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HCO_3^- modified *N*-heterocyclic carbene silver organic porous polymer catalyzes the conversion of low concentration CO_2 into oxazolidinone compounds

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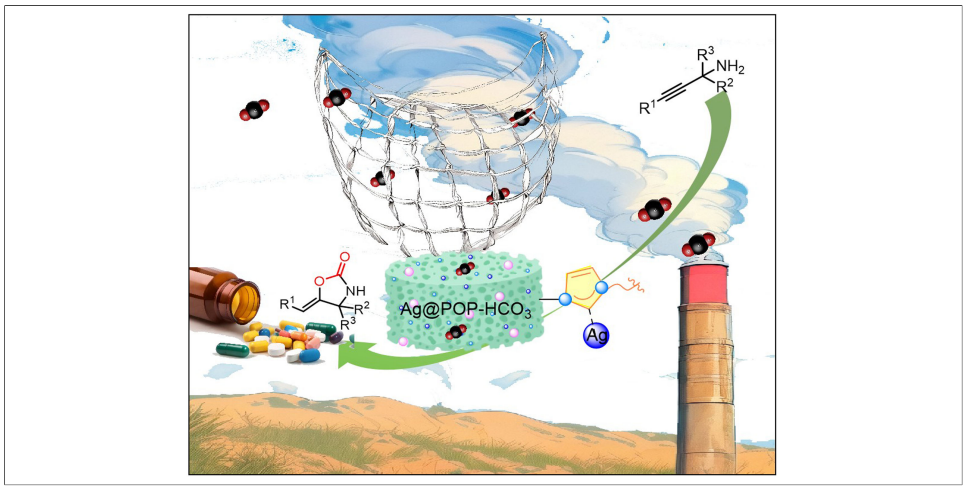

Abstract

Silver metalized organic porous polymer (Ag@POP-HCO_3) was prepared by copolymerizing the HCO_3^- modified *N*-heterocyclic carbene monomer loading silver with divinylbenzene. The *in-situ* conversion of low concentration CO_2 from coal-fired flue gas or air into oxazolidinone compounds was achieved through carboxylation cyclization reaction catalyzed by Ag@POP-HCO_3 under ambient conditions, without the addition of any cocatalyst. Additionally, both SO_2 and NO_2 did not interfere with the reaction at normal concentration presented in flue gas. The Ag@POP-HCO_3 can effectively catalyze the gram reaction, and its catalytic activity is not significantly reduced after being recycled. The introduction of HCO_3^- increased the specific surface area and microporous volumes of the catalyst, enhancing its ability to adsorb CO_2. Furthermore, *N*-heterocyclic carbene and HCO_3^- collaborated to expedite the activation of CO_2, while the coordination of silver serves to activate the substrate. The proposed approach avoids cost issues of traditional carbon capture, utilization and storage technology and promotes green chemical process development.

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INTRODUCTION

The issue of climate change is becoming increasingly severe due to rising global carbon emissions[1]. Carbon capture, utilization and storage (CCUS) technology is considered a key solution to address this issue[2,3]. The process of capturing, utilizing, or storing carbon within the framework of CCUS technology typically involves multiple steps. While this method is crucial for addressing climate concerns, it also presents its own set of challenges, particularly in terms of financial investment and energy usage. For example, the amine-based carbon capture method has become a commonly utilized approach in CCUS technology. This process requires 0.5 to 1 kilogram of amine solution and 1.4 tons of steam to capture a single ton of CO_2[4]. Furthermore, the logistics of transporting captured carbon through pipelines also entail significant financial considerations. The costs associated with this transportation infrastructure can range from $50,000 to $700,000 per mile[4]. In addition, the process of carbon storage requires extensive geological exploration and engineering work, leading to potentially high costs. Furthermore, the conversion of CO_2 into high-value organic chemicals shows promise for carbon utilization[5,6], but it necessitates the use of pure CO_2 obtained after carbon capture and transportation. The aforementioned challenges may currently be influencing the commercial viability of the CCUS technology[7]. *In-situ* CO_2 conversion, as proposed in our previous report[8-10] and by other scientists[11-13], offers an approach to achieve simultaneous capture and utilization of CO_2. This approach has the potential to facilitate the transition from multi-step to one-step CCUS technology, addressing the current challenge the CCUS technology faces.

Oxazolidinones are often used as the core structure of drugs because of their extensive biological activities. The use of CO_2 to synthesize such compounds thus opens up an entirely new source of drugs, helping to reduce the dependence on petrochemicals in traditional pharmaceutical processes, while also contributing to environmental protection and the fight against climate change. However, researchers studying the *in-situ* catalytic conversion of CO_2 into high-value organic chemicals are confronted with a significant challenge due to the strong chemical inertia of CO_2 under normal conditions[14]. This is primarily because: (1) the majority of studies on the catalytic conversion of CO_2 to high-value organic chemicals rely on the use of homogeneous catalysts for converting high-concentration CO_2 and require the participation of alkali or cocatalyst[15-17]. However, these approaches are associated with difficulties in recycling, poor stability, and environmental pollution; (2) the low concentration of CO_2 in flue gas further complicates the process of catalytic conversion for capturing into high-value organic chemicals[18,19]. Therefore, it is imperative and groundbreaking to achieve *in-situ* catalytic conversion of CO_2 in waste gas without relying on homogeneous catalyst, or base and cocatalyst. This could be achieved through designing a specialized heterogeneous catalyst with a large specific surface area and unique active site[20,21].

In recent years, the role of bicarbonate (HCO_3^-) in CO_2 reduction has become increasingly important in the field of chemistry, biology and environmental science[22,23]. Therefore, incorporating it into heterogeneous catalysts may enhance the catalytic conversion ability of CO_2 and is expected to replace the base and cocatalyst in the reaction system. Additionally, metal pre-coordination can be uniformly dispersed on the carrier surface to provide more active sites[24]. Our previous studies have shown that *N*-heterocyclic carbene organic porous polymers (POPs) exhibit superior ability for CO_2 capture and catalytic conversion[8,25]. Therefore, in this study, silver metalized organic porous polymers (Ag@POP-HCO_3) were designed by copolymerizing *N*-heterocyclic carbene monomer modified by HCO_3^- and pre-coordinated silver, with divinylbenzene (DVB). The polymer relies on the established abundant pores and HCO_3^- co-enrichment of CO_2. Additionally, *N*-heterocyclic carbene and HCO_3^- accelerate the activation of CO_2, while the coordination silver serves to activate the substrate. This allows for the *in-situ* conversion of CO_2 in flue gas or air to oxazolidinone compounds through carboxylation cyclization reaction with no cocatalyst at room temperature and ambient pressure. The catalyst is unaffected by atmospheric pollutants (NO_2, SO_2), and

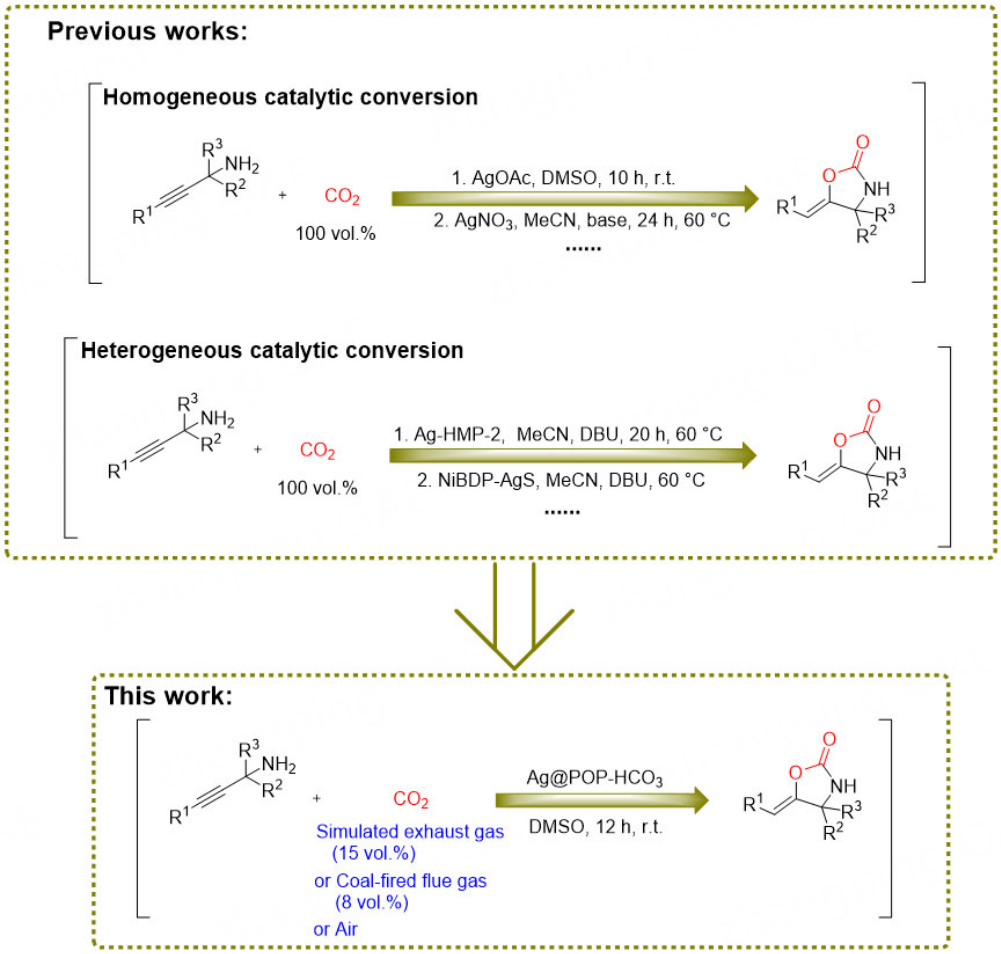


Figure 1. Previous works and this work.

exhibits good selectivity. This approach mitigates the cost and energy issues associated with traditional CCUS technology, thereby facilitating the development of environmentally friendly chemical processes. The comparison between this work and previous reports[26-29] is shown in Figure 1 and Supplementary Table 1.

