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Strategic design of a bifunctional Ag(I)-grafted NHC-MOF for efficient chemical fixation of CO₂ from a dilute gas under ambient conditions†

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The chemical fixation of carbon dioxide into valuable products constitutes a promising step toward reducing the atmospheric CO_2 concentration. Consequently, herein we report the strategic design of a bifunctional catalyst by grafting catalytically active Ag(I) ions onto N-heterocyclic carbene (NHC) sites in a MOF for efficient chemical fixation of CO_2 from a dilute gas to oxazolidinones, bio-relevant commodity chemicals. Indeed, Ag(I)@MOF-NHC demonstrated excellent catalytic activity for efficient fixation of CO_2 from a dilute gas ($CO_2 : N_2 = 13 : 87\%$) with alkynes to afford valuable chemicals, oxazolidinones, under RT and atmospheric pressure (balloon) conditions. The superior activity of the Ag(I) anchored MOF over the individual ($AgNO_3$ and MOF-NHC) components has been ascribed to the synergistic effect between the CO_2-philic NHC and alkynophilic Ag(I) sites exposed in the 1D channels of the MOF. Furthermore, the Ag(I) anchored MOF showed high recyclability without significant loss of catalytic activity and structural rigidity. Overall, this is a unique demonstration of the utilization of dilute CO_2 under environmentally friendly mild conditions and can pave the way for the development of efficient catalytic systems for sustainable utilization of CO_2 from dilute gases.

Introduction

The CO_2 concentration in the environment is increasing rapidly and has reached 412 ppm in 2020 and it is continuing to increase with time resulting in various environmental consequences.[1–5] Hence, there is an urgent requirement to capture and utilize carbon dioxide as a useful C1 source for the synthesis of commodity chemicals/fuels.[6–9,10,11–17] In particular, the flue gases from industries and power plants have the components of CO_2 (5–15%), N_2 (~80%), nitrogen oxide (NO*x*; 0.06–0.4%), and sulfur oxide (SO*x*; 0.02–0.3%) and contribute significantly to the rise in the concentration of atmospheric CO_2.[18] Furthermore, the capture of carbon dioxide from these flue gases having large quantities of N_2 is found to be an energy-demanding process.[19–21] Hence, direct utilization of flue gases/dilute gases as sources of CO_2 for fixation into value-added chemicals offers potential benefits.[22–24] Despite these merits, most of the catalytic systems reported so far still use high purity CO_2 as a feedstock for its conversion into high-

value chemicals.[25–27] Therefore, the design of highly active catalytic systems for simultaneous carbon capture and functionalization from flue gases at low concentrations of CO_2 (~13%) has attracted enormous interest from researchers worldwide.[28–30] Furthermore, out of the various CO_2 functionalization processes known, α-alkylidene cyclic carbonate (α-aCC) production by coupling CO_2 with propargylic alcohols has gained significant interest due to the potential utility of α-aCCs as commodity chemicals for the synthesis of natural products,[31] polymers,[32,33] polyurethanes,[34] *etc.*[35] More importantly, the production of oxazolidinones, an important raw material for antibiotics by a three-component coupling of CO_2 with propargylic alcohols and primary amines under eco-friendly mild conditions is of great significance.[36–38] To achieve this transformation, Ag(I) based catalysts were found to be effective owing to their alkynophilicity promoting the activation of the C≡C bond of alkynes.[39,40] However, most of these studies on Ag(I) catalyzed functionalization of CO_2 with alkynes have been carried out using pure CO_2 under high pressure and/or high-temperature conditions to achieve high yield production of α-alkylidene cyclic carbonates/oxazolidinones,[41–43] whereas, the catalytic systems known for the conversion of CO_2 into fine chemicals using simulated flue gas/dilute CO_2 are very sparse. Hence the catalysts which are active in the capture and conversion of CO_2 from dilute gases

