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ARTICLE

Ag-NPs embedded in two novel Zn₃/Zn₅-cluster-based metal-organic frameworks for catalytic reduction of 2/3/4-nitrophenol

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By utilizing symmetrical pentacarboxylate ligands, 3,5-di(2',5'-dicarboxylphenyl) benzoic acid (H₅L1) and 3,5-di(2',4'-dicarboxylphenyl) benzoic acid (H₅L2), two novel porous Zn-MOFs, [Zn₅(μ₃-H₂O)₂(L1)₂]·3DMA·4H₂O (CTGU-3) and [Zn₃(μ₃-OH)(L2)(H₂O)₃]·H₂O (CTGU-4) have been synthesized under solvothermal condition. CTGU-3 and CTGU-4 exhibit 3D microporous frameworks with **flu** and **dia** topologies and possess unique secondary building units [Zn₅(μ₃-H₂O)₂(RCO₂)₆] and [Zn₃(μ₃-OH)(RCO₂)₃], respectively. Such porous systems create a unique space or surface to accommodate Ag nanoparticles (Ag NPs), which could efficiently prevent Ag NPs from the aggregation and leaching. In this work, two new Ag@Zn-MOFs composites, denoted as Ag@CTGU, have been successfully fabricated through solution infiltration, for the reduction of nitrophenol. Compared with CTGU-4, CTGU-3 shows the enhanced catalytic efficiency toward the reaction when it was used as a catalyst support of Ag NPs. Moreover, gas sorption and luminescent properties of two compounds were also investigated.

Introduction

Nitrophenol and its homologous series have been widely considered as one of the most prevalent organic pollutants in industrial liquid wastes.¹ Even at low concentrations, nitrophenol still causes detrimental effects to the environment and human health.² Thus, it is extremely important to remove these wastes from surrounding efficiently and timely. Among all traditional methods (e.g. ozonation, adsorption, biodegradation and catalytic degradation³) to treat such these wastes, catalytic degradation has been demonstrated to be as a more effective and economical approach not only because this method is feasible, but also because this method could produce many important industrial raw materials such as 4-aminophenol (4-AP) and its homologous series, 2-aminophenol (2-AP) and 3-aminophenol (3-AP) via the reduction of nitrophenol over noble metal NPs in the presence of KBH₄.⁴ However, developing novel noble metal catalysts to realize this type of reactions with high efficiency, convenient operation and economical rewards is extremely important.⁵ Although previous studies have reported that silver nanoparticles (Ag NPs) can be used as catalyst to carry out above reactions,⁶ there is still much

room left for the improvement of their efficiency. In most situations, the use of Ag NPs is mainly limited by its high cost and conglomeration in the catalytic process.⁷ One possible solution is to reduce the usage of Ag via employing porous materials as a support to disperse particles. More importantly, such arrangement would largely improve its conglomeration phenomenon. Moreover, the porous structure of the support is beneficial to the separation of substrates and products.⁸ Although traditional porous materials, such as mesoporous silica, activated carbon and zeolites, have been extensively investigated in the field of catalysis,^{9,10} it is very tedious to prepare these materials with uniform pores and tune the pore sizes. Thus, developing new suitable supports for preparation of the metal-in-pore catalysts still faces many challenges.

Recently, metal-organic frameworks (MOFs) have been demonstrated to represent a new class of permanently microporous materials, which are unique in terms of their extraordinarily high porosities, tunable pores, and diverse functional sites.¹¹ Such unique features have enable MOFs to exhibit great potentials for a broad range of applications, including gas storage, chemical separation, chemical sensing, and heterogeneous catalysis.¹²⁻¹⁴ Over the past years, porous MOFs materials usually come to be known as a potential candidate for gas separation and storage.¹⁵ Moreover, MOFs have been actively employed as host matrices because the incorporation of functional species into their pores can add new properties to MOFs due to the guest-host synergistic effect.¹⁶ Given these advantages, MOFs have been proved to be ideal candidates as host-materials to capture noble metal nanoparticles to limit their migration and aggregation, due to the rigid porous structures of MOFs.^{17,18} Clearly, continuing to work on this direction would not only help to promote the development of this field but also develop new strategies to prepare these

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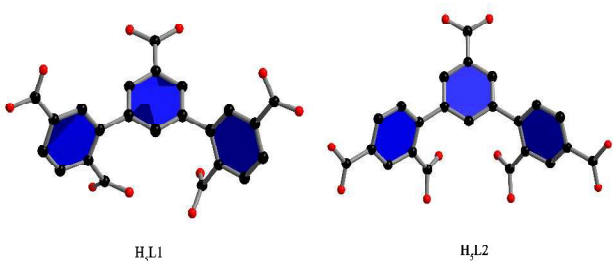
† Electronic Supplementary Information (ESI) available: bond length/angle tables, additional figures and tables. Adsorption isotherm, fluorogram, TGA, FT-IR, UV-Vis spectra and PXRD patterns. See DOI: 10.1039/x0xx00000x

ARTICLE

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composite materials as well as the fundamental researches including the growth mechanism of nanoparticles in the confined space and synergetic effect between subject and object.

