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Porous Organic Polymers with Built-in N-Heterocyclic Carbenes: Selective and Efficient Heterogeneous Catalyst for the Reductive N-formylation of Amines with CO_2

Hui Lv,[b] Wenlong Wang*[a], and Fuwei Li *[b]

Abstract: A series of porous organic polymers (POPs) based on N-heterocyclic carbene (NHC) building blocks have been prepared via the octacarbonyldicobalt complex ($Co_2(CO)_8$)-catalyzed trimerization of terminal alkyne groups. By changing the monomer ratio in the copolymerization, cross-linked POPs with tunable surface areas of 485 to 731 m^2/g and pore volumes of 0.31 to 0.51 cm^3/g were easily prepared. Compared with the analogues homogeneous NHC (SIPr) catalysts, the POPs exhibited enhanced catalytic activity and high selectivity in the reductive functionalization of CO_2 with amines. The extraordinary performance of the sample could be attributed to the combination of the gas enrichment (or storage) effect, enhanced in-pore concentrations of other substrates and advantageous micropore structures of the porous polymers. Meanwhile, these catalysts can easily be separated and recycled from the reaction systems with only a slight loss of activity. This excellent catalytic performance and facile recycling of heterogeneous catalysts make them very attractive. These NHC-containing POPs may provide new platforms for catalytic transformations of CO_2.

Introduction

Carbon dioxide (CO_2) is an abundant, economical and renewable C1 building block and is an alternative to petrochemistry for the production of chemicals.[1] Among the reported chemical syntheses involving CO_2, the reductive N-formylation of amines with CO_2 is a promising route for the synthesis of formamides, which are widely used as solvents and key intermediates in organic syntheses and industry.[2] In addition to metal-based homogeneous catalysts, including those derived from Rh,[3] Ru,[4] Cu,[5] Co,[6] and Zn,[7] metal-free catalyst systems, such as N-heterocyclic carbenes (NHCs),[8] N-heterocyclic olefins (NHOs),[9] 1,3,2-diazaphospholene (NHP-H),[10] ionic liquids (ILs),[11] and organic bases,[2f, 12] have been developed as efficient alternatives. Particularly, in regard to NHCs catalysts, an excellent yield (99%) of N-formylated morpholine can be obtained by using 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidine (IPr) as the catalyst, however, the analogue of IPr, namely, 1,3-bis(2,6-diisopropyl)phenyl-4,5-dihydroimidazol-2-ylidene (SIPr), only gave 24% yield with 5.0 mol% catalyst loading under the same reaction conditions.[22] Notably, the selectivity problem (especially for aromatic substrates with primary amine) that resulted in the double formylation side reaction has not been effectively solved in the majority of homogeneous catalytic systems. Moreover, although significant advances have been achieved in these homogeneous catalysts, the development of efficient reusable heterogeneous catalyst is still highly desirable considering their complicated synthesis and intricate recycling problems associated with homogeneous catalysts.[13] This work is aimed at providing a reusable and highly selective SIPr-based heterogeneous catalyst for the reductive mono-N-formylation of amine with CO_2.

Porous organic polymers (POPs), a class of highly cross-linked amorphous polymers prepared through the direct assembly of several organic building blocks using stable covalent organic bonds, can provide chemically and thermally stable materials with both high surface areas and a wide range of attractive chemical functionalities.[14] In addition to broad applicability in gas sorption and separation fields,[15] they have recently emerged as a new kind of material with promise in heterogeneous catalysis, especially for reaction involving gas because of their gas enrichment capacity.[16] In addition to the built-in catalytic sites, the unique micropore structural environments will exhibit a confinement effect in some catalytic reactions,[14f, 14h, 15d, 16i] which may either improve the product selectivity by favoring the main reaction pathway through chemical size selection, or enhance the catalytic activity through sequestering/confining the reaction substrate in the nanometer-sized pores and then increasing their concentration around the catalytic sites to a level greater than that in solution.

As mentioned before, Cantat and coworkers found that SIPr was much less reactive toward the N-formylation than its analogue, IPr; unfortunately, the latter showed poor selectivity with the standard aniline giving a 35%/31% yield ratio of mono-formylation/double-formylation products, and their investigations also revealed that increasing the steric hinderance of the aryl amine could significantly improve the mono-formylation selectivity, but 4%-11% of the double-formylation products were still produced.[8a] Based on DFT calculations[8b, 17] and the corresponding experimental results with NHCs as the catalyst, it could be envisioned that the double formylation originated from the further activation of the N-H of the amide of the generated

