

Alkyne Activation by a Porous Silver Coordination Polymer for Heterogeneous Catalysis of Carbon Dioxide Cycloaddition

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Supporting Information

ABSTRACT: The widely studied porous coordination polymers, possessing large pores to adsorb waste carbon dioxide gas and further transform it into valuable chemical products, have been attracting research interest, both industrially and academically. The active silver(I) ions endow the specific alkynophilicity to activate $C \equiv C$ bonds of alkynecontaining molecules via π activation. Incorporating catalytic Ag metal sites into the porous frameworks represents a promising approach to construct heterogeneous catalysts that cyclize propargylic alcohols with CO_2 , which is highly desirable for the environmentally benign conversion of carbon dioxide to fine chemicals. We report the preparation of porous coordination polymers (PCPs) with active silver sites and



efficient silver–silver bond formation by carefully modifying the coordination geometries of the silver sites. The decentralized silver(I) chains in the porous frameworks enable the efficient conversion of CO_2 and derivatives of acetylene to α -alkylidene cyclic carbonates in a heterogeneous manner. X-ray structure analysis reveals two kinds of substrate molecules positioned within the pores of the framework, which correspond to trapping and activated modes through the multiple interactions with the functional Ag chains. The example of tandem conversion of simple alkynes and carbon dioxide to α -alkylidene cyclic carbonates is also presented. The well-positioned catalytic silver(I) sites and the crystalline properties of the frameworks facilitated the structural analyses of the intermediates of each catalytic step, providing knowledge of the synergistic nature of the σ and π activation of C=C bonds. The successful catalysis of azide–alkyne cycloaddition and synthesis of propargylic alcohols via terminal alkynes could also give another indicator for the activation properties of Ag sites.

KEYWORDS: silver coordination polymer, carbon dioxide, cyclic carbonates, multiple activation, heterogeneous catalyst

INTRODUCTION

The use and transformation of abundant gaseous waste, such as converting carbon dioxide as a C1 source into valuable chemical products using cheap and easily obtained industrial chemicals, fulfills the requirements of green chemistry and atom economy.^{1–4} The nucleophilic addition of terminal alkynes to various unsaturated electrophiles, which has been extensively studied, enables the introduction of the alkyne functionality.⁵ The resultant propargylic alcohols directly react with CO₂ for conversion into cyclic carbonates with potential biological and commercial value.⁸⁻¹⁰ In general, to ensure this conversion, both catalytic processes require heavy-transition-metal catalysts as well as a subsequent separation and purification of products from the reagents, catalysts, and associated materials.¹¹⁻¹³ A procedure enabling multiple conversions of alkynes via a chain of discrete catalytic steps and a single workup stage is highly desirable for the environmentally benign conversion of carbon dioxide to fine chemicals.¹⁴⁻¹⁶ Recently, reports have shown that silver complexes have the potential to σ -activate terminal alkynes and π -activate internal alkynes of C=C bonds for discrete reactions.¹⁷⁻¹⁹ Most of the studies have concentrated

on homogeneous catalysis using relatively large amounts of Agbased catalysts. However, the low catalytic activity and the leaching of active species make the alkyne activation by silver complexes in the heterogeneous state challenging, and few examples of heterogeneous catalysis for this conversion have been reported.^{20,21}

As one type of typical crystalline porous solid that resembles zeolites, porous coordination polymers (PCPs) are able to utilize a minimum amount of metal ions and organic ligands to build maximum surface areas with predictable, controllable, tailorable, and modifiable pores and cavities.^{22–24} Due to these intrinsic structural attributes, porous coordination polymers have emerged as promising candidates for catalysis because they combine the benefits of heterogeneous catalysis, such as easy postreaction separation and catalyst reusability, with those of homogeneous catalysis, such as high selectivity and controllability.^{25–29} PCP-based catalysis has been recently used for

Received: November 30, 2016 Revised: February 10, 2017 Scheme 1. Representation of the Porous Silver Coordination Polymer for the Carboxylic Cyclization of a Phenyl Propargylic Alcohol with CO_2 to α -Alkylidene Cyclic Carbonates