In this work, we successfully prepared two microporous MOFs, $[\text{Zn}_5(\mu_3\text{-H}_2\text{O})_2(\text{L1})_2]\cdot 3\text{DMA}\cdot 4\text{H}_2\text{O}$ (CTGU-3, CTGU = China Three Gorges University) and $[\text{Zn}_3(\mu_3\text{-OH})\text{L2}(\text{H}_2\text{O})_3]\cdot \text{H}_2\text{O}$ (CTGU-4) by choosing 3,5-di(2',5'-dicarboxylphenyl) benzoic acid ($\text{H}_5\text{L1}$) and 3,5-di(2',4'-dicarboxylphenyl) benzoic acid ($\text{H}_5\text{L2}$) as symmetrical pentacarboxylate ligands (Scheme 1) and Zn salt as metal sources. Structural analysis reveals that two compounds consist of two different unequal SBUs: $[\text{Zn}_5(\mu_3\text{-H}_2\text{O})_2(\text{RCO}_2)_6]$ SBUs and $[\text{Zn}_3(\mu_3\text{-OH})(\text{RCO}_2)_3]$ SBUs, and possess multiple pores, which have been used to embed Ag NPs through solution infiltration. The as-prepared composite catalysts (Ag@CTGU-3 and Ag@CTGU-4) show outstanding catalytic activities toward the reduction of nitrophenol.



Scheme 1. Chemical structures of ligands

Experimental section

Materials and general methods

All reagent used in the experiment were commercially available without further purification. Powder X-ray diffraction (PXRD) was studied on a Rigaku Ultima IV diffractometer ($\text{Cu K}\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$). Thermogravimetric (TG) curves were operated on a NETZSCH449C thermal analyzer with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ under air atmosphere. FT-IR spectra (KBr pellets) were conducted on a Thermo Electron NEXUS 670 FTIR spectrometer. Elemental analyses were performed on a PerkinElmer2400 Series II analyzer. The solid state luminescent spectra and emission lifetime were recorded by the Edinburgh FLS55 luminescence spectrometer at ambient temperature. The UV-vis spectra for samples were obtained on a Shimadzu UV 2550 spectrometer. X-rayphotoelectron spectrometry (XPS) was carried out on an ESCALABMKLL X-ray photoelectron spectrometer by using an Al $\text{K}\alpha$ source. High-resolution Transmission electron microscope (HRTEM) images were taken by a JEOL JEM 2010F at an accelerating voltage of 200 kV.

Synthesis of $[\text{Zn}_5(\mu_3\text{-H}_2\text{O})_2(\text{L1})_2]$ (CTGU-3)

A mixture of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.04 mmol, 11.9 mg), $\text{H}_5\text{L1}$ (0.04 mmol, 18.0 mg) and DMA/ H_2O (4 ml/4 ml) was sealed in a 25 ml Teflon-lined stainless steel vessel, heated to $120 \text{ }^\circ\text{C}$ for 72h, and then cooled to room temperature over 24h. Colorless crystals of CTGU-3 were obtained. Yield: 75% based on $\text{H}_5\text{L1}$. Elemental

analysis (%): calcd for CTGU-3 ($\text{C}_{58}\text{H}_{57}\text{N}_3\text{O}_{29}\text{Zn}_5$): C 43.89, H 3.62, N 2.65; found: C 43.12, H 3.46, N 2.40. FT-IR (KBr, cm^{-1}) (Fig. S1, ESI[†]): 3440 (s), 1620 (s), 1600 (s), 1490 (s), 1410 (s), 1270 (m), 1020 (w), 910 (m), 775 (m).

Synthesis of $[\text{Zn}_3(\mu_3\text{-OH})\text{L2}(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}$ (CTGU-4)

The preparation of CTGU-4 product was similar to that of CTGU-3 by using $\text{H}_5\text{L2}$ in place of $\text{H}_5\text{L1}$. Colorless crystals of CTGU-4 were obtained in 56% based on $\text{H}_5\text{L2}$. Elemental analysis (%): calcd for CTGU-4 ($\text{C}_{23}\text{H}_{20}\text{O}_{15}\text{Zn}_3$): C 37.70, H 2.75; found: C 36.90, H 2.72. FT-IR (KBr, cm^{-1}) (Fig. S2, ESI[†]): 3450 (s), 1620 (s), 1410 (s), 1390 (s), 1360 (s), 1280 (m), 1170 (w), 1020 (w), 914 (m), 781 (s).

Synthesis of Ag@CTGU

The composite catalysts were prepared according to a previously reported method.¹⁹ To load Ag precursors into the channel/surface of CTGU-3, polycrystalline samples (20 mg) were immersed into an aqueous solution of AgNO_3 (20 mg/3 mL) for 24h and vacuum-dried at 273 K. During the period of preparation, AgNO_3 solution was refreshed three times. After filtration, Ag-CTGU-3 was rinsed and soaked in distilled water to remove dissociative AgNO_3 . Then, 3 ml ethanol was added into the system as a reducing agent. This mixed solution was kept for another 10h. Eventually, the composite material Ag@CTGU-3 was obtained and confirmed by XPS and HRTEM measurements. Ag@CTGU-4 was prepared by replacing CTGU-3 with CTGU-4.

Gas sorption measurements

N_2 and CO_2 isotherms were collected using an ASAP 2020 surface area and pore size analyzer in a clean ultra-high-vacuum system. Approximately 120 mg of solvent-exchanged sample was loaded into the sample basket within the adsorption instrument and then degassed under dynamic vacuum at 100°C for 6h to obtain the fully desolvated sample. Volumetric N_2 and CO_2 sorption measurements were performed over the pressure range 0-1 bar at 77K and 298K, respectively.

