

Ag Nanoparticles Supported on a Resorcinol-Phenylenediamine-Based Covalent Organic Framework for Chemical Fixation of CO₂

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Abstract: Covalent organic frameworks are a new class of crystalline organic polymers possessing a high surface area and ordered pores. Judicious selection of building blocks leads to strategic heteroatom inclusion into the COF structure. Owing to their high surface area, exceptional stability and molecular tunability, COFs are adopted for various potential applications. The heteroatoms lining in the pores of COF favor synergistic host–guest interaction to enhance a targeted property. In this report, we have synthesized a resorcinol-phenylenediamine-based COF which selectively adsorbs CO_2 into its micropores (12 Å). The heat of adsorption value (32 kJ mol⁻¹) obtained from the virial model at zero-

Introduction

Rising atmospheric CO₂ concentration has serious implications on global warming triggered climate change. So it is highly desirable to develop stable materials to capture and utilize CO_2 .^[1–3] CO₂ is a small C1 building block for the synthesis a variety of organic molecules,^[4] including heterocyclic molecules.^[5] Although CO₂ is abundant in the atmosphere, it is reluctant to react with other compounds due to its inherent stability and inertness.^[4,6] Developing new activation catalysts to fix CO₂ into value-added products is beneficial. In several reactions, CO_2 is employed as a reactant and gets incorporated into the organic backbone of the product. For example, CO₂ forms cyclic carbonates with epoxides,^[7,8] can carboxylate terminal alkynes, alkenes, amines, propargyl alcohols, propargyl

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loading of CO₂ indicates its favorable interaction with the framework. Furthermore, we have anchored small-sized Ag nanoparticles (\approx 4–5 nm) on the COF and used the composite for chemical fixation of CO₂ to alkylidene cyclic carbonates by reacting with propargyl alcohols under ambient conditions. Ag@COF catalyzes the reaction selectively with an excellent yield of 90%. Recyclability of the catalyst has been demonstrated up to five consecutive cycles. The post-catalysis characterizations reveal the integrity of the catalyst even after five reaction cycles. This study emphasizes the ability of COF for simultaneous adsorption and chemical fixation of CO₂ into corresponding cyclic carbonates.

amines.^[9–13] In this context, propargyl alcohols react with CO₂ to yield α -alkylidene cyclic carbonates, which are important heterocyclic compounds having promising biological activities.^[14] Typically, organometallic compounds serve as catalysts for such conversions. However, the synthesis, storage and utilization of organometallic catalysts are laborious and in some cases, challenging.^[15, 16] Metal-free and metal-based catalysts bring about CO₂ fixation. However, such reactions befall at high pressure of CO_2 and elevated temperatures.^[17-26] The main challenge lies in performing the reaction under ambient conditions without compromising the selectivity and yield of the products. Developing recyclable heterogeneous catalyst bring added advantages. Recently, few supported metal catalysts have been tried for example, Ag NPs/SMR,^[27] AgX@carbon,^[28] ionic liquid supported AgI/OAc^{-.[29]} Nevertheless, in these reports, the role of the support is not demonstrated. To a large extent, this is due to the characterization limitations of these complex composite systems. Using crystalline porous materials such as covalent organic frameworks (COFs) as supports could provide meaningful insights in deciphering the activity of these heterogeneous catalysts.