CO₂ fixation and transformations, such as cycloaddition of epoxides, photochemical reduction, and carboxylation.^{30–33} Our group has also been dedicated to constructing several PCP materials for the catalysis of CO₂ cycloaddition to cyclic carbonates in an asymmetric autotandem conversion or even using raw power plant flue gas as a CO₂ source in the past two years.^{34–37} These developments have inspired the design and preparation of previously poorly established silver-based PCPs for the potential σ and π activation of C=C bonds and tandem transformation of alkyne derivatives to cyclic carbonates directly with CO₂.^{38–40}

From a catalytic perspective, π activation by Ag ions is different, since the silver-based catalytic properties are different from those of the typical Lewis acid catalyst.^{41,42} The fundamental mechanism of silver catalysts promoting π interaction with a triple carbon–carbon bond is electrophilic activation, which requires more space for the direct interactions. However, the construction of three-dimensional PCPs usually relies on the formation of a pattern of multiply connected nodes, and this peculiar structural characteristic remains an ongoing challenge for developing silver-based catalysts in PCP systems due to the unfavorable ability of the catalytic center Ag ions to connect to C=C bonds via π activation.

On the basis of this information, we report the incorporation of the tetrakis(4-carboxyphenyl)ethylene (H₄TCPE) moiety as a four-point connected node to combine alkynophilic silver ions in the porous and coordination frameworks. We envision that the decentralized Ag chains in this structure exhibit excellent potential to activate the π position of C \equiv C bonds, and thus Ag-TCPE represents efficient catalytic capability in a heterogeneous manner for the carboxylative cyclization of propargylic alcohols with carbon dioxide (Scheme 1). The successful catalysis of azide-alkyne cycloaddition also gives another indicator of the activation properties of Ag sites. Additionally, starting from nucleophilic addition of terminal alkynes followed by cycloaddition of propargylic alcohols, without further preparation, the tandem catalytic performance of a silver-based PCP is presented. The intrinsic crystalline properties of the frameworks facilitated deeply structural analyses of the intermediates of each active and catalytic step, providing powerful knowledge of π activation of C \equiv C bonds by Ag sites.

EXPERIMENTAL SECTION

Materials and Instrumentation. All chemicals were of reagent-grade quality, were obtained from commercial sources, and were used without further purification. All starting reagents were obtained from Acros or TCI and used as received. Carbon dioxide (99.995%) was purchased from the Dalian Institute of Special Gases and used as received. The elemental analyses of C and H were performed on a Vario EL III elemental analyzer. Inductively coupled plasma (ICP) analysis was performed on a Jarrel-Ash J-A1100 spectrometer. The powder XRD diffractograms were obtained on a Riguku D/MAX-2400 X-ray diffractometer with a Cu sealed tube ($\lambda = 1.54178$ Å). IR spectra were recorded as KBr pellets on a NEXUS instrument. Thermogravimetric analyses (TGA) were carried out at a ramp rate of 10 °C min⁻¹ under a nitrogen flow with an SDTQ600 instrument. Solution UV-vis spectra were performed on a TU-1900 spectrophotometer. Confocal laser scanning microscopy (CLSM) micrographs were collected by an Olympus Fluoview FV1000 instrument with λ_{ex} 488 nm. Raman spectroscopy (Lab Raman HR Evolution) measurements were performed using a solid-state 683 nm laser. A laser power of 1-2.5% was used to avoid degradation of the sample by the laser beam during the Raman measurements. The morphology of the crystals was observed using a scanning electron microscope (SEM, QUANTA 450, FEI, US) at an accelerating voltage of 20.00 kV and a working distance of 10 mm. All samples were coated with gold before SEM examination. CO₂ sorption isotherms were measured using an Autosorb-IQ-C analyzer of Quantachrome. ¹H spectra were recorded on a Varian INOVA 400 MHz spectrometer. Peak frequencies were referenced versus an internal standard (TMS) for ¹H NMR.

Preparation of Samples. All reagents were used as purchased without further purification. Tetrakis(4-carboxyphenyl)ethylene (H_4TCPE) was prepared according to the methods in the literature⁴³ and characterized by ¹H NMR.