Catalytic measurements

In the reduction of nitrophenol, a desired amount of Ag@CTGU powder (1 mg) was added to 3 ml nitrophenol aqueous solution, in which the concentration was 14 mg/L (4-NP), 60 mg/L (2-NP) and 60 mg/L (3-NP), separately. The reaction was started by adding 3 mg KBH_4 into the reactor. At desired time intervals, the absorbance at concerted wavelength was measure by utilizing the UV-vis spectrophotometer.²⁰

Crystal structure

The diffraction data for CTGU-3/4 was collected on a RigakuXtaLAB mini diffractometer with graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct method and refined by a full-matrix least-squares refinement on F^2 with SHELXTL and Olex2.²¹ All non-H atoms were refined anisotropically. In the two structures, solvent molecules are highly disordered, therefore,

the *SQUEEZE* routine of *PLATON* is used to remove the diffused electron densities resulting from solvent molecules. The final formulation of CTGU-3 and CTGU-4 were calculated from the *SQUEEZE* results combined with TGA analysis. Detailed crystallographic data are summarized in Table 1. Selected angles and bond lengths are listed in Table S1 (ESI†). The crystal structures of two compounds have been deposited and CCDC numbers are 1510773 and 1510774. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

Table 1. Crystal data and structure refinements for CTGU-3 and CTGU-4

Compound	CTGU-3	CTGU-4
Formula	C ₅₈ H ₅₇ N ₃ O ₂₉ Zn ₅	C ₂₃ H ₂₀ O ₁₅ Zn ₃
Formula mass	1587	731
Crystal system	triclinic	orthorhombic
Space group	P -1	Pmn2 ₁
<i>a</i> /Å	12.194(6)	20.137(11)
<i>b</i> /Å	12.647(6)	10.702(6)
<i>c</i> /Å	12.699(6)	11.418(6)
<i>α</i> /°	83.837(11)	90.00
<i>β</i> /°	83.660(13)	90.00
<i>γ</i> /°	77.272(12)	90.00
<i>V</i> /Å ³	1891.7(16)	2461(2)
<i>Z</i>	2	2
<i>D</i> _{calcd} /g cm ⁻³	1.100	0.960
<i>μ</i> /mm ⁻¹	1.615	1.488
<i>F</i> [000]	624	710
Independent refls.	6492	4084
No. of parameters	331	193
^a <i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0496	0.0410
^b <i>wR</i> (<i>F</i> ₂)(<i>I</i> > 2σ(<i>I</i>))	0.1341	0.1131

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

Results and discussion

Crystal structure description for CTGU-3 and CTGU-4

Single-crystal X-ray diffraction analysis revealed that CTGU-3 crystallizes in the triclinic system with *P*-1 space group. The minimum asymmetric unit contains two and a half crystallographically independent Zn centers, one complete L1⁵⁻ ligand and one coordinated water molecule. Zn1 ion is coordinated

to four carboxylato-O atoms from two independent ligands and two oxygen atoms from water ligands, while Zn2 and Zn3 are linked with three carboxylato-O atoms from three different ligands and one oxygen atom from water ligand. Therefore, Zn1 atom adopts a six-coordinated mode to form an octahedron geometry, while, Zn2 and Zn3 bond to four oxygen atoms to form a tetrahedron. More Interestingly, through the linkage of six carboxylates of L1⁵⁻ and two central O atoms, five Zn ions are bonded together to generate a poly [Zn₅(μ₃-H₂O)₂(RCO₂)₆] cluster, acting as secondary building unit (SBU) in this the structure (fig. 1a). Notably, each H₅L1 ligand adopts a μ₄-(η²)-(η¹)-(η¹)-(η²)-(η²) coordination mode to connect metal clusters (fig. 1d). Every SBU is connected with the surrounding eight SBUs by the linkage of five ligands, which could be considered as a 8-connected node. Meanwhile, L1⁵⁻ anion could be viewed as a 4-connected node. Thus, the overall structure of CTGU-3 is 3D (4,8)-*flu* network with the point symbol of (4¹²·6¹²·8⁴)(4⁶)₂. It is noteworthy that the as-obtained (4,8)-connected frameworks are also relatively rare compared to the classical topologies of diamond, NbO, and PtS etc.²² With the expansion of such SBUs, it can be speculated that more porous MOFs with novel SBUs and topologies could be synthesized.

CTGU-4 crystallizes in the orthorhombic system with *Pmn*2₁ space group. The asymmetric unit is composed of one and a half Zn ions, half a L2⁵⁻ ligand, one and a half coordinated water molecule and a half of hydroxyl specie. In the structure, two Zn cations including Zn1 and Zn2, occupancy rates are 1 and 0.5, which are coordinated by carboxylato-O, hydroxyl-O and water-O, show octahedron and tetrahedron coordination geometries, respectively. More importantly, a trimeric [Zn₃(μ₃-OH)(RCO₂)₃] cluster, which is similar to CTGU-3, serving as SBU in this structure (Fig. 2a). The H₅L2 ligand in CTGU-4 is also completely deprotonated, which possesses one type of coordination mode: H₅L2 acts as a connector to link four metal clusters with the μ₄-(η²)-(η¹)-(η¹)-(η²)-(η²) coordination mode. From a topological perspective, every SBU could be defined as a 4-connected node, and the H₅L2 could also be corresponded to a 4-connected vertex, finally, constructing a porous 3D network with *dia* topology (Fig. 2f). A synthetic and structural comparison of CTGU-3 and CTGU-4 demonstrates that the positional heterogeneity of ligands have a profound impact on the final structure of MOFs.

