A MIXED-METAL STRATEGY FOR THE FAST SYNTHESIS OF METAL-ORGANIC FRAMEWORKS UNDER AMBIENT CONDITIONS

Field of Invention

The invention relates to metal organic frameworks (MOFs) having a UTSA-16 structure. In particular, the invention relates to MOFs having good CO_2 capture performance, and methods for making the MOFs that are significantly faster under milder reaction conditions.

Background

The listing or discussion of a prior-published document in this specification should not necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge.

Metal-organic frameworks (MOFs) are porous crystalline materials with a modular synthetic chemistry. Due to high compositional tuneability, they are amenable to precise materials engineering allowing excellent performance in numerous commercially interesting applications. For example, certain MOFs have exhibited large CO_2 uptake capacities, high CO_2 selectivity and prolonged stability making them excellent CO_2 capture sorbents. The development of scalable and sustainable protocols is an essential step towards actual commercial applications of MOFs. This is because most intended MOF applications entail large footprints (e.g., ~3000 tonnes sorbent for a capture unit integrated with a 500 MW coal-based power facility). As such, the environmental impact and cost of manufacture substantially affect the overall economic viability of the process.

UTSA-16 is a highly promising MOF material for CO_2 capture by adsorption due to the isotherm features, mechanism of adsorption, and stability. Almost all reported syntheses for this material are based on the protocol in *Journal of the American Chemical Society* **2005,** *127* (47), 16352-16353, where only the vessel and solvent volume are adjusted to meet the required scale of synthesis. The reported protocol involves mixing the precursor raw materials in 50%/50% ethanol-water mixed solvent, followed by isothermal heating for a fixed duration at 120 °C, corresponding to autogenous pressures of 4 to 6 bar. Such solvothermal synthetic approach requires specialized reactors, introducing additional capital costs for production, and precludes the use of common glass equipment, where typical pressure rating is below 2 bar. Ongoing attempts to scale-up this material are hindered by failure to reduce the synthetic temperature below the boiling point of the solvent. In addition, the prevailing protocol also

necessitates extended crystallization time (up to 2 days). The reaction efficiency, estimated in terms of space-time yield, is 25 kg $(m^3\ day)^{-1}$. This needs to be increased by approximately ten-fold to be commercially viable. The ternary phase equilibria of deprotonated ligand salt in solution (i.e., tripotassium citrate + ethanol + water) involves a liquid-liquid phase separation. In the presence of cobalt salt, viscous gelation occurs. It is understood that mixing is detrimentally affected by high viscosity.

Transitioning from a closed-solvothermal condition to open-reflux synthesis with the usage of safe and cheap solvents is an important step towards scalable protocols. Reflux synthesis of MOFs leverages proven manufacturing process technologies and has been demonstrated in the production of an aluminium fumarate MOF at tonne-scale. The capital equipment cost, safety compliance cost and energy cost may all be reduced when a solvothermal process is replaced with a reflux synthetic process.

Reaction optimization of MOFs are highly system-specific. Most of the reported reflux synthetic protocols described for low-valence MOFs and for high-valence MOFs concern binary systems with a single metal precursor and single organic linker. These protocols do not accommodate the synthesis of materials having higher structural complexity. UTSA-16 possesses a unique chemical feature whereby metal species within distinct structural motifs exhibit different coordination geometries. The commonly accepted crystal-field theory predicts that one of these coordination geometries is significantly more favored in terms of stability. This has direct implications for synthesis, because conditions not conducive for the formation of the less stable motif will substantially compromise the kinetics and accordingly, the yield and efficiency of product formation.

There is therefore a need for improved materials and methods which can produce USTA-16 in a faster time under milder reactions, while retaining good CO_2 capture performance.

Summary of Invention

It has been surprising found that incorporating a secondary metal component provides UTSA-16 analogues with improved CO_2 capture performance that can be formed under significantly milder conditions and in a shorter time. This enables use of conventional laboratory equipment and open-reflux synthesis. The optimized protocols are more compatible with industrial production, paving the way for the mass production of these promising materials.

Aspects and embodiments of the current invention are listed in the following numbered clauses.

1. A metal organic framework (MOF) having a UTSA-16 structure, where the composition comprises:

from 0 to 80 mol% of the total metal in the MOF is a first metal selected from one or more of the group consisting of Cr, Mn, Fe, Ni, Cu, and Co; and

from 20 to 100 mol% of the total metal in the MOF is a second metal selected from one or more of the group consisting of Cd, Mn, and Zn.

2. The MOF according to Clause 1, wherein the second metal is Zn.

3. The MOF according to Clause 1 or Clause 2, wherein the second metal is present in an amount of from 25 to 100 mol% of the total metal present in the MOF.

4. The MOF according to Clause 3, wherein the second metal is present in an amount of from 50 to 75 mol% of the total metal present in the MOF.

5. The MOF according to any one of the preceding clauses, wherein the first metal is selected from Fe and Co.

6. The MOF according to Clause 5, wherein the first metal is Co.

7. The MOF according to any one of the preceding clauses, wherein the first metal is present in an amount of from 25 to 50 mol% of the total metal present in the MOF.

8. The MOF according to any one of the preceding clauses, wherein the second metal preferentially occupies a tetrahedral metal site within the MOF.

9. The MOF according to any one of the preceding clauses, wherein the majority of the first metal, when present, occupies an octahedral metal site within the MOF.

10. The MOF according to any one of the preceding clauses, wherein the first metal, when present, and second metal preferentially occupy an octahedral metal site and a tetrahedral metal site within the MOF, respectively.

11. The MOF according to any one of the preceding clauses, wherein the MOF has a saturated CO_2 uptake of up to 5.0 mmol/g, optionally wherein the MOF has a saturated CO_2 uptake of from 2.5 to 4.5 mmol/g, such as from 3.39 to 3.50 mmol/g.

12. The MOF according to any one of the preceding clauses, wherein the MOF has a breakthrough CO_2 working capacity of up to 2.2 mmol/g, such as from 1.0 to 1.8 mmol/g, such as from 1.65 to 1.70 mmol/g.

13. A method of forming a MOF according to any one of the preceding clauses, wherein the method comprises the step of aging a mixture comprising from a first metal precursor, a second metal precursor, a base, citric acid, a first solvent and a second solvent for a period of time at a temperature of from 15 to 200 °C, wherein:

the first metal precursor is selected from one or more of the group consisting of Cr, Mn, Fe, Ni, Cu, and Co;

the second metal precursor selected from one or more of the group consisting of Cd, Mn, and Zn; and

the metal in the first metal precursor is present in an amount of from 0 to 80 mol% of the total amount of metal in the mixture; and

the metal in the second metal precursor is present in an amount of from 20 to 100 mol% of the total amount of metal in the mixture.

14. The method according to Clause 13, wherein the temperature is from 20 to 150 °C.

15. The method according to Clause 14, wherein the temperature is from 40 to 120 °C, such as temperature of from 60 to 80 °C.

16. The method according to Clause 15, wherein the temperature used results in one or both solvents being refluxed.

17. The method according to any one of Clauses 13 to 16, wherein:

(a) the first solvent is water and the second solvent is an alkyl alcohol (e.g. the alkyl alcohol is methanol, a propanol or, more particularly, ethanol); and/or

(b) the base is a metal hydroxide (e.g. the base is KOH); and/or

(c) the method is performed under ambient atmospheric conditions (e.g. standard pressure).

18. The method according to any one of Clauses 13 to 17, wherein the first and second metal precursors are a metal salt, where the metal is in a cationic form, which is balanced by one or more counterions selected from one or more of halide (e.g. chloride), nitrate, sulfate, hydroxide, oxide, acetate anion, and hydrates thereof

19. The method according to any one of Clauses 13 to 18, wherein:

(a) the second metal precursor is $Zn(OAc)_2$ or a hydrate thereof (e.g. $Zn(OAc)_2 \cdot 2H_2O$); and/or

(b) the metal in the second metal precursor is present in an amount of from 25 to 100 mol%, such as from 50 to 75 mol% of the total metal present in the mixture.

