Double-Helical Ag–S Rod-Based Porous Coordination Polymers with Double Activation: σ-Active and π-Active Functions

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Supporting Information

ABSTRACT: As common coinage metals, silver and silver compounds have very rich application in the organic catalytic reaction. Immobilization of silver compounds on heterogeneous media is the most common way used in industrial catalytic reactions. In this work, we designed and synthesized a new heterogeneous porous silver catalyst, with in situ-formed Ag–S rods as connecting nodes and thiosemicarbazide-functionalized linear ligands, used in both σ- and π-catalytic transformations. Strong Ag–S bonds bypassed the loss of noble silver elements and inhibited the formation of nonporous silver particles which always led to the decrease of yields in homogenous reactions. Furthermore, various derivatives of propargylamines and phenylacetylenes were applied as both σ and π-active substrates with moderate to good yields.

INTRODUCTION

As an important branch of synthetic chemistry, heterocatalysis has received increasing attention because of the potential industrial feasibility, low metallic residues, and low loss of catalysts.1–3 Increasing heterogenous synthetic methods have been applied to the various synthesis of value-added, structurally complex compounds. In terms of high porosity and specific surface area, heterogeneous porous materials offer many advantages over nonporous heterogeneous materials in the field of catalysis.4–6 With the periodic open structures and controllable pores, metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) are appealing porous heterogeneous catalysts for the value-added chemical transformation.7–10

Silver is the most commonly used metal catalyst in both fine organic synthetic and chemical industry.11–16 Given the specificical electronic configuration, silver catalysts could play a characteristic double catalytic activity, σ-activation and π-activation, in chemical transformation.5,17–20 With the versatile catalytic activation,21–23 heterogeneous silver catalysts have been reported, especially immobilizing silver atoms or silver nanoparticles in the pores of MOFs.24–27 In most of these reported silver MOF catalysts, Ag atoms were incorporated as guests in pores through postsynthetic methods or were incorporated into the nodes with relatively weak Ag–N or Ag–O bonds, which could not provide enough chemical stability in σ-activation and π-activation transformation.28,29 Very recently, our group has reported the first example of two silver MOFs consolidated with strong Ag–S cluster nodes used as effective π-active catalysts.30 Herein, we developed the aforementioned synthetic strategy of the catalyst with sulfur-rich ligands, in which double-helical Ag–S rods were used as the basic building blocks with high density of open catalytic sites (named as Ag-MOF-1 here and after, Scheme 1). Given

Scheme 1. Perspective Views of the Construction of the PCPs and the Double Catalytic Activity, σ-Activation and π-Activation

the good chemical stability of Ag–S bonds and the large pores, this catalyst Ag-MOF-1 was applicable for both σ-activation and π-activation transformation of alkynes and CO2.

RESULTS AND DISCUSSION

Synthesis and Structure of Ag-MOF-1. Ligand L was prepared from a Schiff base reaction of thiosemicarbazide and
1,4-phthalaldehyde in a high yield. The target crystalline materials were obtained by slowly diffusing CF₃COOAg into the solution of ligands L. Single-crystal structure analysis suggested that the double-helical rodlike SBUs (secondary building units) formed with silver atoms and bridging sulfur atoms through a glide reflection symmetry. Each Ag atom coordinated to four sulfur atoms from four different ligands in distorted tetrahedral coordinating configuration with an average Ag–S distance of 2.63 Å, in which three of the sulfur atoms were posited at one plane with the center Ag atom and another sulfur atom was served as an axial ligand (Figure 1a).

The counter anions were fixed around the thiourea motifs through H-bonding interactions and were not directly coordinated to Ag atoms, with the minimum distances of 3.18 Å between Ag and O atoms. This opening configuration of Ag sites endows both σ- and π-interaction of Ag atoms with substrates containing unsaturated triple C–C bonds. With linear thiourea-functionalized ligands as linkers between Ag–S rod SBUs, the 3D frameworks were consolidated with the I₄₁₃₂ space group and square channels (Figure 1b–d). The cross-sectional area of the channel is about 12.5 × 18.1 Å². The channel has enough space to charge substrates and provides the possibility for catalyzing the reaction of alkyne derivatives. On the surface of the Ag–S rods, there are abundant H-bonding donors (–NH₂ and –NH–) and H-bonding acceptors (C= N– and sulfur). The potential hydrogen-bonding interactions with substrates can be provided by the donors and acceptors which play an important role in synergistically activation and fixation in catalytic reaction.

