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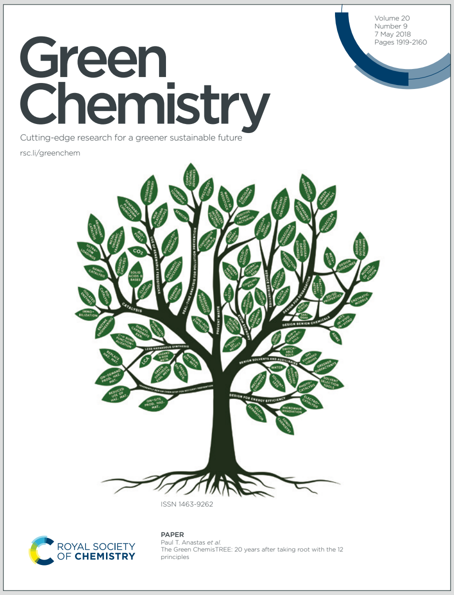

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ARTICLE

A highly stable polyoxovanadate-based Cu(I)–MOF for the carboxylative cyclization of CO_2 with propargylic alcohols at room temperature

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A novel polyoxovanadate-based copper(I)–organic framework, $[Cu^{I}(bib)]_4\{V^{V}_4O_{12}\}$ (V-Cu-MOF, bib = 1,4-bis(1H-imidazoly-1-yl)benzene), is facilely synthesized under mild hydrothermal conditions. The structure of V-Cu-MOF is constructed by cyclic $\{V_4O_{12}\}^{4-}$ polyanion cluster and 1D chain Cu(I)-MOF ($[Cu^{I}(bib)]^{+}$). The presence of $\{V_4O_{12}\}^{4-}$ cluster stabilizes the Cu(I)-MOF with Cu(I) as the center, thereby improving the stability of the V-Cu-MOF and enabling it to stably exist in various solvents and pH = 2-12 solutions. Additionally, the V-Cu-MOF as a heterogeneous catalyst can catalyze the carboxylative cyclization of CO_2 and propargylic alcohols to high value-added α-alkylidene cyclic carbonates at room temperature, the conversion and selectivity are almost 100%. More importantly, no obvious decrease in the yield of the α-alkylidene cyclic carbonate is observed after ten cycles. These results indicate the excellent catalytic activity and sustainability of V-Cu-MOF. Researching the mechanism of the catalytic reaction suggests that the high-density Cu(I) sites in the V-Cu-MOF are the catalytically active centers for activating the C≡C bonds of propargylic alcohols. To the best of our knowledge, this is the first example of polyoxometalate-based metal–organic frameworks catalyst for catalyzing the conversion of CO_2 to value-added α-alkylidene cyclic carbonates at room temperature.

Introduction

Carbon dioxide (CO_2), as a greenhouse gas, has been considered as the main cause of global warming due to its growing concentration in the atmosphere.[1, 2] Meanwhile, comparing with the toxic phosgene and carbon monoxide, CO_2 is recognized as green, cheap and inexhaustible C1 feedstock.[3-5] As a result, transforming CO_2 into high value-added chemicals is an effective strategy that not only reduces the content of CO_2, but also makes full use of this renewable resource.[6-8] Currently, many methods have been reported for chemical conversion of CO_2, mainly including the photocatalytic reduction of CO_2,[9, 10] carboxylation of terminal alkynes with CO_2,[11-13] cycloaddition of aziridines or epoxides with CO_2,[14-17] and carboxylative cyclization of propargylic alcohols with CO_2 etc.,[2, 18-21] among which the cyclization of propargylic alcohols with CO_2 is one of the most efficient route because the obtained products α-alkylidene cyclic carbonates are an important class of heterocyclic compounds in organic synthesis and pharmaceutical chemistry.[22, 23] However, highly active catalysts, high temperature or CO_2 pressure are necessary to realize this cyclization reaction owe to the thermodynamic stability and kinetic inertness of CO_2.[24]

A number of homogeneous catalysts, including inorganic salts,[25-29] organic salts,[30-32] organic phosphorous,[33, 34] transition metal complexes,[35-37] and ionic liquid etc.,[38-41] have been developed to catalyze the cycloaddition of propargylic alcohols with CO_2. Although these homogeneous catalysts exhibit excellent catalytic activity, they suffer from the difficulty in postreaction separation and catalyst reusability. Heterogeneous catalyst is an ideal candidate to resolve above these problems. Hence, various heterogeneous catalysts, such as metal nanoparticles,[42, 43] composite catalysts,[44, 45] and metal–organic frameworks (MOFs) etc.,[46-49] have been explored to catalyze the cyclization of CO_2 with propargylic alcohols. Among them, MOFs are a class of crystalline materials with definite composition and structure, which are constructed by metal ions or clusters and organic ligands.[50, 51] MOFs have been abstracted much attention because their inherent crystal properties that can provide the nature and distribution of catalytically active sites and the potential interactions between catalytic sites and substrate molecules.[52] Recently, many Ag-based and {CuI} cluster-based MOFs catalysts have been employed for the carboxylative cyclization of propargylic alcohols with CO_2.[46-49, 53] In spite of these catalysts show high catalytic effects and the unique advantages of MOFs, they are associated with the utilization of noble metals, stoichiometric additives, low stability, poor recyclability and harsh reaction conditions (high temperature and CO_2 pressure). Therefore, developing efficient, highly stable and sustainable non-noble metal-based

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heterogeneous catalyst to achieve the cyclization reaction of propargylic alcohols with CO_2 under mild conditions still remains challenging.