20. The method according to any one of Clauses 13 to 19, wherein:

(a) the first metal precursor is $Fe(OAc)_2$, $Co(OAc)_2$ or hydrates thereof (e.g. $Co(OAc)_2 \cdot 4H_2O$); and/or

(b) the metal in the first metal precursor is present in an amount of from 25 to 50 mol%, such as from 50 to 75 mol%, such as from 25 to 50 mol% of the total metal present in the mixture.

21. A method of capturing CO_2 comprising the step of exposing a material comprising a MOF as described in any one of Clauses 1 to 12 to an environment containing CO_2.

Drawings

Figure 1. (a) Representation of inorganic building units within UTSA-16 and their respective formation tendencies when using different metal precursors. (b) Representation of monometallic and mixed-metal synthetic approaches for the synthesis of UTSA-16 with different formation kinetics.

Figure 2. (a) PXRD patterns of mixed-metal UTSA-16-type MOFs with varying Zn loadings (*x* represents the feed molar fraction of Zn in mixed Zn/Co precursors). (b) Reported Co–O bond distances of tetrahedral and octahedral Co motifs in UTSA-16. Fourier transforms of k^3-weighted EXAFS data collected at Co K-edge (c) and Zn K-edge (d). (e) Position of first peak maxima of FT-EXAFS data as a function of Zn loading *x*. Up-facing triangle: data from Co K-edge. Down-facing triangle: data from Zn K-edge. (f) The fraction of either metallic species occupying the tetrahedral sites, $Y_{Co,tet}$ and $Y_{Zn,tet}$, as a function of Zn loading *x*. Note that $Y_{Co,tet}$ ($x = 0$) and $Y_{Zn,tet}$ ($x = 1$) are 0.33 based on SCXRD data.

Figure 3. (a) PXRD patterns of UTSA-16-Zn-*0* obtained after incubation for 24 h at various temperatures. (b) PXRD patterns of UTSA-16-Zn-*0.50* obtained after incubation for 24 h at various temperatures. (c) Growth kinetics of UTSA-16-Zn-*x* based on *ex-situ* experiments. Sigmoidal fit (solid line) is presented to guide the eye.

Figure 4. (a) CO_2 isotherms at 298 K of UTSA-16-Zn-*x*. (b) Wet CO_2 (relative humidity: 85%) breakthrough curves at 298 K of UTSA-16-Zn-*x*. (c) Isosteric heat of CO_2 adsorption of UTSA-16-Zn-*x*. (d) IAST selectivity of UTSA-16-Zn-*x* for 10:90 CO_2/N_2 mixed gas at 298 K under varying feed pressures.

Figure 5. Optical micrographs of UTSA-16-Zn-*0.25*. (a,b, scale bar: 50 μm) and UTSA-16(Co) (c,d, scale bar: 200 μm). The droplet is liquid/gel of relatively high viscosity.

Figure 6. FTIR spectra of UTSA-16-Zn-*x*: 400-4000 cm^{-1} (left) and 1000-1800 cm^{-1}(right).

Figure 7. DSLF fits of CO_2 isotherms at 273 and 298 K for UTSA-16-Zn-*x* materials.

Figure 8. Comparison of TGA thermograms (recorded in air, 150-800 °C, heating rate of 5 °C/min) for UTSA-16-Zn-*x* materials.

Figure 9. Photograph of UTSA-16-Zn-*x* against white A4 paper: (from left to right) *x* = 0 (pure Co), 0.25, 0.50, 0.75, 1.00 (pure Zn).

Figure 10. Co K-edge and Zn K-edge XANES spectra of bimetallic UTSA-16-Zn-*x* materials.

Figure 11. Results of the EXAFS fitting. Experimental data are shown as white circles, fitted curves are presented as full lines.

Figure 12. Scheme of home-built breakthrough setup used in this study.

Figure 13. Uncorrected breakthrough curves for UTSA-16-Zn-*x* materials under different conditions. Empty symbols – N_2, filled symbols – CO_2.

Description

It has been surprising found that incorporating a second metal as described herein provides mixed-metal UTSA-16 analogues that can be prepared under milder conditions relative to monometallic UTSA-16. These compounds possess an asymmetric site distribution of the first metal and second metal, and benefit from expanded reaction space and faster reaction kinetics. Additionally, the material disclosed herein may have improved gas separation properties and the underlying structure of UTSA-16 is maintained.

Thus, in a first aspect of the invention, there is provided a metal organic framework (MOF) having a UTSA-16 structure, where the composition comprises:

from 0 to 80 mol% of the total metal in the MOF is a first metal selected from one or more of the group consisting of Cr, Mn, Fe, Ni, Cu, and Co; and

from 20 to 100 mol% of the total metal in the MOF is a second metal selected from one or more of the group consisting of Cd, Mn, and Zn.

In embodiments herein, the word "comprising" may be interpreted as requiring the features mentioned, but not limiting the presence of other features. Alternatively, the word "comprising" may also relate to the situation where only the components/features listed are intended to be present (e.g. the word "comprising" may be replaced by the phrases "consists of" or "consists essentially of"). It is explicitly contemplated that both the broader and narrower interpretations can be applied to all aspects and embodiments of the present invention. In other words, the word "comprising" and synonyms thereof may be replaced by the phrase "consisting of" or the phrase "consists essentially of" or synonyms thereof and *vice versa*.

The phrase, "consists essentially of" and its pseudonyms may be interpreted herein to refer to a material where minor impurities may be present. For example, the material may be greater than or equal to 90% pure, such as greater than 95% pure, such as greater than 97% pure, such as greater than 99% pure, such as greater than 99.9% pure, such as greater than 99.99% pure, such as greater than 99.999% pure, such as 100% pure.

When used herein, the USTA-16 structure is taken to mean that the MOFs disclosed herein share a similar structure to that disclosed in the microporous cobalt citrate framework USTA-16 (University of Texas at San Antonio-16). However, for the avoidance of doubt, the compounds disclosed here use different constituent components.

As noted above, the first metal, when present, may be selected from one or more of the group consisting of Cr, Mn, Fe, Ni, Cu, and Co. For example, the first metal (when present) may be selected from one or both of Fe and Co or, more particularly, the first metal (when present) may be Co. As will be appreciated from the above, the first metal may or may not be present in the MOFs of the current invention. When the MOF is present, the first metal may represent up to 80 mol% of the total metal in the MOF. In particular embodiments of the invention when the first metal is present, it may represent from 25 to 50 mol% of the total metal present in the MOF.

As noted herein, the second metal may be selected from one or more of the group consisting of Cd, Mn, and Zn. In more particular embodiments that may be mentioned herein, the second metal may be Zn.

As will be appreciated, the second metal may be the only metal present in the MOF (i.e. the first metal represents 0 mol% and the second metal represents 100 mol% of the total metal in the MOF), but it may more typically be present in combination with the first metal. Thus, in embodiments of the invention, the second metal may represent from 20 to 80 mol%, such as from 25 to 100 mol%, such as from 50 to 75 mol% of the total metal in the MOF.

Thus, in embodiments of the invention, the MOF may contain:

(a) 0 mol% of the first metal and 100 mol% of the second metal;
(b) 25 mol% of the first metal and 75 mol% of the second metal;
(c) 50 mol% of the first metal and 50 mol% of the second metal;
(d) 75 mol% of the first metal and 25 mol% of the second metal; and
(e) 80 mol% of the first metal and 20 mol% of the second metal,

where 100 mol% represents the total metal in the MOF.

In microporous cobalt citrate framework USTA-16, there are tetrameric [Co_4] clusters and monomeric [$Co(O_2CR)_4$] units, where the Co(II) species adopt octahedral and tetrahedral coordination environments, respectively.