Synthesis of Ag-TCPE. A mixture of H_4TCPE (30 mg, 0.06 mmol) and AgNO₃ (134 mg, 0.2 mmol) was dissolved in 4 mL of a mixed solvent of dimethylformamide (DMF) and DMA in a screw-capped vial. The resulting mixture was kept in an oven at 100 °C for 3 days. After the autoclave was cooled to room temperature, dark red blocklike single crystals were separated, washed with water, and air-dried. Yield: 10% (based on the



Figure 1. (a) Representation of Ag chains linked by each μ_2 -O bridge of the H₄TCPE ligand. (b) Connected mode of Ag chains. (c) Structure of Ag-TCPE showing the three-dimensional network. (d) Schematic representation of the Ag-TCPE network as tiling. Color code: Ag, violet; O, red; C, green. H atoms are omitted for clarity.

crystal dried under vacuum). Anal. Calcd for $C_{15}H_{12}O_6Ag_2$: C, 35.74; H, 2.40; Ag, 42.80. Found: C, 35.90; H, 2.23; Ag, 43.24. IR (KBr): 3436 (br, s), 1593 (s), 1530 (w), 1387 (m), 1196 (vs), 1066 (m), 794 (s) cm⁻¹.

Ag-TCPE@1a. Ag-TCPE was first soaked in a methanol solution (72 h) to remove guest molecules and then fully dried, removing the alcohol molecules, in a vacuum oven (100 °C, 2 h). Crystals of Ag-TCPE@1a were obtained by soaking the treated Ag-TCPE crystals in a (10 mmol) propargyl alcohol dichloromethane solution for 48 h.

Crystallography. X-ray intensity data were measured on a Bruker SMART APEX CCD-based diffractometer (Mo K α radiation, λ 0.71073 Å) using the SMART and SAINT programs.^{44,45} The crystal structure was solved by direct methods and further refined by full-matrix least-squares refinements on F^2 using the SHELXL-97 software, and an absorption correction was performed using the SADABS program.⁴⁶ The remaining atoms were found from successive full-matrix least-squares refinements on F^2 and Fourier syntheses. Non-H atoms were refined with anisotropic displacement parameters. The hydrogen atoms within the ligand backbones were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. In the refinement of crystal data of Ag-TCPE@1a, to

help the stability of the refinement for the encapsulated related substrate molecule, bond distances between several atoms were fixed for the ideal geometrical shape. There are two and a half solvent CH_2Cl_2 molecules within an asymmetric unit. C55, Cl5, and Cl6 had 0.5 occupancy, and one Cl atom was disordered into two parts (Cl0 and Cl2) with their SOF values refined as 0.35 and 0.65, respectively. Crystallographic data for **Ag-TCPEs** are summarized in Table S1 in the Supporting Information.

Catalysis Details. Before the catalysis experiments, solventexchange experiments were carried out to activate the catalysts by removing the coordinated water molecules and solvent. The crystal samples were immersed in methanol for 3 days and then fully dried out at 100 °C under high vacuum for 2 h to produce the activated samples.

Cyclization of Propargylic Alcohols with CO_2 . In a typical reaction, the catalytic reactions were conducted in a 25 mL autoclave reactor with propargylic alcohol (2 mmol) and Ph₃P (2.5 mol %) in 1 mL of CH₃CN, purged with 0.5 MPa of CO₂ under a constant pressure for 10 min to allow the system to equilibrate. The vessel was set in an oil bath with frequent stirring at a temperature of 50 °C for 36 h. At the end of the reaction, the reactor was placed in an ice bath for 20 min and then opened. The catalysts were separated by centrifugation, and a small aliquot of the supernatant reaction mixture was taken to be analyzed by ¹H NMR to calculate the yields of the reaction. The organic phase was collected and then purified by flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to isolate the desired products.