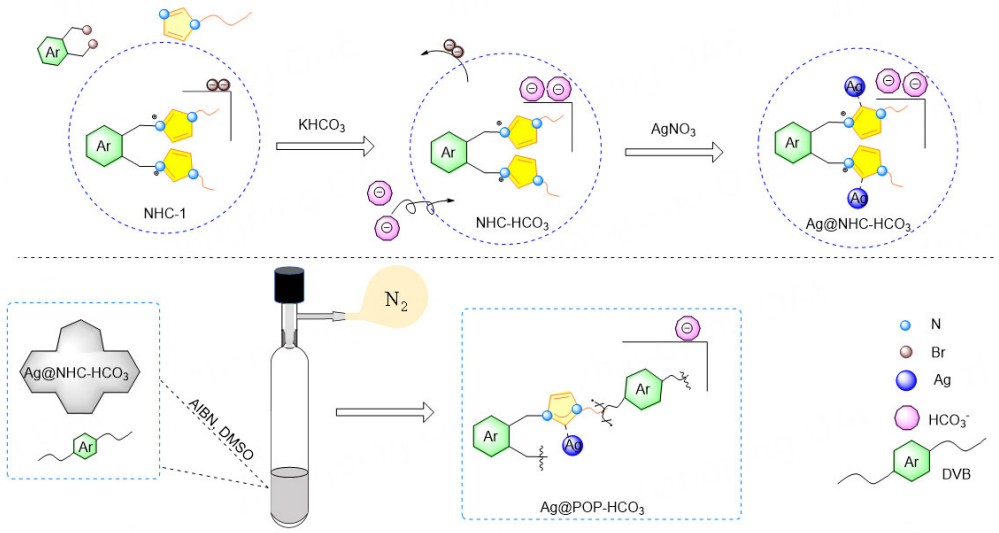
EXPERIMENTAL

Materials and reagents

1,2-Dibromo-methyl benzene, n-vinylimidazole, DVB, azodiisobutyronitrile (AIBN), bis(triphenylphosphine)palladium(II) dichloride [$Pd(PPh_3)_2Cl_2$], palladium(II) acetate [$Pd(OAc)_2$], cuprous iodide (CuI), iodobenzene, 2-methyl-3-butyn-2-amine, *etc.* were purchased from Innochem in Beijing, China. Potassium carbonate ($KHCO_3$) and silver nitrate ($AgNO_3$) were procured from Xilong Science Co., LTD. Solvents such as toluene, ethyl acetate (EA), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) and methanol (MeOH), sulfuric acid (H_2SO_4) are purchased from local suppliers.

Synthetic method of Ag@POP-HCO_3

The monomer (NHC-1) was synthesized by quaternary ammonium reaction of 20.0 mmol 1-vinylimidazole and 10.0 mmol halogenated aromatic hydrocarbons in 20 ml toluene at 90 °C for 24 h[24]. Secondly, NHC-HCO_3 was synthesized by mixing 2 mmol NHC-1 and 4.2 mmol $KHCO_3$ in MeOH at room temperature for 48 h to achieve anion conversion, stirring (400 rpm) at room temperature under shade for 12 h for metal pre-coordination synthesis Ag@NHC-HCO_3. Finally, the polymer Ag@POP-HCO_3 was obtained



Scheme 1. Synthesis path of Ag@POP-HCO_3.

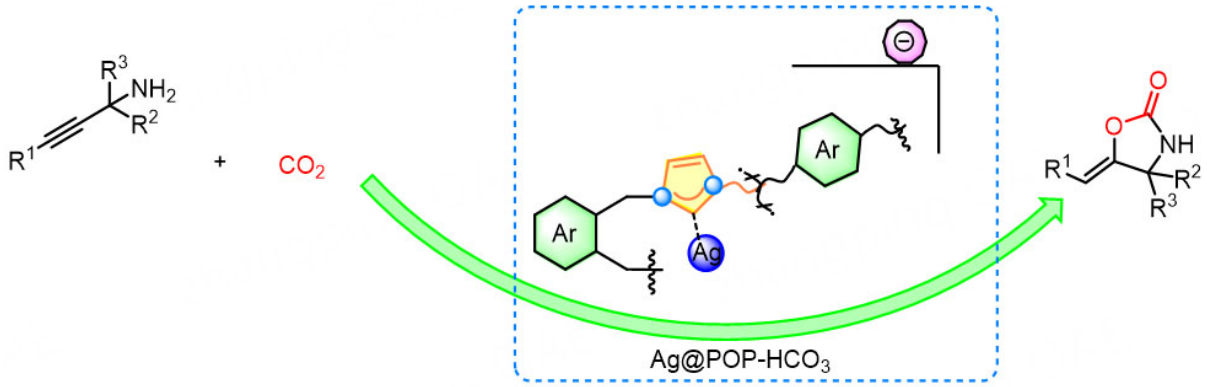
by polymerization in 3 mL DMSO under high pressure of 100 °C for 24 h with 0.10 mmol Ag@NHC-HCO_3 as the polymerization unit, 2.0 mmol DVB as the crosslinker, and 33 mg AIBN as the initiator [Scheme 1].

Characterization methods

The functional groups and structures of the catalysts were investigated by various analytical techniques. These included 1H/13C nuclear magnetic resonance (NMR) spectroscopy (Bruker SBAVance III 400 M, Germany), solid-state ^{13}C NMR (Bruker Avance Neo 400WB 400M, Germany) and Fourier infrared spectroscopy (FT-IR, Thermo Scientific Nicolet iS20, United States). Additionally, the elemental composition of the nanoparticles was further analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific K-Alpha, United States). The morphology and pore distribution of the catalyst were observed and determined by a scanning electron microscope (SEM, ZEISS sigma300, Germany), a transmission electron microscope (TEM, FEI Tecnai F20, United States), and a specific surface area and pore volume analyzer (BET, Kubo-X1000, China). Finally, the active center type of the catalyst was analyzed by *in situ* Raman (Horiba HR Evolution, Japan) and the thermal stability was studied by thermogravimetric analysis (TGA, NETZSCH STA2500, Germany).

The evaluating method of catalyst performance

The carboxylation cyclization reactions between propargyl amines and CO_2 were employed to evaluate the performance of the catalysts proposed by this work [Scheme 2]. The brand of pharmaceutical reagent used in this system is listed in Supplementary Materials. In particular, an appropriate amount of catalyst was carefully weighed and added to a 10 mL branched glass reaction tube. Subsequently, 0.2 mmol of the reaction substrate and a specific quantity of solvent were introduced into the tube. The tube was then connected to CO_2 atmosphere (0-100 vol.% CO_2 /N_2) provided by a balloon. Finally, the reaction tube containing the reaction mixture was then placed in a dark environment and subjected to magnetic stirring (400 rpm) for a certain time at a certain reaction temperature. After the reaction, the yield was determined using high performance liquid chromatography (HPLC Dionex UltiMate 3000) with biphenyl as the internal standard. The structure of the reaction products was elucidated by analyzing $^{1}H/^{13}C$ NMR spectra obtained using a Bruker AVANCE-III 400 spectrometer.



Scheme 2. Carboxylation cyclization of CO_2 with propargyl amines.

RESULTS AND DISCUSSION

Catalytic performance evaluation

The polymer material Ag@POP-HCO_3 was employed as a catalyst to catalyze the model carboxylation cyclization reaction between 2-methyl-4-phenylbut-3-yn-2-amine and CO_2. The reaction conditions, including the choice of solvent, reaction temperature, catalyst dosage, CO_2 concentration and reaction time, were optimized using a univariate method. The optimization conditions resulted in the following: when utilizing 15 vol.% CO_2/N_2 simulated gas as the carbon source and 0.2 mmol propargyl amines as the substrate, it was observed that employing 1 mL of DMSO at room temperature for a reaction time of 12 h resulted in an optimal yield of 77% using 10 mg of Ag@POP-HCO_3 catalyst [Figure 2A-C].

The higher concentration of CO_2 in the carbon source gas leads to a greater yield within the same reaction time (12 h) [Figure 2D]. With the increase of CO_2 concentration to 50 vol.% CO_2/N_2 and 100 vol.% CO_2/N_2, the yield can reach 87% and 93%, respectively. When using air as the carbon source, only a 1% yield of oxazolidinone compounds was obtained. However, no oxazolidinone was produced in the absence of CO_2, such as under a pure N_2 atmosphere. These findings suggested that the carboxylation cyclization reaction between propargyl amines and CO_2 was dependent on the nucleophilic addition and cyclization steps of CO_2.