In embodiments of the invention where only the second metal is present, then by analogy, the second metal will occupy both the octahedral and tetrahedral coordination environments. However, when the first metal is also present, the second metal will preferentially occupy tetrahedral metal sites within the MOF. For example, the majority of the second metal may occupy a tetrahedral metal site within the MOF. When used herein "majority" may mean 51 mol% of the second metal, such as 55 mol%, 60 mol% 70 mol, 75 mol%, 80 mol%, 85 mol%, 90 mol%, 95 mol%, or 99 mol% occupies the tetrahedral metal sites.

Similarly, when only a small amount of the second metal is present (e.g. 20 mol%), then the first metal may occupy both the octahedral and tetrahedral coordination environments. However, the first metal may display a preferential occupation of the octahedral metal sites. For example, the majority of the first metal, when present, may occupy an octahedral metal site within the MOF. When used herein "majority" may mean 51 mol% of the first metal, such

as 55 mol%, 60 mol% 70 mol, 75 mol%, 80 mol%, 85 mol%, 90 mol%, 95 mol%, or 99 mol% occupies the octahedral metal sites.

Thus, in embodiments of the invention, where both the first and second metals are present, then the first metal and second metal preferentially occupy an octahedral metal site and a tetrahedral metal site within the MOF, respectively.

For example, when there is a 50:50 mixture of Zn and Co as the second and first metals, respectively, then 65 mol% of Zn may occupy the tetrahedral metal sites. Further, when there is a 25:75 mixture of Zn and Co as the second and first metals, respectively, then 82 mol% of Zn may occupy the tetrahedral metal sites.

The MOFs disclosed herein may have a specific surface area of from 300 to 1500 m^2g^{-1}, such as from 500 to 1000 m^2g^{-1}, such as from 691 to 863 m^2g^{-1}.

The MOFs disclosed herein may be useful in CO_2 capture. As such, the MOFs of the current invention may display a saturated CO_2 uptake of up to 5.0 mmol/g, optionally wherein the MOF has a saturated CO_2 uptake of from 2.5 to 4.5 mmol/g, such as from 3.39 to 3.50 mmol/g. Additionally or alternatively, the MOFs of the current invention may have a breakthrough CO_2 working capacity of up to 2.2 mmol/g, such as from 1.0 to 1.8 mmol/g, such as from 1.65 to 1.70 mmol/g.

The MOFs disclosed herein may be conveniently prepared. As mentioned, the MOFs disclosed herein may be formed under milder conditions (such as lower temperature or pressure). Thus, in a second aspect of the invention, there is provided a method of forming a MOF as described herein, wherein the method comprises the step of aging a mixture comprising from a first metal precursor, a second metal precursor, a base, citric acid, a first solvent and a second solvent for a period of time at a temperature of from 15 to 200 °C, wherein:

the first metal precursor is selected from one or more of the group consisting of Cr, Mn, Fe, Ni, Cu, and Co;

the second metal precursor selected from one or more of the group consisting of Cd, Mn, and Zn; and

the metal in the first metal precursor is present in an amount of from 0 to 80 mol% of the total amount of metal in the mixture; and

the metal in the second metal precursor is present in an amount of from 20 to 100 mol% of the total amount of metal in the mixture.

Any suitable temperature in the range of from 15 to 200 °C may be used. For example, the temperature may be from 20 to 150 °C, such as from 40 to 120 °C, such as temperature of from 60 to 80 °C. In another embodiment, the temperature may be room temperature (that is, from 20 to 30 °C, such as temperature of about 25 °C).

As noted above, the method makes use of a first and second solvent. As such, the temperature used in the preparation may result in one or both solvents being refluxed. The use of a reflux synthetic process as compared to a solvothermal process may reduce equipment cost, safety compliance cost and energy cost.

Any suitable solvents may be used as the first and second solvent. For example, the first solvent may be water and the second solvent may be an alkyl alcohol (e.g. the alkyl alcohol is methanol, a propanol or, more particularly, ethanol).

Any suitable base may be used in the method disclosed herein. For example, the base may be a metal hydroxide (e.g. the base is KOH).

The method above may be performed under any suitable pressure. For example, the method may be performed under ambient atmospheric conditions (e.g. standard pressure). Again, this may reduce costs associated with the preparation of the MOF.

Any suitable chemical can be used as the first and second metal precursors. As will be appreciated, the chemicals selected will need to include the first and/or second metal to be able to act as a precursor. In embodiments of the invention that may be mentioned herein, the first and second metal precursors may be a metal salt, where the metal is in a cationic form, which is balanced by one or more counterions selected from one or more of halide (e.g. chloride), nitrate, sulfate, hydroxide, oxide, acetate anion, and hydrates thereof.

In particular embodiments that may be mentioned herein, the second metal precursor may be $Zn(OAc)_2$ or a hydrate thereof (e.g. $Zn(OAc)_2 \cdot 2H_2O$). Additionally or alternatively, the metal in the second metal precursor may be present in an amount of from 25 to 100 mol%, such as from 50 to 75 mol% of the total metal present in the mixture.

In particular embodiments that may be mentioned herein,the first metal precursor is $Fe(OAc)_2$, $Co(OAc)_2$ or hydrates thereof (e.g. $Co(OAc)_2 \cdot 4H_2O$). Additionally or alternatively, the metal in

the first metal precursor may be present in an amount of from 25 to 50 mol%, such as from 50 to 75 mol%, such as from 25 to 50 mol% of the total metal present in the mixture.

As noted above, the MOF disclosed herein may be useful in capturing CO_2. Thus, in a third aspect of the invention, there is provided a method of capturing CO_2 comprising the step of exposing a material comprising a MOF as described herein to an environment containing CO_2.

Further aspects and embodiments of the invention will now be described by reference to the following non-limiting examples.

Examples

Pristine UTSA-16(Co) contains tetrameric [Co_4] clusters and monomeric [$Co(O_2CR)_4$] units coexisting in the framework, wherein Co^{II} species adopt octahedral and tetrahedral coordination environments, respectively. In turn, these units form nodes with octahedral and trigonal connectivity, resulting in an anatase-type net. According to the crystal-field theory, the presence of weak-field ligands such as carboxylate and solvent molecules heavily prefers Co^{II} in octahedral coordination. As a result, the low thermodynamic stability of tetrahedral Co^{II} under the prevailing reaction conditions may reduce the driving force for the formation of the corresponding [$Co(O_2CR)_4$] motif, and in turn, kinetically limit the formation process of this material (**Figure 1a**). We hypothesized that the inclusion of Zn^{II} as the secondary metal component may generate a structurally analogous [$Zn(O_2CR)_4$] motif in the framework, because Zn^{II} is known to exhibit tetrahedral geometry in several systems. In a mixed-metal formulation, the one-pot combination of the two metal sources may favor the formation of [Co_4] and [$Zn(O_2CR)_4$] due to their specific coordination preference. Importantly, cationic partitioning can decouple the formation rates of the two motifs from the octahedral-tetrahedral equilibria of the individual precursors, culminating in accelerated formation kinetics of the MOFs (**Figure 1b**). As such, mixed-metal formulations were prepared and analyzed.

Materials and Methods

All the reagents were obtained from commercial sources and used without further purification. Ultrapure water was used as supplied from PU$^+$ purification system (VWR).

Table 1. *List of chemicals*

Chemical	Source
Citric acid, >98%	TCI Singapore
Cobalt acetate tetrahydrate, 98%	Alfa Aesar
Zinc acetate dihydrate, 98+% ACS	Strem Chemicals
Potassium hydroxide, reagent, 98% flakes	Sigma Aldrich
Ethanol, >99.8% ACS	VWR
Methanol, >99.8% ACS	VWR

Powder X-ray diffraction. For phase analysis, PXRD patterns with a 2θ range of 5-40° were collected on a Bruker D8 Advance instrument using Cu K_α radiation (λ = 1.5418 Å). The data were collected at a scanning rate of 2°/min. The FWHM data derived for kinetic experiments were collected on a Rigaku Miniflex 600 diffractometer, also using Cu K_α radiation (λ = 1.5418 Å). The patterns were collected from a 2θ range of 5-15° at a scanning rate of 2°/min.

