AgNPs Embedded in Porous Polymeric Framework: A Reusable Catalytic System for the Synthesis of α-Alkylidene Cyclic Carbonates and Oxazolidinones via Chemical Fixation of CO₂

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Abstract: Porous polymeric frameworks have received great interest over the past few years because of their nonstop growth as crystalline porous polymeric materials connected through covalent bonds and versatile utilities in diverse fields. The production of high-value organic compounds via sustainable and environment-friendly methods is an uphill struggle for researchers. The elegant strategy of using carbon dioxide as a C1 building block is an intriguing platform owing to its non-toxicity, easy accessibility, natural abundance, recyclability, non-flammability, and cheapness. Additionally, CO₂ levels are regarded as the main contributor to the greenhouse effect (the most abundant greenhouse gas across the globe) and the aforementioned strategy needs to mitigate CO₂ emissions. This present study describes the synthesis of silver nanoparticles (AgNPs) embedded in a porous polymeric framework, a reusable heterogeneous catalyst (recyclable over 5 times), TpMA (MC)@Ag. The synthesized catalyst is characterized by using FT-IR, PXRD, XPS, FE-SEM, TEM, EDAX, TGA DTA, and N₂ sorption studies. Additionally, the catalysts can be easily recycled to generate the desired α-alkylidene cyclic carbonates and oxazolidinone compounds under solvent-free conditions. This research demonstrates the potential of nanoporous 2D porous polymeric framework-based materials in the area of catalysis, specially, in CO₂ capture and chemical fixation. These findings offer a promising approach for the chemical fixation of CO₂ into α-alkylidene cyclic carbonates and oxazolidinones from propargylic alcohols utilizing AgNPs embedded in a 2D catalyst, which functions as a potential heterogeneous catalyst under mild conditions (e.g., solvent-free approach).

Keywords: CO₂ fixation; heterogeneous catalyst; oxazolidinones; cyclic carbonates; Ag nanoparticle

