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In-situ cleavage and rearrangement synthesis of an easy-obtained and high stable Cu(II)-based MOF for efficient heterogeneous catalysis of carbon dioxide conversion

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Cycloaddition into cyclic carbonates has been attracted substantial attentions for metal-organic frameworks based catalysis of carbon dioxide (CO_2) chemical fixation, not only due to the contributions that solving the environmental issue of the excessive emission CO_2 , but also providing an effective pathway for the production of value-added fine chemicals. Herein, a Cu(II)-based metal-organic framework (**1**) was synthesized by the in-situ cleavage and rearrangement of *N*,*N'*-bis(4picolinoyl)hydrazine ligand into isonicotinate (INA) moiety as connected node *via* solvothermal synthesis in a high yield. This three-dimensional framework possesses an infinite one-dimensional Cu-O double chains in a ladderlike arrgenment with exposed metal centres, and can be highly stable at least 240 °C and in various solvents. Gas adsorption experiments reveal the well adsorption ability of **1** towards CO_2 with high value of Q_{st} . Cycloaddition of CO_2 with epoxides could successfully occurs by the catalysis of **1** as efficient heterogeneous catalyst, affording almost complete conversion and selectivity under solvent free conditions.

1. Introduction

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Due to the excessive emission of carbon dioxide (CO_2) becoming more and more severe with the rapid development of the society, the efficient capture or transformation of CO2 has become a feasible pathway to solve this environmental issue^{1, 2}. Especially, the combination of capture and successive transformation of CO₂ as the abundant renewable C1 source into value-added fine chemicals is more attractive both industrially and academically³⁻⁶. By far, the CO₂ cycloaddition to epoxides have been the most studied reactions in CO₂ chemical fixation systems, because cyclic carbonates are a class of significant and clean fine chemical intermediate, with nontoxicity, high boiling-point and stable property, which further utilized for the formation of value-added products, such as dialkyl carbonate, phenolic resin and ethanediol, and applied as electrolyte in lithium batteries and capacitors, extraction or annexing agent⁷⁻¹². However, the conversion of the non-polar CO2 with linear structure requires a relative high energy input for C=O bond cleavage because of its high thermodynamic stability. One of the challenges for CO₂ chemical fixation is the activation of CO₂ molecules within a reaction system, which might mainly involve a specific catalyst for the activation¹³⁻¹⁶.

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^b Jiaxing University, School of Entrepreneurship, Jiaxing, 330400, P. R. China. Electronic Supplementary Information (ESI) available: [supplementary structural figures, SEM image and element mapping, GC spectra of the cycloaddition products and the catalysis comparison Table]. See DOI: 10.1039/x0xx00000x Therefore, the rational design and development of materials with high catalytic activity and well-activation ability towards CO_2 molecules under mild conditions, have become one of the most significant research orientations for CO_2 chemical fixation into value-added products¹⁷⁻²².

The coordination-driven metal-organic frameworks (MOFs), which are basically constructed by single metal ions or clusters as secondary building units (SBUs) and organic ligands as connected linkers to form as crystalline solids with longrange ordered network structures, have been draw a great deal of attentions in recent research^{23, 24}. These materials could merge both the advantages of inorganic and organic functionalities within one single system, showing outstanding physical and chemical properties. Besides that, the wider range of synthesis conditions and easy-handled methods endows them a rapid growth of development in recent years^{25, 26}. Especially, the solvothermal synthesis reacted in an autoclave could obtain even more unexpected construction patterns via the cleveage and rearrangement of the starting materials under a relative high temperature and pressure. The construction of MOFs materials with fascinating topology and structures exhibit high surface areas and well-defined porosity, and thus applied in the fields of gas storage, proton conductivity, molecular recognition, and so on²⁷⁻³². In terms of catalysis, the coordinated open metal ions in MOFs could serve as Lewis acid sites to catalyze different types of reactions and these multidimensional porous materials could also provide a microenvironment for the contact and activation between the substrates and the active sites, which greatly promote the developments of MOFs as the ideal heterogeneous catalysts

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among the other traditional catalysts³³⁻⁴⁰. Additionally, due to their specific crystalline construction, it is benefit for the mechanisms for the detailed studied of the catalytic mechanism.