Polyoxometalate-based metal–organic frameworks (POMOFs) are a kind of crystalline hybrid materials that constructed by MOFs and POMs, which have attracted great interest in the field of catalysis because they combine the advantages of MOFs and POMs.[54, 55] In addition, the introduction of POMs into MOFs can enhance the stability of the original MOFs,[56-58] which is crucial for the sustainability of the MOFs catalyst in catalytic reaction. In this work, we successfully synthesized a novel polyoxovanadate-based copper(I)–organic framework, $[Cu^{I}(bib)]_4\{V^{V}_4O_{12}\}$ (V-Cu-MOF, bib = 1,4-bis(1H-imidazoly-1-yl)benzene), which exhibits high solvent and acid/base stabilities. V-Cu-MOF as a heterogeneous catalyst can effectively and selectively catalyze the carboxylative cyclization of various terminal propargylic alcohols with CO_2 to high value-added α-alkylidene cyclic carbonates at room temperature. More importantly, V-Cu-MOF shows excellent recyclability, and the yield of α-alkylidene cyclic carbonate is still up to 97% after ten cycles. To our knowledge, this is the first example of POMOFs catalyst for the cyclization of propargylic alcohols with CO_2 at room temperature.

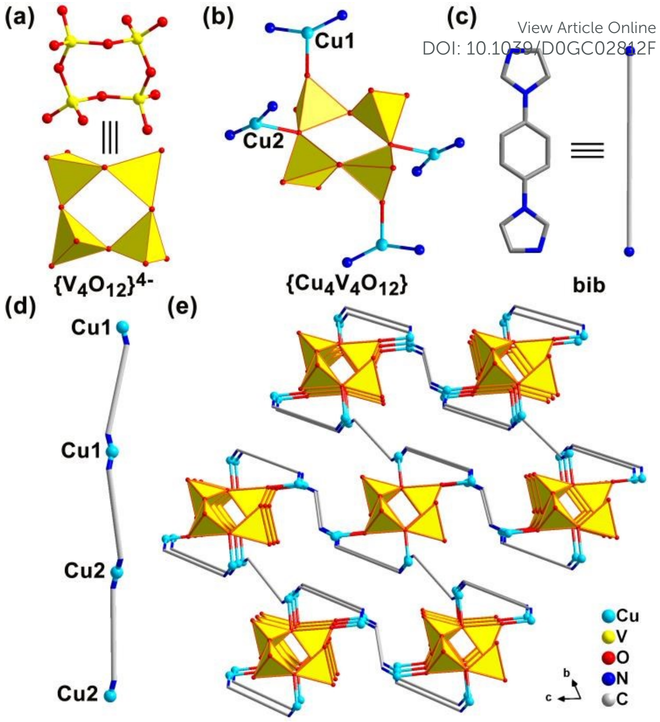

Fig. 1 The structure of V-Cu-MOF. (a) $\{V_4O_{12}\}^{4-}$ polyanion cluster. (b) Bimetallic octanuclear cluster $\{Cu_4V_4O_{12}\}$. (c) Ligand bib. (d) Three connection modes of ligand bib. (e) The 3D frameworks of V-Cu-MOF. Hydrogen atoms are omitted for clarity.

Results and discussion

Crystal structure and characterizations of V-Cu-MOF

Yellow strip V-Cu-MOF crystals were synthesized from $NaVO_3$, $Cu(NO_3)_2·3H_2O$, bib and $N_2H_4·H_2O$ under mild hydrothermal conditions. Single crystal X-ray diffraction analysis reveals that V-Cu-MOF crystallizes in a triclinic space group of P-1 (Table S1). The structure of V-Cu-MOF contains a cyclic $\{V_4O_{12}\}^{4-}$ polyanion cluster that constructed from four distorted VO_4 tetrahedron linked by the vertex-sharing of O atoms, and all V atoms in the cluster exhibit tetrahedral coordination geometry, coordinated by four oxygen atoms (Fig. 1a). The $\{V_4O_{12}\}^{4-}$ cluster in V-Cu-MOF severs as a tetradentate ligand to bond to four Cu atoms by two terminal O atoms and two bridging O atoms, thus obtaining a bimetallic octanuclear cluster $\{Cu_4V_4O_{12}\}$ (Fig. 1b). There are two kinds of copper ions (Cu1 and Cu2) that adopt "T-type" coordination geometry in the cluster (Fig. 1b). The Cu1 ion is ligated by two N atoms from two bib molecules and one terminal O atom from $\{V_4O_{12}\}^{4-}$ cluster, and the Cu2 ion is coordinated by two N atoms from two bib molecules and one bridging O atom from $\{V_4O_{12}\}^{4-}$ cluster (Fig. 1b). In addition, the ligand bib corresponds to a linear bidentate ligand (Fig. 1c), which has three linking modes in V-Cu-MOF (Fig. 1d). Each bimetallic $\{Cu_4V_4O_{12}\}$ cluster is further linked by eight ligands bib to a 3D framework (Fig. 1e).