1. Introduction

The emission of carbon dioxide (CO₂) caused by human activity is responsible for the global environmental crisis and has had a significant impact on the principles of green and sustainable chemistry. CO₂ is an appealing, plentiful, affordable, non-hazardous, and sustainable chemical resource, making it an attractive option for atom economy [1–14]. The use of CO₂ has gained substantial attention in the past decade due to its low cost and potential as a C1 feedstock for various fine chemicals. The sustainable synthesis of value-added chemicals shows great potential for decarbonization of the chemical industry via the utilization of carbon dioxide (CO₂). It is noteworthy that the current chemical production is heavily dependent on carbon feedstocks obtained from fossil fuels. As a result, significant research efforts have been increased to generate CO₂-sequestering materials [15–32]. CO₂ utilization shows tremendous importance in the area of atom economy since it is a fascinating, plentiful, low-cost, non-toxic, and sustainable chemical feedstock [33–38].
key tactics that might be used to conquer this obstacle are a) carbon dioxide capture and sequestration/storage and b) carbon dioxide capture and its utilization [26]. Carbon dioxide conversion into portable compounds like amides, esters, carboxylic acids, aldehydes, and alcohols has gained large attention in current years. In the present context, the utilization of CO$_2$ in the synthesis of 2-oxazolidinones as an environmentally acceptable alternative has significant interest [27–33]. Although there are several ways to incorporate CO$_2$ into 2-oxazolidinones, most of these reactions often need costly, hazardous organic solvents, which have negative health and environmental consequences [34–37]. As the notion of green chemistry, researchers have concentrated their efforts on the development of solvent-free methods [38,39]. In this regard, numerous solvent-free techniques for the synthesis of 2-oxazolidinones via CO$_2$ have been published in the literature. A thorough analysis of this hot study issue appears appropriate for the recent achievements and all the changes that have taken place in this fascinating research field. 2-oxazolidinones are a type of an extremely useful family of N-containing five-membered heterocyclic compounds found in a variety of pharmaceutical substances like toloxatone, cimoxatone, zolmitriptan befloxatone, and others [18], as well as agrochemicals such as phosalone [40–43]. Furthermore, they are present in many anti-bacterial drugs (e.g., Linezolid, Toloxatone, Tedizolid) and are extremely active against multiply resistant infections caused by Gram-positive bacteria, and also frequently utilized in the paint and varnish businesses and the polymer industry. 2-oxazolidinones have also been employed extensively as chemical intermediates [44,45] and chiral auxiliaries in asymmetric synthesis. The utilization of carbon dioxide as the C1 synthon for the generation of oxazolidinones has been extensively recorded in a variety of procedures, such as the cycloaddition of aziridines through CO$_2$ of [33,46] the chemical interaction of 2-aminoalcohols and CO$_2$ [47], carboxylative cyclization of propargylic amines [25,35], and the three-component coupling of propargyl alcohols, primary amines, and CO$_2$. The most appealing approach for producing oxazolidinone out of the procedures is the three-component reaction. Homogeneous catalytic media were employed for the majority of previously published investigations on the one pot three-component coupling process to produce oxazolidinone, along with extreme reaction conditions such as high temperature and high pressure of CO$_2$. However, all of these procedures have specific constraints such as a long reaction time and limited substrate scope. So, it is necessary to develop a technique that operates under moderate reaction circumstances. Propargyl alcohols and amines can absorb CO$_2$ by carboxylative cyclization, terminal alkynes through terminal carboxylation, cycloaddition on epoxides, N-methylation, and N formylation processes [48]. So nowadays, designing appropriate catalysts for CO$_2$ fixation reactions is one of the growing fields of research because of the adaptability of these reactions. One of the most efficient and alluring ways of CO$_2$ reformation is the carboxylative cyclization process for the production of $\alpha$-alkylidene cyclic carbonates from propargyl alcohol. The $\alpha$-alkylidene cyclic carbonates are a family of heterocyclic compounds that are helpful for a number of inorganic synthesis processes [18,49,50]. This group of compounds is often found in natural substances including guaianolide hololeucin, genkwanin I, and cycloolivil, among many others. These substances are mostly used in pharmaceutical, agricultural, and pesticide industries [51]. For the generation of valuable compounds, a number of techniques have been developed till now. These methodologies include metal-supported catalysts, for example, Cu [52], Ag [53–55], palladium [56], zinc [57], tungsten [58], and cobalt [59], along with organocatalysts [60–65], IL-based catalysts [66], and (MOFs) metal-organic frameworks [67]. Meanwhile, many of the previously published approaches have certain drawbacks, including the usage of extreme reaction temperatures, the challenge of recovering the catalyst, and the use of potentially dangerous organic solvents or bases. Owing to the limitations of earlier findings, further research is still needed for the generation of $\alpha$-alkylidene cyclic carbonates within favorable reaction circumstances. Our team has disclosed a catalytic technique in which 2-oxazolidinones and $\alpha$-alkylidene cyclic carbonates are synthesized at RT from carbon dioxide using a heterogeneous porous polymeric framework based on silver metal under solvent-free conditions. The most interesting and
significant subset of porous materials in organic chemistry is the porous polymeric frame- 
work. The porous polymeric framework, a unique family of porous crystalline polymers, 
has appeared as heterogeneous catalysts for different organic reactions. Due to their highly 
ordered, pre-designable, and functionalizable porous architectures [33], polymer catalysts 
enable the exact integration of catalytic centers within the framework matrix. Those are 
extensively used in catalysis [68], adsorption [69,70], sensing [71,72], gas storage [73], and in 
many other important applications [74] due to their intriguing qualities including huge sur-
face area, excellent chemical resistance, structural adaptability, and uncomplicated surface 
functionalization. However, due to the very complex growth procedure containing crystal-
lization, assembly, and polymerization, among other things, generates a well-organized 
and perfectly ordered 2D stacked porous polymeric framework sheet. In general, the docu-
mented building techniques of 2D sp² carbon-conjugated porous polymeric catalysts may 
be classified into two categories: bottom-up and top-down strategy. The catalyst TpMA  
(MC) was synthesized by combining melamine (1,3,5-triazine 2,4,6triamine (Tt)) with 2,4,6-
triformylphloroglucinol (Tp) aldehyde. Previously, many triazine-containing polymers 
were synthesized in the presence of a metal catalyst and at higher temperatures. Due to 
its low reactivity, synthesizing a crystalline porous TpMA (MC) catalyst from a melamine 
building block without the use of a metal catalyst proved extremely difficult. We generated 
a fairly crystalline porous polymeric framework TpMA (MC) after numerous attempts 
with various solvent combinations. The development of metal nanoparticles has garnered 
significant attention in the area of nanotechnology because of their evident characteristics, 
such as geometry, shape, and distribution. Nanoparticles also have an influence on many 
facets of mankind in addition to displaying wholly original or superior characteristics. 
Because of their numerous uses in areas such as catalysis, energy, biomedicine, materials, 
etc., silver nanoparticles, also referred to as Ag NPs, are considered to be among the most 
promising nanoparticles in the nanotechnology sector [66–69]. Ag NPs can be generated 
through a diverse range of methods, including physical, chemical, and biological processes. 
In the physical procedure, expensive machinery and high suction are utilized; in the course 
of the chemical process, the synthesis is facilitated through the utilization of toxic capping 
agents. Hence, they are not environment-friendly, affordable, or viable. As a consequence, 
scientists have focused on synthesizing nanoparticles that are affordable, recyclable, and 
environment-friendly by using natural ingredients and microorganisms [70–73]. In this 
investigation, our group describes the production and characterization of a nanoporous 
polymeric framework assisted with Ag complex (TpMA (MC)@Ag) that is very active at 
fixing CO₂ in chemical processes to synthesize oxazolidinones and α-alkylidene cyclic 
carbonates from propargyl alcohols. The catalyst is particularly effective in producing 
2-oxazolidinones through CO₂ fixation from terminal propargylic amine at 1 atm pressure, 
under mild reaction environment, and in the presence of a stoichiometric quantity of DBU. 
Similarly, the catalyst is particularly efficient at producing α-alkylidene cyclic carbonates 
by carboxylative cyclizing propargylic alcohols with CO₂ at R.T. under 1 bar of pressure 
without solvent. Both catalytic conversions cannot take place without the presence of 
TpMA (MC)@Ag, thus indicating the pivotal role that the catalyst plays in activating and 
trapping CO₂ molecules. Furthermore, it is noteworthy that the heterogeneous catalyst 
can be effortlessly recovered and utilized repeatedly, rendering it highly sustainable. The 
catalyst is recyclable up to five times without appreciable loss of its activity.