In recent years, COFs have fascinated material researchers owing to their modular structural and functional tunability and high surface area.^[30, 31] Rational choice of the building blocks can yield two, three-dimensional porous network with a high degree of crystallinity.^[32, 33] Most importantly, decorating the pore-walls of the mesoporous COFs with heteroatoms furnish space for anchoring/growing catalytic nPs.^[34] COFs find application in diverse fields of research such as gas separation and storage,^[35] heterogeneous catalysis,^[36–38] energy storage and conversion,^[39] biological application^[40] and optics.^[41] Earlier, in our group, we have developed efficient heterogeneous COF-

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based catalysts for organic transformations and electrocatalytic oxygen evolution reaction.[34a,42,43] Several experimental and theoretical inputs reveal that the COF not only provides support for the growth of small-sized nPs but also delivers a synergistic structural and electronic influence on the catalytic process.^[37a] Here, we report a microporous resorcinol-phenylenediamine COF with ability to capture CO₂ selectively. Further, a composite water/chemical-stable catalyst synthesized by growing small-sized silver nPs using this COF as support catalyzes the conversion of propargyl alcohols into their corresponding cyclic carbonates in the presence of CO₂. The fact that the conversion does not transpire in the absence of the COF confirms that the COF plays a key role in trapping and activating the CO₂ molecules. There are few reports on CO₂ conversion using COF where epoxides and propargyl amines are being used as the reagent for chemical fixation.[8d, 13c] But, to the best of our knowledge, this is the first report of COF based heterogeneous catalyst to convert CO_2 into α -alkylidene cyclic carbonates using propargyl alcohols with high selectivity and yields.

Results and Discussion

IISERP-COF15 was synthesized via a simple Schiff base condensation between triformyl-resorcinol and phenylenediamine under solvothermal conditions. The aldehyde and amine were dissolved in a mixture of dioxane and mesitylene (1:1 v/v). To this mixture, 0.5 mL acetic acid (6 N) was added as a catalyst. The mixture was heated in a pyrex tube at 120 °C for three days (Scheme S1). The resulting solid product was cleaned by soxhlet extraction using dimethylformamide (DMF) and tetrahydrofuran (THF). The crystalline nature of COF was confirmed by powder X-ray diffraction.

A two-dimensional (2D) COF structure formed by π -stacking of layers having hexagonal windows was modeled, in agreement with the experimental powder X-Ray diffraction, using the Material Studio Programme (Figure 1). For the structure solution, we opted a similar routine as reported in our earlier works.^[34a, 37a, 42, 43] To ascertain the best possible space group, we have indexed the powder X-ray pattern in the XCELL pro-



Figure 1. (A) Three dimensional structure of the COF viewed along the c-axis showing the hexagonal pores. (B) Single channel view of the COF illustrating the heteroatoms lining its pore-wall. (C) View of π -stacked layers with an *AAA*... arrangement. Color codes; Gray: Carbon; Blue: Nitrogen; Red: Oxygen; White: Hydrogen.

gram which suggested P6 (FOM: >50) space group as the best-fit highest symmetry. So, an initial model was constructed in this hexagonal space group via atomic manipulation. However, the asymmetric dispositioning of the -OH groups of the resorcinol unit lowers the symmetry to Monoclinic. This structure was further geometry-optimized using tight-binding density functional theory algorithm embedded in the Materials Studio. The lowest energy structure adopts a P2/m space group (a = 22.12; b = 22.12; c = 3.52; $\beta = 120^{\circ}$, table S1). The diffraction pattern of this model was refined against the experimental PXRD using the Pawley routine; it yielded an excellent fit (Figure 2A, refined cell: a = 22.04; b = 21.50; c = 3.52; a =89.75°, $\gamma = 89.85^{\circ}$, $\beta = 119.91^{\circ}$; Rp = 4.5 and wRp = 6.56). The experimental PXRD pattern agreed better with the simulated PXRD pattern of the eclipsed form (Figure S1). In this finalized structure, the COF has a uniform one dimensional (1D) pores of size ~14 Å (factoring the van der Waal radii of the atoms), which agrees well with the experimentally determined pore size.