Based on these considerations, we herein presented a Cu(II)-based MOF (noted as 1, $[Cu(OH)(NC_5H_4CO_2)\cdot H_2O]_n)$, synthesized by adding N,N'-bis(4-picolinoyl)hydrazine and $CuCl_2 \cdot 2H_2O$ in a mixable solvent of H_2O and DMF under a solvothermal reaction. In this synthesis, N, N'-bis(4picolinoyl)hydrazine ligand undergoes an in-situ cleavage and rearrangement process into isonicotinate (INA) moiety as connected node, forming a three-dimensional framework constructed by Cu(II) ions and INA. Generally, the obtained compounds synthesized by this approach are in favor of the lowest thermodynamics status, and thus this porous framework exhibits a highly thermal and solvent stabilities, which could maintain its skeleton rise up to 240 °C and after immersed in several solvents for five days. This Cu(II)-based MOF has an infinite Cu-O double chains with the opening active sites, exhibiting a high adsorption ability towards CO₂, and then cycloaddition catalysis of CO₂ with epoxides by 1 as heterogeneous catalyst has also been explored under solvent free conditions.

Experimental

General Methods Details

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The elemental analyses of C, H and N were performed on a Vario EL III elemental analyzer. Inductively coupled plasma (ICP) analysis was performed on a Jarrel-AshJ-A1100 spectrometer. The powder XRD diffractograms were obtained on a Bruker AXS D8 Advance diffractometer instrument with Cu K α radiation (λ = 1.54056 Å) in the angular range $2\theta = 5-50^{\circ}$ at 293 K. Thermogravimetric analyses (TGA) were measured on a SDTQ600 instrument at a ramp rate of 10 °C min⁻¹ in a nitrogen flow. IR spectra were performed by a NEXUS instrument uing KBr pellets. XPS characterization was carried out by using a Thermo Scientific K-Alpha+ spectrometer with Al Ka X-rays (1486.6 eV) as the light source. Scanning electron microscopy (SEM) images were obtained using a NOVA NanoSEM 450 microscope. Gas adsorption measurements were performed using a Quantachrome Autosorb-iQ2 analyzer. ¹H NMR spectra were recorded on a Bruker Avance 400 spectrometer. The GC analyses were performed on Shimadzu GC-2014C with an FID detector equipped with a Wonda Cap Hp-5 Sil capillary column.

Preparation and Synthesis

Synthesis of ligand N,N'-bis(4-picolinoyl)hydrazine was prepared according to the literature methods⁴¹ and characterized by ¹H NMR.

Synthesis of **1**: A mixture of ligand VIEWANCLEDING picolinoyl)hydrazine (24.2 mg, 0.1 mmo) and COCLEDING mg, 0.1 mmol) were dissolved in a mixed solvent of DMF:H₂O = 1:1 (2 mL) in a screw-capped vial, and then heated in a 23 mL Teflon cup at 85 °C for 3 days. After cooling the autoclave to room temperature, green block crystals were observed, washed with water and air-dried. Yield: 77 % (based on the crystals dried in vacuum and the amounts of CuCl₂).

Catalysis experiments

In a typical reaction, the catalytic reaction was conducted in a 25 mL autoclave reactor, purged with 0.5 MPa CO_2 and kept for 15 min to allow the system equilibrated. An oil bath containing the vessel was stirred at 100 °C for 12 h. The general reaction conditions were carefully screened with solvent free. After the reaction, the reactor was cooled to the room temperature by placed in an ice bath for 20 min. A small aliquot of the supernatant reaction mixture was measured by GC to analyze the conversions of the reaction, while the catalysts were separated by centrifugation.

Results and Discussion

Synthesis discussion

Compound 1 was obtained by solvothermal reactions of CuCl₂·2H₂O, and ligand N,N'-bis(4-picolinoyl)hydrazine at 85 °C in DMF/H₂O mixed solvent system. After 3 days heating and cooling to the room temperature, green hexagonal crystals were isolated with the yield of 77%. As shown in Scheme 1, solvothermal synthesis, the N,N'-bis(4during the picolinoyl)hydrazine ligand undergoes an in-situ cleavage and rearrangement process, which the C-N bonds of two amido groups in the ligands have been ruptured and divided into three species. Then the hydroxyl groups from water molecules have been connected to the carbon atoms forming the carboxylic groups and finally two INA ligands have been obtained. Meanwhile, the other hydrogen atoms are linked to the HN-NH fragment and afforded hydrazine molecules. Parallel experiments show that the temperature affects the cleavage and formation of the crystals, increasing or decreasing the reaction temperature, could not obtain the framework 1. Additionally, changing the another Cu(II) salts as starting material, such $Cu(NO_3)_2 \cdot 2H_2O$, CuSO₄·5H₂O as or $Cu(CH_3COO)_2 \cdot H_2O$, also affact the quality of the crystals. Interestingly, when using INA ligands directly to replace N,N'bis(4-picolinoyl)hydrazine ligand the as starting material could not obtained the target crystals under the same conditions. Despite the structure of Cu(II)-INA-based MOF has been synthesized by Williams and co-workers group in 2002⁴², this insitu cleavage and rearrangement solvothermal synthesis provide a feasible approach for the formation of comparative stable materials.