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at low concentrations are of significant interest. In this regard, MOFs have attracted tremendous interest owing to their modular nature which facilitates the introduction of CO_2-philic and catalytically active sites for the simultaneous capture and utilization of carbon dioxide.[44–52] Among the various types of MOFs utilized for the chemical fixation of carbon dioxide, N-heterocyclic carbene (NHC)-based MOFs have gained special interest because the NHC sites can act as potential anchoring sites for catalytic metal ions and also provide CO_2-philicity to the framework.[53–56] Here, the covalent linkage formed between the carbene site and Ag(I) will be beneficial in preventing the possible leaching of Ag(I) during the catalysis. Therefore, herein, we report the application of an NHC-based MOF as an ideal support for grafting catalytically active Ag(I) ions at the NHC sites to obtain Ag(I)@MOF-NHC which acts as an efficient bifunctional catalyst for CO_2-capture and fixation with alkynes.[57,58] Indeed, Ag(I)@MOF-NHC displayed recyclable CO_2 uptake and excellent catalytic activity for efficient cyclization of CO_2 with propargylic alcohols/primary amines to afford α-aCCs/oxazolidinones in high yields from a dilute gas ($CO_2 : N_2$ = 13 : 87%) at RT and 1 atm pressure. Furthermore, the catalyst was highly recyclable and quite stable for multiple cycles of usage. The present work demonstrates the rational design of MOF-based heterogeneous catalysts for the highly recyclable conversion of CO_2 into value-added oxazolidinones from dilute CO_2 gas under mild conditions.

Results and discussion

The MOF-NHC was prepared by adopting a reported procedure with a slight modification (see the ESI†).[59] The powder X-ray diffraction (PXRD) plots of the as-synthesized MOF corroborated the phase purity of the sample (Fig. 1a). As shown in Scheme 1, the NHC sites lined in the 1D channels of the MOF were applied to graft Ag(I) ions to generate an Ag(I)@MOF-NHC hybrid.

The powder X-ray diffraction (PXRD) pattern of Ag(I)@MOF-NHC was found to match well with that of the pristine MOF indicating that the framework structure is maintained even after the immobilization of Ag(I) ions at the NHC sites (Fig. 1a). Additionally, FTIR spectra showed shifting of the –C–N stretching band from 1704 cm^{-1} in MOF-NHC to 1179 cm^{-1} in Ag(I)@MOF-NHC due to the formation of –C≡N⁺ after Ag(I) incorporation at the NHC sites (Fig. S2†). Furthermore, the UV-Vis spectra of the Ag(I) grafted sample showed absorption bands at 208 and 271 nm owing to $\pi \rightarrow \pi^*$ transitions from the ligand (Fig. S3†). Furthermore, the incorporation of Ag(I) into the framework was ascertained from microwave plasma atomic emission spectroscopy (MP-AES) analysis and was found to be about 6.8% (Fig. S4†) and 22.6% NHC sites were occupied by Ag(I) ions. The XPS studies were carried out to validate the anchoring of Ag(I) at the NHC sites (Fig. 1b). The survey spectra of Ag(I)@MOF-NHC display the presence of elements Ag, Zn, C, N, and O in the sample. The Zn(II) spectra show
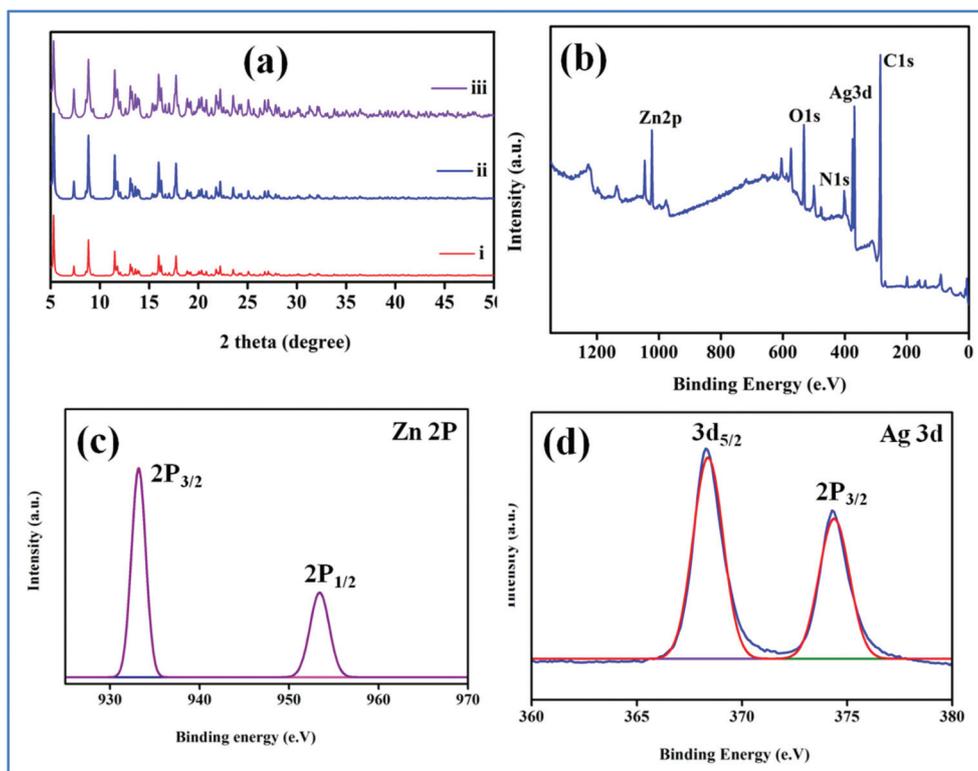
Fig. 1 (a) PXRD pattern of (i) a simulated MOF, (ii) Ag(I)@MOF–NHC, and (iii) recovered Ag(I)@MOF–NHC, and (b) survey scan of Ag(I)@MOF–NHC, (c) Zn 2p, and (d) Ag 3d.