ICP-OES. The metal compositions of mixed-metal UTSA-16 MOFs were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 7300DV, Perkin Elmer). UTSA-16 samples were digested in 5% HNO_3 aqueous solution, which allowed complete dissolution of the MOF. The solutions were transferred to low density polyethylene tubes (Fisher Scientific) for further tests.

FTIR-ATR spectroscopy. Fourier-transform infrared attenuated total reflectance (FTIR-ATR) spectra were recorded on a Bruker Vertex 70 spectrometer.

UV-Vis spectroscopy. Solid-state UV-Vis spectra were collected with a Shimadzu UV-2450 spectrophotometer in the range of 400-800 nm using $BaSO_4$ as the standard.

XPS analysis. The photoelectron spectra (XPS) were collected using monochromatized Al K_α radiation ($h\nu$ = 1286.71 eV) at 15 kV on a Kratos Axis Ultra XPS system (Kratos Analytical). The measured binding energies (BEs) were referenced according to C 1*s* peak (BE set at 284.5 eV) that corresponds to C−C bonds. The fit of Co high-resolution spectra considered individual peaks for the sites with octahedral coordination environment (O_h), the sites with tetrahedral coordination environment (T_d), with the remaining contributions lumped into a single satellite signal. The fitting was performed simultaneously for the Co $2p_{3/2}$ and Co $2p_{1/2}$ orbitals after Shirley background subtraction. The peak full width at half maximum (FWHM) was constrained to be equivalent for either orbital, whereas the area ratios were constrained

to be 2:1 according to spin-orbit splitting. A similar fitting was undertaken for the Zn 2p region but without the satellite contribution.

TGA experiments. Thermogravimetric analysis (TGA) data were collected using a Shimadzu DTG-60AH under an air flow of 30 mL/min. The samples were heated to 900 °C at a heating rate of 10 °C/min.

EXAFS analysis. X-ray absorption fine structure (XAFS) spectra were collected in transmission mode at room temperature at the XAFCA beamline of the Singapore Synchrotron Light Source. The Co and Zn K-edge spectra were processed following the conventional procedure using the IFEFFIT package.

Synthetic and Activation Procedure

General Procedure 1. Solvothermal synthesis of UTSA-16-Zn-*x* materials

UTSA-16(Co) (or UTSA-16-Zn-*0*) was synthesized with reference to those reported in *Journal of the American Chemical Society* **2005,** *127* (47), 16352-16353. Briefly, $Co(OAc)_2 \cdot 4H_2O$ (1 mmol), KOH (3 mmol), and citric acid (1 mmol) were mixed in H_2O (2.5 mL) to yield a homogeneous aqueous solution. The solution was transferred into a Teflon-lined reaction vessel (15 mL). Next, absolute ethanol (2.5 mL) was introduced while manually stirring the vessel contents. To prepare the bimetallic UTSA-16-Zn-*x* materials, varying amounts of $Co(OAc)_2 \cdot 4H_2O$ were replaced by $Zn(OAc)_2 \cdot 2H_2O$ maintaining the overall stoichiometry of the metal precursor with respect to the ligand and KOH. The reaction mixtures were introduced into a preheated oven (Memmert UF) at 120 °C, kept at that temperature for 2 days, and subsequently retrieved and cooled to room temperature. The protocols yield large single crystals (UTSA-16-Co) or powder which was recovered by centrifugation at 5000 rpm and washed with copious amounts of absolute methanol.

General Procedure 2. Growth of UTSA-16-Zn-*x* single crystals

UTSA-16-Zn-*x* single crystals can be grown at lower temperatures.

To grow **UTSA-16-Zn-*1.00*** single crystals, 500 µL of 0.8 M $Zn(OAc)_2 \cdot 2H_2O$ solution in water was mixed with 500 µL of 0.8 M tripotassium citrate solution in water to yield a clear solution. Then 500 µL of 1 vol.% ethanol in water was added. The homogeneous reaction mixture was transferred to a loosely capped scintillation vial and incubated in a preheated oven at 80 °C.

Crystals observable by optical microscope were recovered after approximately 24 h and kept in mother solution prior to SCXRD characterization.

To grow **UTSA-16-Zn-*0.25*** single crystals, 375 µL of 0.8 M $Co(OAc)_2 \cdot 4H_2O$ solution in water was first mixed with 500 µL of 0.8 M tripotassium citrate solution in water. Next, 125 µL of 0.8 M $Zn(OAc)_2 \cdot 2H_2O$ solution in water and 500 µL of 1 vol.% ethanol in water were sequentially added. The same heating and storage protocols were used as **UTSA-16-Zn-*1.00*** (ICP result: 63.3% Co and 36.7% Zn).

It is noted that the single crystal recipe involves an open system where solvent is lost through evaporation. Hence the measured Co/Zn composition may reasonably differ from the feed and differ for different synthetic conditions. In all cases, however, strong preferential occupancy of sites was observed.

General Procedure 3. Activation of UTSA-16-Zn-*x* materials

Powder samples were exchanged with fresh methanol daily to dissolve excess ligand or metal precursors. The samples were dried under dynamic vacuum at room temperature for 24 h to yield dry solid products. All samples tested in adsorption measurements were activated (see Examples 6 and 7). For characterization, samples were activated beforehand but may be exposed to environment or solvent in the course of the characterization.

Example 1. Synthesis and characterization of UTSA-16-Zn-*x* materials

Mixed-metal MOF samples containing Co and Zn – denoted as UTSA-16-Zn-*x*, where *x* represents the feed molar fraction of Zn in the mixed Zn/Co precursors, and *x* = 0, 0.25, 0.50, 0.75 or 1.00 – were prepared by a one-pot synthetic method in accordance with General Procedure 1.

Structural Characterization

Bulk-phase characterization confirms that all of the samples have the same phase. Powder X-ray diffraction (PXRD) measurements confirm a sole crystalline phase identical to that of UTSA-16 (**Figure 2a)**. Fourier-transform infrared spectroscopy (FTIR) data also confirm the successful synthesis of UTSA-16-type MOFs (**Figure 6)**. The elemental distributions, as measured by inductively coupled plasma optical emission spectrometry (ICP-OES) against Co and Zn standards, agree well with the feed compositions (**Table 2**).

In line with the changing sample colour (**Figure 9**), XPS and UV-Vis spectroscopy data collectively suggest that the distribution of octahedral-tetrahedral species is a function of metal composition in the mixed-metal MOFs.

- The XPS analyses support a decreased T_d spectral contribution relative to O_h when the Zn loading was increased from 0 to 50%.
- The band position of octahedral Co^{2+} occurs at approximately 540 nm (suggesting a reddish-pink colour), whereas the band position of tetrahedral Co^{2+} occurs at around 650 nm. F(R) for monometallic Zn compound (***x*** = 1.00) is close to zero. F(R) for the monometallic Co compound (***x*** = 0) incorporates contributions from both octahedral and tetrahedral Co, consistent with the crystal structure. For the case of ***x*** = 0.50, the contribution at around λ = 625 nm is significantly diminished. This is consistent with a situation whereby Co_{tet} is replaced by Zn_{tet}, since the latter has minimal spectral contribution.

The site occupancies within the bulk mixed-metal MOFs were assessed by measuring room temperature extended X-ray absorption fine structure (EXAFS) spectra of mixed-metal samples with varying Zn loadings (*x* = 0, 0.25, 0.50, 0.75, 1.00) at the Co and Zn K-edges. X-ray absorption near edge structure (XANES) spectra (**Figure 10**) indicate similar valence state of the samples.