Azide–Alkyne Cycloaddition. The catalytic reaction was conducted in a 2 mL glass vial with a tetrafluoroethylene lid. To a mixture of phenylacetylene (1 mmol) and benzyl azide (1 mmol, 1 equiv) in 0.1 mL of water was added the catalyst (1 mol % loading, based on each Ag site). The mixture was then stirred at 50 °C for 24 h. The reaction mixture was diluted with dichloromethane (10 mL). The catalysts were separated by centrifugation. Subsequently, 10 mL of water was added, and the organic layer was extracted with dichloromethane and dried over anhydrous sodium sulfate. The organic phase was concentrated under vacuum and purified through silica gel column chromatography (ethyl acetate/hexanes) to afford the pure product. All reported yields are isolated yields.

Tandem Conversion of Alkyne and CO₂ to α -Methylene Cyclic Carbonates. In a typical reaction, the catalytic reaction was conducted in a 25 mL autoclave reactor, with the addition of 2 mmol of phenylacetylene and acetone (1.5 equiv, 0.22 mL) in the presence of the catalyst Ag-TCPE (1.0 mol %), t-BuOK (5 mol %), Ph₃P (5 mol %), and 1 mL of CH₃CN, which were directly placed in the reactor and then purged with 0.5 MPa CO₂ under constant pressure for 10 min to allow the system to equilibrate. The vessel was set in an oil bath with frequent stirring at a temperature of 40 °C for 72 h. At the end of the reaction, the reactor was placed in an ice bath for 20 min and then opened. The catalysts were separated by centrifugation, and the reaction mixture was taken to be analyzed by ¹H NMR to calculate the yields of the reaction using durene as an internal standard. The yields of the general reactions with different substrates are indicated in Table S4 in the Supporting Information.

RESULTS AND DISCUSSION

The synthesis of Ag-TCPE began with AgNO₃ and H₄TCPE in a solvothermal reaction at 100 °C in a DMF/DMA mixed solvent. Single-crystal X-ray structural analysis revealed that Ag-TCPE crystallized in the C2c space group. The asymmetric unit of this structure contains two independent, four-coordinate Ag(I) ions, bound in a tetrahedral fashion with identical coordination modes (neglecting the Ag…Ag interactions). Ag1 and Ag2 are bridged by two μ_2 -O atoms from the carboxylic groups of two H₄TCPE ligands and anchored by another oxygen atom of the H₄TCPE ligand and one lattice water molecule, which can be considered as a potential catalytic metal site after guest-molecule exchange, which would remove the lattice water and solvent molecules (Figure 1). For each H₄TCPE ligand, one oxygen atom of the carboxylic groups acts as a μ_2 -O bridge, whereas the other oxygen acts only as a μ -O bridge to link each layer of the Ag chains. Notably, the Ag...Ag distances between the silver pair bridged by one carboxylic group of 2.85 Å (shorter than 3.44 Å, the Ag…Ag van der Waals radius) indicate an argentophilic interaction. Considering the weak Ag...Ag interaction between monatomic-bridged silver pairs, the silver atoms are cross-linked to form one-dimensional chains (Figure 1b). The close bonding of the Ag atoms facilitates long-range charge and electron transfer and endows the strong activating capacity. These functional Ag chains, distributed on the tube walls, rather than the vertexes of the framework, reduce the steric hindrance and at the mean time

magnify effective contact regions of both sides, providing a beneficial feature to capture and activate specific molecules.