Bond valence sum (BVS) calculations[59] reveal that oxidation states of all V and Cu ions in compound V-Cu-MOF are +5 and +1, respectively (Table S2). Moreover, the oxidation states of V and Cu ions in V-Cu-MOF are further confirmed by X-ray photoelectron spectroscopy (XPS), and two typical peaks with bonding energies of 517.5 eV and 932.26 eV can be assigned to V(V) $2p_{3/2}$ and Cu(I) $2p_{3/2}$, respectively (Fig. S1).[55, 60] The phase purity of V-Cu-MOF is demonstrated by the experimental powder X-ray diffraction (PXRD), which is matched well with the simulated peaks from the crystallographic studies (Fig. S2). The Fourier transform infrared (FTIR) spectrum of V-Cu-MOF is shown in Fig. S3. The characteristic bands in 930-1000 cm^{-1} and 600-910 cm^{-1} are attributed to ν(V=O) and ν(V-O-V), respectively.[61] The bands in the region of 1100-1600 cm^{-1} arise from ν(C=C) of ligand bib.[62]

The stability of V-Cu-MOF

The structural stability of catalyst is important for its practical application, thus we systematically investigate the stability of V-Cu-MOF. The thermal stability of V-Cu-MOF is confirmed by thermogravimetric analysis (TGA), it can be seen that V-Cu-MOF exhibits high thermal stability, up to 350 °C (Fig. S4). Subsequently, we explore the solvent and acid/base stabilities of V-Cu-MOF by soaking it in various organic solvents (Toluene, DCM = dichloromethane, Dioxane, MeOH = methanol, ACN = acetonitrile, DBU = 1,8-diazabicyclo-[5.4.0]underc-7-ene) for 7 days and pH aqueous solutions (pH = 1-13) for 12 hours. The PXRD patterns (Fig. 2) and FTIR spectra (Fig. S5) of the experimental V-Cu-MOF are well consistent with those of the fresh prepared V-Cu-MOF, suggesting that V-Cu-MOF has excellent solvent stability and acid/base stability (pH= 2-12). To our knowledge, the stability of V-Cu-MOF is significantly higher than the most Cu(I)-MOFs that have been reported,[13, 48, 49] which may be attributed to the

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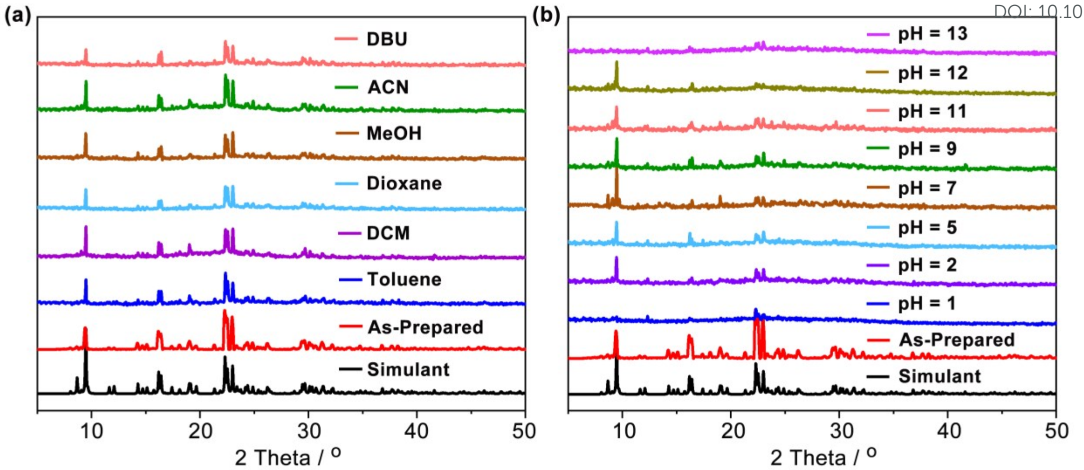

Fig. 2 (a) PXRD patterns of V-Cu-MOF after immersing in various solvents for 7 days; (b) PXRD patterns of V-Cu-MOF after immersing in different pH solutions for 12 hours.

introduction polyoxovanadates into the Cu(I)-MOF, similar phenomenon have been observed and discussed for the other kinds of POMOFs as well.[56-58]

Catalytic performance of V-Cu-MOF for the cyclization of propargylic alcohols with CO_2