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Scheme 1. The representation of the in-situ cleavage and rearrangement of ligand N,N'-bis-(4-picolinoyl)-hydrazine with Cu(II) ions forming framework **1** *via* solvothermal synthesis.

Structural description

Single-crystal X-ray structural analysis revealed that the asymmetric unit of 1 contains one Cu(II) ion, one halfdeprotonated INA ligand, one coordinated water molecule and one lattice water molecules (Figure S1). Each Cu(II) ion is fivecoordinated in a tetragonal pyramid configuration with a CuO₄N coordination environment, including one nitrogen atom and one carboxylate oxygen atom from two INA ligands, three μ_3 -O bridges from the coordinated water molecules with Cu-O bond lengths ranging from 1.970(9) to 2.242(9) Å and Cu-N bond length of 1.981(11) Å, respectively. The μ_3 -O bridges connect each Cu ions for an infinite one-dimensional Cu-O double chains in a ladderlike arrgenment, and one Cu ion connected with one oxygen is regarded as one stair. The INA ligands are wellordered arranged and only one oxygen of the carboxylic group in each ligand, together with the nitrogen from pyridine ring is coordinated, acting as a μ_2 -bridge to link each Cu-O double chains which extended to three-dimensional frameworks with one-dimensional channels (Figure S2). The channels, where the lattice water molecules reside, are shaped as square. Two channels are edge-sharing each other, and the INA ligands are located as sides with lengths of the square channels approximately 10.16 ×11.21 Å while the diagonal distances of the square channel are ranged from 13.69 to 14.87 Å (Figure S3). From the side view of the structure, as shown in Figure 1a and 1b, the morphology modes of coordinated ligands from each side of Cu-O double chains shows C₂ symmetry. The whole frameworks is like a skyscraper, with each Cu-O double chain acting as a steel pillar and each INA ligand as the linker with a centrum-centrum distance of 3.53 Å between each layer, indicating an obvious $\pi \cdots \pi$ interactions (Figure 1c and 1d). After removing the free water molecules in the lattice, the effective free volume of 1 was proven to be 59.3% of the crystal volume by the calculation of PLATON program. Topologically, each ligand and Cu-O double chain could be abstracted as the 2connected nodes. The overall 3D structure was represented as a (2,2)-connected kgd topology with the Schläfli symbol of 4⁶·6⁴·7·8.



Figure 1. (a) Perspective view of **1** along the *c* axis; (b) 3D structure of **1** showing the skyscraper-liked arrangement; (c) and (d) The presentation of the coordinated ligands INA with a centrum-centrum distance of 3.53 Å between each layer. Colour code: Cu, turquoise; N, blue; O, red; C, gray. Lattice solvent molecules and H atoms are omitted for clarity.

Thermal and solvent stabilities

The stability of 1 was conducted by thermogravimetric analysis from room temperature to 900 °C at a ramp rate of 10 °C min⁻¹ in nitrogen flow. As shown in Figure 2a, two steps of weight loss process were observed, including a small and a severe weight loss process. The slow weight loss of 8.25% from 60 to 240 °C is due to the removal of one lattice H₂O molecule in 1 (calcd. 8.15%), indicating that the skeleton of 1 is stable at least 240 °C. From 240 to 275 °C, the weight loss tendency is suddenly intensified and the 42.75% (calcd. 41.7%) weight loss could be attributed to the decomposing of the organic INA ligand without the coordinated N and O atoms. This analysis indicated that 1 exhibited a good thermal stability within the temperature range from the room temperature to 240 °C. Moreover, the temperature-depended PXRD patterns of sample 1 was further performed from 150 to 360 °C with 30 °C intervals. From 150 to 240 °C, sample 1 exhibited the similar PXRD patterns and same as the fresh pattern, while PXRD patterns has been changed above 270 °C. PXRD results are consistent with the thermogravimetric analysis, demonstrating the high thermal stability of the framework 1.