With the rod SBUs consolidated by the strong Ag–S bond, Ag-MOF-1 exhibited good stability. A significant stable platform ranging from 25 to 220 °C could be observed from the thermogravimetry (TG) analysis curve (Figure 2b). After soaking in various solvents for 24 h, the similar powder X-ray diffraction (PXRD) pattern with the as-synthetic crystals was observed (Figures 2a and S3). Furthermore, the well-proportioned green fluorescence of Ag-MOF-1 absorbing fluorescein, in the confocal laser scan microscopy photograph, indicated the thorough penetration of fluorescein into the channels of Ag-MOF-1 (Figure 2c,d). Both of these results suggested that the good stability of 1D channels of Ag-MOF-1 in solution.

Characterizations and Catalytic Experiments. Because of the specific d-electron configuration, the activation between Ag and unsaturated C–C bonds with the π-interaction has been well-known. The π-catalysis experiments initially focused on the cycloaddition transformation of propargylamine and CO₂ as the negative-cost C₁ source 31–34 (Table 1). The reaction was conducted in a 10 mL Schlenk tube with a 1 mmol of propargylamine and 1 atm CO₂ at room temperature. In the presence of 1.5 mmol of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), a 20 mg Ag-MOF-1 catalyst afforded almost

![Figure 1](image1.png)

**Figure 1.** (a) Distorted tetrahedral coordinating configuration of Ag atoms; (b) connecting configuration between ligands and Ag–S rods; (c) Ag–S rods with open sites of Ag atoms; and (d) 3D frameworks of Ag-MOF-1 with the 1D channel.

![Figure 2](image2.png)

**Figure 2.** (a) Simulated and experimental PXRD pattern of Ag-MOF-1; (b) the TG curve; (c,d) the confocal laser-scanning microscopy, dark field (c) and light field (d).
Table 1. \( \pi \)-Active Catalysis with Various Propargylamine Derivatives and \( \text{CO}_2 \).\(^a\)

| Compound | Reaction Condition | Yields |
|----------|-------------------|-------|
| \( \text{Ag-MOF-1} \) | MeCN, 0.1 MPa \( \text{CO}_2 \), RT, 24 h | 95% |
| 91% | 87% |
| 55% | 52% | 52% |

\(^a\)The yields were determined using \( ^1 \text{H} \) NMR spectroscopy.

Table 2. \( \sigma \)-Active Catalysis with Various Terminal Alkynes and \( \text{CO}_2 \).\(^a\)

| Compound | Reaction Condition | Yields |
|----------|-------------------|-------|
| \( \text{Ag-MOF-1} \) | Alcohol, 0.4 MPa \( \text{CO}_2 \), RT, 24 h | 79% |
| 73% | 68% | 62% | 61% | 58% |

\(^a\)Yield of isolated pure products.

Conducted in a 10 mL autoclave reactor with 1 mmol of phenylacetylene and 0.4 MPa \( \text{CO}_2 \) at 50 °C. In the presence of 1.5 mmol of \( \text{Cs}_2\text{CO}_3 \), a 20 mg \( \text{Ag-MOF-1} \) catalyst afforded 79% conversion of the aforementioned reaction within 24 h. Homogeneous \( \text{CF}_3\text{COOAg} \) exhibited significantly less catalytic activation. Only trace yield was obtained with \( \text{Ag}_2\text{S} \) as catalysts or without any catalysts. Alcohol was selected as the optimized solvent. Moderate pressure (0.4 MPa) was needed to increase the solubility of \( \text{CO}_2 \) in alcohol. Furthermore, \( \text{Ag-MOF-1} \) was applied to various alkyne derivatives with moderate yield under optimized conditions. In both of these \( \sigma/\pi \)-activation catalyses, simple homogeneous silver salt exhibited significantly less catalytic activation, which may be due to the formation of nonporous heterogeneous silver particles, and the specific surface area of nonporous silver particles was much less than that of well-dispersed \( \text{Ag-S} \) rods in porous frameworks.