In view of the excellent stability and high-density Cu(I) active sites, the catalytic activity of V-Cu-MOF was explored by the carboxylative cyclization of propargylic alcohols with CO_2. 2-methyl-3-butyn-2-ol (**1a**, 1.0 mmol) was selected as model substrate to optimize the reaction conditions, and the catalytic reaction was conducted in ACN (1.0 mL), 0.4 MPa CO_2 pressure, mesitylene as internal standard (1 mmol), and catalyst (0.025mmol, 2.5% mol) at 25 °C. For a better dispersion in ACN, the V-Cu-MOF crystals were ground and the Brunauer–Emmett–Teller (BET) surface area of used V-Cu-MOF was 4.2 m^2/g (Fig. S6). The catalytic process was monitored by gas chromatography with flame ionization (GC-FID) and the product was identified by ^1H NMR spectra. As shown in Table S3, the individual catalyst V-Cu-MOF and other raw materials ($NaVO_3$, $Cu(NO_3)_2{\cdot}3H_2O$ and bib) were hardly to catalyze the reaction (Table S3, Entry 1-5). It should be noted that V-Cu-MOF showed negligible activity together with co-catalyst triethylamine (TEA) or diisopropylethylamine (DIPEA) (Table S3, Entry 7-8), but when DBU was added as co-catalyst in combination with V-Cu-MOF, the yield of the desired product α-alkylidene cyclic carbonate can reach to 99% (Table S3, Entry 9). In addition, the DBU was alone employed as catalyst, it was ineffective for the reaction (Table S3, Entry 6), indicating that V-Cu-MOF was an excellent catalyst for the cyclization of propargylic alcohols with CO_2 to generate α-alkylidene cyclic carbonate and there was some synergistic effect between V-Cu-MOF and DBU.

Subsequently, the examinations of other reaction parameters (reaction temperature, CO_2 pressure, amount of DBU, and reaction time) were performed based on the catalytic system of V-Cu-MOF/DBU, and the results were summarized in Fig. 3. To clearly display the influence of these parameters, the reaction time was reduced to 6 hours. Firstly, the yield of the target product α-alkylidene cyclic carbonate is decreased with increasing reaction temperature (Fig. 3a), which is attributed to the production of some by-products with elevating the temperature.[63] Hence, the proper reaction temperature is 25 °C, and the CO_2 pressure is explored at this temperature. The yield of the product exhibits a rising trend as the pressure of CO_2 is enhanced from 0.1 MPa to 0.8 MPa (Fig. 3b). However, the improvement of yield turns slower after exceeding 0.4MPa, so the moderate CO_2 pressure is 0.4 MPa. Then the effect of amount of DBU is investigated. The yield is increased with the amount of DBU added, but the enhancement of yield is unworthy when the amount of DBU added over 30 μL (Fig. 3c), indicating the suitable amount of DBU is 30 μL (0.2 mmol). Finally, the dependence of yield on the reaction time is studied, and the result is recorded in Fig. 3d. It can be seen that the yield of α-alkylidene cyclic carbonate can reach 99% within 10 hours, thus the appropriate reaction time is 10 hours. According to the above experimental results, the optimal reaction conditions of V-Cu-MOF catalyzes the cyclization of propargylic alcohols with CO_2 to produce α-alkylidene cyclic carbonate are 25 °C, 0.4 MPa CO_2 pressure, 30 μL of DBU as co-catalyst and 10 hours.

Next, we investigate the catalytic behaviors of V-Cu-MOF toward the cyclization of a series of propargylic alcohols with CO_2 under the optimal reaction conditions. As shown in Table 1, V-Cu-MOF could catalyze the transformation of terminal propargylic alcohols with different substituents (methyl, ethyl, *sec*-butyl, cyclopentyl, and cyclohexyl) to the corresponding high value-added α-alkylidene cyclic carbonates in almost quantitative yield. It should be noted that the yield of **2h** decreased to 88% under identical conditions, which may be caused by the steric hindrance effect. However, the yield of **2h** can be improved to 95% by appropriately extending the reaction time (12 hours). These results demonstrated that V-Cu-MOF is an efficient and selective catalyst for the carboxylative cyclization of CO_2 with propargylic alcohols to α-alkylidene cyclic carbonates.