Previous research has been confirmed that SBUs can be used as building units instead of single metal ions in the MOFs engineering.²³ As an effective strategy, SBUs undoubtedly help to shed light on the prediction, design, and synthesis of the target product, in which, SBUs are established under the appropriate chemical conditions. Up to now, many famous framework materials such as MOF-5, UIO-66, MIL-101, and HKUST-1 have been synthesized base on SBUs and usually consist of two, three or more metal centers. In this work, two distinct SBUs, consisting of three and five metal centers, have been successfully directed to generate two novel Zn-MOFs. Note that both SBUs were assembled under the same temperature, solvent, ration of reactant and pH value, indicating that the ligand with carboxyl group in a different location is the main reason for the structure differences between CTGU-3 and CTGU-4.

Actually, several microporous metal-organic frameworks (MMOFs) have been reported in previous literature, in which the

ligand is isometric with H₅L1 and H₅L2. Liu et al. utilized a similar pentacarboxylate ligand to prepare two anionic MMOFs, JLU-Liu5 and JLU-Liu6, based on rare ternary SBU (The coordination mode of ligand is $(\eta^1:\eta^2-\mu_3)-(\eta^1:\eta^1-\mu_2)-(\eta^1:\eta^1-\mu_2)-(\eta^1:\eta^1-\mu_2)-(\eta^1:\eta^2-\mu_3)-\mu_{12}$).²⁴ Qian groups also prepared a novel MMOF, ZJU-72, which possesses paddle-wheel Cu₂(CO₂)₄ SBU and shows prominent separating

property of gas mixture (The coordination mode of ligand is $(\eta^1:\eta^1-\mu_2)-(\eta^1:\eta^1-\mu_2)-(\eta^1:\eta^1-\mu_2)-(\eta^1:\eta^1-\mu_2)-\mu_8$).²⁵ Combined with above examples, it is clear that the location of functional groups in similar ligands can produce profound influence on the final SBU and MOF structure.

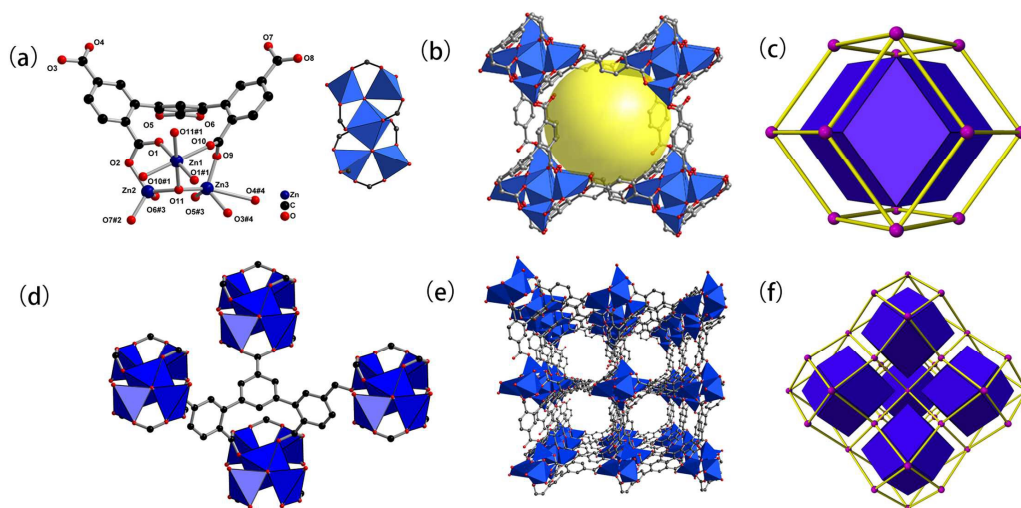


Fig. 1 (a) Coordination environments of the Zn ions and $[Zn_5(\mu_3-H_2O)_2(RCO_2)_6]$ SBU in CTGU-3. Symmetry code: #1 = 2-x, 1-y, 1-z; #2 = x, 1+y, z; #3 = 1-x, 1-y, 1-z; #4 = x, y, 1+z. The hydrogen atoms are omitted for clarity. (b), (e) View of the novel 3D frameworks of CTGU-3 along the *a* axis. (d) Defined a 4-connected node based on SBUs. (c), (f) Schematic representation and natural tiling of the (4,8)-connected **flu** network of CTGU-3.