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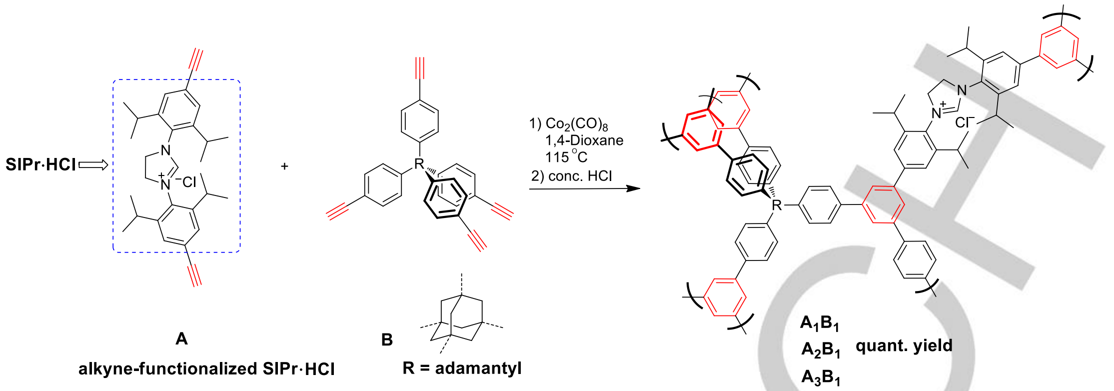

Scheme 1. Synthesis of SIPr·HCl-incorporated POPs A_1B_1, A_2B_1, and A_3B_1 using cobalt-catalyzed acetylene trimerization reaction.

[NHCH]$^+$[carbamate]$^-$ intermediate by the second NHC in the homogeneous reaction system.[17] Therefore, the development of a functional POP with NHC catalytic sites built in to the rigid catalyst and at suitable distances from each other to prevent the formation of undesirable '[NHCH]$^+$[carbamate]$^-$—NHC' intermediate might prevent formation of the double N-formylation product. Further, we expected the catalytic activity might also be improved due to the substrate sequestering/confining effects. As part of our continuing studies on the development of recyclable N-heterocyclic carbene-based catalysts,[14f, 18] herein, we report the synthesis of a series of POPs catalysts with built-in NHC precursors (SIPr·HCl) via the ($Co_2(CO)_8$)-catalyzed trimerization[19] of terminal alkyne groups at the para-position of benzene rings without influencing the steric and electronic properties of SIPr (Scheme 1); as expected, they showed enhanced catalytic activity and selectivity in the N-formylation of a wide range of amine compounds with CO_2 and silane and could be stably recycled and reused for five runs without loss of activity.

Results and Discussion

First, FT-IR (Figure 1) and solid-state NMR spectra (Figure 2) were collected to confirm the structures of the synthesized A_1B_1, A_2B_1 and A_3B_1 POPs. Their spectra were consistent with a high degree of trimerization of the terminal alkynes of A and B, because the C-H stretching peak of the C≡C-H group between 3000-3300 cm^{-1} and the C-C stretching peak of the -C≡C- group at approximately 2200 cm^{-1} are absent in all the IR spectra. This result suggests that the alkyne groups in the starting materials were converted to benzene rings in the POPs. The representative solid-state NMR spectrum of A_1B_1 is shown in Figure 2, and the peaks at 25 and 28 ppm correspond to the carbon atom of the $-CH_3$ group and the tertiary carbon atom of the $-CH(CH_3)_2$ group, respectively. The signals from 40-55 ppm are attributed to the secondary carbon ($-CH_2$) and the quaternary carbon atom connected to the phenyl group (Ar-C) of adamantane. The peaks between 120-160 ppm are from the aromatic groups.

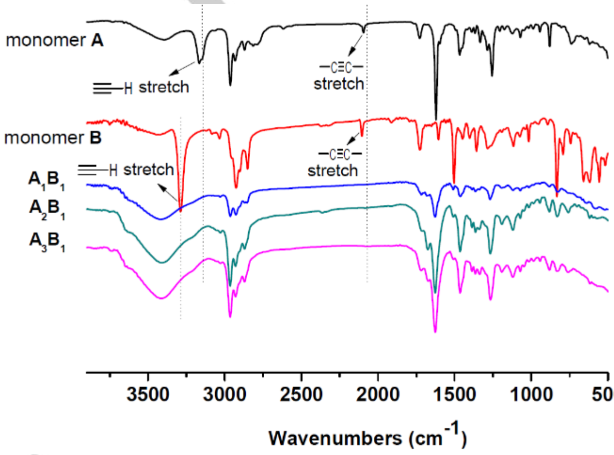

Figure 1. Comparison of the FT-IR spectra of monomer A, monomer B, and POPs

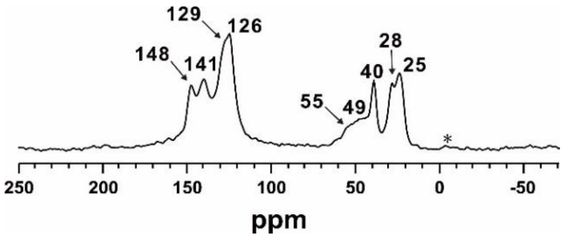

Figure 2. Representative solid-state NMR spectrum of POP A_1B_1.