Recyclability of V-Cu-MOF

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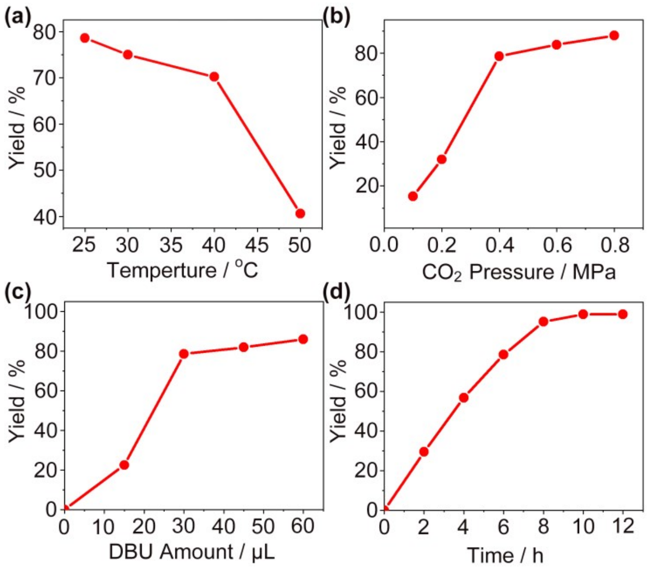
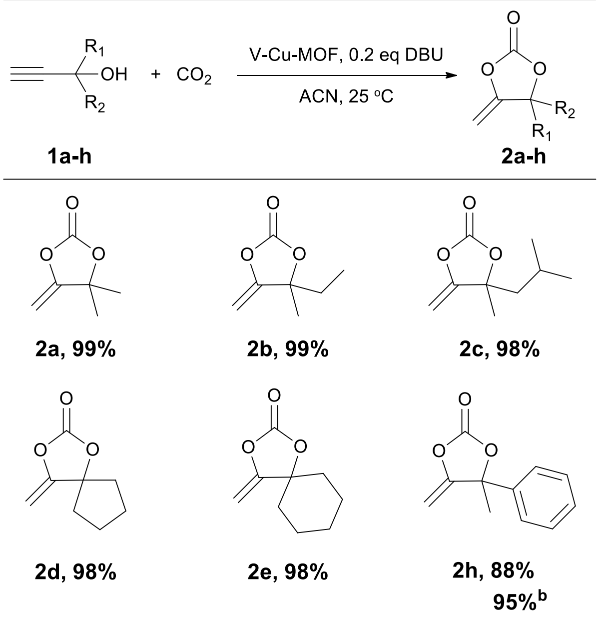


Fig. 3 The influences of reaction conditions on the carboxylative cyclization of propargylic alcohols with CO_2. (a) The effect of reaction temperature. (b) The effect of CO_2 pressure. (c) The effect of DBU amount. (d) The effect of reaction time. Reaction conditions: **1a** (1.0 mmol), V-Cu-MOF (0.025 mmol), mesitylene (internal standard, 1.0 mmol), DBU (0.2 mmol), ACN (1.0 mL), 25°C, 6 hours. The yields were determined by GC.

Having identified highly catalytic activity and wide generality exhibited by V-Cu-MOF, the recyclability of the catalyst is subsequently investigated by employing **1a** as model substrate, which is vital for practical application. Firstly, a leaching test was performed to further confirm the heterogeneity of the catalyst V-Cu-MOF. As shown in Fig. 4a, the removal of the V-Cu-MOF by centrifugation after 2 hours, and the resulting solution was maintained for another 10 hours under the same conditions, but no additional **2a** was produced. To our delight, there was no significant decrease in the catalytic activity of V-Cu-MOF after ten runs (the yield of **2a** was maintained at 99-97%) (Fig. 4b), indicating excellent sustainability of V-Cu-MOF. The PXRD patterns and FTIR spectra of the recovered catalyst matched well with the fresh catalyst (Fig. 4c, d), suggesting its structural integrity. In addition, there was no obvious difference in XPS results, which demonstrated the well-maintained oxidation states of V ions and Cu ions in the catalyst before and after the catalytic reaction (Fig. 4e, f). These results indicate that V-Cu-MOF has highly structural stability and reusability.

Table 1 Carboxylic cyclization of various propargylic alcohols with CO_2 over V-Cu-MOF. [a]



1a-h **2a-h**

2a, 99% **2b, 99%** **2c, 98%**

2d, 98% **2e, 98%** **2h, 88%**
95%[b]

[a] Reaction conditions: substrate (1 mmol), catalyst (0.025 mmol), 0.4MPa CO_2, DBU (0.2mmol), ACN (1 mL), 25ºC, 10hours. Yield was determined by GC and mesitylene as internal standard. [b]12hours.