After absorbing substrate molecules, phenylacetylene, the characteristic peak of substrate molecules could be observed clearly in laser Raman confocal spectra (Figure 3a).\(^{40} \) The peaks at 1000 and 2112 cm\(^{-1} \) in Raman spectra were assigned to the ring-breathing vibration and \( \text{C} = \text{C} \) vibration, respectively. These emerging characteristic peaks confirmed the substrate molecules could diffuse into the pores of \( \text{Ag-MOF-1} \). Given the intrinsic crystallization of MOFs, guest molecules in the pores of MOFs could be directly observed by X-ray technology. Soaking \( \text{Ag-MOF-1} \) crystals in phenylacetylene solution, phenylacetylene molecules could diffuse into the pores and be fixed through multiple hydrogen bonding interactions and \( \pi-\pi \) stacking interactions with the aryl and thiosemicarbazide motifs on the intrasurface of the pores (Figure 3b). In traditional impress, the \( \text{Ag-S} \) compound was typically inert in the catalytic reaction. In many \( \text{Ag-catalytic processes, sulfate and sulfur-containing compounds were typical toxic reagents, which could inhibit catalytic activation. In this work, through a delicate design of ligands and synthetic methods, a well-oriented and separated rodlike \( \text{Ag-S} \) compound was synthesized and fixed in the porous frameworks with open catalytic sites. The open sites of \( \text{Ag-S} \) rods provided catalytic activation. Thiosemicarbazide motifs provided hydrogen-bonding sites interacting with substrate molecules. Both open sites of \( \text{Ag-S} \) rods and hydrogen-bonding sites on thiosemicarbazide motifs synergistically facilitated the \( \sigma \) and \( \pi \)-active transformation. Time-dependent \( ^1 \text{H} \) NMR spectra of reaction mixture solution in \( \sigma \) and \( \pi \)-catalytic processes clearly showed the gradual transformation, in which the peaks of reactants decreased and the peaks of products increased (Figure 3c,d).

**CONCLUSIONS**

In conclusion, we developed our previous reported synthetic methodology about the design and synthesis of \( \text{Ag-S} \)-based porous frameworks. A new \( \text{Ag-S} \)-based porous framework with double-helical \( \text{Ag-S} \) rods as connecting nodes and linear thiosemicarbazide-functional ligands was synthesized and used in both \( \sigma \) and \( \pi \)-catalytic transformation with moderate to good yields for various propargylamine derivatives and phenylacetylene derivatives. The strong \( \text{Ag-S} \) bond provided enough chemical stability, bypassing the formation of nonporous heterogeneous particles which could decrease the catalytic efficiency in a homogenous catalytic process with simple soluble silver salts as catalysts. The rich hydrogen-bonding sites in pores enhanced the interaction between frameworks and reactants. Intrinsic crystallization of MOFs endowed the direct observation of the phenylacetylene-containing crystal in situ. Good chemical stability, effective synergistic interaction of open sites on \( \text{Ag-S} \) rods and H-bonding sites, and clear mechanism endowed this catalyst-designed methodology with great advantages in \( \text{Ag-catalytic industrial reaction.} \)
for 24 h. Then, a yellow product was isolated by 0.5 mL acetic acid in 150 mL of alcohol was stirred at 80 °C (0.13 g, 1 mmol), thiosemicarbazide (0.19 g, 2.2 mmol), and a ramp of 10 °C/min. A microscopy micrographs with FV1000 instrument was used to record confocal laser scanning microscopy micrographs with 10831 λex = 488 nm. A Thermo Fisher-Schlenk tube. The reaction solution was degassed with CO2 for 20 min, and then, the reaction was sustained with 1 atm CO2 at room temperature for 1 day. The yields were determined by using 1H NMR spectroscopy.

**Synthesis of Substrates.** The substrates in Table 1 were purchased from Energy Chemical and used without further purification. The substrates in Table 2 were prepared according to previous ref 30.