In exploring the use of POPs with built-in NHC precursors for the catalytic formylation of amines with CO_2, we sought to investigate how the micropore environment affects the reaction activity; therefore, three POPs with different monomer ratios were synthesized via the same procedures. The N_2 adsorption and desorption isotherms of A_1B_1, A_2B_1 and A_3B_1 are shown in Figure 3a. The nitrogen sorption of these three POPs displayed a combination of type I and type II sorption isotherm curves along with a large adsorption at low pressure ($P/P_0 < 0.1$), which is indicative of the coexistence of micro- and mesopores in the framework. Compared with A_3B_1 (S_{BET} = 485 m^2/g) and A_2B_1 (S_{BET}

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= 525 m^2/g), A_1B_1 has the greatest surface area (S_{BET} = 731 m^2/g), and this is mainly because of the high ratio of the tetrahedral alkyne monomer B. The large and rigid monomer B with its four alkyne groups stretching to four sides in a tetrahedral way can expand the pore volume, and further generate a hierarchical pore structure, which is very beneficial for the diffusion and mass transfer process. From the relative BET-derived pore size distribution plots (Figure 3b), we can conclude that these three POPs have almost the same pore size distribution but different pore volumes. The results of the BET surface areas and pore volumes are listed in Table 1.

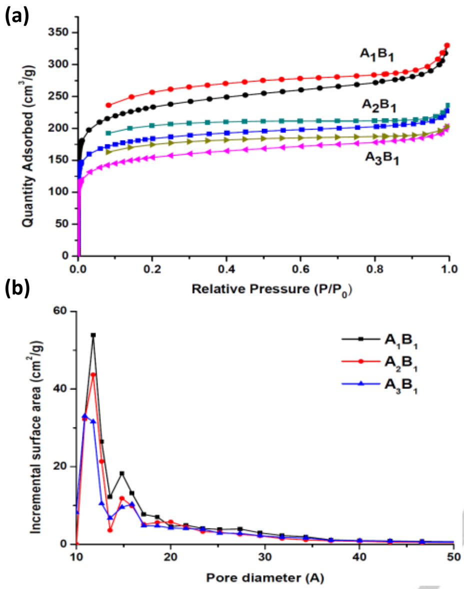


Figure 3. (a) Nitrogen isotherms measured at 77 K for POPs A_1B_1, A_2B_1 and A_3B_1. (b) pore size distribution plots for A_1B_1, A_2B_1 and A_3B_1 caculated by NLDFT method.

Table 1. Pore and surface properties of POPs with built-in NHC precursors.

Entry	POP	BET surface area (m^2/g)	Total pore volume (cm^3/g)
1	A_1B_1	731	0.51
2	A_2B_1	525	0.34
3	A_3B_1	485	0.31

In addition, the CO_2 sorption isotherms for the three samples at 273 K are presented in Figure 4. No saturation was observed for any of the three POPs in the 900 mmHg range, which suggests higher CO_2 absorption capacities can be achieved at higher pressures. POPs A_1B_1, A_2B_1 and A_3B_1 exhibited CO_2 uptakes of 36, 34 and 28 cm^3/g, respectively. Compared with the difference between the BET surface areas of the three POPs from the N_2 adsorption experiments, the gap in the CO_2 absorption capacity is narrower, and this is probably because of the enhanced interactions between the N atoms of the imidazole ring and CO_2 in the nanopores of these materials. This direct observation of CO_2 uptake shows that this kind of POP is very attractive for catalytic transformations involving CO_2. The order of catalytic activities of three POPs AxBy is $A_1B_1 > A_2B_1 > A_3B_1$ (refer to Table 2), which is consistent to their CO_2 absorption capacity order $A_1B_1 \approx A_2B_1 > A_3B_1$. This difference of catalytic activity correlates well with the gas enrichment (or storage) effect.

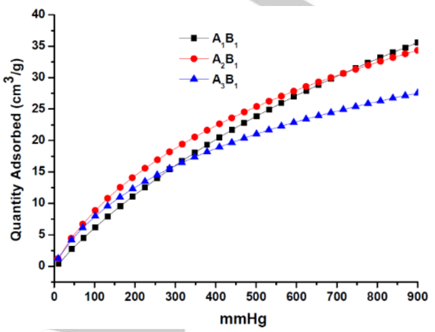
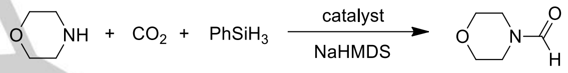


Figure 4. CO_2 adsorption isotherms at 273 K for A_1B_1, A_2B_1 and A_3B_1.