The skeleton of the Ag-TCPE extends the chains to form 3D frameworks with large quadrilateral channels of $15.4 \times 15.4 \text{ Å}^2$ along the *c* direction. The overall framework is depicted by a Schläfli symbol of $\{6^4.8^2\}_2\{6^6\}$. In the absence of guests, the PLATON program gives a free void volume of 52.6% of the crystal volume of Ag-TCPE, approximately 2930 Å³ per unit cell. Dye-uptake studies were performed by soaking the crystals in a methanol solution containing 2',7'-dichlorofluorescein and exhibit 9.8% uptake based on Ag-TCPE's weight (Figure S8 in the Supporting Information). Additionally, confocal laser scanning microscopy of the guest-adsorbed crystals gave a strong green fluorescence response (λ_{ex} 488 nm) that can be assigned to the emission of fluorescein (Figure S9 in the Supporting Information). The uniform distribution of the dye molecules throughout the crystals suggests that the dyes penetrated deeply into the channels, rather than remaining on the external surface.47 These results give potent evidence of porous characteristics and the capacity of adsorbing and accommodating substrate molecules in its pores. The unsaturated metal sites in the MOF created by structural defects would increase its interaction with CO₂ molecules and thus improve its CO₂ uptake capacity and promote high selectivity and efficient chemical transformations. The CO₂ adsorption measurements at 273 and 298 K are reversible and show q steady rise with an uptake of 56.4 cm³ g⁻¹ (corresponding to 2.52 mmol g⁻¹) and 42.2 cm³ g⁻¹ (corresponding to 1.88 mmol g⁻¹) for Ag-TCPE at 1 bar, respectively (Figure S10 in the Supporting Information). This suggests a sound interaction between the Ag-TCPE framework and CO₂ molecules. These features also render Ag-TCPE a solid sorbent material for CO₂ capture.

Our catalytic experiments were initially performed on the carboxylic cyclization of phenyl propargylic alcohols as a model for reaction with carbon dioxide. In a typical experiment, reactions were conducted in an autoclave reactor with propargylic alcohol (2 mmol) and CO₂ purged to 0.5 MPa in 1 mL of CH₃CN at 50 °C. ¹H NMR analysis revealed that Ag-TCPE (0.5 mol % loading, based on each Ag site) could act as an effective heterogeneous catalyst for this catalysis reaction in the presence of 2.5 mol % triphenylphosphine (Ph_3P) and afforded nearly complete conversion within 36 h. No rearrangement side product, such as α_{β} -unsaturated ketone, was observed after the reaction. In the control experiments, no detectable conversion occurred in the absence of catalysts, and Ph₂P itself was ineffective under the given reaction conditions. However, Ph₃P also plays a significant role in the catalytic system, as there is no carboxylative product without adding it (Table 1, entry 6). Notably, other silver(I) salts, such as AgNO₃, AgOAc, and AgSO₃CF₃ displayed negative activity under identical conditions (Table 1, entries 1-3). The simple mixture of AgNO3 and H4TCPE could also not afford the detected conversion under the same reaction conditions (Table 1, entry 4). When other additives were used to replace Ph₃P, such as TBABr (tetra-n-butylammonium bromide), TBUP (trin-butylphosphine), and DBU (1,8-diazabicyclo[5.4.0]undec-7ene), all of them gave low yields under identical conditions (Table 1, entries 7-9). Internal propargylic alcohols with various substituted R¹ groups were subject to carboxylative cyclization (Table 2). No significant conversion was observed under identical reaction conditions, and all reactions gave excellent yields. Additionally, 2-methyl-3-butyn-2-ol (2i) and 3Table 1. Control Experiments of Carboxylic Cyclization of Propargylic Alcohols with $CO_2^{\ a}$



^{*a*}Reaction conditions unless specified otherwise: propargylic alcohols (2 mmol), catalyst (0.5 mol %), additive (2.5 mol %), and CH₃CN (1 mL) under CO₂ (0.5 MPa), 50 °C and 36 h. ^{*b*}The yields were determined by ¹H NMR analysis using durene as internal standard. ^{*c*}H₄**TCPE** (0.05 mmol). ^{*d*}Solvent free.

Table 2. Ag-TCPE-Catalyzed Cyclization of Propargylic Alcohols with CO_2^a



^{*a*}Reaction conditions unless specified otherwise: propargylic alcohols (2 mmol), catalyst (0.5 mol % loading, based on each Ag site), Ph₃P (2.5 mol %), and CH₃CN (1 mL) under CO₂ (0.5 MPa), 50 °C, and 36 h. ^{*b*}The reaction time was 20 h. The yields were determined by ¹H NMR analysis using durene as internal standard.

methyl-1-pentyn-3-ol (2j) as substrates have also been investigated and give excellent yields (>99%) within 20 h of the reaction under an identical catalytic system, which enlarges the feasibility of the catalyst Ag-TCPE. Increasing the bulk of substituted R¹ or R² groups (i.e., 2e,h) caused the yield to decrease. The size selectivity of the substrates suggested that the catalytic processes occurred within the pores of the catalysts.