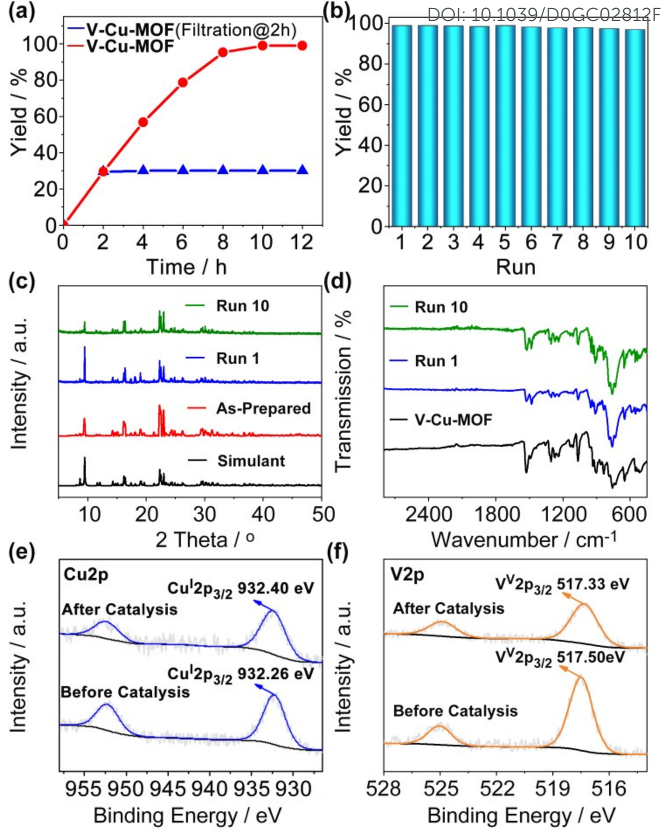


Fig. 4 (a) Catalyst V-Cu-MOF filtered after 2 h. (b) Recycling tests for **1a** with CO_2 cycloaddition using V-Cu-MOF. (c) PXRD patterns of V-Cu-MOF: before and after catalytic reactions. (d) FTIR spectra of V-Cu-MOF: before and after catalytic reactions. (e, f) XPS spectra of Cu(I) and V(V) in V-Cu-MOF: before and after catalytic reactions.

Compared with the reported heterogeneous catalysts for the cyclization of propargylic alcohols with CO_2, the V-Cu-MOF showed the following advantages. First of all, V-Cu-MOF exhibited comparable catalytic activity with noble metal-based catalysts (Table S4, Entry 1-3). Secondly, V-Cu-MOF demonstrated high stability and recyclability (the yield of **2a** can reach 97% after ten runs), whereas the leaching of active species was severe in certain MOF-based catalysts (Table S4, Entry 9-12). Third, with the assistance of catalytic amount of additives, V-Cu-MOF could achieve the cycloaddition of propargylic alcohols with CO_2 at room temperature, while high reaction temperature (Table S4, Entry 4-8) or stoichiometric

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additives (Table S4, Entry 1-2) were required in some catalytic systems. Therefore, V-Cu-MOF can be considered as a green and sustainable catalyst for the carboxylative cyclization of propargylic alcohols with CO_2 to obtain high value-added α-alkylidene cyclic carbonates.

Reaction mechanism of V-Cu-MOF for catalyzing the cyclization of propargylic alcohols with CO_2

It is well known that the activations of the C≡C bond and hydroxyl group in the propargylic alcohols are considered as two crucial processes for the carboxylative cyclization of the propargylic alcohols with CO_2.[47, 64] According to our experimental results and the reported literatures,[27] we speculate that the DBU is used for activation the hydroxyl group of the propargylic alcohol and Cu(I) in V-Cu-MOF is utilized for activation the C≡C bond of the propargylic alcohol in our V-Cu-MOF/DBU catalytic system. To confirm our assumptions, firstly, the propargylic alcohol **1a**, and the mixture **1a**/DBU and **1a**/V-Cu-MOF are examined by ^1H NMR spectra analysis and the results are recorded in Fig. 5. The ^1H signal of O-H in **1a** appears at δ = 5.30 ppm and presents a sharp single peak (Fig. 5a). The ^1H signal of the mixture of **1a**/V-Cu-MOF (Fig. 5b) is similar to that of O-H in **1a**, suggesting that V-Cu-MOF cannot activate the hydroxyl group of the substrate **1a**. However, the ^1H signal of the mixture of **1a**/DBU shifts obviously and changes into a broad peak (Fig. 5c), which indicates that DBU can activate the alcoholic hydroxyl through the formation of hydrogen bonding.[65] Subsequently, a series of control experiments are carried out using ligand bib, $[Et_4N]_4\{V_4O_{12}\}\cdot 2H_2O$ and CuI as catalyst, respectively, to confirm the active site of the V-Cu-MOF in the carboxylative cyclization of **1a** with CO_2 (Table S5). $[Et_4N]_4\{V_4O_{12}\}\cdot 2H_2O$ (Fig. S7) was synthesized according to the literature,[66] in which $\{V_4O_{12}\}^{4-}$ had the same structure as that in V-Cu-MOF. These results demonstrate that ligand bib and $[Et_4N]_4\{V_4O_{12}\}\cdot 2H_2O$ as catalyst exhibit no catalytic activity under the optimal reaction conditions (Table S5, Entry 1-2). However, the yield of **2a** is 99% when the CuI is used as catalyst (Table S5, Entry 3), indicating that the Cu(I) in V-Cu-MOF is the catalytically active site for the cyclization reaction. Although the homogeneous CuI catalyst exhibits comparable catalytic activity with the V-Cu-MOF catalyst, the V-Cu-MOF shows excellent recyclability without significant decrease in yields over ten catalytic cycles (Fig. 4b). Moreover, Cu(I) is widely employed as catalyst for activation the C≡C bond in organic synthesis,[67] thus we deduce that Cu(I) in V-Cu-MOF is the catalytically active site that activates the C≡C bond of the substrate **1a**.