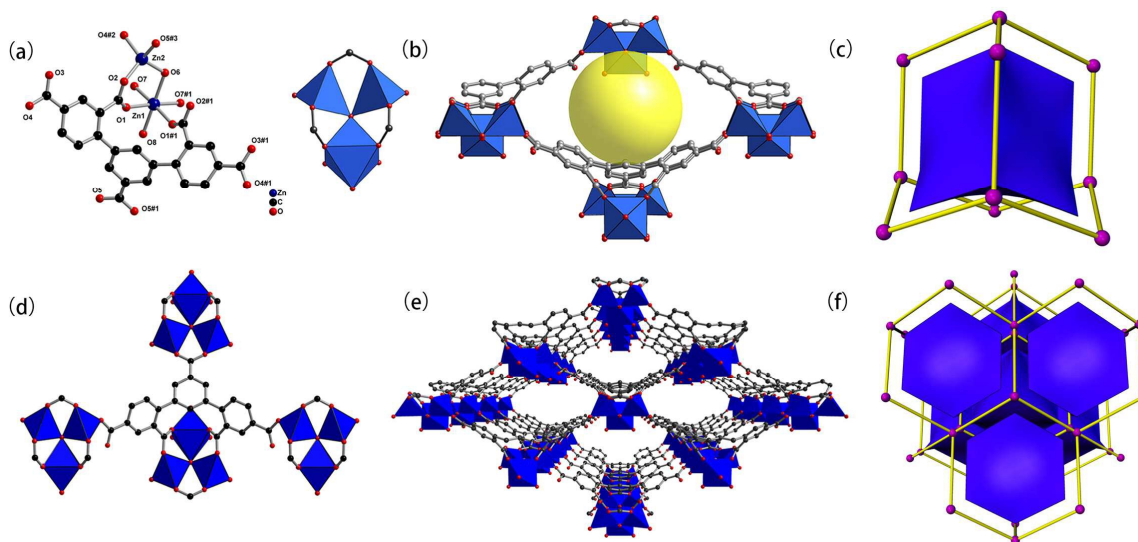


Fig. 2 (a) Coordination environments of the Zn ions and $[Zn_3(\mu_3-OH)(RCO_2)_3]$ SBU in CTGU-4. Symmetry code: #1 = -x, y, z; #2 = -x+1/2, 2-y, 1/2+z; #3 = x, 1+y, z. The hydrogen atoms are omitted for clarity. (b), (e) View of the novel 3D frameworks of CTGU-4 along the *a* axis. (c), (f) Schematic representation and natural tiling of the (4,4)-connected **dia** network of CTGU-4.

Sorption properties

It is noteworthy that CTGU-3 has one dimensional (1D) rectangle shape channels with dimensions of approximately $18.9 \text{ \AA} \times 16.9 \text{ \AA}$ along the a axis (Fig. 1e) and two other channels along the b and c axis. Whereas, there are only one kind of channel belongs to CTGU-4 with dimensions of around $16.9 \text{ \AA} \times 11.7 \text{ \AA}$ along the a axis (Fig. 2e).

The total accessible volume of two compounds is ca. 50.2% and 59.5% respectively, calculated by using the PLATON program.²⁶ In virtue of the high accessible volume, and prominent pore structure, we investigated their adsorption performance for N_2 at 77 K and CO_2 at 298 K. The N_2 sorption isotherm of CTGU-3 reveals typical reversible type-I sorption behavior, which represents the characteristic of microporous materials, corresponding to a BET surface area of $639.63 \text{ m}^2/\text{g}$ (Langmuir surface area of $928.91 \text{ m}^2/\text{g}$) (Fig. 3). CTGU-4 was also investigated by adsorption-desorption isotherm measurements, as expected, obtaining no appreciable absorption data (Fig. S3, ESI[†]), which indicated that CTGU-3 and CTGU-4 have differences within pore structure.

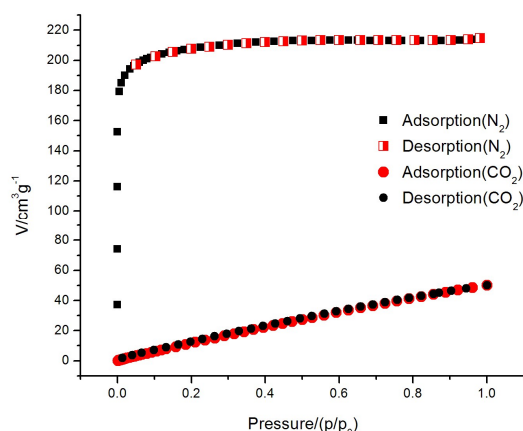


Fig. 3 N_2 and CO_2 sorption isotherms for CTGU-3 at 77 K (298 K).

PXRD and thermal analysis

To verify the phase purity of the bulky materials, X-ray power diffraction (PXRD) experiments have been carried out. The PXRD experimental and computer-simulated patterns are in good agreement with each other, indicating phase purity of the as-synthesized products (Fig. S4 and Fig. S5, ESI[†]). Additionally, thermogravimetric analysis of CTGU-3 and CTGU-4 has been performed in the temperature range of 30–800°C. The TGA curves of CTGU-3 and CTGU-4 are similar and present two main steps of weight loss corresponding to the loss of coordinated water molecule, solvent molecules and decompose of organic ligands. CTGU-3 shows the first mass loss of 6.20% below 149°C due to the release of the coordinated water and lattice water molecules (calcd: 6.80%). The second step displays a weight loss of 16.20% from 160°C to 287°C, indicating the departure of DMA molecules

(calcd: 16.40%). The third step is from 315°C to 500°C, where the $\text{H}_5\text{L1}$ began to decompose with the weight loss of 46.8% (calcd: 50.18%). For the latter, the weight loss between 60°C and 140°C corresponds to the release of lattice water and coordinated water molecules (obsd: 12.20% and calcd: 12.30%). The removal of organic components occurs at 310°C.