Figure 2. (*a*) Thermogravimetric analysis of **1**; (*b*) PXRD patterns of sample **1** (red) under different temperature.

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Figure 3. (*a*) IR spectra of fresh **1** (red) and samples after immersed in various solvents; (*b*) PXRD patterns of fresh **1** (red) after immersed in various solvents and its calculated pattern based on the single-crystal simulation (black).

To further examine the solvent stabilities of 1, the fresh crystals were immersed in several solvents, including DMF, DMSO, water, THF, CH₃CN and acetone for five days. The immersed samples were measured by IR and PXRD. The IR spectra of the samples after immersed in different solvents were shown in Figure 3a, and all of them exhibited the characteristic peaks of the fresh samples without the significant change. In addition, these immersed samples were further measured by PXRD, and the PXRD patterns could all wellconsistent with that of the fresh sample and calculated pattern based on the single-crystal simulation, indicating that the frameworks are preserved and the tested samples are in a pure phase. These results give a clear proof that framework 1 can be highly stable and well maintain the skeleton of its structure immersed in these solvents. The high chemical stability of 1 in water or multiple organic solvents provides a superior opportunity and ideal platforms for the applications of various valuable organic transformations using 1 as the potential heterogeneous catalyst.

XPS analysis and SEM

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XPS analysis was further performed to study the electronic state of elements in **1**. As shown in Figure 4, the peaks for C, O, N and Cu at their respective binding energy could be identified in the XPS full scan survey. The HRXPS C 1s spectrum could be further separated to three peaks at 288.0, 285.4 and 284.6 eV for C-O bond of carboxyl groups from INA ligands, C-N bond and C-C bond of pyridine ring from INA ligands, respectively. The deconvoluted HRXPS N 1s spectrum has showed two crossed peaks at 399.8 and 399.4 eV, attributed to N-C and N-Cu, respectively. The HRXPS Cu 2p spectrum showed a peak at 934.3 eV, which were ascribed to Cu^{2+} ($2p_{3/2}$), and this Cu^{2+} ($2p_{3/2}$) peak was further deconvoluted into two peaks at 934.6 and 933.8 eV, corresponding to Cu-O and Cu-N bonds, respectively ^{43, 44}.

The morphological of the single crystal of 1 was estimated by SEM. The SEM image displayed a rod-like morphology of crystal **1** (Figure S4). The element mapping analysis demonstrated the presence of Cu, O and N in the test region, further confirming the composition of **1**.



Figure 4. (*a*) XPS survey spectra of 1; (*b*) C 1s XPS spectrum of 1; (*c*) N 1s XPS spectrum of 1; (*d*) Cu 2p XPS spectrum of 1.

Gas adsorption properties

Gas adsorption experiments have been examined to evaluate the porosity for 1. Due to the coordinated water and lattice water in the crystal 1, the samples were firstly immersed in ethanol to exchange these solvent molecules before the measurement. The samples were further treated by the outgassing process at 100 °C under high vacuum for 6 h and then the activated samples were obtained for the measurement. As shown in Figure 5a, a representative type I sorption behavior, attributed to the typical microporous materials, was exhibited for N₂ adsorption isotherms at 77 K with a saturated uptake of 58.87 $\mbox{cm}^3\mbox{g}^{-1}$ at 1.0 bar. The Brunauer-Emmett-Teller (BET) surface of 1 calculated from the adsorption isotherm were 217.60 m² g⁻¹ (Langmuir surface area of 231.75 m² g⁻¹). However, the N₂ adsorption experiments revealed that almost no N₂ adsorption could be observed at 273 K. Additionally, two reversible and steady rising adsorption isotherms have been observed in the CO₂ adsorption measurements at 273 and 298 K, with the uptake of 58.7 cm³ g⁻¹ and 50.2 cm³ g⁻¹ for **1** at 1 bar, respectively (Figure 5b).

At zero loading, the calculated Q_{st} using the virial method of CO₂ was 31.3 kJ mol⁻¹ (Figure S5). This value was higher than most of the typical MOFs materials, such as MOF-5 (17 kJ mol⁻¹) and HKUST-1 (30 kJ mol⁻¹), demonstrating a strong adsorption



Figure 5. (*a*) N_2 adsorption isotherms of **1** at 77 K; (*b*) CO_2 adsorption isotherms of **1** at 273 and 298 K, respectively. Filled shape, adsorption; open shape, desorption.