Under the optimal reaction conditions, POP-HCO_3 and Ag@POP-Br (these synthesis methods are shown in Supplementary Schemes 1 and 2) were also utilized as catalysts to facilitate the conversion of low concentration CO_2 through the model reaction, respectively. Both materials are components of the structure of Ag@POP-HCO_3. The results showed that POP-HCO_3 did not yield any target products, while Ag@POP-Br resulted in a relatively low yield of only 24% [Figure 3A]. However, Ag@POP-HCO_3 outperformed both catalysts with a resulting yield of 77%. These findings indicate that both silver and HCO_3^- active sites in the polymer materials are essential for catalyzing the carboxylation cyclization reactions.

To investigate the impact of HCO_3^- on the catalytic performance, different Ag@POP-HCO_3 materials with varying HCO_3^- content were synthesized by adjusting the reaction ratios of NHC and $KHCO_3$ to establish the anionic environment of NHC-1 in the Ag@POP-HCO_3 synthesis process. The catalytic performance for the model reaction was then evaluated [Figure 3B]. When the reaction ratios of NHC-1 and $KHCO_3$ ranged from 1:0 to 1:2, the yield increased up to 77% due to rising HCO_3^- content in the Ag@POP-HCO_3 material. However, there was no significant increase in yield when changing the ratio of NHC and $KHCO_3$ to 1:3. This is because the theoretical reaction ratio of NHC and $KHCO_3$ is 1:2; increasing it to 1:3 did not raise the HCO_3^- content in the Ag@POP-HCO_3. These findings further confirm that HCO_3^- is an effective active site in

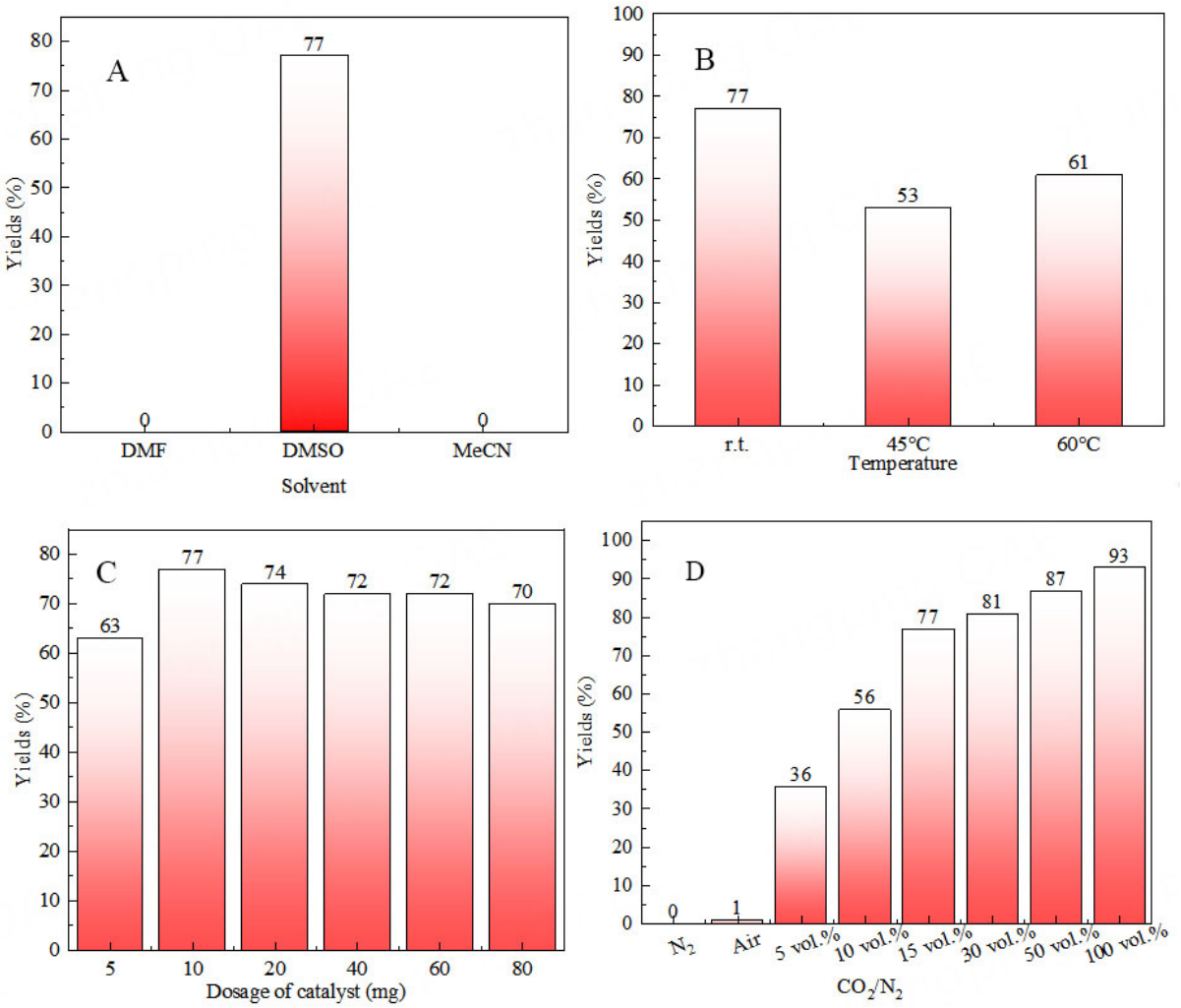


Figure 2. Under the ambient pressure of low concentration CO_2 and other different conditions, the catalyst reacted with 0.2 mmol propargyl amines for 12 h and the yields are as follows. (A) Solvent type (1 mL); (B) DMSO (1 mL), temperature; (C) DMSO (1 mL), dosage of catalyst at r.t.; (D) DMSO (1 mL), 10 mg catalyst catalyzes the conversion of different concentrations of CO_2 at r.t. DMSO: Dimethyl sulfoxide.

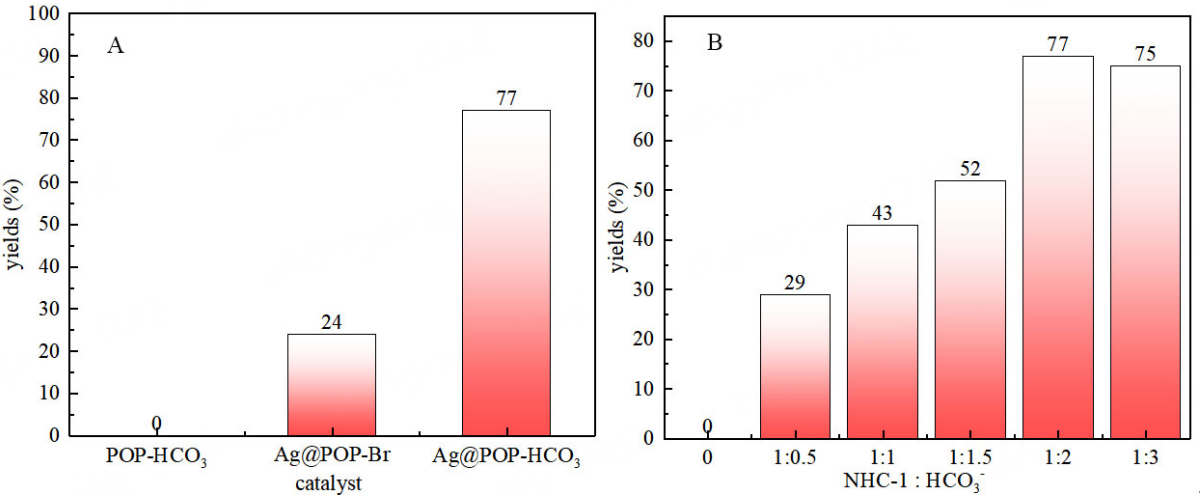


Figure 3. Under the environment pressure of 15 vol % CO_2, DMSO (1 mL), the catalytic reaction yield of 10 mg catalyst with different structures stirred for 12 h are as follows. (A) Catalyst screening; (B) Influence of bicarbonate content. DMSO: Dimethyl sulfoxide.

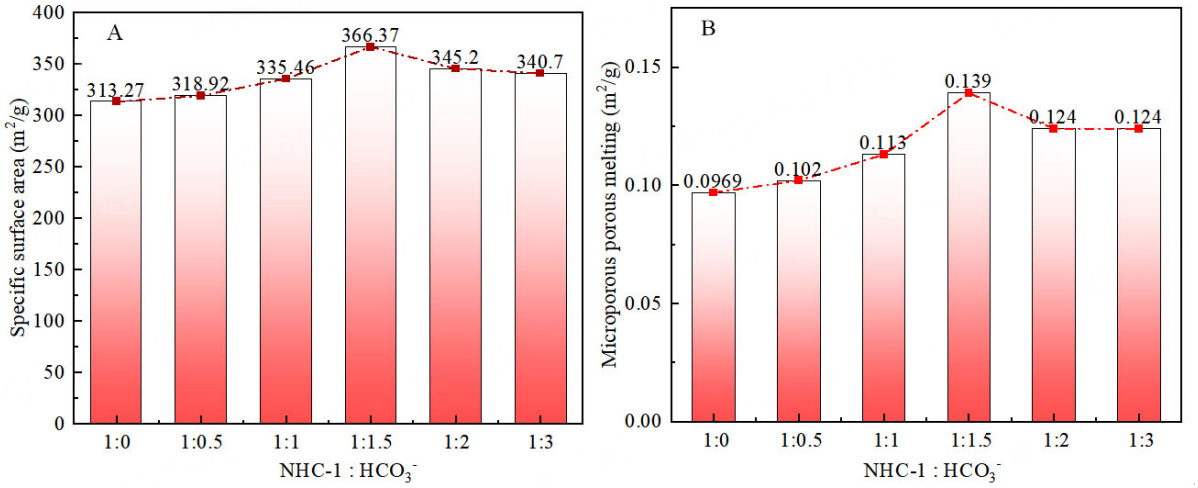


Figure 4. Specific surface area and microporous fusion of polymers with different NHC-1 and HCO_3^- ratios. (A) Specific surface area; (B) Microporous porous melting.

the Ag@POP-HCO_3 catalyst.