The catalytic efficiency of **Ag-TCPE** was compared with that of **Ni-TCPE2**, a previously reported framework containing identical amounts of catalyst sites for each ion and a similar framework skeleton as a reference.³⁴ The fact that no detectable amounts of the carboxylic cyclization products were found under identical reaction conditions indicates that the effect of the metal ions on this type of reaction is specific to typical π activation of Ag ions. As is shown in Figure 2a, the removal of Ag-TCPE by filtration after 12 h shut down the reaction, and no additional conversions were observed for another 24 h under the same reaction conditions. This observation suggested that Ag-TCPE is a true heterogeneous catalyst in the catalytic system and is stable enough to ensure that no leaching of metal ions occurs during the catalysis process.⁴⁸ For the heterogeneous catalysts, recyclability is an essential feature for them to be considered for practical use in industrial applications. The residual Ag-TCPE from the reaction isolated by simple filtration was used for successive runs with freshly added Ph₃P. The yields of cyclic carbonates were not significantly affected in additional cycles (Figure 2b), although the loss of small amounts of the catalyst is unavoidable. The XRD patterns and IR spectroscopy (Figures S5 and S7 in the Supporting Information) of the reused crystals did not exhibit any significant changes. Dye-uptake studies revealed that the dyeuptake ability of the recovered catalyst (8.9%) was nearly identical with that of the original catalyst, confirming the chemical stability of fresh Ag-TCPE and that recovered after each cycle.

One of the most outstanding features of the porous materials is their ability to accommodate molecules within their pores; the robust crystallinity of these networks facilitates the X-ray analysis of the encapsulated products.49,50 The definitive identification of the captured structure gives more information on the intermediate process of the catalytic reactions and has become an increasingly general method for catalytic studies. As postulated in the literature, the well-positioned catalytic Ag(I) sites and the crystalline properties of the frameworks facilitate deep structural analyses of the intermediates of the catalytic steps and provide knowledge of the activation nature of the $C \equiv C$ bonds.^{51,52} Fortunately, the quality of substrate 1aimpregnated Ag-TCPE crystals was sufficient for X-ray structure analysis (noted as Ag-TCPE@1a). While the cell dimensions of the crystals are almost the same as those of the original, the strong interactions between the substrates and the frameworks lead to a change in symmetry from the space group C2/c to the space group $P2_1/n$. Clearly, the asymmetric unit of this structure contains four independent Ag(I) ions, each bound in a tetrahedral fashion with identical coordination modes. As shown in Figure 3, two different types of 1a molecules were observed positioned close to the functional Ag chains within the frameworks. One type of 1a molecule exhibited a weak Ag…O coordinate bond (the Ag…O separation of 2.81 Å). It is postulated that this type of interaction has the potential to supply the driving force for the substrate trapping in the cavity of catalyst Ag-TCPE. Several cooperative Ag…C interactions were also found, which corresponded to the aromatic rings stabilizing the encapsulated mode. The distances between the Ag ions and the aromatic atoms of 3.29–3.33 Å were well within the reported range, ^{53,54} probably providing additional driving force to fix the substrate close to the catalytic sites with the potential activated bonds well-positioned near the active silver sites. Another type of 1a molecule exhibited stronger Ag…C interactions relevant to the aromatic rings, with the average separation compressed from 3.30 to 3.00 Å, but showed much weaker Ag…O interactions relevant to the hydroxyl group of propargylic alcohol (Ag---O 3.46 and 2.81 Å). The weak but significant Ag…C interactions corresponding to the C \equiv C bonds were also found in this type of interaction mode with the shortest intermolecular separation of 3.16 Å. If the first type of substrate-framework interactions was related to the trapping of the substrates, the latter is



Figure 2. (a) Catalytic traces of cyclization performed under optimal conditions with the catalyst Ag-TCPE filtered after 12 h. (b) Recycling experiments at each run.