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ability of **1** towards $CO_2^{45, 46}$. We attributed this high value of Q_{st} and adsorption ability of **1** towards CO_2 to the strong interactions between the unsaturated Cu centers in **1** and the quadrupole of CO_2 .

Catalysis experiments

Considered the high stability, CO₂ adsorption ability and the extended di-copper chains with exposed metal centres of 1 after the activation, cycloaddition catalysis of CO₂ and epoxides by 1 as heterogeneous catalyst has been explored. First of all, the optimize reaction system under various reaction conditions were conducted for the cycloaddition of styrene oxide with CO₂ as a model reaction. As shown in Figure 6a-6c, the conversions were increased with the rise of the temperature, CO_2 pressure and the amount of catalyst within certain scope, affording almost complete conversion, and further increasing could not lead to higher conversions. While this catalysis could all exhibit a well selectivity without any rearrangement side products observed under various conditions. Generally, the catalytic reaction was carried out in an autoclave reactor by the addition of 4 mmol epoxide with CO₂ purged at 5 atm at 100 °C without any solvents for 12 h, in the presence of 0.5 mol% 1 (per Cu site) heterogeneous catalyst and co-catalyst as the of tertbutylammonium bromide (TBABr, 0.5 mol%), afforded >99% conversion and >99% selectivity. Control experiments have also been performed and the results showed that the other raw materials involved in the synthesis of 1 could hardly catalyze this reaction under the same condition, which demonstrated that assembly of the metal centers with organic ligands into one framework can greatly improve catalytic efficiency. Additionally, the base TBABr also plays a significant role in this catalysis process and the control experiment indicated that there was no cycloaddition product without adding it, however, TBABr itself was ineffective to catalyze this cycloaddition reaction, proving the synergistic effect of MOF catalyst 1 with TBABr as co-catalyst. The kinetic tracking of the reaction was also performed (Figure 6d). Under the optimize reaction conditions, there was a very low conversion in the first two hours, while most of the substrates were converted into the final product after 8 h reaction time and almost quantitatively converted after 12 h. After 6 h reaction, the catalyst 1 was removed by filtration, but no additional conversions were observed for the next 6 h of the same catalytic system. This result gave a proof that the catalytic reaction has been shut down after the filtration of catalyst 1, and thus 1 was a true and stable heterogeneous catalyst in the catalytic system without leaching of metal ions occurs during the catalysis process. To the best of our knowledge, the high catalytic efficiency of 1 is comparable to the other reported Cu-based MOFs catalysts⁴⁷⁻⁵¹ with a relative low addition of the base TBABr, which are significantly less than the other metal-based MOFs catalysts, for the cycloaddition of CO2 to epoxides under the similar conditions (Table S1).



Figure 6. (*a*) The effect of temperature on the conversion and selectivity of cycloaddition catalysis under given conditions; (*b*) the effect of the CO_2 pressure on the conversion and selectivity of cycloaddition catalysis under given conditions; (*c*) the effect of the amount of catalyst on the conversion and selectivity of cycloaddition catalysis under given conditions; (*d*) the effect of reaction time on the conversion and selectivity of cycloaddition catalysis and selectivity of cycloaddition catalysis under given conditions; (*d*) the effect of reaction time on the conversion and selectivity of cycloaddition catalysis and leaching test by removing the catalyst after 6 h reaction.

It is worth mentioning that 1 showed the excellent catalytic activity substrates of various epoxides with CO₂ under the same conditions (Table 1). No significant variation in the conversion was observed when the phenyl group in epoxides was substituted for the aliphatic chain (Entry 2, >99%), and when increasing the carbon chain length, a 93% conversion could be afforded under the same conditions (Entry 3). Additionally, glycidyl phenyl ether as the starting substrate also gave >99% of the corresponding cyclic carbonates (Entry 4), and the benzyl glycidyl ether (Entry 5) was converted to the respective product with 96% conversion. The slightly decreased catalytic capability for Entry 3 and 5 could be attributed to the steric hindrance of the larger epoxides, which might impede the diffusion rate into the catalyst cavities for the activation. Generally speaking, these results could draw a conclusion that the synthesized catalyst 1 exhibited the potential development for further practical applications of CO₂ chemical fixation into value-added chemicals.