In order to further verify the experimental results, the specific surface area and microporous fusion of NHC-1 and HCO_3^- proportional polymers were determined by N_2 adsorption and desorption curves [Figure 4, Supplementary Figures 1 and 2]. The higher the HCO_3^- content, the larger the specific surface area and microporous melting of the catalyst. When NHC-1: HCO_3^- = 1:1.5, the specific surface area and micropore porosity are the largest. The specific surface area is 366.37m^2/g, and the micropore volume is 0.139 m^3/g. However, due to the small number of active sites of HCO_3^- compared with the NHC-1: HCO_3^- = 1:2 polymer, the catalytic conversion rate of HCO_3^- to oxazolidinone was only 52%. When NHC-1: HCO_3^- = 1:3, the specific surface area and micropore volume of the catalyst remain basically unchanged. Furthermore, increasing the ratio of NHC-1 to HCO_3^- to 1:3 does not increase the HCO_3^- content in Ag@POP-HCO_3. Based on the above experimental results, it is proved that HCO_3^- is an important influencing factor of the catalytic system.

Increasing the usage of DVB in the polymerization process for the materials will increase both the specific surface area and micropore volume, potentially benefiting the catalytic performance[30,31]. However, it will decrease both the silver and HCO_3^- active sites, negatively affecting the catalytic performance. Therefore, an optimum polymerization ratio needs to be sought to balance both sides of the conflict. Experimental data revealed that the best catalytic conversion of low concentration CO_2 to oxazolidinone occurs when Ag@NHC-HCO_3: DVB = 1:20 [Figure 5]. According to Figure 6, Supplementary Figures 3 and 4, the presence of DVB in the polymer benefits the increase in specific surface area and micropore volume of the polymer. As shown in Figure 7, Ag@POP-HCO_3 has significant selectivity for CO_2 adsorption at both 0 °C and 25 °C. Comparison of the CO_2 adsorption isotherms of Ag@POP-Br and Ag@POP-HCO_3 (1:20) showed that introduction of HCO_3^- anions into the catalyst led to enhancement of CO_2 adsorption capacity. Additionally, there was a positive correlation between adsorption performance for CO_2 and the increase in DVB usage [Figure 8]. Although the maximum CO_2 capacity belonged to the polymer material Ag@POP-HCO_3 (1:30), optimal catalytic performance occurred with a polymerization ratio of 1:20 for Ag@POP-HCO_3, indicating that an ideal equilibrium state was achieved in terms of distribution of active center, pore structure and adsorption capacity of the catalyst when using a ratio of 1:20.

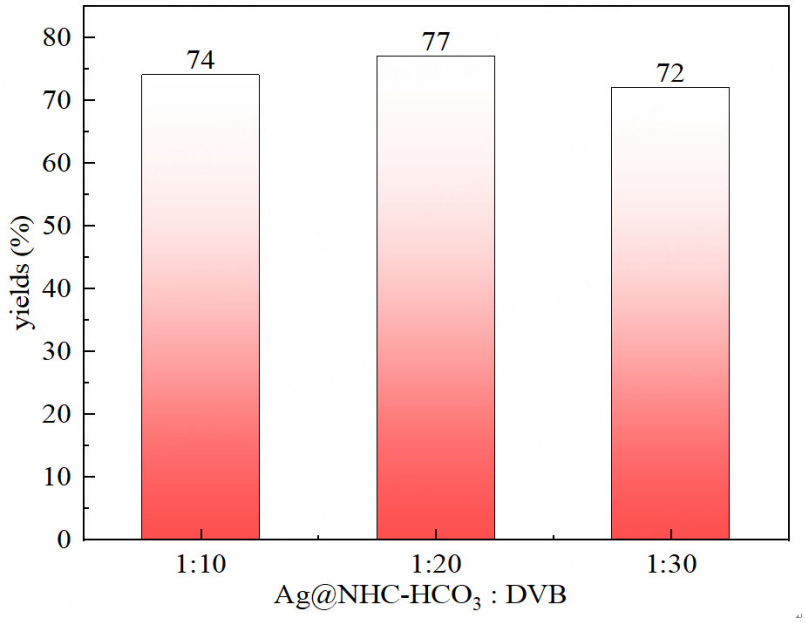


Figure 5. The effect of different polymerization ratios on the catalytic effect.

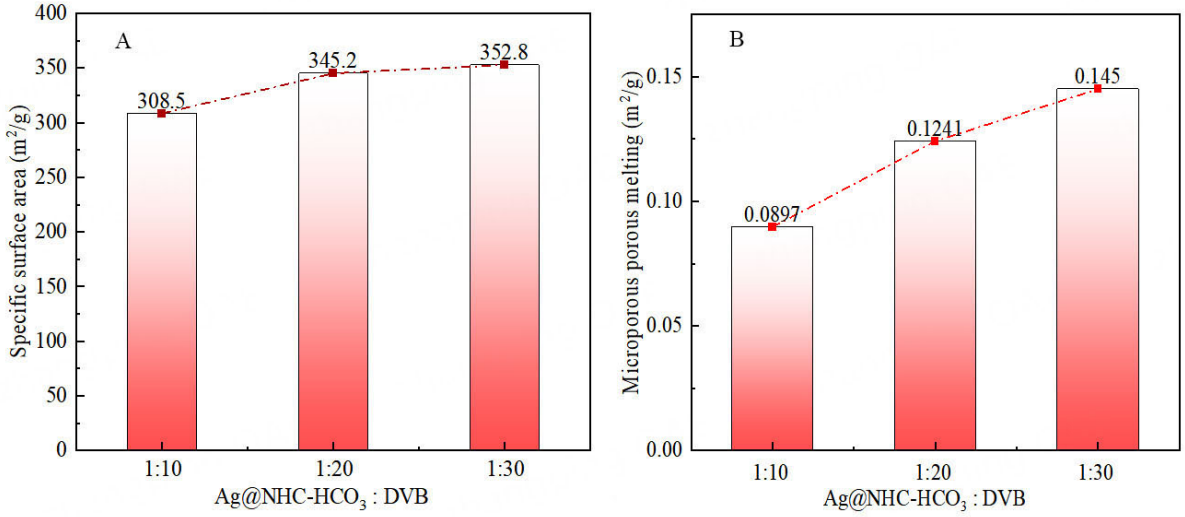


Figure 6. Specific surface area and microporous fusion of polymers with different NHC-1 and HCO_3^- ratios. (A) Specific surface area; (B) Microporous porous melting.

Mechanistic considerations

Following the successful construction and optimization of the internal structure, the micro-structure of the optimized catalyst Ag@POP-HCO_3 (1:20) was characterized and verified. The specific surface area of Ag@POP-HCO_3 (1:20) material is 345.2 m^2/g and the micropore volume is 0.1241 cm^3/g. The adsorption and desorption curve of Ag@POP-HCO_3 exhibits type IV isotherm features [Figure 9]. The analysis of the pore size distribution curve indicated a pore size of approximately 3 nm for the polymer material, demonstrating characteristics of mesoporous materials.

The ^{13}C NMR spectrum of NHC-HCO_3 revealed an increase in HCO_3^- peaks, indicating the successful replacement of original Br^- in NHC-1 by HCO_3^- through the reaction of NHC-1 with $KHCO_3$. The solid-state

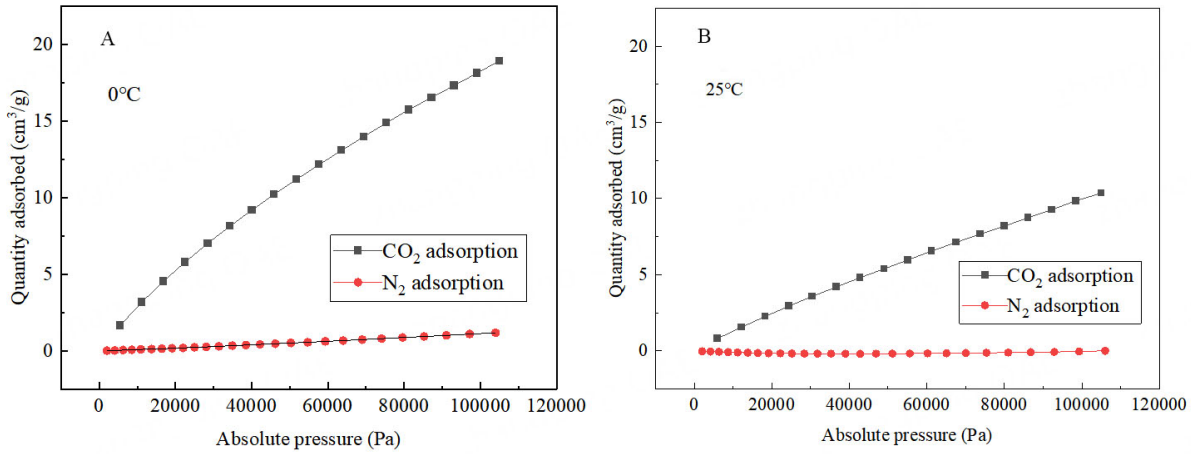


Figure 7. (A) Comparison of adsorption isotherms of carbon dioxide and N_2 at 0 °C of Ag@POP-HCO_3; (B) Comparison of adsorption isotherms of carbon dioxide and N_2 at 25 °C of Ag@POP-HCO_3.