Figure 3. Structure of propargylic alcohol impregnated crystals Ag-TCPE@1a and enlarged views showing the positions of the substrate and multiple-type interactions between the Ag ions and substrates.

possibly related to the π activation of the C=C bonds. These morphological differences can be attributed to the dynamic interaction process from molecular trapping to the substrate activation stage. From a mechanistic viewpoint, the dynamic reversible weak Ag…O coordinate bonds first form to trap the molecules of 1a within the pores of the catalyst, fix the molecules close to the catalytic sites via the weak Ag…C (aromatic ring) interactions, position the C=C bonds close to the silver chains, and finally form Ag…C (C=C bond) interactions, thus leading to a decrease in the electron density in the triple bonds and the direct activation of them. This unique decentralized structural distribution of Ag chains endows the catalyst Ag-TCPE with the specific alkynophilicity.

Raman and ¹H NMR measurements of the crystals Ag-TCPE@1a were also carried out to verify the existence and activation of propargylic alcohol molecules (Figure 4). In comparison with the Raman spectrum of the free Ag-TCPE, the spectrum of Ag-TCPE@1a exhibits two new peaks at 990 and 2225 cm⁻¹, which correspond to the characteristic peak of C=C stretching.⁵⁵ The obvious red shifts from 997 and 2230 cm⁻¹ of free propargylic alcohol suggest the adsorption and the activation of 1a within the channels of Ag-TCPE. The ¹H NMR signal of the OH group shifted from δ 3.41 to 3.46 ppm, providing further evidence for the activation process. Additionally, there is a small emerging peak at 3.54 ppm next to 3.46 ppm, which is attributed to the hydrogen-bonding interaction between Ag-TCPE and 1a, leading to the enhancement of O nucleophilicity. These two signals of the OH group also match well with the trapping and activated modes of 1a captured by the X-ray structure analysis.

To further examine the π -activation behavior of our Ag-based PCP catalyst in the catalytic reactions, azide-alkyne cycloaddition was performed. This reaction, as a representative example of "click" reactions, has been extensively studied and widely employed in organic synthesis, medicinal chemistry, and polymer science.^{56,57} Nevertheless, only a few studies regarding silver-based catalysts have been reported.^{58–60} In the presence of Ag-TCPE with a mixture of benzyl azide (1.0 mmol) and phenylacetylene (1.0 mmol) in 0.1 mL of H₂O, the substrate exhibited 90% conversion after 24 h. Other phenylacetylene substrates exhibited excellent to moderate yields under identical conditions (Table 3). As is known, the synthesized silver phenyl acetylide intermediate with Ag ions fixed to the terminal $C \equiv C$ bond cannot be directly reacted with benzyl azide because there is no further π activation of extra Ag catalytic sites.⁶¹ These results fully demonstrate that the framework structure and decentralized Ag centers in our catalyst are beneficial for the π activation to promote the catalysis.

Having established the π -activation behavior of the **Ag**-**TCPE**-catalyzed carboxylative cyclization protocol, we investigated the possibility of tandem conversion of alkyne and carbon dioxide to α -alkylidene cyclic carbonates in related reactions. Acetone and phenylacetylene were selected as the first step to examine the conversion of propargylic alcohol (reaction 1, Figure 5, top scheme). When phenylacetylene and acetone were mixed in the presence of the catalyst **Ag**-**TCPE** and *t*-BuOK (potassium *tert*-butoxide) was added at room temperature under solvent-free conditions, the desired product was isolated with considerable yields. Other terminal alkynes with various alkyl substituents on the phenyl moiety at the para



Figure 4. (a) Raman spectra of Ag-TCPE impregnated with propargyl alcohol (Ag-TCPE@1a, blue) and free Ag-TCPE (black). The inset gives the Raman spectrum of free propargyl alcohol (1a). (b) Photographs and ¹H NMR spectra of substrate 1a (top) and the treated crystals Ag-TCPE impregnated with propargyl alcohol (bottom) in CD_3CN-d_3 .