2. Results and Discussion

The two-dimensional porous polymeric catalyst TpMA (MC) and silver metal-incorporated 
TpMA (MC)@Ag catalyst were synthesized as the following schematic diagram, Scheme 1, 
shows, and the Supporting Information file shows the detailed procedure.
2.1. Characterization Techniques

2.1.1. Powder X-ray Diffraction (PXRD) Analysis

PXRD patterns of the nanoporous polymeric catalyst TpMA (MC)@Ag described the intense unique peak at $2\theta = 6.3^\circ$ which was attributed to the reflection of greatest intensity from Miller plane (100) (Figure 1). This peak is joined by tiny peaks located at $2\theta = 11.7^\circ$, $14.1^\circ$, and $15.2^\circ$ that are attributed to the (110), (200), and (210) facets correspondingly. The extensive peak of $\sim 27.3^\circ$ corresponds to the (001) plane and can be attributed to the $\pi-\pi$ stacking of the porous polymeric catalyst TpMA (MC)@Ag layers. The wide-angle XRD patterns of AgNPs embellished porous polymeric framework match to an FCC structure. As a result, the porous polymeric catalyst TpMA (MC)@Ag nanomaterial exhibited three additional diffraction peaks from (111), (200), and (220) reflections, and it can be categorized as the peak for the FCC model of reactive metallic Ag. The broad-angle XRD graphs certainly demonstrated the loading of reactive metallic AgNPs on the outer surfaces of the crystalline porous polymeric frameworks. The calculated d-spacing value is $3.4 \text{ Å (d001)}$ between the (001) facets and was determined through the implementation of Bragg’s equation, whereby $n = 1$ is assigned to the 001 reflection planes, $n\lambda = 2d001\sin \theta$, where $\lambda = 0.15406$ nm. Scherrer’s equation was used to evaluate the particle sizes of Ag NPs, which were estimated to be in the range of 14 to 20 nm. The (111), (200), (220), and (311) facet Ag NPs sizes are found to be 19.45 nm, 14.77 nm, and 16.65 nm, 18.97 nm, respectively, using the Debye–Scherrer formula (SI). The TEM results are consistent with the calculated values derived from Scherrer’s equation. PXRD patterns of the catalyst remain almost the same after several runs, proving the reusability of the porous polymeric catalyst TpMA (MC)@Ag catalyst (Figure S4).

![Scheme 1](image1)  
**Scheme 1.** Schematic diagram for the synthesis of porous polymeric catalyst TpMA (MC)@Ag.

![Figure 1](image2)  
**Figure 1.** Powder XRD of porous polymeric catalyst TpMA (MC)@Ag.
2.1.2. Fourier Transform Infrared (FT-IR) Spectroscopy

The successful generation of the porous polymeric catalyst TpMA (MC)@Ag was confirmed by FT-IR spectroscopy (Figure 2). The presence of C=O at 1643 cm\(^{-1}\) confirmed the formation of the aldehyde. The N-H stretching frequency of the primary amine (3464 cm\(^{-1}\)) and C=O group (1643 cm\(^{-1}\)) of aldehyde vanished in the synthesized porous polymeric framework, indicating that starting materials were completely utilized after porous polymeric framework production. The FT-IR spectra of the freshly prepared porous polymeric framework (porous polymeric catalyst TpMA (MC)) exhibit two bands at 1232 cm\(^{-1}\) and 1523 cm\(^{-1}\), owing to C-N and C=C bonds correspondingly, which indicate the generation of a \(\beta\)-ketoenamine link in the framework. Furthermore, an absorption band appeared at 2923 cm\(^{-1}\) corresponding to C–H asymmetric stretching vibration (Figure S2). It is noteworthy that all abovementioned characteristic bands were also present in the porous polymeric framework TpMA (MC) @Ag, but with slight positional shifts. This observation serves to confirm the attachment of silver nanoparticles within the porous polymeric framework.

![Figure 2. FT-IR spectra of porous polymeric catalyst TpMA (MC)@Ag catalyst, Triformyl phloroglucinol (TFP), and Melamine.](image)

2.1.3. X-ray Photoelectron Spectroscopy (XPS) Analysis

XPS analysis of porous polymeric catalyst TpMA (MC)@Ag matrix was performed to identify the oxidation state and elemental composition of silver nanoparticles grafted onto the abovementioned matrix. Figure 3 reveals individual information about carbon, silver, nitrogen, and oxygen atoms of porous polymeric catalyst TpMA (MC)@Ag from XPS whereas Figure 3a shows the wide-range XPS spectrum of complexes.

Figure 3a depicts the wide-range XPS of the complex, where C 1s, N 1s, and O 1s components were observed, with corresponding binding energies of 284.5, 398.9, and 531.3 eV, respectively. The high-resolution C 1s picture on deconvolution exhibits bands at 288.4, 287.3, 286.2, and 284.5 eV, which correspond to the binding energies of C=O, C=N, C-N, and C=C, respectively, as shown in the XPS spectra of porous polymeric catalyst TpMA (MC)@Ag. The XPS spectrum of the Ag 3d (Figure 3b) is divided into three sections: Ago, Ag\(_{\ldots}N=\), and Ag\(_{\ldots}O\). The existence of metallic Ag is shown by the peaks at 368.50 eV and 374.55 eV corresponding to Ag 3d\(_{5/2}\) and Ag 3d\(_{3/2}\). The corresponding band gap is calculated to be 6.0 eV.