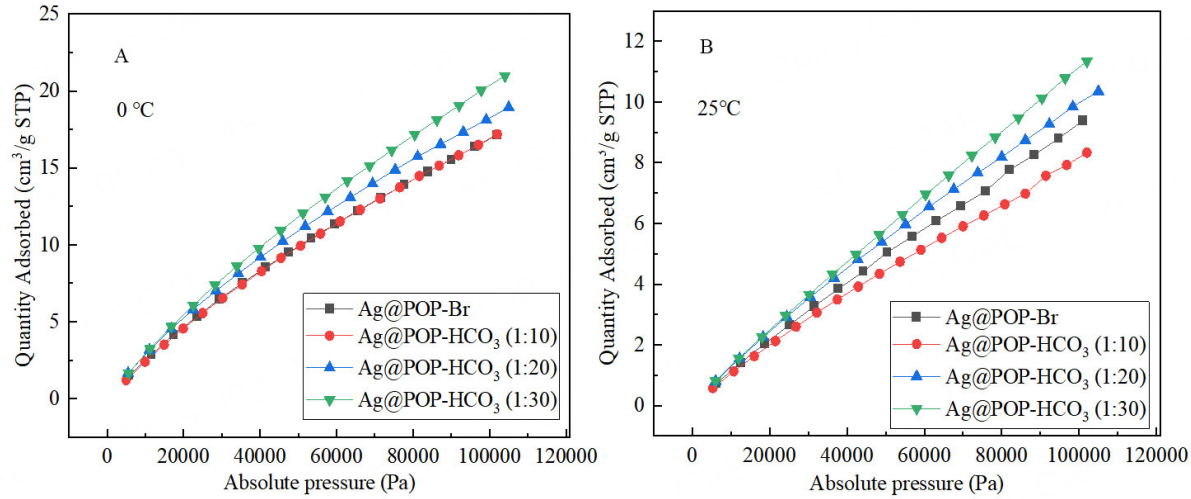


Figure 8. (A) CO_2 adsorption curve at 0 °C; (B) CO_2 adsorption curve at 25 °C.

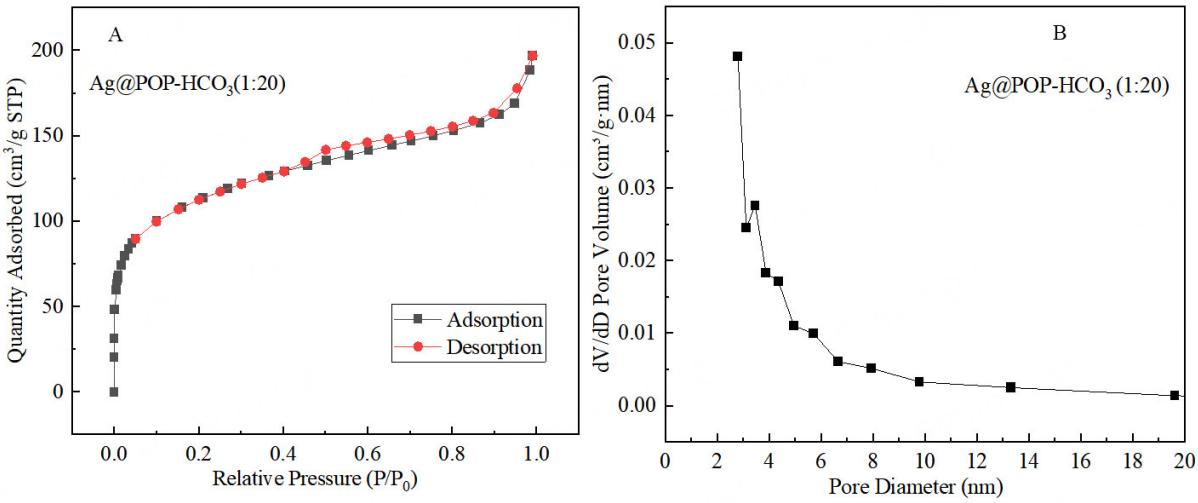


Figure 9. (A) Specific surface area of the catalyst; (B) Microporous melting of catalyst.

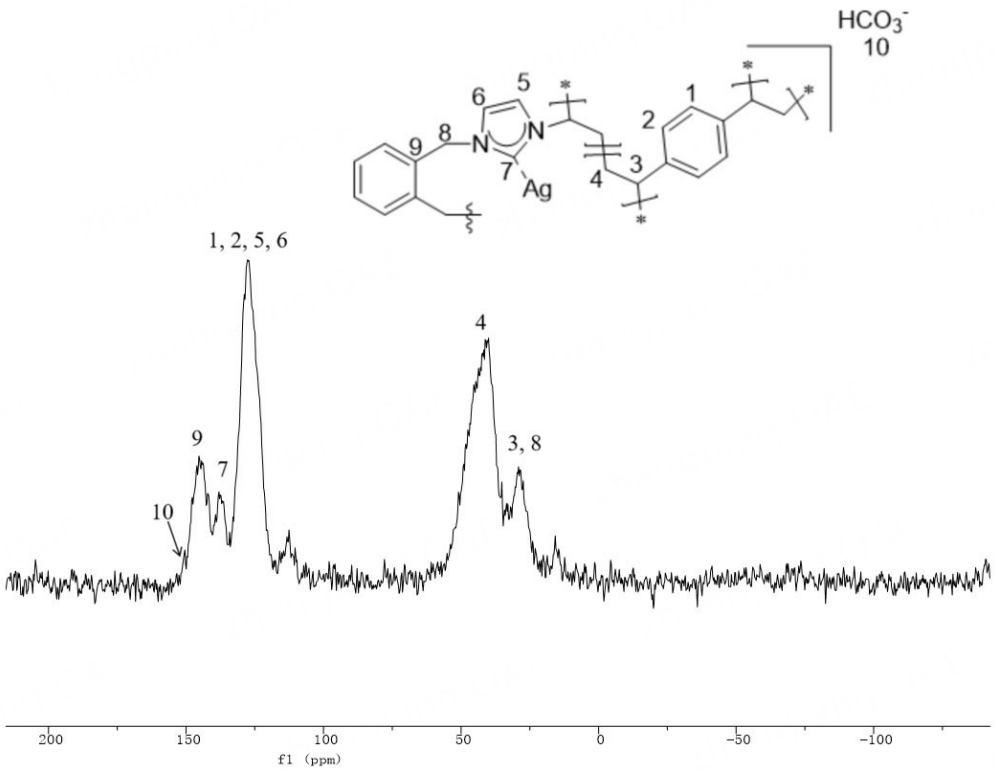


Figure 10. ^{13}C NMR spectrum of solid nuclear magnetic vibration at Ag@POP-HCO_3

C NMR spectrum of Ag@POP-HCO_3 [Figure 10] shows vibration peaks at 29 ppm caused by methylene units (C3, C8) attached to the benzene ring, wide overlapping peaks at 40-60 ppm attributed to polyethylene (C4) vibration, vibration peaks at 128 ppm, 138 ppm, and 145 ppm associated with C signals from imidazole and aromatic rings, and a spike at 150 ppm due to HCO_3^-[32].

The FT-IR spectra of Ag@POP-HCO_3, Ag@POP-Br and POP-HCO_3 polymers are exhibited in Figure 11A. The peaks observed at 3,100-2,850 cm^{-1} can be attributed to the stretching vibrations of aliphatic C-H bonds, while a bending vibration peak of around 710 cm^{-1} is caused by aromatic C-H. These findings suggest DVB unit presence in the structure of the polymers[33,34]. Peaks observed at 1,600 cm and 1,156 cm are separately induced by the vibration of the aromatic ring and imidazole ring skeleton (C-C)[35], while peaks at 1,640 cm and 1,445 cm arise from C=N and C-N bonds[36,37], indicating that imidazole framework of Ag@POP-HCO_3 remains undamaged after $KHCO_3$ modification and silver loading.

TGA [Figure 11B] in N_2 atmosphere shows that the catalyst Ag@POP-HCO_3 has excellent thermal stability. It did not exhibit significant mass loss until it reached a temperature above 400. However, a rapid increase of mass loss was observed between 400 °C and 500 °C, indicating substantial polymer decomposition. Further mass loss above 500 °C was attributed to imidazole ring decomposition[8,9]. However, as the temperature increases, the polymer will undergo carbonization, eventually resulting in a non-volatile carbon skeleton and metal residues.