Solid-state magic-angle spinning NMR (SS-MAS NMR) spectrum reveals the characteristics of chemical shifts. Peaks in the range of $\delta = 110$ to 120 ppm have been assigned to the aromatic carbons. Notably, the presence of a peak at $\delta = 182$ ppm suggests that the -OH groups are tautomerised to keto form in the COF (Figure S2). $^{[34a,41a]}$ Further, the peak at $\delta =$ 148 ppm is seen due to the imine bond formation in the COF. While the characteristic chemical shift due to C=C-N is obtained at $\delta =$ 134 ppm signifying the existence of the COF in the keto form under the ambient conditions. The Infra-Red (IR) stretching band at 1607 cm^{-1} is assigned to the vibration of -C=O bonds. Peaks at 1513 and 1457 cm⁻¹ are observed due to the stretching of C=N and C=C-N bonds, respectively (Figure S3).^[34a] Thermo gravimetric analysis (TGA) shows that the COF is stable up to 300 °C (Figure S4). An initial mass loss (29%) due to the loss of occluded solvent molecules trapped within the COF pores is observed. This substantial solvent loss reflects the porosity. The observed thermal stability is corroborated by the variable temperature PXRD (VTPXRD), where it is observed that the COF retains its crystallinity even after heating at 250 °C (Figure S5).

The permanent porosity of the COF was determined using N₂ adsorption at 77 K. The COF exhibits a type-I adsorption isotherm with a saturation N_2 uptake of 15 mmolg⁻¹. The COF has remarkably high Brunauer-Emmet-Teller (BET) and Langmuir surface areas 1230 and 1540 m²g⁻¹, respectively, calculated from the N₂ at 77 K isotherm (Figures 2B and S6). The isotherm, when fitted with the non-local density functional theory (NLDFT) yields a pore-size of 12 Å and a pore volume of 0.6332 cm³g⁻¹ (inset of Figure 2B). The solidity of IISERP-COF15 has been validated under various harsh chemical conditions such as 6 N HCl, 6 N H₂SO₄, 6 N NaOH and even in boiling water for 24 hours (Figure 2C). Further, 77 K N₂ adsorptions carried out on the post-chemically-treated samples and the extracted pore size distributions; confirm the structural stability which corroborates well with the retention of crystallinity observed from the PXRD (inset of Figure 2C). Thus, IISERP-COF15 can be a suitable candidate for practical gas separation appli-

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Figure 2. (A) Pawley fitting of the powder XRD of the COF. (B) N_2 adsorption isotherm collected at 77 K; the surface areas are presented. Inset shows the pore size distribution of the COF obtained using the NLDFT model. (C) Stability of the COF to different chemical treatment is demonstrated by the N_2 adsorption isotherms and the associated pore-size distribution (inset) carried out using the treated samples. (D) CO_2 adsorption isotherms at different temperatures. (E) Heat of adsorption (HOA) for the CO_2 . (F) Selectivity plots demonstrating selective CO_2 capture by the COF.

cations where a harsh thermal and chemical environment is encountered. The presence of micropores lined by the heteroatoms may manifest favorable interactions with the trapped CO_2 molecules. In order to verify this, CO_2 adsorptions were performed at four different temperatures. The COF shows moderate CO_2 uptake at room temperature (2.5 mmolg⁻¹, 1 bar). It exhibits a plentiful saturation CO_2 uptake of 15 mmolg⁻¹ at 195 K (Figure 2D). The zero-loading heat of adsorption (HOA) values were 32 kJ mol⁻¹ and 33 kJ mol⁻¹ as estimated from virial and DFT calculations, respectively