The recycling test has been performed to evaluate the stability of catalyst **1** in this catalytic system, since the recyclability is another essential feature of the catalysts for further practical applications. After the reaction, the catalyst was recycled by simply filtration, and washed with acetone to remove the adsorbed species. As shown in Figure 7a, the recycled catalyst **1** could be reused for successive four cycles without significant loss of catalytic performance (>99%, 98.2%, 95% and 92.8% conversions, respectively and all >99% selectivity) and the PXRD patterns of the catalyst **1** were

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Table 1. 1-catalyzed cycloaddition of various epoxides with CO₂.

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Conditions: epoxide substrates (4 mmol), 1 (5 mol%), TBABr (0.5 mol%), CO₂ (5 atm), 12 h, 100 °C.



Figure 7. (*a*) Recycling experiments of styrene oxide with CO_2 under optimal conditions at each run; (*b*) PXRD patterns of catalysts after used.

maintained. From a structure point of view, the MOF could contact with the substrates by the multiple potential intermolecular interactions, such as hydrogen bonding and $\pi \cdots \pi$ interactions of the multi-aromatic rings in the backbone of MOF to enter its accessible pores and activate them by the unsaturated Cu(II) centers as Lewis activity site. A possible mechanism of 1-catalyzed cycloaddition of epoxide with CO₂ was proposed and illustrated as Figure 8. In the present work, the Lewis acidic Cu(II) centers could activate the oxygen atom in epoxy ring, and meanwhile, TBABr attacked the less-hindered methylene carbon atom in the activated epoxy ring, leading to the ring open with Cu(II) ion coordinated to oxygen atom and Br⁻ anion coordinated to carbon atom of the epoxide substrate. Then, the activated Cu coordinated bromo-alkoxide intermediate reacted with CO₂ to form a tetrel bond with the oxygen atom in the intermediate and a C-O bond between the intermediate and the negatively charged oxygen of CO₂ with Cu(II) site binding. In the final step, the cyclic carbonate was produced via the removal of bromide ion and ring-closing of the metal carbonate intermediate and the catalyst and TBABr were regenerated at the same time^{52, 53}.



Figure 8. Proposed mechanism of **1**-catalyzed cycloaddition of epoxide with CO₂.

In order to testify the above speculative mechanism of the potential interaction between catalyst **1** and substrate styrene oxide, FT-IR of **1** before and after soaked in styrene oxide for 3 days have been further explored. As shown in Figure S7, two new bands in the spectrum of **1** after soaked (**1**@styrene oxide) were observed at 1252 and 985 cm⁻¹, assigned to the antisymmetric stretching vibration and symmetric stretching vibration of C-O-C in the free styrene oxide molecules, respectively, but with weaker intensities, which might attribute to the C-O···*M* interaction between the styrene oxide molecules and Cu(II) centers. These results indicated that the porous catalyst **1** could interact with the substrate styrene oxide within its accessible cavities during the catalytic process, which was benefit for the next activation step.

Conclusions

In conclusion, a new synthesis approach of Cu(II)-INA-based metal-organic framework has been presented by the cleavage and rearrangement of N,N'-bis(4-picolinoyl)hydrazine ligand into INA moiety as connected node to coordinate with Cu(II) ions via solvothermal synthesis. The obtained MOF with an infinite Cu-O double chains and exposed metal centres, exhibited a highly thermal and solvent stabilities, together with the adsorption ability towards CO2. Cycloaddition catalysis of CO_2 with epoxides by **1** as heterogeneous catalyst has been explored and suggested almost complete conversion and selectivity under solvent free conditions. Mechanism studies revealed that the Cu-nodes in MOF could serve as efficient Lewis active catalytic sites for the catalysis. Additionally, the Cu(II)-INA-based MOF catalyst displayed a wide scope for a range of epoxides with high conversions and could be reused for four cycles without the decrease of the catalytic activity, indicating its potential development for further practical

applications of \mbox{CO}_2 chemical fixation into value-added chemicals.

Author Contributions

Lan Qin: Investigation, Writing – original draft.

Yu Pan: Investigation.

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Lei Yu: Formal analysis, Investigation.

Ranran Huai: Investigation.

Yong Dou: Investigation, Visualization.

Lu Yang: Conceptualization, Writing – review & editing, Funding acquisition.