The SEM image reveals that the polymer Ag@POP-HCO_3 is formed through the accumulation and superposition of particles, resulting in irregular pore structures conducive to the enrichment of CO_2 in waste gas [Figure 12A]. TEM images demonstrate that the silver particles are uniformly dispersed within the polymer [Figure 12B and Supplementary Figure 5]. This can be attributed to the benefits of the method of

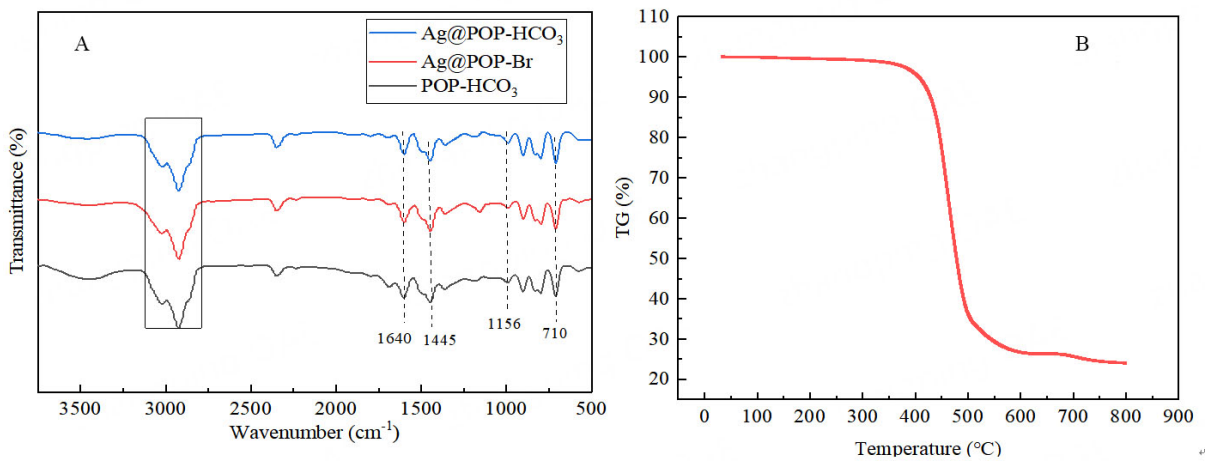


Figure 11. (A) FT-IR spectra of Ag@POP-HCO_3, Ag@POP-Br and POP-HCO_3; (B) Thermogravimetric analysis diagram of Ag@POP-HCO_3.

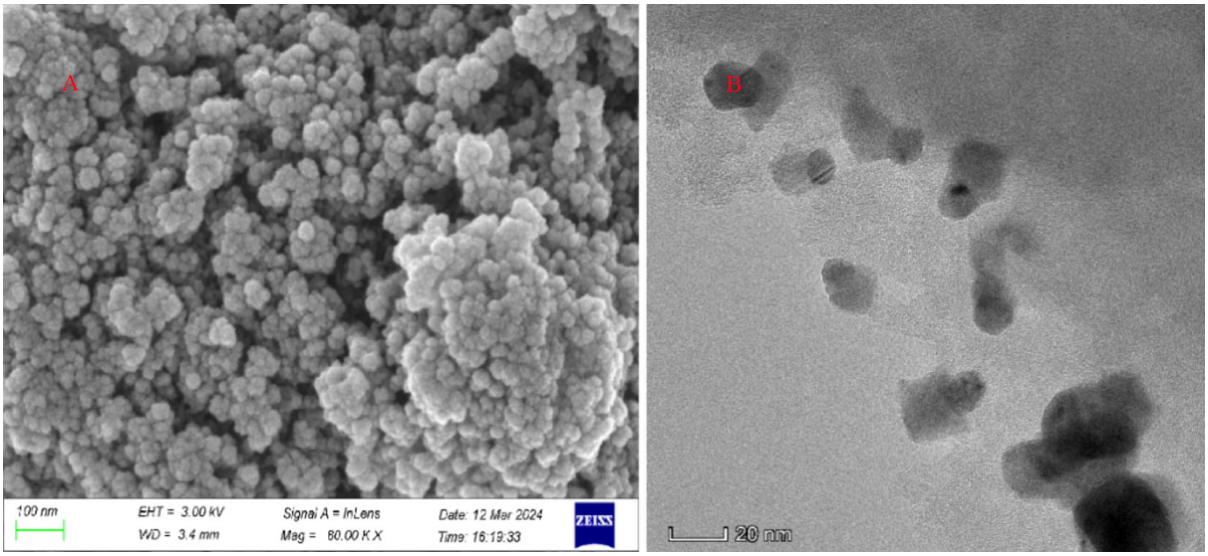


Figure 12. (A) 100 nm SEM image of catalyst before cycling; (B) TEM image of catalyst before cycling. SEM: Scanning electron microscope; TEM: transmission electron microscope.

metal pre-coordination, where the metal coordinated NHC-HCO_3 to form a metal complex monomer (Ag@NHC-HCO_3), and then copolymerizes with the crosslinking agent, ensuring the dispersion of metallic silver and preventing cluster phenomena[10].

The XPS diagram [Figure 13 and Supplementary Figure 6] clearly indicates the binding energy of N 1s at 399.7 eV. A distinct O 1s electron binding energy is observed at 532.5 eV, providing further evidence that HCO_3^- has successfully replaced Br^-[38,39] although a minute quantity of Br^- remains. The peaks at 368.6 eV and 374.7 eV correspond to Ag 3d, representing the bimodal structure of Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively, confirming the successful loading of metal Ag[40,41].

In situ Raman spectra of Ag@POP-HCO_3 under CO_2 and N_2 atmosphere were depicted in Figure 14A. Peaks at 1,207 cm^{-1} and 2,233 cm^{-1} are clearly observed in the spectrum of Ag@POP-HCO_3 under CO_2, but not under N_2 atmosphere. The peak at 1,207 cm^{-1} corresponds to the tensile vibration of CO_2 adsorbed on N, while the peak at 2,233 cm^{-1} is derived from the antisymmetric stretching of the adsorbed CO_2 on the *N*

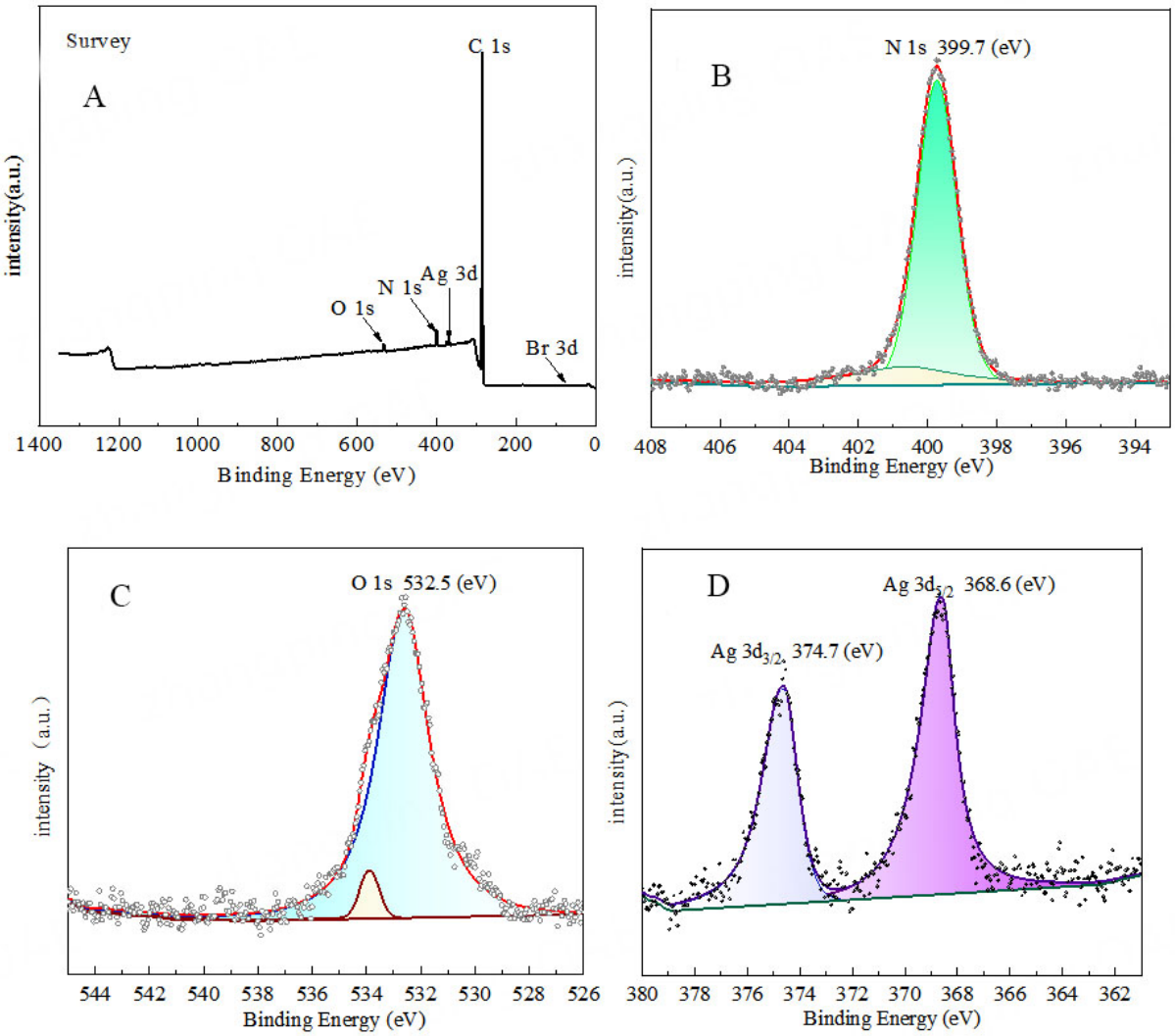


Figure 13. High resolution XPS spectrum. (A) Ag@POP-HCO_3; (B) N 1s; (C) O 1s; (D) Ag $3d_{3/2}$, Ag $3d_{5/2}$. XPS: X-ray photoelectron spectroscopy.