Luminescent properties

Two compounds are assembled from luminescent rigid ligands and d^{10} configuration ions of Zn, therefore, the solid-state photoluminescent spectra of two compounds, free $\text{H}_5\text{L1}$ and $\text{H}_5\text{L2}$ ligands were measured at room temperature. For CTGU-3, excited at 325 nm, it gives rise to an emission band at 435 nm (Fig. S10, ESI[†]). The emission spectrum of CTGU-4 exhibits an emission band at 405 nm nearby with excitation maximum at 310 nm (Fig. S11, ESI[†]) and the maximal emission peaks of free $\text{H}_5\text{L1}$ and $\text{H}_5\text{L2}$ ligand appear at 437 ($\lambda_{\text{ex}} = 390 \text{ nm}$) and 470 nm ($\lambda_{\text{ex}} = 400 \text{ nm}$), respectively (Fig. S8,S9, ESI[†]). Compared with that of free ligands, the emission bands of CTGU-4 is blue-shift, which should be ascribed to the metal-ligand coordinative interactions.²⁷ The emission of CTGU-3 and CTGU-4 can probably be assigned to the intraligand transfer. Apparently, the spectral differences between CTGU-3 and CTGU-4 are associated with the structure disparity, which has been reported in previously literature.²⁸ Besides, the emission lifetime of two compounds are 4.11 ns and 3.20 ns (Fig. S12, 13 ESI[†]).

Catalysis activities

As stated, composite catalysts were produced according to the related literature.¹⁹ To get a further insight into the structure of Ag@CTGU, high-resolution transmission electron microscopy (HRTEM) was used to investigate the dispersion and size distribution of the Ag NPs in the channel or on the surface. HRTEM images revealed that the AgNPs were crystalline and highly dispersed with an average particle size of $4 \pm 2 \text{ nm}$ (Ag@CTGU-3) and $6 \pm 2 \text{ nm}$ (Ag@CTGU-4) (Fig. 4a, 4d). Although the particles measured by TEM are larger than the pore size of CTGU, the porous structure may still offer steric restriction to confine and prevent the growth of Ag NPs. As shown in Fig. 4b and Fig. 4e, two images clearly display a lattice fringe with an interplanar distance of 0.23 and 0.20 nm, corresponding to (111) and (200) lattice plane of face center cubic Ag. Meanwhile, X-ray photoelectron spectroscopy (XPS) were operated to confirm the existence of Ag (Fig. 4c, 4f), there are two specific peaks with binding energies of 369 and 375 eV due to the Ag $3d_{5/2}$ and Ag $3d_{3/2}$ electrons of Ag^0 .

The ease of the synthesis of composite catalysts based on well-dispersed AgNPs provides opportunities for applications, especially with respect to the catalytic reduction of nitrophenol. Meanwhile, the degradation of nitrophenol in aqueous solutions is often chosen as a model reaction to study the catalytic performance of composite materials. Thus, in order to research the catalytic activity of Ag@CTGU-3 and Ag@CTGU-4, the degradation experiment was conducted in a typical way, in which

4-NP and its isomerides were chosen as reaction substrates.

Generally, the aqueous solution of 4-NP, 2-NP and 3-NP shows a strong absorption peak at 317, 277 and 272 nm. After the addition of KBH_4 , the absorption peak of nitrophenol red-shifted to 400, 390 and 414 nm, respectively, which corresponded to a color change of light yellow to yellow-green due to the formation of nitrophenolateion.²⁹ Besides, each of three nitroaromatics exhibits a negligible change in the adsorption spectroscopy after the addition of KBH_4 , indicating that KBH_4 itself has no catalytic activity for the reaction. However, when the as-prepared catalysts were added, the absorption of substrates significantly decreases at the monitored wavelength. Ultimately, for Ag@CTGU-3,

Table 2 Catalytic activities of Ag@CTGU for the reduction reaction

Catalysts	reaction substrate		
	4-NP	2-NP	3-NP
Ag@CTGU-3	$8.64\text{ s}^{-1}\text{ g}^{-1}$	$3.33\text{ s}^{-1}\text{ g}^{-1}$	$4.50\text{ s}^{-1}\text{ g}^{-1}$
Ag@CTGU-4	$3.03\text{ s}^{-1}\text{ g}^{-1}$	$8.50\text{ s}^{-1}\text{ g}^{-1}$	$1.58\text{ s}^{-1}\text{ g}^{-1}$

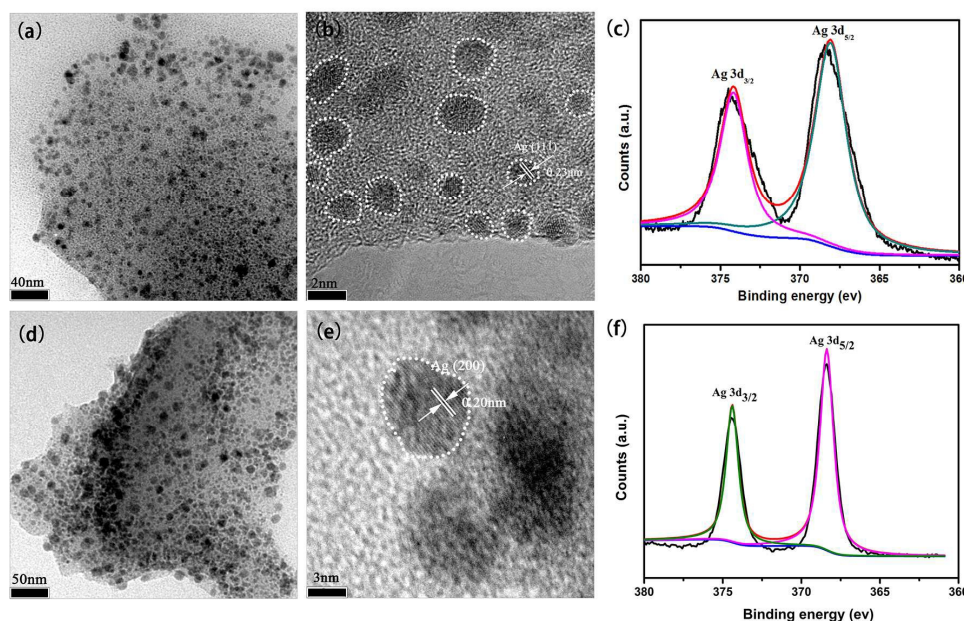


Fig. 4 (a), (b) are the TEM images of Ag@CTGU-3, (d), (e) for Ag@CTGU-4. (c), (f) X-Ray photoelectron spectroscopic (XPS) analysis of Ag@CTGU.