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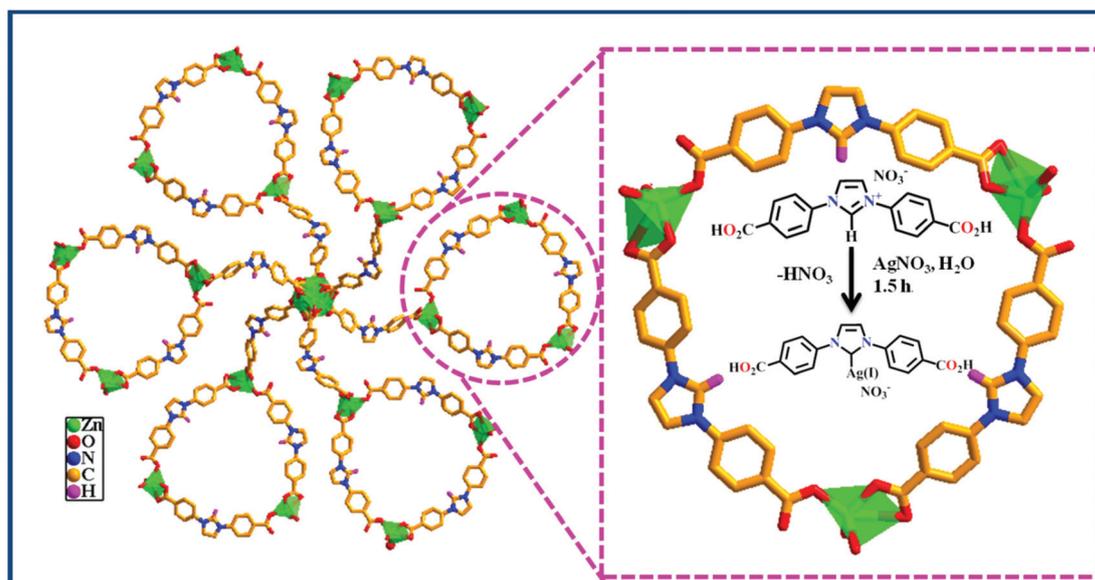
Scheme 1 Schematic representation of the preparation of Ag(ɪ)@MOF-NHC.