The BET method was used to determine the specific surface areas of the UTSA-16-Zn-*x* materials. Adsorption data were collected at 77 K. The obtained specific surface areas are listed below in Table 3.

Table 2 (Table S.4.1) *Calculated Co-Zn ratios for UTSA-16-Zn-x materials from ICP-OES compositional analyses*

Sample	Measurement					Average	s	x	Average	Feed
1-1	Co	12.882	12.875	12.917	ppm	12.891	0.022	0.281	**29.9**	**25**
1-1	Zn	5.032	5.019	5.035	ppm	5.029	0.008		%	%
1-2	Co	17.998	18.114	18.121	ppm	18.078	0.069	0.318		
1-2	Zn	8.385	8.422	8.426	ppm	8.411	0.022			
2-1	Co	9.060	9.037	9.028	ppm	9.042	0.016	0.520	**50.3**	**50**
2-1	Zn	9.821	9.793	9.795	ppm	9.803	0.015		%	%
2-2	Co	10.677	10.682	10.715	ppm	10.691	0.021	0.487		
2-2	Zn	10.123	10.142	10.128	ppm	10.131	0.010			
3-1	Co	5.119	5.156	5.138	ppm	5.138	0.018	0.759	**76.4**	**75**
3-1	Zn	16.162	16.205	16.198	ppm	16.188	0.023		%	%
3-2	Co	5.018	4.996	5.020	ppm	5.012	0.013	0.770		
3-2	Zn	16.775	16.727	16.740	ppm	16.747	0.025			
4-1	Co	0.008	0.006	0.007	ppm	0.007	0.001	1.000	**100.0**	**100**
4-1	Zn	15.802	15.767	15.812	ppm	15.794	0.024		%	%
4-2	Co	0.006	0.006	0.007	ppm	0.007	0.000	1.000		
4-2	Zn	14.028	14.118	14.031	ppm	14.059	0.051			

Table 3. *Calculated BET surface areas of UTSA-16-Zn-x materials*

x	BET S.A. ($m^2 g^{-1}$)
0.00	691
0.25	791
0.50	863
0.75	670
1.00	834

Example 2. Asymmetric site distribution of Co and Zn within UTSA-16-Zn-x

The asymmetric site distribution of Co and Zn within UTSA-16-Zn-x is proven using X-ray absorption spectroscopy.

Fourier-transformed EXAFS data at the Co and Zn K-edge for all the MOF samples are shown in **Figures 2c,d**. Overall similarity of the peak profiles in the R range of 0.8 – 3.2 Å suggests substantially similar coordination environments being adopted by Co and Zn in the mixed-metal MOFs. On the other hand, the peak positions of the mixed-metal samples diverge noticeably across the Co and Zn K-edges (**Figure 2e**). The peak maxima fall in the range of 1.59 – 1.60 Å for the Co K-edge and 1.51 – 1.53 Å for the Zn K-edge, compared to 1.53(6) and 1.55(4) Å for the respective monometallic MOFs. These are statistically significant deviations ($\Delta R > 0.06$ Å). Since the average bond lengths for tetra-coordinated and hexa-coordinated cobalt in UTSA-16 differ significantly (**Figure 2b**), the concerted displacement of peak positions in opposite directions for either element, amidst a preserved crystalline structure, suggests displacement of Co at a specific site by doping Zn element.

Quantitation of the site distribution based on EXAFS data was performed by simultaneous fitting of Co and Zn K-edges of the mixed-metal samples according to the previous treatment of metal site doping in oxide materials (*Physical Review B* **2002,** *66* (22), 224405). The path amplitudes were parameterized using the fraction of either metallic species occupying the tetrahedral sites, $Y_{Co,tet}$ and $Y_{Zn,tet}$. The amplitude parameters were referenced to the monometallic Co and Zn samples, for which the site occupancy has been established prior by SCXRD (*Journal of the American Chemical Society* **2005,** *127* (47), 16352-16353). Other parameters are defined as described below. Results of the combined EXAFS fitting of eight independent data sets are shown in **Figure 11**, while the values of the obtained fitting parameters are reported in Tables 4 and 5. The fits show satisfactory overall agreement with the experimental data. The obtained $Y_{Co,tet}$ indicates that majority of Co species are situated in the octahedral sites for the mixed-metal samples, whereas $Y_{Zn,tet}$ evidences a strong tetrahedral preference for Zn (**Figure 2f**). At $x = 0.25$, Zn occupies 60.3% of tetrahedral sites. This value increases to 84.4% and 93.5% when the x value increases to 0.50 and 0.75, respectively. This strongly indicates an asymmetric site distribution in the mixed-metal materials.

Fit parameterization

The reported and collected crystal data for UTSA-16 (Co) and UTSA-16 (Zn) were imported and the relevant scattering paths were generated using the FEFF programme. Paths with length below 2.5 Å were considered for the fitting. Four path parameters, S_0^2, E_0, ΔR, and σ^2 are considered for each path. The path degeneracy, N, was kept as specified by the FEFF software.

A single global E_0 was specified as a refinable parameter for each edge.

In the monometallic samples, i.e. $\boldsymbol{x}$ = 0 and $\boldsymbol{x}$ = 1, S_0^2 is parameterized as a single refinable parameter. The contribution for the Co_{tet}—O and Co_{oct}—O single scattering paths were weighted by 0.33 and 0.67 respectively, according to their stoichiometry within the solved crystal structure. For UTSA-16-Zn-*x* ($\boldsymbol{x}$ = 1), an analogous weighting scheme was specified. In the bimetallic samples, the distribution between octahedral and tetrahedral sites in the structure was parameterized as $Y_{Co,tet}$ *(x = 0.25)*, $Y_{Zn,tet}$ *(x = 0.25)*, etc. and introduced as a weighting factor. These were then referenced to S_0^2 of the monometallic samples. In other words, S_0^2 of the Co_{tet}—O scatterer in $\boldsymbol{x}$ = 0.25 is defined as ($S_{0,\,x=0}^2 \times Y_{Co,tet}$ *(x = 0.25)*), whereas S_0^2 of the Co_{oct}—O scatterer is [$S_{0,\,x=0}^2 \times$ (1- $Y_{Co,tet}$ *(x = 0.25)*)].

ΔR is parameterized as a single refinable parameter for each edge, weighted by the respective R_{eff} of each path.

The Debye-Waller factors of Co_{tet}—O, Co_{oct}—O, Zn_{tet}—O, Zn_{oct}—O were reasonably expected to differ, and a single refinable parameter was defined for each.

All the parameters were freely varied during the simultaneous fit of all the eight datasets, resulting in the calculation of the global R-factor.

Fitted ΔR and σ^2 converge to physically reasonable values, which are summarized below. Note that the amplitude reduction factor (S_0^2) is slightly above the typical range (0.7 – 1.1) for both edges.