(Figure 2E). This optimal HOA value supports a balanced reversible physisorption-desorption of CO₂. Further, the ideal adsorption solution theory (IAST) was employed to calculate the selectivity of CO₂ over other gases (Figure 2F). The CO₂/N₂ selectivity is obtained employing a typical composition of 15CO₂:85N₂ and it is observed that the COF has substantially high CO₂ selectivity at two different temperatures (65 at 298 K and 73 at 273 K, @ 1 bar). The selectivity values are comparable to the recently reported COFs.^[35] The CO_2/CH_4 selectivity has also been calculated using a typical composition of 50 CO₂:50 CH₄ and the COF reveals selective capture of CO₂ over methane at 1 bar (selectivity: 9.3 at 298 K and 6.4 at 273 K) (Figures S7–S10, Tables S2–S4). These studies indicate that the COF pores have active sorption sites for selective CO₂ capture. The COF has a spherical morphology as evidenced from scanning electron microscopic images. The energy dispersive X-Ray analysis and the mapping show homogeneous distribution of elements in the COF (Figures S11-S13). Inspired by the substantial selective CO₂ capacity, we decided to perform chemical fixation of CO₂ using the COF. However, the neat COF did not catalyze any CO₂ conversion (see SuppInfo). Realizing that Aq can be an active metal for CO₂ conversion,^[10] we have utilized the micropores of the COF to grow small-sized uncapped silver nPs. Here, COF is actually serving as the stabilizing agent for the growth of nPs. The heteroatoms in the structure have an interaction with the metal nPs which holds the nPs firmly, preventing the leaching from the support. To impregnate the nPs, the COF is suspended in dimethylsulphoxide (DMSO) along with AgNO₃. The mixture was heated at 80 °C for 24 hours under an N₂ atmosphere. The treatment generates small-sized Ag nPs on the COF. The PXRD of the composite has the characteristics low angle peaks of the COF and the peaks due to Aq nPs at higher 2θ values: 38.1° (*hkl*: 111), 44.1° (200), 64.1° (220) and 77.1° (311) (JCPDS file no: 89-3722) (Figure 3 A).^[44] Interestingly the Ag@COF composite did not exhibit any appreciable N₂ uptake even at 77 K, however, it shows a substantial amount of CO₂ capacity (1.3 mmol g⁻¹) at 298 K and 1 bar (Figures S9 and S10).

The composite has a spherical morphology comparable to the parent COF (Figure S11). The EDX analysis reveals that the composite has $\approx 5\%$ Ag loading, which is further verified by inductively coupled plasma (ICP) analysis (6.3% Ag loading). Elemental mapping verifies the homogeneous distribution of Ag on the COF (Figures S11, S14-S18). The phase of the silver was

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Figure 3. (A) PXRD of the Ag@COF. Inset is showing the indexed peaks of the Ag nano particles (B) High resolution TEM image of the Ag@COF. The lattice fringes of the planes of Ag nPs are indexed accordingly. (C) XPS spectrum of the Ag nP showing the splitting of 3d orbital. (D) Details of CO₂ fixation reaction with yields, TONs, and TOFs.

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determined by high-resolution transmission electron microscopic (HRTEM) studies. Lattice fringes with d-spacing of 0.235 and 0.20 nm appear due to the Ag (*111*) and Ag (*200*) planes, respectively (Figure 3 B). A statistical estimate from the TEM images unveils the average size of the Ag nPs to be 3–5 nm (Figures S19, S20, S21). The heteroatoms in the COF's backbone help the growth of such small-sized nPs. Further, X-ray photoelectron spectroscopy prominently distinguishes the Ag⁰ nPs. Two spin-orbit doublets are obtained at 368.7 (3d_{5/2}) and 374.6 eV (3d_{3/2}) with 6 eV spacing corresponding to the Ag⁰ (Figure 3 C). No peaks corresponding to the oxidized form of Ag were observed.^[45]

The Ag $3d_{5/2}$ appears at 368.7 (instead of 368.2 eV) due to the interaction of Ag with C=N (Ag $^{0\delta+}$).^[45] The peak at 399.7 eV for N1s spectrum corresponds to the Ag-N interaction, which corroborates the slight positive shift of the Ag $3d_{5/2}$ peak. The satellites of Ag peaks result in asymmetric lineshapes.^[45] Ag–O interaction is also observed in the O1s spectrum (530.8 eV for Ag–O) (Figure S22).^[46] All these observations acknowledge that the COF can be well-suited support to grow small-sized Ag nPs on the COF.