The peaks at 375.39 eV and 369.44 eV are attributed to Ag\(_{\ldots}N=\), while those at 373.45 eV and 367.45 eV are attributed to Ag\(_{\ldots}O\), according to the literature. The Ag in Ag\(_{\ldots}N=\) and Ag\(_{\ldots}O\) must also exist as Ago since the difference in spin energy is also
6.0 eV. Ago strongly binds to the N sites and O sites in the porous polymeric framework, as indicated by a small change in binding energy compared to that of metallic Ag. As a result, the nitrogen and oxygen atoms in this porous polymeric catalyst played a significant role in anchoring Ago. As observed in the N 1s image of porous polymeric catalyst TpMA (MC)@Ag, the presence of Ag...N= can be attributed to the band observed at 401.47 eV, which has the ability to bind with the silver centers. Additionally, the high-resolution N 1s image also reveals bands appearing at 398.22 eV and 399 eV which correspond to sp2 hybridized C-N=C in the triazine functional group and C=N, respectively. The XPS spectra with high resolution demonstrate the O 1s peaks at 531.0 eV and 532.4 eV (Figure 3e). Interaction between Ag-O can also be detected in the O1s spectrum, where the Ag-O peak is observed at 531 eV [75]. These various observations collectively establish the successful incorporation of silver nanoparticles in the COF.

**Figure 3.** (a) Wide-range XPS survey spectrum of porous polymeric catalyst TpMA (MC)@Ag porous polymeric framework and narrow-range XPS spectra of (b) Ag 3d, (c) C 1s, (d) N 1s, and (e) O 1s elements of porous polymeric catalyst TpMA (MC)@Ag.

2.1.4. BET Surface Area Measurement

N₂ adsorption–desorption isotherms were executed at a temperature of 77 K to investigate the internal porosity present in the porous polymeric framework material embedded with silver nanoparticles. The N₂ sorption isotherm exhibited by the sponge-like porous polymeric framework TpMA (MC), a covalent organic framework, demonstrates a type I behavior, while simultaneously displaying certain patterns like type IV pattern, as Figure 4 depicts. The presence of several micropores in catalyst TpMA (MC) is suggested by the excessive N₂ adsorption within the low-pressure range of 0–0.1 bar. The observed surface area and pore volume of the resultant porous polymeric framework are estimated to be 364 m²g⁻¹ and 0.30 ccg⁻¹, respectively. The pore size distribution of porous polymeric catalyst TpMA (MC)@Ag was evaluated through the application of the Barrett Joyner Halenda (BJH) technique. The distribution of pore size of the TpMA (MC)@Ag catalyst using N₂ at 77 K revealed the presence of mesopores with a pore dimension of 2.06 nm. BET surface area of the reused TpMA (MC)@Ag catalyst was around 256 m²g⁻¹ and the pore size was reduced to 1.26 nm (Figure S3). This reduction in pore size and BET surface area indicates the blockage of some pores in the porous polymer.
2.1.5. Microscopic Analysis

SEM images, as Figure 5a–d show, reveal that the catalytic system of porous polymeric catalyst TpMA (MC) and TpMA (MC)@Ag comprises numerous indistinguishable particles, which exhibit a remarkable resemblance to rock-like morphology. The porous polymeric catalyst TpMA (MC)@Ag catalytic system is entirely insoluble in the majority of common organic solvents. The FESEM images of the porous polymeric catalyst TpMA (MC)@Ag material suggest the presence of primarily uniform particles that appear to be haphazardly aggregated. The TEM image of TpMA (MC) (Figure 6g–i) provides insight by demonstrating that the layered sheet-like porous materials consisted of micropores and mesopores, featuring a microcrystalline arrangement. The HRTEM images (Figure 6) of the silver-decorated polymeric catalyst TpMA (MC)@Ag reveal a layered sheet-like morphology with an average particle diameter of 14–20 nm, as well as a random void, present in the catalyst. A TEM image of low-resolution displays uniform distributions of silver nanoparticles on TpMA (MC)@Ag polymer. From the HR-TEM image of TpMA (MC)@Ag, the specific portion (yellow box) demonstrates that some of the silver nanoparticles present on the surface of the polymer exhibit remarkable lattice fringes. The corresponding SAED pattern, as Figure 6f shows (based on the yellow-framed portion), exhibits remarkable lattice fringes and characteristic diffraction rings at (111), (200), (220), and (311) that align with the PXRD spectrum of TpMA (MC)@Ag (Figure 1) which show the successful loading of silver. The calculated lattice spacings of silver (d = 0.235 nm and 0.204 nm) are attributed to the (111) and (200) plane of silver, respectively (Figure 1). Additionally, EDAX recommended that the silver loading in the polymeric compound be at 2.53 wt%.

Figure 4. (a) N\textsubscript{2} adsorption–desorption curve of porous polymeric catalyst TpMA (MC)@Ag. (b) Corresponding pore size distribution of the catalyst TpMA (MC)@Ag.

Figure 5. FE-SEM images of the porous polymeric catalyst TpMA (MC) and TpMA (MC)@Ag materials at two different scales (a-d), (e,f) EDAX of porous polymeric catalyst TpMA (MC) and TpMA (MC)@Ag, and (g) particle size distribution plot.
Reduced quantity of catalyst stacking (10 mg) in the presence of a base (DBU) led to a decrease in the reaction. Reduced quantum yield of 2-oxazolidinones (Table 6).

2.1.6. TGA Analysis of Porous Polymeric Catalyst TpMA (MC)@Ag

Figure 7 presents the TGA plot of TpMA (MC)@Ag and TpMA (MC) catalysts. The thermal degradation process for both the catalysts are observed to be very slow at the temperature range of 160 °C to 450 °C. Both TpMA (MC)@Ag and TpMA (MC) catalysts show a similar type of thermal degradation process. After reaching the aforementioned temperature range, it was observed that the rate of degradation accelerated significantly. This suggests that the catalyst is capable of maintaining thermal stability up to 450 °C. Nevertheless, it is important to note that prior to reaching this temperature limit, the catalyst undergoes a minor loss in mass. This loss can be attributed primarily to the detachment of surface-adsorbed H₂O molecules and other adsorbed gases present within the porous structure of the catalyst.