-heterocyclic carbene[42]. These findings demonstrate that *N*-heterocyclic carbene in Ag@POP-HCO_3 can effectively activate CO_2. In addition, elemental analysis and atomic absorption were performed on the catalyst, and the content of N and silver was measured to be 0.9% and 0.046 wt%, respectively [Supplementary Table 2].

The reaction kinetics were investigated using a 15 vol.% CO_2/N_2 gas mixture as the carbon source [Figure 14B]. It was observed that after 12 h, the yield almost reached a plateau. Further extending the reaction time to 24 h resulted in only a 6% increase in yield. Additionally, when the catalyst was filtered out at 3 h and no longer participated in the subsequent CO_2 reaction, the reaction almost stopped. This confirms that this catalytic system operates through a heterophase catalytic mechanism.

Based on aforementioned experimental results, we propose a possible mechanism for Ag@POP-HCO_3 catalyzing the carboxylation cyclization of propargyl amines with low concentration CO_2 [Scheme 3]. Firstly, CO_2 is co-enriched by the pores and HCO_3^- anions of Ag@POP-HCO_3 catalyst. During the enrichment process, CO_2 is initially adsorbed by the pores and then captured by HCO_3^- anions. The solvent DMSO exhibits strong water absorption, which allows for species transformation of HCO_3^- and CO_2, thereby

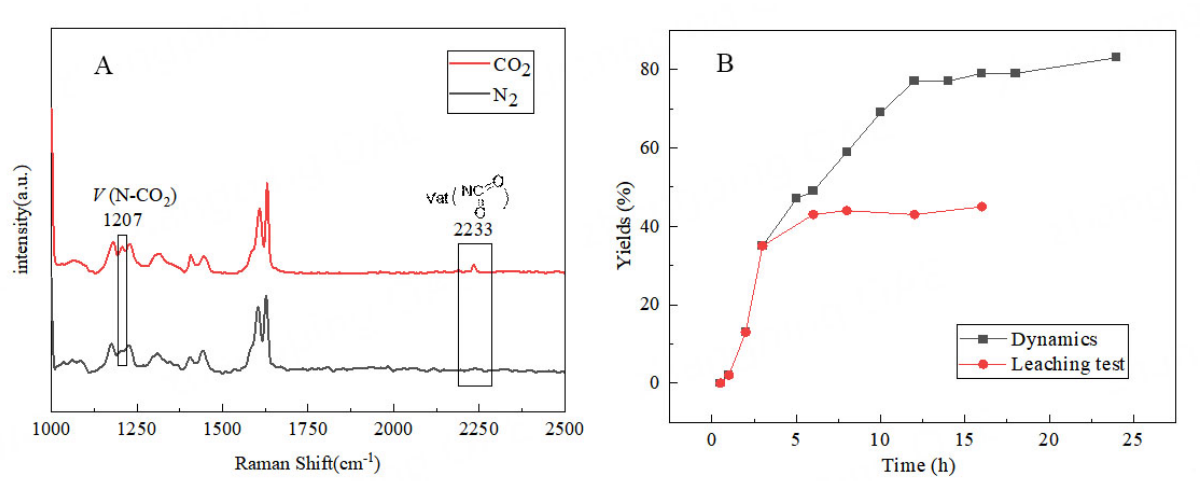
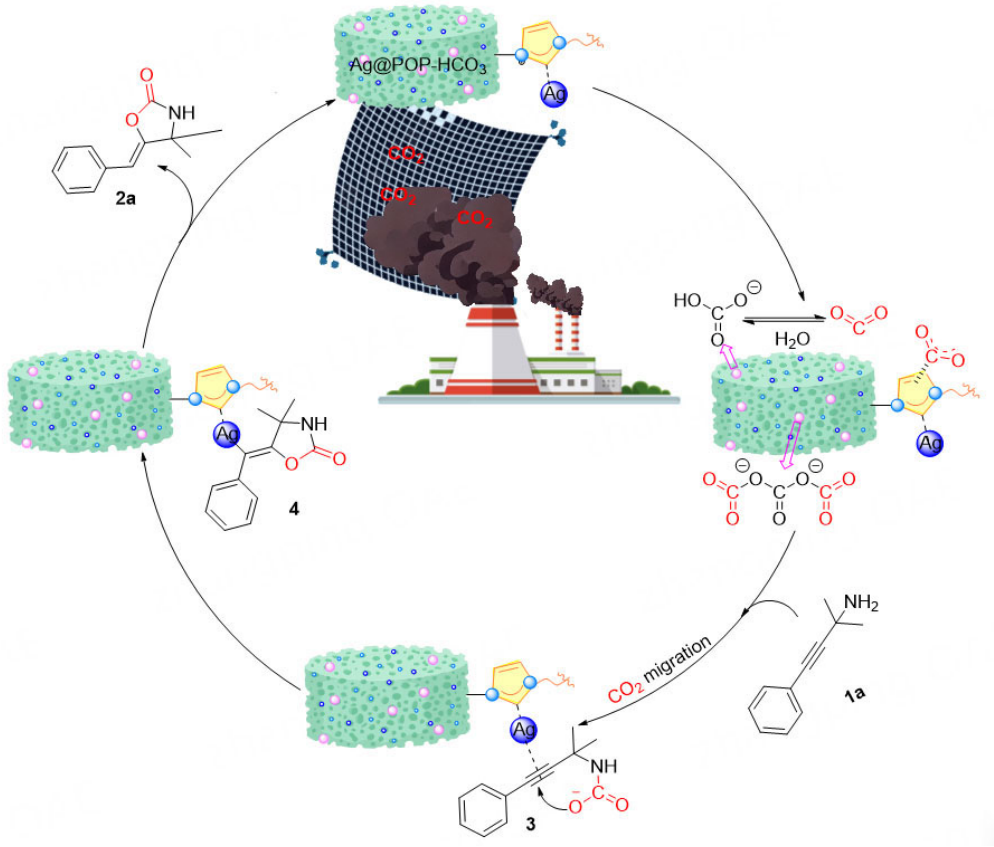


Figure 14. (A) *In situ* Raman spectra of Ag@POP-HCO_3 under CO_2 and N_2 atmosphere; (B) Reaction kinetics and leaching experiments.



Scheme 3. Possible mechanism for Ag@POP-HCO_3 catalyzing the carboxylation cyclization of propargyl amines with coal-fired flue gas.

enhancing the capability of the catalyst Ag@POP-HCO_3 to enrich CO_2. Subsequently, the enriched CO_2 is activated by carbene N. The Ag in the catalyst interacts with the C≡C bond of propargyl amine through empty orbitals and π electrons to active propargyl amine. The activated CO_2 and propargyl amines are converted into carbamate intermediates **3**. Carbamate intermediate **3** is converted to vinyl-silver intermediate **4** by intramolecular cyclization. Finally, oxazolidinone **2a** was produced by *in-situ* demetallization, and the catalyst Ag@POP-HCO_3 was regenerated.

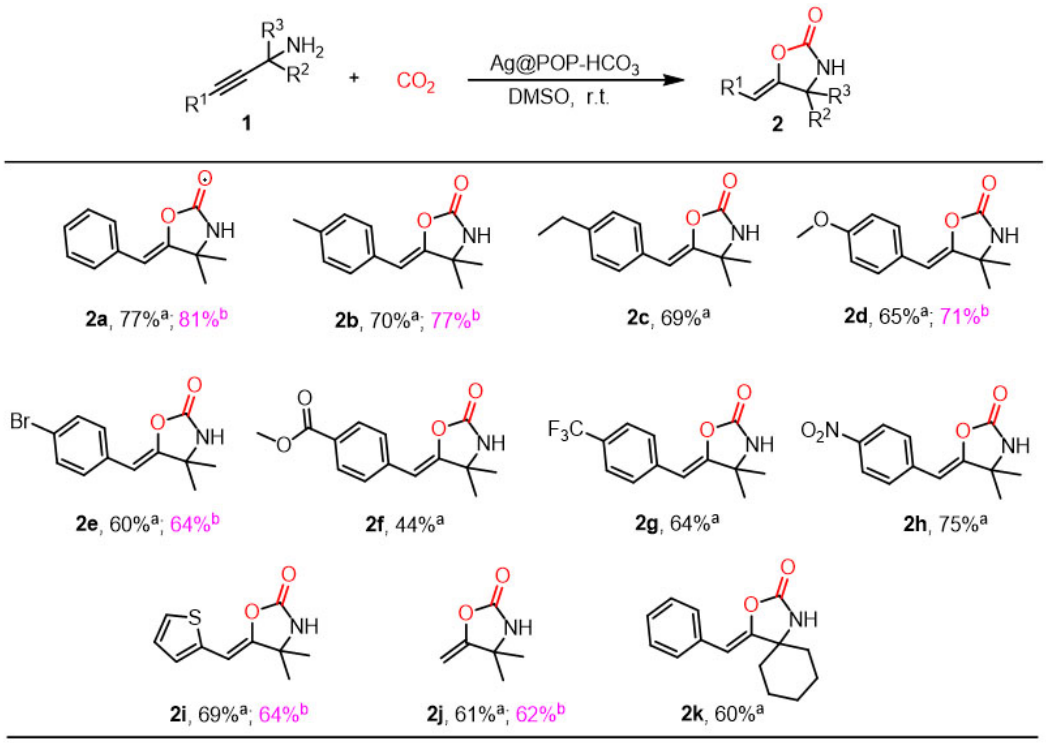


Figure 15. Suitability studies of substrates. Reaction conditions: (a) Propargyl amines 1 (0.2 mmol), catalyst (10 mg), 15 vol.% CO_2/N_2, DMSO (1 mL), 12 h, r.t.; (b) Propargyl amines 1 (0.2 mmol), catalyst (10 mg), coal-fired flue gas, DMSO (1 mL), 36 h, r.t.