Table 4. *Parameters obtained by combined fitting of eight datasets at Co and Zn K-edges*

Parameter	Value	Parameter	Value
N_{ind}	28	N_{para}	16
$S_0^2{}_{Co}$	1.176 ± 0.116	$S_0^2{}_{Zn}$	1.149 ± 0.206
ΔE_{Co}, *eV*	–0.94 ± 1.34	ΔE_{Zn}, *eV*	4.96 ± 2.46
$Y_{Co,tet}$ *(x = 0.25)*	0.18 ± 0.07	$Y_{Zn,tet}$ *(x = 0.25)*	0.82 ± 0.14
$Y_{Co,tet}$ *(x = 0.50)*	0.12 ± 0.07	$Y_{Zn,tet}$ *(x = 0.50)*	0.65 ± 0.14
$Y_{Co,tet}$ *(x = 0.75)*	0.08 ± 0.07	$Y_{Zn,tet}$ *(x = 0.75)*	0.38 ± 0.13
$\Delta R_{,Co}$, *Å*	–0.02 ± 0.01	$\Delta R_{,Zn}$, *Å*	–0.01 ± 0.01
σ^2 (Co_{tet}—O), *Å²*	0.0103 ± 0.0038	σ^2 (Zn_{tet}—O), *Å²*	0.0058 ± 0.0025
σ^2 (Co_{oct}—O), *Å²*	0.0071 ± 0.0011	σ^2 (Zn_{oct}—O), *Å²*	0.0094 ± 0.0036

Parameter	Value	Parameter	Value
Global R-factor	0.0072		

Table 5. *Individual goodness-of-fit information of eight datasets at Co and Zn K-edges*

Individual R-factors, Co K-edge		Individual R-factors, Zn K-edge	
x = 0	0.01526	*x = 1*	0.00645
x = 0.25	0.00705	*x = 0.25*	0.00111
x = 0.50	0.00827	*x = 0.50*	0.00169
x = 0.75	0.00878	*x = 0.75*	0.00253

Example 3. Synthesis and characterization of UTSA-16-Zn-*0.25* and UTSA-16-Zn-*1.00* materials

The further possibility of determining site occupancy by SCXRD arises due to the three-electron difference between Co and Zn incorporated in the samples. To prepare samples of suitable size for the data collection of SCXRD, a modified protocol was adopted. Specifically, large single crystals of UTSA-16-Zn-*1.00* and UTSA-16-Zn-*0.25* were grown according to General Procedure 2.

The unconstrained refinement of occupancy factors in the octahedral and tetrahedral sites indicates near full occupation of the tetrahedral site by Zn, whereas the Zn occupancy in the octahedral site is approximately 20% for UTSA-16-Zn-0.25. This model agrees well with the diffraction data (see Table 6). The regressed occupancies correspond to a bulk composition of 68.3% Co and 31.7% Zn within the single crystal (ICP result: 63.3% Co and 36.7% Zn).

Single-crystal X-ray Diffraction (SCXRD)

Single-crystal X-ray diffraction data of *UTSA-16-Zn-1.00* and *UTSA-16-Zn-0.25* were collected at 100 K on a Bruker D8 Venture diffractometer. The data integration and reduction were processed with SAINT software. A multi-scan absorption correction was applied to the collected reflections. The structure was solved by the direct method using SHELXTL and was refined on F2 by full-matrix least-squares technique using the SHELXL-2014/7 package within the WINGX programme. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in successive difference Fourier maps and they were treated as riding

atoms using SHELXL default parameters. The structures were examined using the Adsym subroutine of PLATON to assure that no additional symmetry could be applied to the models.

Table 6. *Crystal data and structure refinement for* ***UTSA-16-Zn-1.00*** and ***UTSA-16-Zn-0.25***

Identification code	***UTSA-16-Zn-1.00***	***UTSA-16-Zn-0.25***
Empirical formula	$C_{12}H_8KO_{14}Zn_3$	$C_{12}H_8KO_{16}Co_{2.05}Zn_{0.95}$
Formula weight	611.45	630.21
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Tetragonal	Tetragonal
Space group	I -4 2 d	I -4 2 d
Unit cell dimensions	a = 12.8873(10) Å α= 90°. b = 12.8873(10) Å β= 90°. c = 30.445(4) Å γ = 90°.	a = 12.7869(6) Å α = 90°. b = 12.7869(6) Å β = 90°. c = 30.2946(12) Å γ = 90°.
Volume	5056.4(10) $Å^3$	4953.3(5) $Å^3$
Z	8	8
Density (calculated)	2.203 Mg/m^3	1.691 Mg/m^3
Absorption coefficient	3.608 mm^{-1}	2.512 mm^{-1}
F(000)	3384	2488
Theta range for data collection	2.555 to 29.903°.	2.57 to 28.4°.
Index ranges	-18<=h<=18, -18<=k<=18, -42<=l<=36	-17<=h<=16, -16<=k<=17, -40<=l<=40
Reflections collected	53272	24136
Independent reflections	3662 [R(int) = 0.1718]	3111 [R(int) = 0.0595]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3662 / 0 / 127	3111 / 0 / 149
Goodness-of-fit on F^2	0.951	0.981
Final R indices [I>2sigma(I)]	R1 = 0.0570, wR2 = 0.1377	R1 = 0.0263, wR2 = 0.0555
R indices (all data)	R1 = 0.0710, wR2 = 0.1452	R1 = 0.0315, wR2 = 0.0576

Identification code	***UTSA-16-Zn-1.00***	***UTSA-16-Zn-0.25***
Absolute structure parameter	0.014(12)	0.016(8)
Largest diff. peak and hole	1.524 and -0.669 e.Å^{-3}	0.34 and -0.35 e.Å^{-3}

Example 4. Effect of Zn loading on temperature-dependent crystallization

Temperature-dependent crystalization of UTSA-16(Co) (viz. UTSA-16-Zn-*0*) and UTSA-16-Zn-*0.50* were compared.

Temperature-dependent crystallization

The reaction mixtures (corresponding to UTSA-16-Zn-*0* and UTSA-16-Zn-*0.50)* were prepared in accordance with General Procedure 1 except that the heating was done for 24 h in preheated ovens at the defined temperatures (60, 80, 100 °C), or at room temperature (25 °C).

The samples were recovered by centrifugation at 5000 rpm, washed with copious amounts of absolute MeOH before being dried in a vacuum oven for PXRD tests. Due to significant Co content in the samples, the samples exhibited high signal-to-noise ratio owing to X-ray absorption when using Cu Kα radiation source (Rigaku Miniflex). Hence, the samples were background-subtracted and filtered by Savitsky-Golay function using instrument-accompanying processing software (Rigaku PDXL). The same processing method was performed for all samples in **Figures 3a and 3b**. The intensity metrics for samples of different compositions are not directly comparable because of the absorption phenomena.

Results

In the case of the monometallic parent MOF (UTSA-16-Zn-*0*), a sticky gel was deposited from which violet prismatic crystals emerged. XRD patterns collected on products crystallized from incubation for 24 h at 25, 60, 80, and 100 °C (**Figure 3a**) indicate that the solids obtained at low temperatures (25 and 60 °C) are primarily amorphous. When the temperature increased to 80 °C, peaks corresponding to UTSA-16 arose after 24 h. At 100 °C, large single crystals observable by optical microscope began to form (**Figure 5**). For UTSA-16-Zn-*0.50*, characteristic PXRD peaks may be observed even by standing the reaction mixture at room temperature for 24 h (**Figure 3b**).

Example 5: Effect of Zn loading on induction time

The effect of Zn loading on the formation kinetics was estimated by *ex-situ* PXRD studies. The MOF formation kinetics was estimated by the inverse of the full-width at half-maximum (FWHM) of the dominant PXRD peak at ca. 7.5°, which was further normalized by the long-time average for comparability across different Zn loadings.

Method

For accurate estimation of induction time, the composition was optimized to ensure a homogenous starting solution. In light of salting-out effects, it is necessary to balance the solvent composition to suppress liquid-liquid phase separation. Here, a starting solution of M^{II}(acetate)-K_3(citrate) (0.4 M in 15 vol% aqueous EtOH solution) was used.