![Figure 6](image_url)  
**Figure 6.** TEM images of porous polymeric catalyst TpMA (MC)@Ag at different scales: (a) 100 nm, (b) 50 nm, (c) 10 nm, (d) 2 nm, (e) part of (d), shows unclear lattice fringes of some AgNPs, (f) SAED pattern of porous polymeric catalyst TpMA (MC)@Ag material, and (g-i) TEM images of only TpMA (MC) catalyst.

![Figure 7](image_url)  
**Figure 7.** Thermogravimetric (TGA) analysis of porous polymeric catalyst TpMA (MC) and TpMA (MC)@Ag.
2.2. Catalytic Activity

2.2.1. Generation of 2-Oxazolidinones over Porous Polymeric Catalyst TpMA (MC)@Ag Porous Polymeric Framework via Carboxylative Cyclization of Terminal Propargyl Alcohol and Amine

Carboxylative cyclization of propargyl alcohols and amines with carbon dioxide to produce 2-oxazolidinones have received a lot of interest recently [76,77]. Numerous catalytic systems centered around metals, including Cu [78], Pd [79], Au, Ru, and Ag [80,81], as well as protic ionic liquids, organo-catalysts like super bases, and heterocyclic carbenes, have found application in the synthesis of 2-oxazolidinones using the aforementioned method. However, a common limitation of the aforementioned catalytic systems is their reliance on homogeneous reaction conditions, leading to difficulties in terms of recyclability and reusability of the catalysts. Additionally, in most instances, high-pressure CO\(_2\) has been utilized as part of the process. In a few earlier reports, 2-oxazolidinones were produced using the carbon dioxide fixation method from propargyl alcohols and amines. In this instance, we were able to make 2-oxazolidinones from amines and propargyl alcohols using CO\(_2\) fixation in environment-friendly, ambient circumstances using noble metals like Ag without the need for supercritical or high-pressure CO\(_2\), solvents, or additives, etc (Scheme 2). Initially, using a CO\(_2\) balloon, the reaction involving (1A) and (1B) was conducted without the presence of any catalyst at room temperature (Table 1, entry 1). After 6 h of reaction, no product appeared. After that, the same reaction was seen with our synthesized catalyst TpMA (MC)@Ag (15 mg) without base; to our pleasure, after 6 h of reaction, 48% of the required product was obtained (Table 1, entry 2). Afterward, we investigated the impact of varying catalyst incorporation in the reaction. Reduced quantity of catalyst stacking (10 mg) in the presence of a base (DBU) led to a decrease in the rate of product yield (Table 1, entry 3). Conversely, an excessive weight of catalyst incorporation did not result in a substantial increase in the product yield percentage (Table 1, entry 4). As a result, 15 mg of catalyst loading was determined to be appropriate for the catalytic process at RT (Table 1, entry 5), and 35% product yield was recorded with just TpMA (MC) in the reaction (Table 1, entry 6). Likewise, a 35–29% yield was achieved using the silver salt (AgNO\(_3\), AgI, AgOAc) catalyst (Table 1, entry 7–9). As a result, Ag metal porous polymeric framework TpMA (MC) had an impact on the catalytic process. Instead of DBU, diverse categories of bases were used, for instance, DIPEA, DABCO, t-BuOK, NEt\(_3\), K\(_2\)CO\(_3\), Cs\(_2\)CO\(_3\), etc., whereby (12–36%) yield was obtained (Table 1, entry 10–15). So, the maximum final product amount (97%) was achieved while 15 mg porous polymeric framework was employed for 6 h without solvent and in the assistance of the base DBU (1 mmol). We also examined the influence of the DBU quantity on the catalytic activity. When 3 mmol of DBU was used, no significant change in the final product amount was observed (Table 1, entry 16). In a solvent-free environment at room temperature (RT), we studied the rate of change in mentioned reaction over time under the influence of porous polymeric catalyst TpMA (MC)@Ag catalyst (15 mg). Derived from the collected data, the kinetic graph (yield % vs. time) is constructed, as Figure 8 depicts. The illustration distinctly showcases the effective catalytic synthesis of 2-oxazolidinones, reaching its maximum yield within 6 h of reaction time. After determining the optimal reaction conditions, we conducted an investigation encompassing a diverse range of substrates. This involved using (1A) and (2A), as well as aromatic and aliphatic amines, all under atmospheric CO\(_2\) pressure. Table 2 presents the outcomes of the above reaction.

The reaction involving (1A) and (1B), as well as the reaction between (1A) and (2B), were significantly faster, completing in only 6 h and yielding nearly the same amount of the desired product (97%) for both cases (entry 1 and 2). However, when (2A) was substituted by (1A) in the reaction, the product yield decreased. This reduction in yield was attributed to the steric hindrance caused by the cyclohexyl group of the alcohol and the reactivity of aromatic amines (Table 2, entry 3 and 4). Substrates (4B) and (5B) containing electron-donating groups (-CH\(_3\), -OCH\(_3\)) produced oxazolidinones with slightly improved
yields (Table 2, entry 5–7). Conversely, substrates containing electron-withdrawing groups (Cl, Br) resulted in the corresponding oxazolidinones with slightly lower yields.