Application research of catalyst

The carboxylation cyclization reactions were conducted under optimized reaction conditions using 15 vol.% CO_2/N_2 as a carbon source and various substituents of propargyl amines (For the synthesis procedure, see Supplementary Schemes 3 and 4)[27,43] as substrate [Figure 15]. In addition to the model substrate (**1a**), benzene substituents, including electron-donating substituents (**1b-1d**), electron-withdrawing groups (**1f-1h**), all successfully participated in the carboxylation cyclization reaction in considerable yields. Additionally, successful completion of carboxylative cyclization reaction was also observed when the propargyl amines skeleton contained a heterocyclic structure (**1i**) or a terminal alkyne structure (**1j**). The study also investigated changes in substituents at R^2 and R^3 positions (**1k**), resulting in a 60% yield.

In order to access the potential applications of the Ag@POP-HCO_3 catalytic system in actual flue gases, the impact of co-existing SO_2 and NO_2 on the model reaction was investigated using simulated flue gases as a carbon source [Table 1]. The results indicated that, with both SO_2 content of up to 428 mg/m^3 and NO_2 content of up to 221 mg/m^3, there was no significant negative impact on the reaction, which maintained a relatively stable yield [Figure 16A]. It is worth noting that SO_2 and NO_2 content in actual flue gases are usually less than 400 mg/m^3 and 200 mg/m^3, respectively. Therefore, it can be concluded that the catalytic system proposed in this work is also available for actual flue gases.

In practical application, a coal-fired flue gas (containing 8 vol.% CO_2) collected from a coal-fired power plant in Guilin was treated with Ag@POP-HCO_3 catalyst. This resulted in the successful conversion of CO_2 to oxazolidinone (**2a**), with a remarkable yield of 50%. When reaction time was extended to 24 h and 36 h, the yield reached 62% and 81%, respectively [Figure 16B]. When benzene substituents with electron-donating substituents (**1b, 1d**), halogen substituents (**1e**) and propargyl amine scaffolded with the heterocyclic

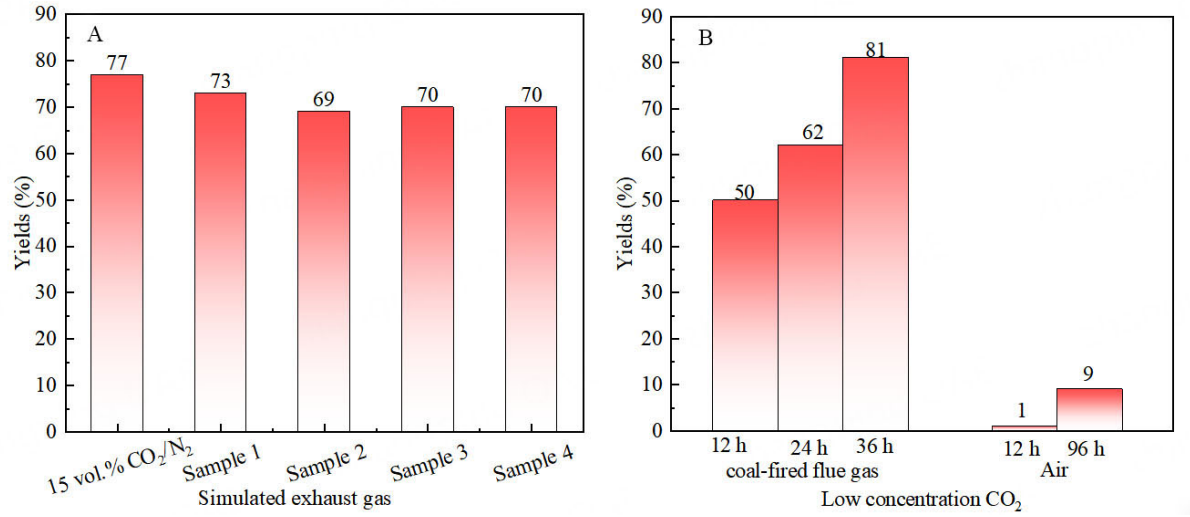
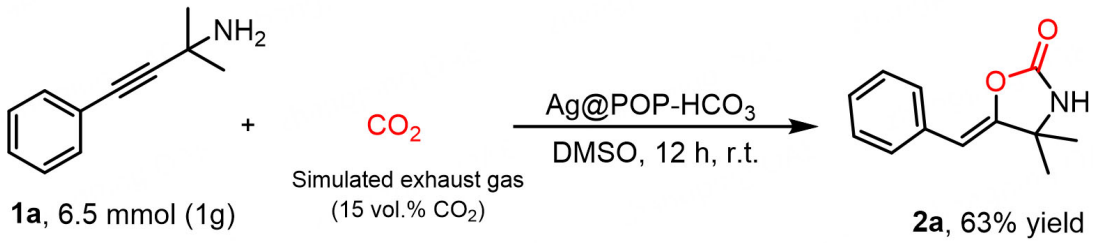


Figure 16. (A) The influence of SO_2 and NO_2 contents on the reaction; (B) Ag@POP-HCO_3 for fixing CO_2 in coal-fired flue gas and air.



Scheme 4. Gram test results. DMSO: Dimethyl sulfoxide.

Table 1. The components of simulated exhaust gases

Simulated exhaust gas	Content of components
Sample 1	15% CO_2, 71 mg/m³ SO_2, 51 mg/m³ NO_2, 1.0% O_2, 0.05% CO, N_2 balance
Sample 2	15% CO_2, 134 mg/m³ SO_2, 107 mg/m³ NO_2, 1.0% O_2, 0.05% CO, N_2 balance
Sample 3	15% CO_2, 294 mg/m³ SO_2, 221 mg/m³ NO_2, 1.0% O_2, 0.05% CO, N_2 balance
Sample 4	15% CO_2, 428 mg/m³ SO_2, 1.0% O_2, 0.05% CO, N_2 balance

structure (**1i**) or a terminal alkyne structure (**1j**), they could react with coal-fired flue gas, and form the corresponding oxazolidinones in 62%-77% yields [Figure 15]. Furthermore, the catalyst was used to catalyze the carboxylation cyclization reaction of propargyl amines with CO_2 in real air. Initially, the yield was only 1% during the 12 h reaction time; however, after extending the reaction time to 96 h, the yield increased to 9% [Figure 16B]. This experimental data strongly demonstrate that Ag@POP-HCO_3 catalyst exhibits high selectivity and catalytic activity for CO_2, even in actual flue gas environments containing pollutants such as SO_2 and NO_2.

The model reaction of carboxylation cyclization was conducted on a gram scale [Scheme 4] with a yield of 63% within 12 h reaction time. The Ag@POP-HCO_3 catalyst recovered from the previous reaction was utilized to react propargyl amines with CO_2 in simulated flue gas under optimal reaction conditions. It was observed that the catalyst could be recycled [Supplementary Figure 7]. These findings further provide strong evidence for the practicality of the Ag@POP-HCO_3 catalyst.

CONCLUSION

In summary, we have successfully synthesized an organic porous polymer material named Ag@POP-HCO_3 for catalyzing the *in-situ* conversion of low concentration CO_2 from coal-fired flue gas or air into oxazolidinone compounds through carboxylation cyclization reaction under ambient conditions. The main results obtained are as follows:

This process does not require the addition of any cocatalyst. The abundant pore structure and large specific surface area of the material provide a basis for achieving excellent adsorption capacity of CO_2.

The introduction of HCO_3^- to *N*-heterocyclic carbene further enhances the adsorption capacity. Silver loaded by a pre-coordinated method ensures that silver particles are uniformly dispersed within the polymer. Furthermore, the catalyst exhibits excellent thermal stability below 400 °C.

Ag@POP-HCO_3 catalyst exhibits exceptional performance in the carboxylation cyclization of low concentration with various propargyl amines. The catalyst demonstrates broad substrate adaptability and is effective for actual flue gas, unaffected by co-existing both SO_2 content of up to 428 mg/m^3 and NO_2 content of up to 221 mg/m^3. It is exciting that the catalyst effectively converts low concentrations of CO_2 in coal-fired flue gas and real air to oxazolidinone.

The proposed catalytic approach has the potential to be scaled up and developed into a one-step CCUS technology, which can effectively address the cost issues associated with traditional CCUS technology. This advancement also promotes the development of green chemical processes.

DECLARATIONS

Authors' contributions

Conceptualization, methodology, supervision, funding acquisition, writing - review and editing: Liang, Y.
Conceptualization, investigation, data curation, writing - original draft: Yang, J.
Investigation, data curation: Chen, W.
Conceptualization, methodology: Chen, P.
Conceptualization, discussion: Fang, P.
Conceptualization, supervision, funding acquisition, writing - review and editing: Pan, Y.

Availability of data and materials

The experimental data and associated test results are published as Supplementary Materials in the journal.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Supplementary Materials

Supplementary Materials

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