"Reaction conditions: alkyne (1.0 mmol), benzyl azide (1.0 mmol), catalyst (1 mol % loading, based on each Ag site) and H_2O (0.1 mL) at 50 °C and 24 h. The yields were calculated using the isolated product.

position also produced the corresponding propargylic alcohols in good to excellent yields (Figure 5a). To verify the potential interactions between **Ag-TCPE** and phenylacetylene, the phenylacetylene-uptake test was performed. After the catalyst **Ag-TCPE** was added to water with 20 μ L of phenylacetylene sitting on the top, the organic layer gradually faded and disappeared after 1 h, showing a fast uptake of phenylacetylene molecules (Figure S13 in the Supporting Information). This result reveals that the porous **Ag-TCPE** is capable of quickly adsorbing the substrate phenylacetylene into its pores.

According to the above catalysis results for starting with phenylacetylene and propargylic alcohol as substrates, respectively, our protocol worked well for both internal and terminal carbon–carbon triple bonds. A three-component catalytic system for tandem reactions, consisting of phenylacetylene, acetone, and CO_2 , has been established (reaction 3, Figure 5, top scheme). The tandem reactions occurred smoothly and gave the targeted carboxylative cyclization products with ultimate 93% conversion and 73% selectivity for **Ag-TCPE** (100[carbonate]/([carbonate] + [propargylic alcohol]) %). Control experiments showed that the presence of CH₃CN as solvent could effectively avoid the reaction of CO_2 with alkyne forming the unwanted propiolic acid in this tandem reaction system.^{62,63} From the view of the plausible mechanism, the smooth conversion of phenylacetylene into cyclic

carbonates can be attributed to the dual-activation patterns of the Ag-based catalysts. The fast adsorption of phenylacetylene molecules is believed to facilitate the proximity between Ag ions and the alkyne deprotonation by the additive base. Subsequent nucleophilic addition of the activated terminal alkyne to the carbonyl group generates the oxygen-centered anion of the propargylic alcohol.⁶⁴ Consequently, the terminal alkyne is occupied via the protodemetalation process of σ coordinated Ag ions. However, the short distance facilitates further π activation of the internal alkynes by Ag ions. The next conversion occurs in the presence of CO₂ and added Ph₃P, which plays a key role in the promotion of CO₂ fixation and activation. The nucleophilic attack on the silver propargylic alcohol carbonate intermediate, which was generated by π activation of the $C \equiv C$ bonds, gives the corresponding carboxylative cyclization product via a protodemetalation process.

CONCLUSION

In conclusion, a porous Ag(I)-based coordination polymer was synthesized by incorporating the tetraphenylethylene moiety as the backbone. The unique decentralized silver(I) chains in the frameworks endow the specific alkynophilicity to activate $C \equiv C$ bonds, enabling the efficient conversion of CO₂ and derivatives of acetylene to α -alkylidene cyclic carbonates in a heterogeneous manner. The substrate propargylic alcohol could enter the pores of catalyst Ag-TCPE and have multiple interactions with Ag sites. The trapping and activated modes of propargylic alcohol molecules have been captured within one single-crystal structure. π activation and σ activation of the substrates enabled successful tandem conversion of the phenylacetylene and carbon dioxide to α -alkylidene cyclic carbonates in a singlesystem catalysis reaction for the first time. The well-positioned catalytic silver(I) sites and the crystalline properties of the frameworks facilitated the structural analyses of the activation intermediates and verified the existence of π activation of C \equiv C bonds, which were further examined by the reaction of azidealkyne cycloaddition. This work provides a highly promising approach for achieving continuous conversion by constructing a dual-activation catalytic center in a single system, in which the porous materials act as a microscopic chemical reactor for the interaction and fast transport of the substrate molecule in its cavities.



Figure 5. (top) Scheme of the tandem catalytic conditions. (a) Yields of the reaction of various phenylacetylene and acetone catalyzed by **Ag-TCPE**. (b) Conversion and selectivity of the tandem carboxylative cyclization catalyzed by **Ag-TCPE**.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b03404.

Experimental details, crystal data, additional catalytic information, and NMR spectra for the products and substrates (PDF) Crystal data for Ag-TCPE (CIF)

Crystal data for Ag-TCPE@1a (CIF)

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Notes

The authors declare no competing financial interest.

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