three nitroaromatics were decomposed completely in the presence of catalysts and KBH_4 within the time of 8 min to 11 min, while 20–26 min for Ag@CTGU-4. Interestingly, under normal circumstances, the absorbance of the reaction mixture at 400 nm gradually decreased as the reaction proceeded, along with a concomitant increase of the 300 nm peak corresponding to 4-aminophenol. Nevertheless, the characteristic peak of 4-aminophenol did not appear when Ag@CTGU was used as the catalyst, presumably as a result of the formation of intermediate products in the limited pore space of CTGU.³⁰ In the control experiment, the CTGU support shows no catalytic activity towards the target reaction. Furthermore, to test the recyclability of Ag@CTGU, catalyst was recovered from the reaction mixture by filtration, washed with distilled water, and reused directly for the next run under the same conditions. Finally, the catalyst can be successfully recycled and reused for up to three times (Fig. S17, S18 ESI†).

To study the reduction rate of nitrophenol over the different composite catalysts, the kinetics of each reaction were further investigated. As shown in Fig. 5, in each case, liner relationship between $\ln(C_t/C_0)$ and reaction time is obtained, implying that such a catalytic reaction could be of pseudo-first-order reaction, which has been observed in several similar catalytic progress.³¹ The related value of k was calculated from the slope as summarized in Table 2. For a quantitative comparison, the activity parameter $k = k/M$ was introduced,³² where M is the total mass of the catalyst added in the reaction. Thus, the reaction rate constants per unit mass were calculated to be $8.64\text{ s}^{-1}\text{ g}^{-1}$ (Ag@CTGU-3) and $3.03\text{ s}^{-1}\text{ g}^{-1}$ (Ag@CTGU-4) for the reduction of 4-NP, respectively. According to the literature, Au/ZSBA-PL catalyst and the Ag/POM-2 composites have good activity parameters of about 2.36 and $3.69\text{ s}^{-1}\text{ g}^{-1}$ respectively,³³ which is superior to some other catalysts measured under similar conditions. (Table. S2, ESI†). Obviously, in this work Ag@CTGU-3/4 composites show excellent catalytic activities for the reduction of nitrophenol.

The results revealed that both catalysts exhibited outstanding catalytic activities due to the pore structure of their support and highly dispersed Ag NPs, allowing effective mass transfer process. Compared with Ag@CTGU-4, Ag@CTGU-3 shows the enhanced catalytic efficiency, which might be attributed to the size-dependent catalytic property of Ag NPs and the surface area of support (A smaller Ag NPs would possess faster electron transfer rate on their surface, a higher surface area would guarantee the diffusion rate of substrate). Although we have demonstrated that support could be a key factor in the catalytic processes, there is still a long way to understand the nature of this effect.

In accordance with the above experimental results and traditional theory about the catalytic reduction of nitrophenol by Ag NPs, we propose a possible catalytic mechanism pathway for the reaction (Fig. 6).³⁴ Taking 4-NP as an example, nitrophenol is

adsorbed by the CTGU support. At meanwhile, borohydride ions react with the Ag NPs in the Ag@CTGU composite material and transfer active hydrogen and electrons to them, which result in the electron transfer takes place from BH_4^- to 4-NP through adsorption the nitrophenol molecules onto the catalyst surface at a later stage. Thus, the catalytic efficiency is highly dependent on the size of Ag NPs and the contacting opportunity between catalyst and reactant. Compared to nanoporous substrates, the permanent porosity of the CTGU can promote the transport of 4-NP and 4-AP. Besides, the strong interaction between Ag NPs and the support also can prevent the agglomeration of Ag NPs. This makes the Ag NPs more accessible for the substrate.