Zhen Zhou: Resources, Writing – review & editing, Funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 M. Z. Jacobson, *Energy Environ. Sci.*, 2009, **2**, 148-173.
- 2 L. Li, N. Zhao, W. Wei, Y. H. Sun, Fuel, 2013, 108, 112-130.
- P. Markewitz, W. Kuckshinrichs, W. Leitner, J. Linssen, P. Zapp,
 R. Bongartz, A. Schreibera, T. E. Müller, *Energy Environ. Sci.*, 2012, 5, 7281-7305.
- 4 S. Dabral, T. Schaub, Adv. Synth. Catal., 2019, 361, 223-246.
- 5 W.-G. Cui, G.-Y. Zhang, T. L. Hu, X.-H. Bu, *Coordin. Chem. Rev.* 2019, **387**, 79-120.
- 6 D.-C. Liu, D.-C. Zhong, and T.-B. Lu, *EnergyChem*, 2020, **2**, 100034.
- 7 Y.-N. Gong, B.-Z. Shao, J.-H. Mei, W. Yang, D.-C. Zhong and T.-B. Lu, Nano Res., 2021, DOI: 10.1007/s12274-021-3519-4.
- 8 X. B. Lu, D. J. Darensbourg, *Chem. Soc. Rev.*, 2012, **41**, 1462-1484.
- 9 H. M. He, J. A. Perman, G. S. Zhu, S. Q. Ma, *Small* 2016, **12**, *46*, 6309-6324.
- 10 C. Martín, G. Fiorani, A. W. Kleij, ACS Catal., 2015, 5, 1353-1370.
- 11 Z. Zhou, L. Yang, Y. F. Wang, C. He, C. Y. Duan, *Current Organic Chemistry*, 2018, **22**, 1809-1824.
- 12 T, K. Pal, D. De, P. K. Bharadwaj, *Coord. Chem. Rev.*, 2020, **408**, 213173.
- 13 E. M. Beccalli, G. Broggini, M. Martinelli, S. Sottocornola, *Chem. Rev.*, 2007, **107**, 5318-5365.
- 14 Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun.*, 2015, **6**, 5933.
- 15 I. Omae, Coordin. Chem. Rev., 2012, 256, 1384-1405.
- 16 P.-Z. Li, X.-J. Wang, J. Liu, J. Liang, J. Y. J. Chen and Y. L. Zhao, *CrystEngComm*, 2017, **19**, 4157-4161.
- 17 S.-L. Hou, J. Dong, B. Zhao, Adv. Mater., 2019, 1806163.
- 18 J. W. Maina, C. Pozo-Gonzalo, L. X. Kong, J. Schütz, M. Hillc, L. F. Dumée, *Mater. Horiz.* 2017, **4**, 345-361.
- 19 G. Sneddon, A. Greenaway, H. H. P. Yiu, *Adv. Energy Mater*. 2014, **4**, 1301873.