The final composition of a 10 mL solution comprises 1.5 mL EtOH, 8.5 mL H_2O, 4 mmol of M^{II}(acetate), and 4 mmol of citric acid neutralized with 12 mmol KOH. The 4 mmol of M^{II}(acetate) will be further apportioned into the two metals, keeping all other reagent quantities constant. For example, a 50/50 solution (x = 0.5) may be prepared with 2 mmol of **$Co(OAc)_2 \cdot 4H_2O$** and 2 mmol of **$Zn(OAc)_2 \cdot 2H_2O$** with 4 mmol of citric acid neutralized with 12 mmol KOH in 5 mL H_2O as solvent. Then, 1.5 mL EtOH + 3.5 mL H_2O solution is added to start the experiment. Different relative amounts of Co/Zn can be prepared by varying the relative ratio of M^{II}(acetate) without changing the total molar amount. For example, 25/75 (x = 0.75) and 75/25 (x = 0.25) mixtures can be prepared using 1 mmol of **$Co(OAc)_2 \cdot 4H_2O$** and 3 mmol of **$Zn(OAc)_2 \cdot 2H_2O$** or 3 mmol of **$Co(OAc)_2 \cdot 4H_2O$** and 1 mmol of **$Zn(OAc)_2 \cdot 2H_2O$**, respectively. The concentration of EtOH is strongly correlated with solid precipitation; to avoid immediate formation of solid, EtOH was added as a dilute solution (<30 %) in water. The samples were incubated in a preheated oven at 65 °C, removed at fixed intervals and ice quenched. The products were centrifuged (8,000 rpm for 3 min), dried under vacuum at room temperature, and subject to PXRD measurements. The time for products recovery was minimized and kept constant between samples with different Zn loadings. For samples with no solid isolated after the centrifugation, the FWHM is reported as 0.

Results

Figure 3c indicates the induction time, defined as the time where the product shows noticeable crystallinity, decreases noticeably as the Zn content in the system is increased.

Even a modest Zn loading (x = 0.25) can greatly reduce the induction time to around 70 min These results inform a certain feasibility to obtain mixed-metal UTSA-16 materials at ambient pressure within reasonable synthetic durations (< 48 h).

In **Figure 3c**, the experiments are performed at T = 65 °C. The product crystallizes in less than 1 hour. This temperature is below the boiling point of the solvent, which allows the reaction to be operated at ambient pressure using a simple reflux setup. It is apparent from **Figure 3c** that the reaction time can be manipulated by adjusting the structure composition. This property can be used to manipulate other parameters beyond reaction time, such as temperature, by accommodating appropriate process trade-offs.

Example 6. Carbon capture performance of UTSA-16-Zn-x

Gas sorption experiments

The gas isotherms were measured up to 1 bar using a Micromeritics ASAP 2020 surface area and pore size analyzer. Before the measurements, the samples were degassed under reduced pressure (< 10^{-2} Pa) at 150 °C until the outgas rate was below 5 μm Hg/min. UHP grade N_2 and CO_2 were used for gas sorption measurements. Oil-free vacuum pumps and oil-free pressure regulators were used to prevent contamination of the samples during the degassing process and isotherm measurement. The temperatures of 77, 273, and 298 K were maintained with a liquid nitrogen bath, an ice water bath, and under room temperature, respectively.

Fitting of CO_2 isotherms

Measured CO_2 isotherms were fitted using the dual-site Langmuir Freundlich (DSLF) isotherm model,

$$q = \frac{q_{sat,A} b_A p^{\alpha_A}}{1+b_A p^{\alpha_A}} + \frac{q_{sat,B} b_B p^{\alpha_B}}{1+b_B p^{\alpha_B}} \quad \text{Eq. 1}$$

The model accounts for site inhomogeneity by defining two adsorption sites A and B with distinct saturation capacities and affinity parameters.

Here, q is the amount of adsorbed gas, q_{sat} is the amount of gas adsorbed at saturation (mmol g^{-1}), b is the Langmuir-Freundlich affinity parameter (kPa^{-1}), and α is a dimensionless exponent.

The simultaneous fitting at 298 K and 273 K was performed by inbuilt Solver function in Microsoft Excel, where the temperature dependence is described by independent *b* terms.

Table 7. *DSLF isotherm parameters for UTSA-16-Zn-x materials*

x	$q_{sat,A}$	$b_{A,298}$	$b_{A,273}$	α_A	$q_{sat,B}$	$b_{B,298}$	$b_{B,273}$	α_B
0.25	2.367	0.028	0.222	1.528	2.754	0.028	0.064	0.684
0.50	2.158	0.029	0.220	1.530	2.752	0.029	0.064	0.681
0.75	2.173	0.030	0.237	1.514	2.706	0.030	0.067	0.678
1.00	2.449	0.027	0.213	1.562	2.716	0.027	0.063	0.703

Fitting of N_2 isotherms

Measured N_2 isotherms were fitted using the single-site Langmuir (SSL) isotherm model,

$$q = \frac{q_{sat} bp}{1+bp} \qquad \text{Eq. 2}$$

Due to low curvature of the isotherms, independent fitting for samples with different Zn loadings led to large variance in the obtained parameters. To reduce the number of free parameters, the q_{sat} values of the individual UTSA-16-Zn-*x* sample were restrained to a common value scaled by their N_2 uptake at 100 kPa. This restraint is supported by the substantial agreement of the isotherms, their isostructural nature, and very similar adsorption behaviour with respect to CO_2.

Table 8. *SSL isotherm parameters for UTSA-16-Zn-x materials*

x	q_{sat} (mmol g^{-1})	b (kPa^{-1})
0.25	1.3322	0.00156
0.50	1.1947	0.00166
0.75	1.2387	0.00153
1.00	1.2599	0.00154

Results

Single component CO_2 and N_2 isotherms were collected for UTSA-16-Zn-*x* at 273 and 298 K. The shape of CO_2 isotherms and total uptake of CO_2 at 1 bar are substantially similar to that of the parent Co one. In addition, several other parameters obtained by analysing the

isotherms, such as isosteric heat of CO_2 adsorption (Q_{st}) and CO_2/N_2 selectivity calculated by ideal adsorbed solution theory (IAST) are also identical (**Figure 4; Figure 7; and Table 9**), suggesting similar CO_2 capture performance between UTSA-16-Zn-*x* and UTSA-16(Co).

***Table 9**: Summary of performance metrics for adsorptive CO_2 capture at 298K*

x	**0.25**	**0.50**	**0.75**	**1.0**
CO_2 uptake (mmol g^{-1})	3.39	3.18	3.20	3.50
$-Q_{st}$ (kJ mol^{-1})	35.4	34.3	35.3	34.8
IAST CO_2/N_2 selectivity 1 bar, 15:85 feed	190	206	212	228

Example 7. Competitive adsorption of UTSA-16-Zn-x under dynamic conditions

Breakthrough experiments were also performed using simulated flue gas (15/85 CO_2/N_2 feed) to analyze competitive adsorption under dynamic conditions.

Breakthrough experiments

The breakthrough experiments were conducted using a home-built setup shown in **Figure 12.** The MOF samples (700 to 900 mg) were packed into a stainless-steel column (L = 7 cm, D = 0.46 cm) and held in place using quartz wool and steel mesh.

The feed flow rates during the experiment were controlled using mass flow controllers (error: 0.1 sccm). The total flow rate through the column was set to 3 sccm. These were stabilized using a bypass line and switched to flow through the adsorbent column immediately prior to the experiment.

The gas composition at the exit of the column was determined by a mass spectrometer (Hiden QGA). To precisely determine the flow rates, Ar was introduced at a fixed flow rate of 3 sccm to the effluent gas as an internal reference to calibrate the mass flow rate. The upstream and downstream pressures were recorded. The original breakthrough plots were obtained as relative compositions vs. elapsed time and then converted to mole fraction normalized with the mole fraction at the inlet vs. elapsed time plots.

The performance evaluation is based on 3 experiments:

- *Dry feed (RH = 0%) –*

The column was activated by purging a constant He flow of 10 sccm through the column at 120 °C for 24 h. The feed gas was a (15 ± 1)/(85 ± 1) CO_2/N_2 mixture prepared by mixing dry gas upstream of the column.

- *Wet feed (RH = 85%) –*

The column was activated by purging a constant He flow of 10 sccm through the column at 120 °C for 24 h. The feed gas was a (15 ± 1)/(85 ± 1) CO_2/N_2 mixture with relative humidity of around 85%; the moisture was introduced by passing the N_2 stream through a water bubbler at room temperature prior to mixing.