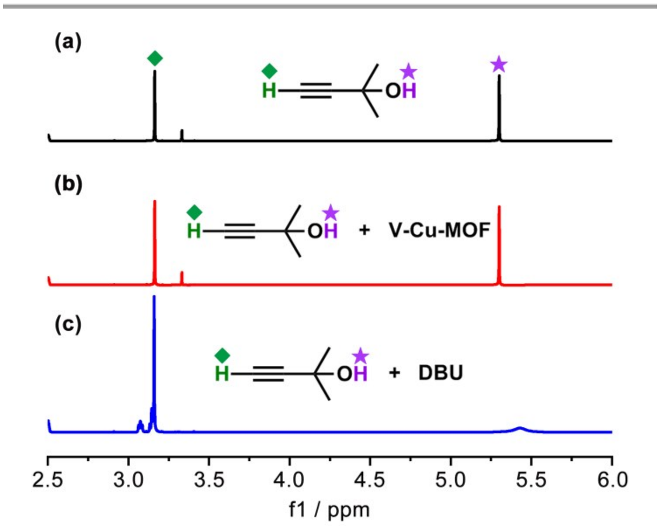
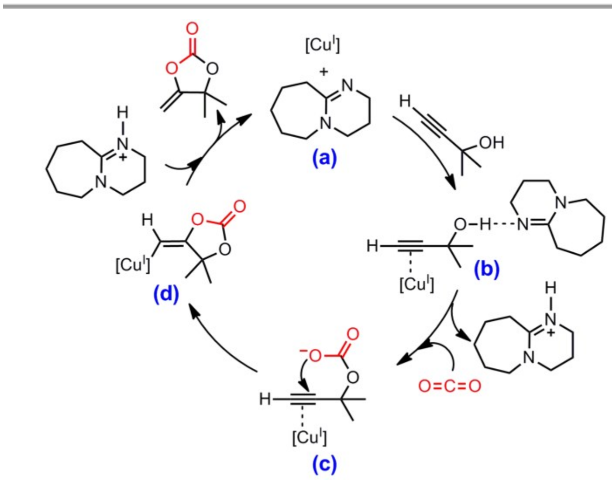


Fig. 5 Activation of the hydroxyl proton by different systems (^1H-NMR in D_6-DMSO). (a) Substrate **1a**. (b) **1a**/V-Cu-MOF. (c) **1a**/DBU.

Based on the above discussion, a possible mechanism for the carboxylative cyclization of propargylic alcohols with CO_2 by V-Cu-MOF is proposed in Scheme 1. Initially, in the system of DBU and V-Cu-MOF (**a**), the DBU abstracts proton from the alcoholic hydroxyl of the propargylic alcohol by forming hydrogen bonding and the Cu(I) in V-Cu-MOF interacts with the C≡C bond of the propargylic alcohol through its empty orbital and π electron of C≡C bond to generated the intermediate **b**. Then CO_2 is inserted via the resulting alcohol anion nucleophilic attack on the carbon atom of CO_2, the intermediate **c** is obtained. Subsequently, the intramolecular cycloaddition of the transition **c** produces the vinylcopper intermediate **d**.[68] Finally, the α-alkylidene cyclic carbonate is generated by proto-demetallation and the catalyst returns to the original (**a**).

Conclusions



Scheme 1 A proposed catalytic mechanism of the V-Cu-MOF/DBU system. Note: [Cu^I] = V-Cu-MOF

In conclusion, we synthesized a novel POVs-based MOF, V-Cu-MOF, and its unique composition and structure makes it have high solvent and acid/base stabilities. The V-Cu-MOF can heterogeneously catalyze the cyclization of various terminal propargylic alcohols with CO_2 to obtain high value-added α-alkylidene cyclic carbonates at room temperature, displaying excellent catalytic activity and selectivity. More importantly, the V-Cu-MOF exhibits significant sustainability, the yield of α-alkylidene cyclic carbonate is still as high as 97% after ten cycles. This work demonstrates that the recyclability of MOFs-based catalyst can be improved by introducing POMs into MOFs to construct POMs-based MOFs, which provides an insight on designing efficient and highly robust catalyst for transforming CO_2 to fine chemicals.

