57 (2018) 1–6, https://doi.org/ 10.1002/anie.201811506.
- [46] J.Y. Hu, J. Ma, Q.G. Zhu, Q.L. Qian, H.L. Han, Q.Q. Mei, B.X. Han, Zinc(II)catalyzed reactions of carbon dioxide and propargylic alcohols to carbonates at room temperature, Green Chem. 18 (2016) 382, https://doi.org/10.1039/ C5GC01870F
- [47] X.Y. Guo, Z. Zhou, C. Chen, J.F. Bai, C. He, C.Y. Duan, New rht-type metal-organic frameworks decorated with acylamide groups for efficient carbon dioxide capture and chemical fixation from raw power plant flue gas, ACS Appl. Mater. Interfaces 8 (2016) 31746–31756, https://doi.org/10.1021/acsami.6b13928.

- [48] M.L. Ding, H.L. Jiang, Incorporation of imidazolium-based poly(ionic liquid)s into a metal-organic framework for CO₂ capture and conversion, ACS Catal. 8 (2018) 3194–3201, https://doi.org/10.1021/acscatal.7b03404.
- [49] L.Y. Jing, F. Yang, B. Yuan, G. Yan, L.X.W. Lou, Hierarchical hollow nanoprisms based on ultrathin Ni-Fe layered double hydroxide nanosheets with enhanced electrocatalytic activity towards oxygen evolution, Angew. Chem. Int. Ed. 57 (2017) 172–176, https://doi.org/10.1002/ange.201710877.
- [50] Z.H. Su, Z.F. Zhao, B.B. Zhou, Q.H. Cai, Y. Zhang, Three novel coordination polymers constructed from [Cu(CN)] chains, CrystEngComm 13 (2011) 1474–1479, https://doi.org/10.1039/C0CE00483A.
- [51] D.Y. Shi, R. Zheng, M.J. Sun, X.R. Cao, C.X. Sun, C.J. Cui, C.S. Liu, J.W. Zhao, M. Du, Semiconductive copper(I)-organic frameworks for efficient light-driven hydrogen generation without additional photosensitizers and cocatalysts, Angew. Chem. Int. Ed. 56 (2017) 14637–14641, https://doi.org/10.1002/ ange.201709869.
- [52] J.C. He, J. Li, Q.X. Han, C. Si, G.Q. Niu, M.X. Li, J.P. Wang, J.Y. Niu, Photoactive metal-organic framework for the reduction of aryl halides by the synergistic effect of consecutive photo-induced electron-transfer and hydrogen-atom transfer processes, ACS Appl. Mater. Interfaces 12 (2020) 2199–2206, https://doi.org/ 10.1021/acsami.9b13538.
- [53] S.J. Li, G. Li, P.P. Ji, J.W. Zhang, S.X. Liu, J. Zhang, X.N. Chen, A giant Mo/Ta/W ternary mixed-addenda polyoxometalate with efficient photocatalytic activity for primary amine coupling, ACS Appl. Mater. Interfaces 11 (2019) 43287–43293, https://doi.org/10.1021/acsani.9b16694.
- [54] Z.L. Shi, J. Li, Q.X. Han, X.Y. Shi, C. Si, G.Q. Niu, P.T. Ma, M.X. Li, Polyoxometalate-supported aminocatalyst for the photocatalytic direct synthesis of imines from alkenes and amines, Inorg. Chem. 58 (2019) 12529–12533, https:// doi.org/10.1021/acs.inorgchem.9b02056.
- [55] L. Capaldo, D. Merli, M. Fagnoni, D. Ravelli, Visible light uranyl photocatalysis: direct C-H to C-C bond conversion, ACS Catal. 9 (2019) 3054–3058, https://doi. org/10.1021/acscatal.9b00287.
- [56] I.B. Perry, T.F. Brewer, P.J. Sarver, D.M. Schultz, D.A. Dirocco, D.W.C. MacMillan, Direct arylation of strong aliphatic C–H bonds, Nature 560 (2018) 70–75, https:// doi.org/10.1038/s41586-018-0366-x.