- *Water-saturated sorbent bed (sat. col.) –*

The column was activated by purging a constant He flow of 10 sccm through the column at 120 °C for 24 h. For pre-saturation, a wet purge stream was prepared by passing a N_2 stream through a water bubbler at room temperature prior to mixing. The purge stream was sent through the column for 72 h until a stable water signal was detected by the mass spectrometer. Then, the column was briefly activated under constant He flow (10 sccm) at room temperature. This condition has been observed by us to enable near complete desorption of N_2/CO_2 but minimal desorption of adsorbed H_2O. The experiment was then performed using 'wet feed' conditions. Under these conditions, the MOF-packed columns showed negligible uptake for either component.

The mean residence time within the adsorption column was obtained by performing a mass balance using the inlet and exit gas molar flow rates, i.e.

$$\bar{t} = \int_0^t \left(1 - \frac{F_t}{F_0}\right) dt \qquad \text{Eq. 3}$$

The obtained residence time was corrected by the residence time of a control experiment using a blank tube under the same pressure drop and feed conditions. The validity of this correction depends on a linear additive relationship for retention time and band broadening characteristics of the experiment. Uncorrected breakthrough curves (**Figure 13**) and obtained residence time after correction are presented in Table 10).

Results

The saturated CO_2 uptakes of UTSA-16-Zn-*x* are in the range of 1.65–1.70 mmol g^{-1} with substantial tolerance to moisture (**Figure 4**). These are slightly lower than that of the parent Co MOF (1.82 mmol g^{-1}), in similar fashion to the static CO_2 uptake results.

The maximum productivity of CO_2 (q_{max}) is in good agreement with the single-component static uptake (1.8 mmol g^{-1} and 1.94 mmol g^{-1} respectively for ***x*** = 0.5 and 1). In general, there is a slightly lower capacity (-2.3%) when transiting from dry to RH = 85% feed, due to competitive adsorption by H_2O.

Table 10. *Obtained dynamic adsorption parameters from column breakthrough measurements*

Run	$\bar{t}_{CO_2}$ min g^{-1}	$q_{CO_2,max}$ mmol g^{-1}
***x* = 0, RH = 0%**	96.5	1.86
***x* = 0, RH = 85%**	91.8	1.84
***x* = 0.5, RH = 0%**	84.02	1.69
***x* = 0.5, RH = 85%**	81.91	1.65
***x* = 1, RH = 0%**	84.47	1.70
***x* = 1, RH = 85%**	82.4	1.66

Summary

In summary, we have shown that the replacement of rate-limiting tetrahedral Co species within UTSA-16 by Zn can dramatically accelerate the formation kinetics of these MOFs, affording mild synthetic conditions suitable for the mass production of those materials. The new UTSA-16-type MOFs exhibit CO_2 capture performance identical to that of the parent Co one, with substantial tolerance to moisture.

The invention yields mixed-metal composites from a known binary (single metal/single linker) MOF with suitable structure, which possess improved synthetic robustness compared to the monometallic materials. Optimized protocols derived from this strategy are more compatible

with scaled-up production, which will accelerate the process development of the concerned materials for various commercial applications.

Claims

1. A metal organic framework (MOF) having a UTSA-16 structure, where the composition comprises:

a first metal selected from one or more of the group consisting of Cr, Mn, Fe, Ni, Cu, and Co present in an amount of up to 80 mol% of the total metal in the MOF; and

from 20 to 80 mol% of the total metal in the MOF is a second metal selected from one or more of the group consisting of Cd, Mn, and Zn.

2. The MOF according to Claim 1, wherein the second metal is Zn.

3. The MOF according to Claim 1 or 2, wherein the second metal is present in an amount of from 50 to 75 mol% of the total metal present in the MOF.

4. The MOF according to any one of the preceding claims, wherein the first metal is selected from Fe and Co, optionally wherein the first metal is Co.

5. The MOF according to any one of the preceding claims, wherein the first metal is present in an amount of from 25 to 50 mol% of the total metal present in the MOF.

6. The MOF according to any one of the preceding claims, wherein the second metal preferentially occupies a tetrahedral metal site within the MOF.

7. The MOF according to any one of the preceding claims, wherein the majority of the first metal, when present, occupies an octahedral metal site within the MOF.

8. The MOF according to any one of the preceding claims, wherein the first metal, when present, and second metal preferentially occupy an octahedral metal site and a tetrahedral metal site within the MOF, respectively.

9. The MOF according to any one of the preceding claims, wherein the MOF has a saturated CO_2 uptake of from 3.39 to 5.0 mmol/g, optionally wherein the MOF has a saturated CO_2 uptake of from 3.39 to 4.5 mmol/g, such as from 3.39 to 3.50 mmol/g.

10. The MOF according to any one of the preceding claims, wherein the MOF has a breakthrough CO_2 working capacity of up to 2.2 mmol/g, such as from 1.0 to 1.8 mmol/g, such as from 1.65 to 1.70 mmol/g.

11. The MOF according to any one of the preceding claims, wherein:
the first metal is Co;
the second metal is Zn; and
the MOF has a saturated CO_2 uptake of from 3.39 to 5.0 mmol/g.

12. The MOF according to any one of the preceding claims, wherein:
the first metal is Co;
the second metal is Zn;
the MOF has a saturated CO_2 uptake of from 3.39 to 5.0 mmol/g; and
the first metal, when present, and second metal preferentially occupy an octahedral metal site and a tetrahedral metal site within the MOF, respectively.

13. A method of forming a MOF according to any one of the preceding claims, wherein the method comprises the step of aging a mixture comprising from a first metal precursor, a second metal precursor, a base, citric acid, a first solvent and a second solvent for a period of time at a temperature of from 15 to 200 °C, wherein:
the first metal precursor is selected from one or more of the group consisting of Cr, Mn, Fe, Ni, Cu, and Co;
the second metal precursor selected from one or more of the group consisting of Cd, Mn, and Zn; and
the metal in the first metal precursor is present in an amount of up to 80 mol% of the total amount of metal in the mixture; and
the metal in the second metal precursor is present in an amount of from 20 to 80 mol% of the total amount of metal in the mixture.

14. The method according to Claim 13, wherein the temperature is from 20 to 150 °C,
optionally wherein the temperature is from 40 to 120 °C, such as temperature of from 60 to 80 °C.

15. The method according to Claim 14, wherein the temperature used results in one or both solvents being refluxed.

16. The method according to any one of Claims 13 to 15, wherein:
(a) the first solvent is water and the second solvent is an alkyl alcohol (e.g. the alkyl alcohol is methanol, a propanol or, more particularly, ethanol); and/or
(b) the base is a metal hydroxide (e.g. the base is KOH); and/or

(c) the method is performed under ambient atmospheric conditions (e.g. standard pressure).

17. The method according to any one of Claims 13 to 16, wherein the first and second metal precursors are a metal salt, where the metal is in a cationic form, which is balanced by one or more counterions selected from one or more of halide (e.g. chloride), nitrate, sulfate, hydroxide, oxide, acetate anion, and hydrates thereof

18. The method according to any one of Claims 13 to 17, wherein:

(a) the second metal precursor is $Zn(OAc)_2$ or a hydrate thereof (e.g. $Zn(OAc)_2 \cdot 2H_2O$); and/or

(b) the metal in the second metal precursor is present in an amount of from 25 to 100 mol%, such as from 50 to 75 mol% of the total metal present in the mixture.

19. The method according to any one of Claims 13 to 18, wherein:

(a) the first metal precursor is $Fe(OAc)_2$, $Co(OAc)_2$ or hydrates thereof (e.g. $Co(OAc)_2 \cdot 4H_2O$); and/or

(b) the metal in the first metal precursor is present in an amount of from 25 to 50 mol%, such as from 50 to 75 mol%, such as from 25 to 50 mol% of the total metal present in the mixture.

20. A method of capturing CO_2 comprising the step of exposing a material comprising a MOF as described in any one of Claims 1 to 12 to an environment containing CO_2.