binding energy peaks at 933.2 and 953.2 eV corresponding to $2p_{3/2}$ and $2p_{1/2}$, respectively (Fig. 1c). The Ag(ɪ) spectra show two distinct binding energy peaks at 368.3 and 374.3 eV which are assigned to $2p_{3/2}$ and $2p_{1/2}$, respectively (Fig. 1d). It is worth noting that, these peaks were found to be slightly shifted in comparison with the corresponding peaks (368.9 and 374.9 eV) observed in AgNO₃ which rule out the presence of a silver salt.[31] Furthermore, the Ag(ɪ) spectra observed here match very well with that of the Ag(ɪ)@NHC complex (368.25 and 374.28 eV) reported in the literature[60,61] which confirms
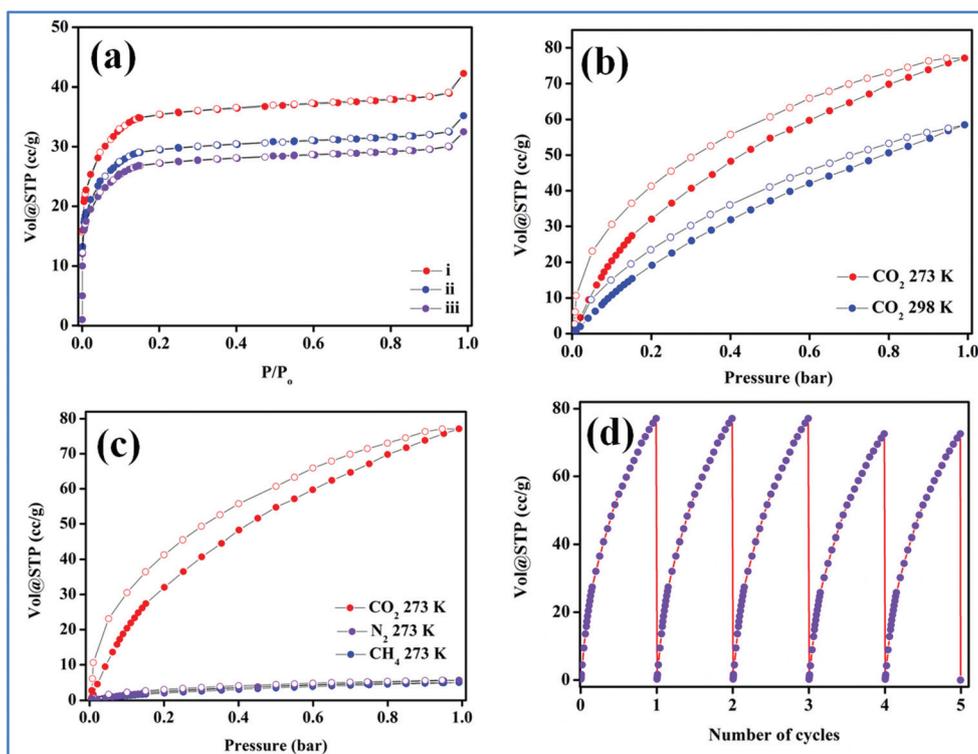
Fig. 2 (a) N₂ adsorption isotherm of (i) MOF-NHC, (ii) Ag(ɪ)@MOF-NHC, and (iii) recycled Ag(ɪ)@MOF-NHC after catalysis, (b) CO₂ adsorption isotherms at 273/298 K, (c) selective CO₂ adsorption plot, and (d) CO₂ adsorption recyclability.

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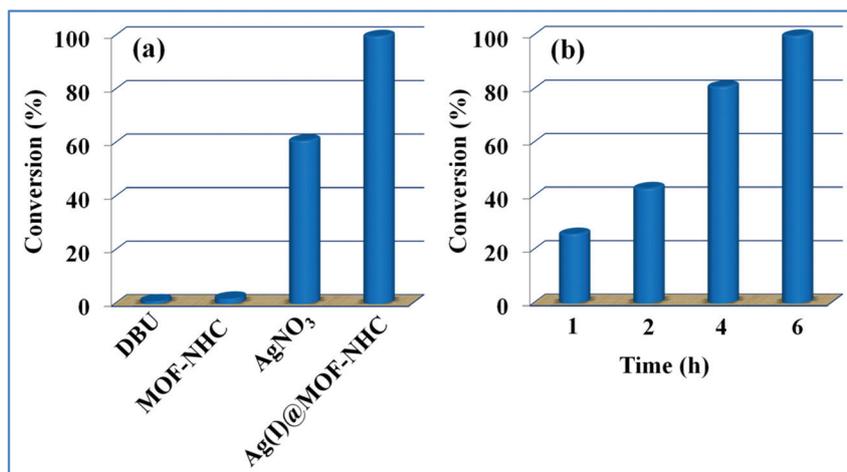
Fig. 3 Catalytic optimizations by varying the catalyst (a) and reaction time (b).

the grafting of Ag(ɪ) ions at the NHC sites. Moreover, scanning electron microscopy (SEM) images showed a rod-like morphology of MOF-NHC and notably, the morphology was maintained despite the anchoring of Ag(ɪ) ions (Fig. S5a and S5b†). The embedding of Ag(ɪ) in MOF-NHC was further supported by energy dispersive spectroscopy (EDS) analysis (Fig. S6a and S6b†).