- 20 A. C. Kathalikkattil, R. Babu, J. Tharun, R. Roshan, D. W. Park, Catal. Surv. Asia., 2015, **19**, 223-235. DOI: 10.1039/D1CE00888A
- F. Guo and X. L. Zhang, *Dalton Trans.*, 2020, **49**, 9935-9947.
 W. S. Liu, L. J. Zhou, G. Li, S. L. Yang and E. Q. Gao, *ACS*
- *Sustainable Chem. Eng.*, 2021, **9**, 1880–1890.
- 23 A. Schoedel, M. Li, D. Li, M. O'Keeffe, O. M. Yaghi, *Chem. Rev.*, 2016, **116**, 12466-12535.
- 24 B. Li, H. M. Wen, Y. J. Cui, W. Zhou, G. D. Qian, B. L. Chen, Adv. Mater., 2016, 28, 8819-8860.
- 25 Z. J. Zhang, M. J. Zaworotko, Chem. Soc. Rev., 2014, 43, 5444-5455.
- 26 H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science*, 2013, **341**, 1230444.
- 27 J. R. Li, J. Sculley, H. C. Zhou, Chem. Rev., 2012, 112, 869-932.
- 28 P. Ramaswamy, N. E. Wong, G. K. H. Shimizu, *Chem. Soc. Rev.*, 2014, **43**, 5913-5932.
- 29 L. Yang, D. P. Zhang, H. Yan, Y. H. Dong, Z. Zhou, S. N., *Inorg. Chem.* 2019, 58, 4067-4070.
- 30 W. P. Lustig, J. Li, Coord. Chem. Rev. 2018, 373, 116–147.
- 31 H.-Y. Li, S.-N. Zhao, S.-Q. Zang, J. Li, Chem. Soc. Rev., 2020, 49, 6364-6401.
- 32 X. Lu, Y. Zhao, X.-L. Wang, G.-C. Liu, N. Xu, H.-Y. Lin and X. Wang, *CrystEngComm*, 2021, **23**, 3828-3837.
- 33 M. L. Ding, Rob. W. Flaig, H.-L. Jiang, O. M. Yaghi, Chem. Soc. Rev., 2019, 48, 2783-2828.
- 34 Z. Zhou, C. He, J. H. Xiu, L. Yang, C. Y. Duan, J. Am. Chem. Soc. 2015, 137, 15066-15069.
- 35 J. W. Liu, L. F. Chen, H. Cui, J. Y. Zhang, L. Zhang, C. Y. Su, Chem. Soc. Rev. 2014, 43, 6011-6061.
- 36 S. S. Dhankhar; B. Ugale, C. M. Nagaraja, *Chem. Asian J.*, 2020, 15, 2403-2427.
- 37 A. H. Chughtai, N. Ahmad, H. A. Younus, A. Laypkov, F. Verpoort, Chem. Soc. Rev., 2015, 44, 6804-6849.
- 38 M. H. Beyzavi, C. J. Stephenson, Y. Liu, O. Karagiaridi, J. T. Hupp, O. K. Farha, Front. Energy Res., 2015, 2, 63.
- 39 C. Wang, J. Ying, X.-Y. Zhang, B.-Y. Zhang, A.-X. Tian and X.-L. Wang, *CrystEngComm*, 2021, 23, 2424–2431.
- 40 J.-H. Deng, J. Luo, Y.-L. Mao, S. Lai, Y.-N. Gong, D.-C. Zhong and T.-B. Lu, *Sci. Adv.*, 2020, 6, eaax 9976.
- 41 M. Du, Z.-H. Zhang, X.-G. Wang, X.-J. Zhao, *Inorg. Chim. Acta*, 2009, **362**, 1358-1360.
- 42 C. Z-J. Lin, S. S-Y. Chui, S. M-F. Lo, F. L-Y. Shek, M. M. Wu, K. Suwinska, J. Lipkowski, I. D. Williams, *Chem. Commun.*, 2002, 1642-1643.
- 43 S. Mao, J.-W. Shi, G. Sun, Y. Zhang, X. Jia, Y. Lv, B. Wang, Y. Xu, Y. Cheng, *Chem. Eng. J.*, 2021, **404**, 126533.
- 44 N. K. Gupta, S. Kim, J. Bae, K. S. Kim, Chem. Eng. J., 2021, 411, 128536.
- 45 G. Verma, S. Kumar, T. Pham, Z. Niu, L. Wojtas, J. A. Perman, Y. S. Chen, S. Q. Ma, *Cryst. Growth Des.*, 2017, **17**, 2711-2717.
- 46 J.-S. Choi, W.-J. Son, J. Kim, W.-S. Ahn, *Microporous Mesoporous Mater.*, 2008, **116**, 727-731.
- 47 X. Y. Guo, Z. Zhou, C. Chen, J. F. Bai, C. He, C. Y. Duan, ACS Appl. Mater. Interfaces, 2016, 8, 31746-31756.
- 48 J. Ai; X. Min, C. Y. Gao, H. R. Tian, S. Dang, Z. M. Sun, *Dalton Trans.*, 2017, **46**, 6756-6761.
- 49 J. M. Gu, X. D. Sun, X. Y. Liu, Y. Yuan, H. Y. Shan, Y. L. Liu, *Inorg. Chem. Front.*, **2020**, *7*, 4517-4526.
- 50 Z. J. Tavakoli, CO2 Util., 2020, 41, 101288.
- 51 A. K. Gupta, N. Guha, S. Krishnan, P. Mathur, D. K. Rai, J. CO₂ Util., 2020, **39**, 101173.
- 52 V. Guillerm, Ł. J. Weseliński, Y. Belmabkhout, A. J. Cairns, V. D'Elia, Ł. Wojtas, K. Adil, M. Eddaoudi, Nat. Chem., 2014, 6, 673-680.
- 53 X. Huang, Y. Chen, Z. Lin, X. Ren, Y. Song, Z. Xu, X. Dong, X. Li, C. Hu, B. Wang, *Chem. Commun.*, 2014, **50**, 2624-2627.