Dispersion of active metal nPs on this CO_2 selective COF synergistically funds to the facile conversion of CO_2 to cyclic carbonates. The catalyzed reaction was performed under ambient conditions employing a CO_2 balloon. Typically this reaction is done under high pressure and temperature, but our catalyst does it under mild conditions. 1 mmol of propargyl alcohol and 0.1 mmol of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)

were dissolved in 3 mL of DMF and the mixture was charged with a CO₂ balloon (table S5). 10 mol% catalyst was used in the reaction. It takes four hours to achieve complete conversion of the propargyl alcohol to α -alkylidene cyclic carbonates. We have used different substitutions at the propargyl alcohol and in each case; \approx 90% yield of the cyclic carbonate was obtained (Figures S23–S32). The turnover numbers (TON) are greater than 150 and turn over frequencies (TOF) are around 40 h⁻¹, which speak well for this relatively cheaper noble metal catalyst (Figure 3 D). However, the TON is not remarkably high because only certain facets of the Ag nPs are exposed to the surface for catalytic activity. Also, the atoms in the core of the cluster are not accessible to the reactants.^[34a, 36b]

For a heterogeneous catalyst, recyclability is a critical aspect. For this Ag@COF catalyst, we registered complete retention of activity for up to five cycles of the cyclic carbonate formation (Figure 4A). The post catalysis samples were characterized via PXRD, IR, SEM, TEM and XPS (Figures 4B and 4C). The PXRD shows that the peaks for the COF and the Ag are retained. However, after five reaction cycles, the intensities of the Ag peaks increase slightly, while the FWHM drops. This is due to the agglomeration of the nPs during the reaction. We performed EDX (Figures S16 and S17) and ICP analysis of the supernatant solution and found hardly any trace of Ag metal indicating no leaching of Ag during catalytic cycles. This could mean that the agglomeration of Ag nPs happens by the rolling of the Ag particles on the COF support without leaving the surface. Lattice fringes from the TEM of the spent catalyst were

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Figure 4. (A) A histogram plot showing recyclability of the Ag@COF catalyst via the retention of activity over five consecutive cycles. (B) Comparison of the PXRD patterns and (C) IR spectra of the different Ag@COF samples. (D) Ag 3d XPS spectra of the spent-catalyst.

indexed to the Ag (111) and Ag (200) planes confirming the existence of Ag⁰ in the composite (Figure S21). The XPS spectra corroborate the observations. The Ag $3d_{5/2}$ and Ag $3d_{3/2}$ peaks are obtained at 368.6 and 374.6 eV along with two satellites at 370.2 and 376 eV, respectively (Figure 4D). All these studies indicate that Ag@COF is an effective heterogeneous catalyst for the chemical fixation of CO₂.

The mechanism for this kind of reaction has been well established in the literature.^[27-29] In a typical reaction, Ag nP helps to activate the alkyne bonds by coordination. DBU deprotonates the alcoholic -OH group of the propargyl moiety. This facilitates the formation of cyclic carbonates after an intramolecular ring closure reaction. Finally, the Ag@COF regains its original form. To support the claim, we have performed cyclic voltammetry (CV) of the COF and Ag@COF. In CV, the irreversible oxidation peak at 0.12 V vs. NHE corresponding to the Ag/Ag⁺, indicates that the composite is redox-active (Figure S33). This indirectly signifies that the catalyst undergoes redox reaction during the CO₂ fixation, which is expected in accordance with the earlier proposed mechanism.^[47] Here, COF is not only providing support for the growth of Ag nPs but also adsorbs CO₂ selectively to promote the reaction. The lodging of the Ag nPs and the CO₂ in close proximity within the nano-confinement of the micropores could be crucial.