![Scheme 2. Synthetic scheme of one-pot three-component 2-Oxazolidinone synthesis using TpMA (MC)@Ag as heterogeneous catalyst.](image)

### Table 1. Optimization table for 2-Oxazolidinone synthesis.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mg)</th>
<th>Base (mmol)</th>
<th>T/h</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>TpMA (MC)@Ag (15 mg)</td>
<td>-</td>
<td>6</td>
<td>48</td>
</tr>
<tr>
<td>3</td>
<td>TpMA (MC)@Ag (10 mg)</td>
<td>DBU (1)</td>
<td>6</td>
<td>79</td>
</tr>
<tr>
<td>4</td>
<td>TpMA (MC)@Ag (20 mg)</td>
<td>DBU (1)</td>
<td>6</td>
<td>97</td>
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<td>DBU (1)</td>
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<td>6</td>
<td>35</td>
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<td>DIPEA (1)</td>
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<td>DABCO (1)</td>
<td>6</td>
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<td>16</td>
<td>TpMA (MC)@Ag (15 mg)</td>
<td>DBU (3)</td>
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### Table 2. Substrate variation for the synthesis of 2-Oxazolidinones.

<table>
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<tr>
<th>Entry</th>
<th>Alcohol</th>
<th>Amine</th>
<th>Product</th>
<th>T/h</th>
<th>Yield (%)</th>
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<td>(5C)</td>
<td>6</td>
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</tr>
<tr>
<td>6</td>
<td>(1A)</td>
<td>(4B)</td>
<td>(6C)</td>
<td>6</td>
<td>88</td>
</tr>
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<td>7</td>
<td>(1A)</td>
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<td>(7C)</td>
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<td>90</td>
</tr>
<tr>
<td>8</td>
<td>(1A)</td>
<td>(6B)</td>
<td>(8C)</td>
<td>6</td>
<td>70</td>
</tr>
</tbody>
</table>

Reaction condition: Propargyl alcohols (5 mmol), amines (5 mmol), CO₂ (1 atm), porous polymeric catalyst TpMA (MC)@Ag (15 mg), RT, DBU (1 mmol).

Figure 8. Kinetic study curve of 2-Oxazolidinone.
2.2.2. Carbon Dioxide Fixation in $\alpha$-Alkylidene Cyclic Carbonate Synthesis with Porous Polymeric Catalyst TpMA (MC)@Ag

The synthesized catalyst TpMA (MC) showed excellent catalytic activity in the CO$_2$ fixation process, which generates cyclic carbonates from propargyl alcohol. Many scientific groups have previously reported the propargyl alcohol to cyclic carbonate production via carbon dioxide fixation [82]. In light of such studies, we attempted the most efficient and environment-friendly method of product synthesis employing the Ag-loaded porous polymeric catalyst TpMA (MC)@Ag.

For the reaction optimization, we utilized (1A), base, and CO$_2$. Firstly, we conducted the reaction at room temperature using (1A) (5 mmol) as a model substrate in the absence of any solvent under CO$_2$ (1 atm) atmosphere. In the absence of a catalyst, the reaction was allowed to run for 4 h. We found no product yield (Table 3, entry 1). After 4 h at RT, the intended product was produced with 36% yield in the presence of 1 mmol DBU catalyst (Table 3, entry 2).

After 4 h of reaction, 60% yield of the product was achieved using porous polymeric catalyst TpMA (MC)@Ag (15 mg) catalyst in the absence of any base (Table 3, entry 3). When several other silver catalysts, such as AgOAc, AgNO$_3$, and AgI, were tested with a constant base and its amount (5 mg each), the yields ranged from 23% to 51% (Table 3, entry 4–6). In the course of our experimentation, we carried out the reaction using a range of bases, substituting DBU with both organic bases such as DIPEA, t-BuOK, TBD, DABCO, and NEt$_3$, as well as inorganic bases like Cs$_2$CO$_3$ and K$_2$CO$_3$, among others, in several trials. Nonetheless, the substitution did not result in a significant increase in the percentage of product yield, contrary to the outcomes we obtained with the DBU base (Table 3, entry 7–13). When 15 mg of porous polymeric framework catalyst was used for 4 h in the absence of any solvent and assisted with 1 mmol base DBU, the optimal product yield (95%) was obtained (Table 3, entry 14). We also investigated the influence of base DBU quantity on the catalytic process. There was no influence on the yield of the product observed when DBU more than 1 mmol was used (Table 3, entry 15). In order to conduct a more comprehensive screening of catalytic reactions, we introduced variations in the catalyst loading during the reaction. Upon analysis of Table 3, it was ascertained that a catalyst loading of 15 mg is sufficient to obtain the maximum percentage of product yield (Table 3, entry 16–17). Further experimentation revealed that when the reaction time was altered from 4 to 6 h, that did not result in any additional yield (Table 3, entry 18). When utilizing TpMA (MC) porous polymeric framework as a catalyst in lieu of porous polymeric catalyst TpMA (MC)@Ag, a minute quantity of product was detected (Table 3, entry 19). Hence, it can be surmised that the loading of Ag nanoparticles on the TpMA (MC) porous polymeric framework surface functions as an active center in the proposed reaction of catalysis.