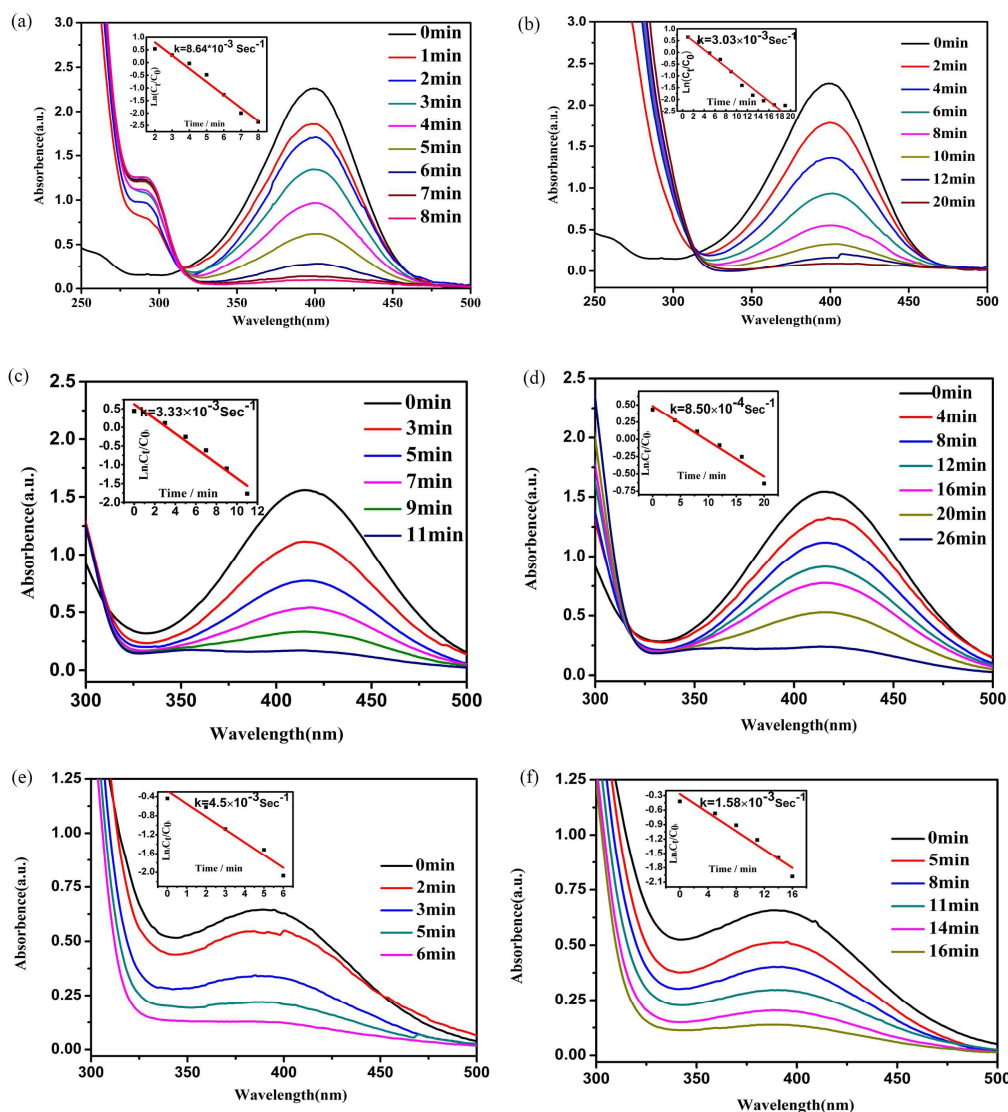


Fig. 5 (a) UV-vis spectra showing gradual reduction of 4-NP, 2-NP (c) and 3-NP (e) over Ag@CTGU-3 and Ag@CTGU-4 (b, d, f). Insert: the relationship between $\ln(C_t/C_0)$ and reaction time (t).

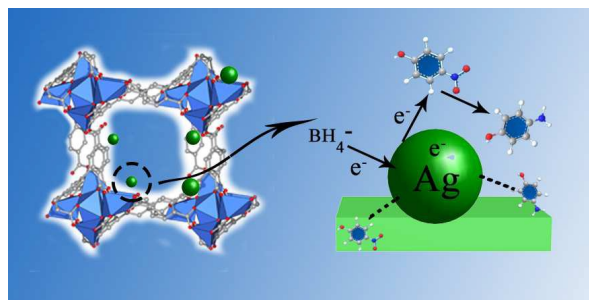


Fig. 6 Mechanism of the catalytic deduction of nitrophenol with the Ag@CTGU.

Conclusions

In summary, two novel 3D metal-organic frameworks with Zn nodes and pentacarboxylate linker have been constructed under solvothermal conditions and the as-prepared material can be employed as a catalytic support of Ag NPs. CTGU-3 features a 3D framework with *flu* topology based on H₃L1 ligand and [Zn₅(μ₃-

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H₂O)₂(RCO₂)₆] SBUs. Similarly, CTGU-4 presents a porous MOF with *dia* topology, which possesses [Zn₃(μ₃-OH)(RCO₂)₃] SBUs and 1D channels along *a* axis. Gas-sorption measurements for two compounds reveal that CTGU-3 has a considerable surface area (Langmuir 928.91 m²/g) and big differences compared to CTGU-4 within pore system. More importantly, our work demonstrated that solution infiltration of two different Zn-MOFs with AgNO₃ results in uniformly distribution of AgNPs with size related to the MOF structure and pore dimensions. Catalytic experiments indicated that two composite catalysts, Ag@CTGU-3 and Ag@CTGU-4, show different activities during the progress, which might be attributed to the wide variations caused by the support. Therefore, it has been confirmed that MOFs can be elegantly employed as hosts to provide solid catalysts with NPs size and catalytic activities regulatable based on their crystalline pore structure or surface. Currently, further efforts on the synthesis of porous MOFs based on SBUs and the application in solid catalysts support are underway.

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Graphical Abstract

Ag-NPs embedded in two novel Zn₃/Zn₅-cluster-based metal-organic frameworks for catalytic reduction of 2/3/4-nitrophenol

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Two novel microporous Zn-MOFs consist of two different unequal SBUs: [Zn₅(μ₃-H₂O)₂(RCO₂)₆] SBUs and [Zn₃(μ₃-OH)(RCO₂)₃] SBUs and possess multiple pores, which have been used to embed Ag NPs through solution infiltration. The resulted composite catalysts show outstanding catalytic activities toward the reduction of nitrophenol.