Gas adsorption analysis

To ascertain the microporous nature of MOF-NHC, N_2 adsorption measurements were performed for the pristine and Ag(ɪ) doped samples at 77 K. As can be seen from Fig. 2a, the N_2 adsorption isotherm showed a type-I plot with a BET surface area (S_{BET}) of 91 m^2g^{-1} which was found to be about 38 m^2g^{-1} lower than that of the parent MOF-NHC (129 m^2g^{-1}). The pore size distribution measurements revealed a microporous nature with pore diameters of 10.1 and 6.6 Å for MOF-NHC and Ag(ɪ)@MOF-NHC, respectively (Fig. S7†). This decrease in the surface area of the Ag(ɪ) anchored sample could be ascribed to a partial loss of porosity due to the grafting of Ag(ɪ) ions at the NHC sites. Furthermore, the CO_2 sorption isotherms showed a type-1 plot with an uptake of 78/59 cm^3g^{-1} observed at 273/298 K (Fig. 2b). By following the Freundlich–Langmuir equation (Fig. S8 and S9†) the prediction of the CO_2 adsorption at saturation was determined.[62] Moreover, the interaction energy (Q_{st}) of CO_2 with Ag(ɪ)@MOF-NHC was estimated using the Clausius–Clapeyron equation[63] and the value was found to be 39.2 kJ mol^{-1} (Fig. S10†). This relatively high value of Q_{st} represents the favorable interaction of CO_2 with the basic NHC sites lined in the 1D channels of the framework.[64,65] In addition, the hysteresis behavior observed in CO_2 adsorption isotherms indeed supports the favorable interaction of CO_2 with the NHC sites.[66–68] Furthermore, a selective gas adsorption study (Fig. 2C) revealed negligible uptake of CH_4 and N_2 with the estimated Henry selectivity constants of 58 and 53 for CO_2/CH_4 and CO_2/N_2, respectively (Fig. S11†). Interestingly, Ag(ɪ)@MOF-NHC demonstrated highly recyclable CO_2 uptake

characteristics and almost retained its adsorption capacity even after five cycles of reuse (Fig. 2d).

Catalytic utilization of CO_2 at atmospheric pressure and RT

The availability of catalytically active alkynophilic Ag(ɪ) and CO_2-philic NHC sites in the 1D pores of the MOF prompted us to study the utilization of Ag(ɪ)@MOF-NHC as a heterogeneous

Table 1 Catalytic utilization of CO_2 under atmospheric pressure and RT conditions[a]

Sl. no.	Substrate	Product	Conversion[b] (%)	TON[c]
1			>99	993
2			93	931
3			88	882
4			75	754
5			68	681

[a] Reaction conditions: propargylic alcohol (2 mmol), Ag(ɪ)@MOF-NHC (0.01 mmol), DMF (2 mL), DBU (0.2 mmol), RT, 1 atm CO_2 (balloon), and time (6 h). [b] The conversions were determined by ^1H NMR analysis. [c] TON = number of moles of product/number of moles of catalyst.

Table 2 Comparison of the catalytic activity of Ag(i)@MOF–NHC with reported catalysts

Sl. no.	Catalyst	Pressure (bar)	Time (h)	Temperature (°C)	Yield (%)	Ref.
1	Ag@RB-POP	10	12	30	94	75
2	PAzo-POP-Ag	10	18	25	100	76
3	Cu–In–MOF	5	10	50	99	77
4	V–Cu–MOF	4	10	25	99	78
5	AgI, IL1	1	03	45	93	79
6	TMOF-3-Ag	1	06	30	99	32
7	MOF-SO₃Ag	1	24	25	99	36
8	Dy–Cu MOF	1	05	30	95	80
9	Cu(i)@NHC-MOF	1	12	25	99	81
10	Ag(i)@MOF-NHC	1	06	25	>99	This work
11	Ag(i)@MOF-NHC	1 (dilute CO₂)	12	25	>99	This work

catalyst for the fixation of CO_2 with propargylic alcohols. In this regard, 2-methyl-3-butyn-2-ol was used as a representative example for propargylic alcohols and various reaction conditions were tested by changing the catalyst and reaction time as shown in Fig. 3. As seen from Fig. 3b, the yield of the product increases with time and a slight deviation from linearity at higher reaction times could be attributed to partial masking of the catalyst surface by the substrates and products as the reaction proceeds.[69–71] Under the optimized conditions, the use of 0.01 mmol of Ag(i)@MOF-NHC as a catalyst along with DBU (0.2 mmol) resulted in more than 99% conversion of 2-methyl-3-butyn-2-ol to the respective α-alkylidene cyclic carbonate with a selectivity of 100% within 6 h under atmospheric pressure (balloon) and RT conditions (Fig. S12†). Here, the role of DBU is facilitating the deprotonation of propargylic alcohol.[29,72,73] Furthermore, the catalytic reaction carried out using pristine MOF-NHC as the catalyst under the optimized reaction conditions showed no formation of the product, highlighting the necessity of Ag(i) sites for catalyzing the coupling of CO_2 with propargylic alcohols (Fig. 3), whereas the use of $AgNO_3$ (homogeneous) as a catalyst rendered about 58% conversion of 2-methyl-3-butyn-2-ol under the optimized conditions (Fig. 3 and S13†). Although the homogeneous reaction resulted in the moderate conversion of the alcohol, it suffered from the limitations of catalyst recycling and product separation from the reaction mixture. The superior performance of Ag(i)@MOF-NHC over the parent samples can be ascribed to synergistic participation of alkynophilic Ag(i) and CO_2-philic NHC sites projected in the 1D pores of the framework. The scope of this catalytic reaction was extended for the coupling of CO_2 with various propargylic alcohols under the optimized conditions and the results obtained are summarized in Table 1 (Fig. S14–S17†). Based on the yield of α-alkylidene cyclic carbonates formed (Table 1), it can be realized that with an increase in the size of the substrates, the yield of α-aCC decreases, and this could be ascribed to the limited diffusion of the larger substrates into the pores of the framework. To further understand the effect of substrate size on the catalytic yield, the structure of the propargylic alcohols was optimized using Gaussian09[74] at the B3LYP/6-311 g (d, p) level and the optimized structures are given in Table S1†. From the optimized structures, it is evident that the propargylic