The reaction’s conversion rate was measured with the involvement of the porous polymeric catalyst TpMA (MC)@Ag (15 mg) in neat reaction conditions at RT, and the data were plotted to create a kinetic curve (% of conversion vs. time), as Figure 9 exhibits. The diagram distinctly illustrates that the catalyzed $\alpha$-alkylidene cyclic carbonate reaction progresses seamlessly and reaches completion within 4 h. Table 4 summarizes the substrate scope for different propargyl alcohol derivatives to investigate the influence of replacements at $R_1$ and $R_2$ positions on the yield of the reaction (3A), a non-substituted propargyl alcohol that provides no product (Table 4, entry 2). On the variation at $R_1$ and $R_2$ position, the greatest yield was found for $R_1 = R_2 = Me$ (Table 4, entry 1). The outcome was supported by the fact that the gem dimethyl group encourages cyclization due to their mutual repulsion; “gem effect” describes this phenomenon. The reaction speed was delayed when the alkyl groups became more bulky (Table 4, entry 3–6). However, in other instances, the reaction took longer to complete (Table 4, entry 4–6). On the other hand, under optimal reaction circumstances, the internal propargylic alcohol showed no reactivity and remained unreacted, leading to the absence of the expected product (Table 4, entry 7).
Table 3. Optimization table for catalytic α-alkylidene cyclic carbonate synthesis.

<table>
<thead>
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<th>Base (mmol)</th>
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<th>Yield (%)</th>
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<td>-</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
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<td>TpMA (MC)@Ag (5)</td>
<td>DBU (1)</td>
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<td>AgOAc (5)</td>
<td>DBU (1)</td>
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<td>AgNO₃ (5)</td>
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Table 4. Substrate scopes for the fixation of CO$_2$ onto propargyl alcohols.

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Reaction condition: Substrate (5 mmol), porous polymeric catalyst TpMA (MC)@Ag (15 mg), DBU (5 mmol), CO$_2$ (1 bar), RT.

Figure 9. Kinetic study curve of α-alkylidene cyclic carbonate.
2.2.3. Reaction Mechanism

According to earlier findings [47,53,83–88], Scheme 3, illustrates a possible mechanistic pathway for the catalytic formation of α-alkylidene cyclic carbonates and 2-oxazolidinones using CO₂ fixation from propargylic alcohol. Initially, propargylic alcohol’s hydroxyl group can be attacked by the strong organic base (DBU), which can then capture the proton. The presence of Ag in the catalyst can ignite the propargylic alcohol’s alkyne portion, which leads to the formation of a hybrid with the Ag-loaded catalyst. In contrast to other inert systems, such as the N₂ molecule, the presence of an internal CO connecting dipole causes CO₂ amphiphilic. The LUMO is located on the C center, whereas the molecular orbital with the greatest occupancy (HOMO) is located on the O centers. Therefore, nucleophilic attack on the center of carbon is quite vulnerable (e.g., when the DBU base activates the propargylic alcohol, the O atom may connect with the C center of CO₂), whereas electrophiles and the O center participate (e.g., activated alkyne moiety). In the potential intermediate, bond formation takes place between the Ag species and the alkyne component following a nucleophilic attack initiated by the oxygen center of CO₂ [87–89]. The adduct has been shown to be beneficial in the inclusion of CO₂ to produce the carbamate salt. Afterwards, intramolecular cyclization takes place. Following the release of the porous polymeric catalyst TpMA (MC)@Ag catalyst, the required α-alkylidene cyclic carbonate product is obtained. The resulting cyclic carbonate serves as an intermediate in the production of oxazolidinones, where it is nucleophilically attacked by amines to yield another carbamate species. Subsequently, this intermediate actively engages in a ring-closing reaction, resulting in the formation of the corresponding oxazolidinone product and the liberation of a water molecule as a byproduct. Scheme 4 presents a comparative analysis of our present methodology with previous research findings concerning the catalytic formation of α-alkylidene cyclic carbonates and oxazolidinones from propargylic alcohol using carbon dioxide fixation processes. The majority of earlier research [62–65] on the catalytic synthesis of α-alkylidene cyclic carbonates was conducted under homogeneous conditions. As a consequence of this, in such instances, the catalyst’s recoverability and reusability are problematic. Once more, each of the methods needed high pressure CO₂ (≥1 MPa). For the manufacture of the identical chemicals, a few reports [22,43] were generated under heterogeneous catalytic conditions. However, there are still the same restrictions about the usage of high-pressure carbon dioxide (1 MPa) and one technique [47] that was carried out using acetonitrile solvent. Our method performs under circumstances of heterogeneous catalysis without solvents at atmospheric CO₂ pressure. Additionally, it produces an exceptionally high proportion of the desired product at ambient temperature.

All earlier published processes for the synthesis of oxazolidinones were carried out under homogenous catalytic conditions and generated an excellent yield of the target product (81–92.5%) at ambient to very high pressures (2 MPa) of CO₂ [90,91] (Table 5). The oxazolidinone synthesis described in this study was carried out utilizing atmospheric-pressure CO₂ and a heterogeneous catalyst without the use of solvents, and at room temperature, it produces an exceptionally elevated yield of the intended product.
Table 5. Comparison between the catalytic generation of oxazolidinones and α-alkylidene cyclic carbonates from propargylic alcohol via CO₂ fixation reactions between this work with previous reports.

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α-alkylidene cyclic carbonate

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<td>TpMA (MC)@Ag [Heterogeneous Catalyst] + CO₂ → RT, 4 h</td>
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</tbody>
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2.3. Reusability of Porous Polymeric Catalyst TpMA (MC)@Ag

The fundamental characteristics of a heterogeneous catalyst are its simple and economical synthetic procedure, recyclability, and recoverability. The reusability of the synthesized porous polymeric catalyst TpMA (MC)@Ag was evaluated using the catalyst up to 5 cycles in both reaction schemes regarding synthesizing 2-oxazolidinone and α-alkylidene cyclic carbonates under optimized reaction conditions (Figure 10). The TpMA (MC)@Ag catalyst was taken out from the reaction mixture using an extraction technique. After the reaction finished, the catalyst was washed using methanol and dried around 50 to 60 degrees Celsius. Following the drying method, the regenerated porous polymeric catalyst TpMA (MC)@Ag was used optimally in the preparation of 2-oxazolidinones and α-alkylidene cyclic carbonates. Five runs of the porous polymeric catalyst TpMA (MC)@Ag material may be successfully recycled without significantly reducing the output yield.