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Experimental

Materials and instrumentation

All of the reagents and solvents are of analytical grade, purchased from commercial sources and used without further purification. The ligand bib and the substrates propargylic alcohols were bought from Jilin Province Extension Technology Co., Ltd. Elemental analyses (C, H and N) were performed on a PerkinElmer 2400 CHN elemental analyzer. V and Cu were analyzed using a PLASMA-SPEC(I) ICP atomic emission spectrometer. The Fourier transform infrared (FTIR) spectra were collected on an Agilent Technologies Cary 630FTIR spectrophotometer in the range 400-4000 cm^{-1}. Thermogravimetric analysis (TGA) was conducted under a nitrogen atmosphere with a heating rate of 10 °C min^{-1} on an SDT 2960 Simultaneous DSC-TGA TA Instruments up to 600 °C. Powder X-ray diffraction (PXRD) measurements were performed on a SmartLab instrument with Cu Kα (λ = 1.5418 Å) radiation and X-ray 40 kV/ 30 mA over the angular range 2θ 5°-50° at a scan rate of 10° min^{-1}. Nitrogen adsorption/desorption measurements was taken by ASAP 2020 V4.00 instrument at 77K. X-ray photoelectron spectra (XPS) were collected using a Thermo ESCALAB 250 X-ray photoelectron spectrometer. The yields of α-alkylidene cyclic carbonates were confirmed by gas chromatography (GC) using a Shimadzu GC-2014 instrument equipped with an SH-Rtx-Wax column. The α-alkylidene cyclic carbonates were identified by ^1H NMR spectra and the ^1H NMR spectra were recorded using a Bruker Avance 500 (^1H: 500 MHz) system at ambient temperature. Data are reported as chemical shifts in ppm relative to TMS (0.00 ppm) for ^1H. The following abbreviations are used to explain the multiplicities: s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, and m = multiplet.

Synthesis of V-Cu-MOF

$NaVO_3$ (21 mg, 0.17 mmol) and $N_2H_4{\cdot}H_2O$ (80%, 3.1 μL, 0.05 mmol) were added into 9.50 mL of H_2O. Then a solution of bib (21 mg, 0.1 mmol) in DMF (0.5 mL) and $Cu(NO_3)_2{\cdot}3H_2O$ (121 mg, 0.5 mmol) were consecutively added into above mixture and the resulting mixture was stirred for 1 hour at room temperature. The pH value of the mixture was adjusted with 1M HCl to 4.46. Then the mixture was placed in a 23 mL Teflon reactor and kept under autogenous pressure at 130 °C for 3 days. Then the mixture was cooled to room temperature at a rate of 10 °C per hour, and yellow strip crystals were obtained (yield: 101 mg, 85% based on Cu). Elemental analysis for $C_{48}H_{40}N_{16}O_{12}V_4Cu_4$: C, 38.67%; H, 2.70%; N, 15.03%; V, 13.67%; Cu, 17.05%; found: C, 38.58%; H, 2.64%; N, 14.94%; V, 13.59%; Cu, 16.93%; FTIR (cm^{-1}, Fig. S3): 1534(s), 1489(m), 1441(w), 1356(m), 1323(m), 1308(m), 1276(m), 1240(m), 1072(m), 935(s), 909(s), 838(m), 758(s), 657(m), 557(w), 533(s).

Crystallography

Single-crystal X-ray diffraction (SXRD) data of V-Cu-MOF were collected on a Bruker diffractometer using Mo Kα radiation (λ = 0.71073 Å) at 293 K. The empirical absorption correction was based on equivalent reflections. The structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2 using the SHELXTL crystallographic software package. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms of the organic molecule were placed based on geometrical considerations and were included in the structure factor calculation. CCDC 2022351 contains the crystallographic data for V-Cu-MOF. Crystal data and structure refinement are summarized in Table S1.

Cyclization of Propargylic alcohols with CO_2

In a typical reaction, propargylic alcohol (1.0 mmol), mesitylene (internal standard, 1.0 mmol), DBU (0.2 mmol), catalyst (0.025 mmol), and ACN (1.0 mL) were added to a 10 mL autoclave reactor with an internal Teflon insert. Then, the reactor was charged with 0.4 MPa CO_2, and the mixture was stirred for 10 hours at 25 °C. At the end of reaction, the catalyst was centrifuged and a small aliquot of the supernatant was taken and diluted with ACN to be analyzed by gas chromatography (GC) to calculate the yield of α-alkylidene cyclic carbonate. The resulting organic phase was collected and purified by column chromatography silica gel (petroleum ether / ethyl acetate) to afford the target product.

Recycling experiment of V-Cu-MOF

The reusability of the catalyst V-Cu-MOF was tested using 2-methyl-3-butyn-2-ol (**1a**) as the substrate. After the completion of the first catalytic reaction, the catalyst was recovered by centrifugation and then washed three times with ACN. The recovered V-Cu-MOF was dried under air and reused for the next run under the same conditions.

Conflicts of interest

The authors declare no competing financial interest.

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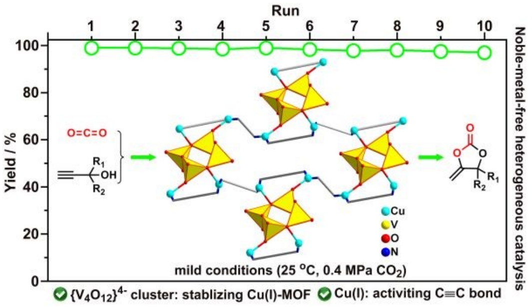

A novel polyoxovanadate-based Cu(I)–organic framework (V-Cu-MOF) was synthesized and utilized as a heterogeneous catalyst for the cyclization of CO_2 with propargylic alcohols to obtain high value-added α-alkylidene cyclic carbonates, performing high catalytic activity and sustainability.