alcohols that are bigger underwent a lower conversion in comparison with the smaller ones. A comparison of the catalytic activity for the coupling of propargylic alcohols with CO_2 revealed that Ag(i)@MOF-NHC demonstrates superior catalytic activity over various catalysts reported in the literature (Table 2).

Table 3 Catalytic utilization of CO_2 from the dilute gas ($CO_2 : N_2$ = 13 : 87%)[a]

Sl. no.	Substrate	Product	Conversion[c] (%)	TON[d]
1			99	990
2[b]			29	292
3			91	911
4			85	853
5			73	734
6			64	641
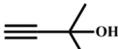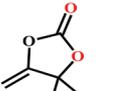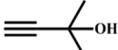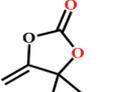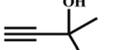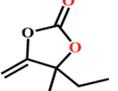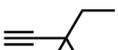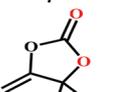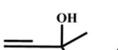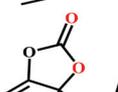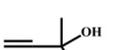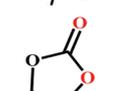
[a] Reaction conditions: propargylic alcohol (2 mmol), Ag(i)@MOF-NHC (0.01 mmol), DMF (2 mL), DBU (0.2 mmol), RT, dilute CO_2 gas ($CO_2 : N_2$ = 13 : 87%, balloon), and 12 h. [b] Continuous bubbling of laboratory air. [c] The conversions were determined by ¹H NMR analysis. [d] TON = number of moles of product/number of moles of catalyst.

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Catalytic utilization of CO_2 from dilute gases

The excellent performance of Ag(I)@MOF-NHC towards the utilization of CO_2 (99.99%) under atmospheric pressure and RT conditions encouraged us to test its activity using dilute carbon dioxide with a composition similar to that of dry flue gas ($CO_2 : N_2$ = 13 : 87%). To our delight, the test reaction carried out with dilute CO_2 showed about 56% conversion of propargylic alcohol, 2-methyl-3-butyn-2-ol, to the respective α-alkylidene cyclic carbonate within 6 h under the optimized conditions. Furthermore, by increasing the reaction time to 12 h, the yield of the product increased to >99% with 100% selectivity (Fig. S18 and S19†). This excellent activity of Ag(I)@MOF-NHC further motivated us to extend the reaction to other propargylic alcohols under optimized conditions with dilute CO_2 (13%). Interestingly, Ag(I)@MOF-NHC was able to convert a series of propargylic alcohols to the corresponding α-alkylidene cyclic carbonates with 100% selectivity (Table 3).

Towards exploring the potential application of our catalyst in carbon capture and utilization (CCU) from atmospheric air, the catalytic activity of Ag(I)@MOF-NHC was tested by bub-

bling laboratory air, and notably, about 29% of 2-methyl-3-butyn-2-ol was converted into 4,4′-dimethyl-5-methylene-1,3-dioxolan-2-one in 24 h. This observation signifies the potential application of Ag(I)@MOF-NHC toward the fixation of CO_2 from direct air (Fig. S20†).