Conclusions

Chemical fixation is an important route to develop a cleaner and greener approach for CO_2 mitigation. Heterogeneous catalysts are the most competent participants along this line. Here, we have established a COF-based catalyst which effectively converts CO_2 to α -alkylidene cyclic carbonates with propargyl alcohols. The high surface area and the microporous structure of the COF enable selective CO₂ sorption over N₂ and CH₄. The heat of adsorption value suggests the facile regeneration of CO₂. The COF hosts small Ag NPs which effectively convert the CO₂ to cyclic carbonates. The composite has remarkable cyclability with retention of the catalytic sites. The COF is not just a support for the NPs but it also serves as an active matrix to adsorb CO₂ and brings the reactants together to the surface of the catalyst. Our findings enlighten the role of COF in heterogeneous catalysis and encourages designing recyclable heterogeneous catalysts for different CO₂-assisted organic transformations.

Experimental Section

Synthesis of IISERP-COF15: 0.2 mmol triformyl resorcinol and 0.2 mmol phenylene diamine were dissolved in a solvent combination of 4 mL dioxane and 4 mL mesitylene. The mixture was stirred for 1 hour and then 0.5 mL of 6 N acetic acid was added to it. The final reaction mixture was transferred in a pyrex tube and heated at 120 °C for 3 days. Dark brown precipitate was obtained which was filtered and finally washed through soxhlet extraction using DMF, THF mixture. Yield (82%), Formula for COF C₃₆N₆O₄H₂₄, M. Wt. 604.623 g mol⁻¹, CHN Observed is C=85.29; H=3.81; N=10.85. calcd C=79.97; H=4.48; N=15.55.

Stability studies of IISERP-COF15: To study the stability of IISERP-COF15, it was soaked in $6 \times HCI$, $6 \times H_2SO_4$, $6 \times NaOH$ and even boiled in water. Samples were characterized by Powder X-Ray Diffraction (PXRD), Infra-Red spectroscopy (IR) and porosity measurements.

Synthesis of Ag@COF: Silver nPs have been encapsulated in the COF by simply heating the mixture of COF and $AgNO_3$ in dimethyl sulfoxide (DMSO).^[10] In a typical synthesis, 100 mg of COF was dis-

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persed in 20 mL of Ethanol. A 5 mL solution (DMSO) containing 15 mg of AgNO₃ was added to it followed by sonication. The mixture was heated at 80 °C for 24 hours. After that the mixture was cooled, filtered and washed with dimethyl formamide (DMF) and ethanol. The solid product was dried under vacuum. 6.3% Ag content was quantified by Inductively Coupled Plasma (ICP) analysis. CHN: C=83.51; H=4.75; N=11.68.

General procedure of catalytic reaction: 10 mol% Ag@COF was dispersed in 3 mL of DMF and 1 mmol propargyl alcohol, 0.1 mmol 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) were added to it. The reaction was performed at room temperature under CO₂ atmosphere (CO₂ balloon). The reaction was completed within 4 hours. Crude mixture was centrifuged to get the solid catalyst back and the product mixture was extracted with dichloromethane and washed with saturated NaCl solution to get rid of DMF. Finally the product mixture was purified using column chromatography on silica gel with 10% ethyl acetate and hexane mixture as eluent. The products were characterized by 1 H, 13C Nuclear Magnetic Resonance spectroscopy (NMR), High Resolution Mass Spectroscopy (HRMS).

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Conflict of interest

The authors declare no conflict of interest.

Keywords: CO₂ capture · Covalent organic frameworks · Cyclic carbonates · Propargyl alcohols · Silver nanoparticles

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FULL PAPER

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 Ag Nanoparticles Supported on a
 Resorcinol-Phenylenediamine-Based Covalent Organic Framework for Chemical Fixation of CO₂



A covalent organic framework derived out of simple building blocks adsorbs CO₂ selectively. Silver nanoparticles are grown into the COF. The composite catalyses the chemical cyclisation of CO_2 with propargyl alcohols.