![Figure 10. TpMA (MC)@Ag catalyst recycling in the production of (a) oxazolidinones and (b) α-alkylidene cyclic carbonates using propargylic alcohols.](image)

2.4. Heterogeneity Test

Hot filtration examination was implemented to ascertain the heterogeneous nature of the porous polymeric catalyst TpMA (MC)@Ag for the generation of α-alkylidene cyclic carbonates and oxazolidinones through propargylic alcohols. In the beginning, the catalyst-assisted reaction yielded 95 and 97%, respectively, of the intended product after 4 and 6 h
of optimization, respectively. After the catalyst was removed from the reaction mixture, the reaction continued for six hours. The filtrate, as well as the isolated catalyst, porous polymeric catalyst TpMA (MC)@Ag, were analyzed using the ICP-AES method. There was no detectable metal present in the filtrate. The ICP-AES technique was employed to evaluate the Ag metal loading of the porous polymeric catalyst TpMA (MC)@Ag following the initial and fifth cycles of catalysis. As a consequence, the loading of Ag metal in the new porous polymeric catalyst TpMA (MC)@Ag catalyst (2.53%) had no discernible effect on the findings. However, the blocking of the catalyst’s active regions during successive catalytic cycles may result in a dramatic reduction in catalytic activity after the 6th reaction cycle.

Moreover, we conducted TEM, FE-SEM, and IR investigations over the regenerated catalyst to validate its heterogeneous character. The shape and particle size of the recycled catalyst were virtually equal to those of the freshly manufactured porous polymeric catalyst TpMA (MC)@Ag catalyst. The FT-IR study and TEM image of the regenerated catalyst revealed no significant modifications.

3. Conclusions

The present study demonstrates the design, synthesis, and complete characterization of the Ag NPs embedded in a porous polymeric framework, namely, porous polymeric catalyst TpMA (MC)@Ag. The catalyst exhibits improved efficacy in the formation of oxazolidinones and α-alkylidene cyclic carbonates using diverse unsaturated alcohols (e.g., propargylic alcohols) as starting substrates. In the presence of a strong organic DBU base, diverse unsaturated alcohols were employed at room temperature, yielding the expected α-alkylidene cyclic carbonates with relatively improved yield and excellent selectivity. On the other hand, oxazolidinones were potentially high-yielding even at room temperature through three-component reaction in the presence of aromatic/aliphatic amines, CO₂, and propargylic alcohols. The development of this catalytic protocol under solvent-free conditions makes the methodology non-hazardous and environmentally friendly. It should be noted that the porous polymeric catalyst TpMA (MC)@Ag can be regenerated and recyclable with the same catalytic efficacy. Additionally, the nanoporous porous polymeric framework not only acts as a support for silver metal, but also as a promising material featuring carbon dioxide adsorption capability. These findings represent a significant advancement in the field of porous polymeric framework-based heterogeneous catalysis and provide momentum for the development of reusable heterogeneous catalysts for diverse CO₂ conversions.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal13121467/s1, Figure S1: Picture of porous polymeric catalyst (a) TpMA (MC) and (b) Ag metal-loaded catalyst, TpMA (MC)@Ag, Figure S2: FT-IR spectroscopy of reused TpMA (MC)@Ag catalyst and TpMA (MC) polymeric catalyst, Figure S3: BET isotherm of reused TpMA (MC)@Ag catalyst, Figure S4: PXRD of reused catalyst, Figure S5: (a–b) HRTEM image of reused catalyst and (c–d) FE-SEM image of reused catalyst, Figure S6: 1H NMR of 3-Cyclohexyl-5,5-dimethyl-4-methylene-oxazolidin-2-one, Figure S7: 1H NMR of 4 methylene-1-oxa-3-azaspiro*4.5+decan-2-one, Figure S8: 1H NMR 3 Benzyl 4 methylene 1 oxo 3 azaspiro *4.5+decan 2 one, Figure S9: 1H NMR of 3--(4 4 methylene 1 oxo 3 azaspiro *4.5+decan 2 one, Figure S10: 1H NMR of 5,5 dimethyl 3--(4 methylbenzyl 4 methyleneoxazolidin 2 one, Figure S11: 1H NMR of 3--(4 5,5 dimethyl 4 methyleneoxazolidin 2 one, Figure S12: 1H NMR of 3 butyl 5,5 dimethyl 4 methyleneoxazolidin 2 one, Figure S13: 1H NMR of 3 Benzyl 5,5 dimethyl 4 methylene oxazolidin 2 one, Figure S14: 1H NMR of 4,4 dimethyl 5 methylene 1,3 dioxolan 2 one, Figure S15: 1H NMR of 4 ethyl 4 methyl 5 methylene 1,3 dioxolan 2 one, Figure S16: 1H NMR of 4 ethyl 4 methyl 5 methylene 1,3 dioxolan 2 one, Figure S17: 1H NMR of 4 methyl 5 methylene 4 phenyl 1,3 dioxolan 2 one, Figure S18: 1H NMR of 4 methylene 1,3 dioxaspiro *4.5+decan 2 one, Table S1: The grain size of Ag NPs.

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