Encouraged by the high activity of Ag(I)@MOF-NHC, the substrate scope of the reaction was extended for the synthesis of oxazolidinone, a valuable commodity chemical for antibiotics, via a three-component reaction of propargylic alcohol, CO_2, and primary amines. Hence, the activity of Ag(I)@MOF-NHC was studied by using propargylic alcohol, 2-methyl-3-butyn-2-ol, and the dilute gas ($CO_2 : N_2$ = 13 : 87%) along with n-butyl amine as an example for primary amines. To our delight, the catalytic reaction resulted in the respective oxazolidinone with > 99% yield within 12 h even when using a low concentration of CO_2 at 1 atm and RT (Fig. S21†). The substrate scope of the reaction was further broadened for the coupling of different primary amines such as isobutylamine, n-hexylamine, cyclohexylamine, and benzylamine (Table 4). Interestingly all of these catalytic reactions proceeded to afford the respective oxazolidinones with >99% yield (Table 4). Furthermore, to explore the generality of this process, the cata-

Table 4 Catalytic fixation of CO_2 into oxazolidinones from the dilute gas[a]

Sl no.	Propargylic alcohol	Primary amine	Product	Conversion (%)
1				99
2				99
3				99
4				99
5				99
6				89
7				86

[a] Reaction conditions: propargylic alcohol (2 mmol), primary amine (2 mmol), DMF (2 mL), DBU (0.2 mmol), Ag(I)@MOF-NHC (0.01 mmol), dilute CO_2 gas (1 atm), and 12 h.

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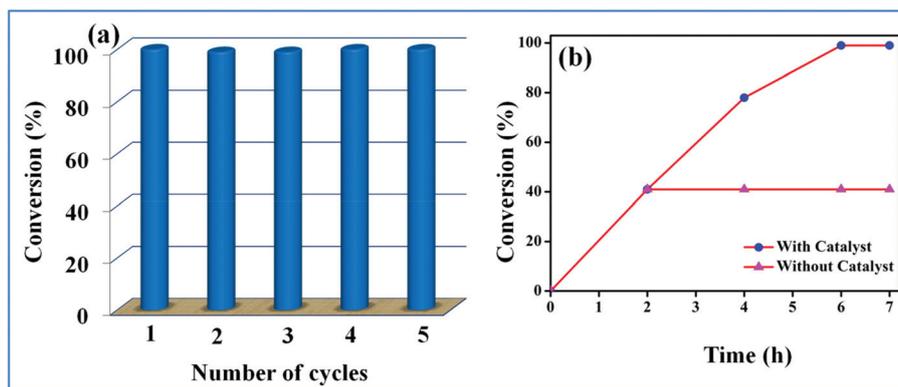
Fig. 4 (a) Recyclability and (b) Catalyst leaching test.

lytic reactions were carried out keeping amine constant (*n*-butylamine) and varying the propargylic alcohols. Interestingly, these three-component reactions of alcohol, 2-ethyl-3-butyn-2-ol/3-ethyl-1-pentyn-3-ol, with CO_2 and *n*-butylamine resulted in the respective oxazolidinones in 89/86% yield maintaining a product selectivity of 100% (Table 4). It is worth highlighting that, to the best of our knowledge, Ag(I)@MOF-NHC represents the first example of a MOF-based catalyst known for the fixation of CO_2 to value-added oxazolidinones from a dilute gas containing about 13% of CO_2 under RT and 1 atm (balloon) conditions.

Leaching and recyclability tests

Recyclability and chemical stability are key parameters of a heterogeneous catalyst. Notably, Ag(I)@MOF-NHC was highly recyclable for several cycles with negligible loss in catalytic performance (Fig. 4a and S22†). The catalyst was recovered by centrifugation followed by filtration and utilized for subsequent catalytic cycles after washing with methanol and activating at 120 °C for 12 h. The recovered catalyst after five cycles was characterized using various techniques to affirm its crystalline phase and structural stability. The powder X-ray diffraction
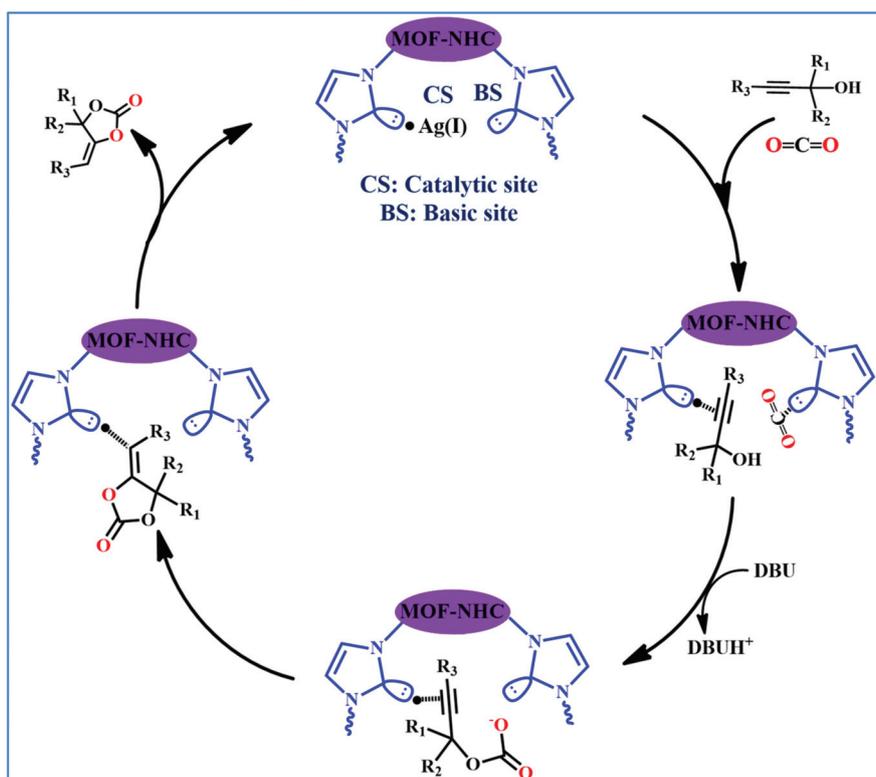
Scheme 2 Proposed mechanism for the coupling of CO_2 with propargylic alcohol catalyzed by Ag(1)@MOF-NHC.