**α-Activation Catalysis Experiments.** Propargylamine (1 mmol) and acetonitrile (5 mL), in the presence of 1.5 mmol of DBU and 20 mg Ag-MOF-1 catalyst, were added in a 10 mL Schlenk tube. The reaction solution was degassed with CO2 for 20 min, and then, the reaction was sustained with 1 atm CO2 at room temperature for 1 day. The yields were determined by isolating pure products.

**Isolation Method of Products of the α-Catalysis Experiments.** The organic phase was collected and then purified by flash column chromatography on silica gel (n-hexane/ethyl acetate) (v/v = 1:1) to isolate the desired products.

**Isolation Method of Products of the π-Catalysis Experiments.** The reaction mixture was diluted with water (30 mL) and extracted with n-hexane (2 × 20 mL). The aqueous layer was acidified with aqueous HCl (6 N, 20 mL) at low temperatures and then extracted with ethyl acetate (4 × 30 mL). The combined organic layers were washed with water.

### EXPERIMENTAL SECTION

**Materials and Measurements.** All chemicals were of reagent grade quality and were obtained from commercial sources and used without further purification. A Rigaku Smart Lab XRD instrument with a sealed Cu tube (λ = 1.54178 Å) was used in PXRD measurements. A Varian INOVA 500 M spectrometer was used to perform 1H NMR with tetramethylsilane as the internal reference. Dalian Institute of Special Gases provided carbon dioxide (99.995%), which can be used as received. Raman spectroscopy (Lab Raman HR Evolution) measurements were performed using a solid-state 633 nm laser, and a laser power of 25% was used. A JASCO FT-IR-430 instrument was used to record the structures in direct methods, which was refined on F2 by the full-matrix least-squares method with the program SHELXL-97.

**Synthesis of Ligand (L).** A mixture of 1,4-phthalaldehyde (0.13 g, 1 mmol), thiosemicarbazide (0.19 g, 2.2 mmol), and 0.5 mL acetic acid in 150 mL of alcohol was stirred at 80 °C for 24 h. Then, a yellow product was isolated by filtration and washed with ether three times to get dry products. Yield: 99%, 0.28 g. (The 1H NMR spectrum was Figure S4).

**Synthesis of Ag-MOF-1.** CF3COOAg was dissolved in acetonitrile to form solution 1 (0.02 mol/L). The ligand L was dissolved in N,N-dimethylformamide (DMF) to form solution 2 (0.02 mol/L). Then, 1 mL solution 2 was dropped into the lower layer of the glass tube. 5 mL mixed solution (DMF: acetonitrile v/v = 1:1) was used as the intermediate layer. 1 mL solution 1 was used as the upper layer. The tube was sealed and stored in the dark for 1 month. The colorless crystals were afforded. Yield: 60% (based on Ag).

**Single-Crystal Analysis.** X-ray intensity data were carried out on a Bruker SMART APEX charge-coupled device-based diffractometer (Mo Kα radiation, λ 0.71073 Å) with the SAINT and SMART programs. The SAINT software was used in the data integration and reduction. Empirical absorption correction, which was applied to the collected reflection, worked with SADABS. SHELXTL was used to solve the structures in direct methods, which was refined on F2 by the full-matrix least-squares method with the program SHELXL-97.

**Isolation Method of Products of the π-Catalysis Experiments.** The organic phase was collected and then purified by flash column chromatography on silica gel (n-hexane/ethyl acetate) (v/v = 1:1) to isolate the desired products.

**Isolation Method of Products of the π-Catalysis Experiments.** The reaction mixture was diluted with water (30 mL) and extracted with n-hexane (2 × 20 mL). The aqueous layer was acidified with aqueous HCl (6 N, 20 mL) at low temperatures and then extracted with ethyl acetate (4 × 30 mL). The combined organic layers were washed with water.
and brine, dried over Na₂SO₄ and filtered. The solvent was removed under vacuum to afford the acid products.36

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00742.

Experimental details, crystal data, additional catalytic information, ¹H NMR spectra, and gas chromatography–mass spectrometry spectra for the products (PDF)

Crystal data of Ag-MOF-1 (CIF)

Crystal data of the Ag-MOF-1 guest (CIF)

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Notes

The authors declare no competing financial interest.

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