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pattern of the recycled sample closely resembles that of the original sample, indicating its structural rigidity (Fig. 1a). Furthermore, FTIR and UV-Vis spectra of the recovered sample were similar to those of the original sample (Fig. S2 and S3†). Additionally, the N_2 adsorption isotherm revealed a BET surface area of 83 $m^2 g^{-1}$ which is slightly reduced in comparison with that of the as-synthesized sample (91 $m^2 g^{-1}$) supporting that the porous framework structure is maintained even after five cycles of catalysis (Fig. 2a). Furthermore, the SEM analysis revealed the retention of the rod-like morphology of the sample even after the catalysis (Fig. S5c†). Importantly, the MP-AES analysis of the reaction filtrate disclosed the nonexistence of $Zn(II)/Ag(I)$ ions which unambiguously rules out the leaching of metal ions during the catalysis (Fig. S4†).

Plausible mechanism

A proposed mechanism for the utilization of CO_2 *via* the carboxylation of propargylic alcohol by Ag(I)@MOF-NHC is presented in Scheme 2. The catalytic reaction proceeded with a polarization of the C≡C bond of propargylic alcohol at the alkynophilic Ag(I) sites. To confirm this polarization step, both the parent and Ag(I) anchored MOFs were treated with propargylic alcohol, 2-methyl-3-butyn-2-ol, for 3 h and then the MOFs were recovered, washed with ethanol thoroughly, and dried at 80 °C for 12 h. Interestingly, the FT-IR spectra of the recovered sample of Ag(I)@MOF-NHC showed stretching bands at 2124 cm^{-1} corresponding to the C≡C bond of 2-methyl-3-butyn-2-ol, while, no peak of the C≡C bond of the alcohol was observed in the case of a pristine MOF, confirming the polarization of the π-electron of the alcohol by Ag(I) sites (Fig. S23†). This step of the alkyne bond activation is accompanied by CO_2 polarization at the free NHC sites projected in the pores of the framework.[82] Then the deprotonation of propargylic alcohol by DBU takes place with the concomitant CO_2 insertion step. Finally, a ring-closure reaction takes place resulting in the formation of the desired product, α-alkylidene cyclic carbonate, and the subsequent elimination of the product allows the catalytic cycle to continue. Meanwhile, the addition of primary amines led to the aminolysis of α-alkylidene cyclic carbonates to generate oxazolidinones as shown in Scheme S2.†

Conclusion

A novel approach for the facile anchoring of Ag(I) ions on a basic NHC-based MOF for the rational incorporation of catalytic and CO_2-philic sites suitable for simultaneous CO_2 capture and conversion to high-value chemicals, oxazolidinones, from dilute CO_2 gas under RT and 1 atm (balloon) conditions is presented. This study revealed that the presence of basic NHC sites enhances the framework's CO_2-philicity and the local concentration of carbon dioxide at the catalytic sites for its efficient conversion into value-added chemicals. Indeed, Ag(I)@MOF-NHC exhibited excellent catalytic activity owing to the synergistic cooperation between alkynophilic Ag(I) and basic NHC sites. To the best of our knowledge, Ag(I) @MOF-NHC is the first example of an MOF-based recyclable catalyst demonstrating the conversion of CO_2 from a dilute gas into value-added chemicals under the conditions of RT and 1 atm pressure. This study could pave the way for the development of efficient bifunctional catalysts for the sustainable utilization of CO_2 from dilute/flue gases.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

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