Table 2. Catalytic performances in different reaction systems.[a]



Entry	Catalyst	Loading[b] (mol%)	Base (mol%)	Yield[c] (%)
1	A_1B_1	2	2	98
2	A_2B_1	2	2	89
3	A_3B_1	2	2	86
4	–	–	2	37
5	A_1B_1	2	–	22
6	–	–	–	0
7	$(A\text{-}CO_2)_1B_1$	2	–	50
8	A	2	2	42
9	SIPr·HCl	2	2	60
10	SIPr-CO_2	2	2	16

[a] Reaction conditions: morpholine (0.5 mmol), phenylsilane (0.75 mmol), dry THF (2 mL), CO_2 (4 atm) room temperature, 24 h. [b] Equivalent to the amount of SIPr. [c] GC yield using n-hexadecane as an internal standard.

To begin with the catalytic investigation, we explored the possibility of using morpholine as the substrate in a heterogeneous system. Morpholine (0.5 mmol), CO_2 (4 atm), $PhSiH_3$ (0.75 mmol), NaHMDS (2 mol%) and A_1B_1 (10 mg, equivalent to 2 mol% SIPr, as a catalyst) were loaded into a stainless-steel autoclave and stirred at room temperature for 24 h. As a result, the corresponding N-formylmorpholine was

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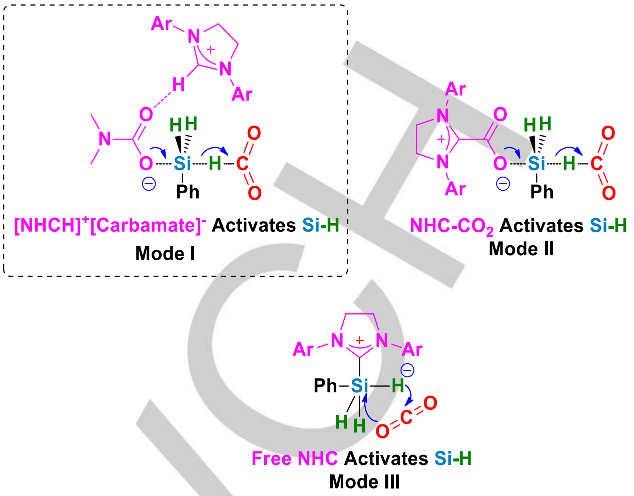
obtained in 98% GC yield (Table 2, entry 1). For comparison, we then investigated A_2B_1 and A_3B_1 as catalysts (2 mol% loading and 4 atm of CO_2), and slightly lower yields were obtained (89% and 86%, Table 2, entries 2 and 3). This is possibly because of the lower surface areas and pore volumes of A_2B_1 and A_3B_1 compared with A_1B_1; moreover, the higher proportion of hydrophobic adamantane moieties in A_1B_1 could further enhance the solvophobic encapsulation ability of the hydrophobic substrate in polar media, increasing the catalyst efficiency.

Control experiments showed that only 37% yield was obtained (Table 2, entry 4) when catalyst was removed from the reaction system; when base was removed from the catalytic system, only 22% yield was achieved (Table 2, entry 5); Further control experiments showed that this reaction did not occur in the absence of both the catalysts and base (Table 2, entry 6). These three results suggest that the catalyst[11a] and base[2f] both can catalyze this reaction. It is worth noting that when the NHC·HCl-built-in POP was treated with an equivalent of base (NaHMDS), free N-heterocyclic carbene is immediately generated, and the ***carbene-based activation mode*** was more reasonable according to literature reports.[8b, 8c, 17] Scheme 2 shows the three most likely activation modes for such N-formylation with a ***carbene-based catalyst***. According to the results of the DFT calculations reported by Li's group,[17] activation mode **I**, i.e., $[NHCH]^+[carbamate]^-$ (generated through a carbene process), was the most favorable species based on free energy; and in the activation mode **II**, the free energies of the NHC-CO_2 adduct and its subsequent transition state with silanes were higher than that of the $[NHCH]^+[carbamate]^-$ process. Therefore, the formation of an NHC-CO_2 species was theoretically unfavorable in this reaction. To confirm this theoretical prediction, porous polymeric materials $(A\text{-}CO_2)_1B_1$ and molecular SIPr-CO_2 were prepared (Supporting Information), and their catalytic efficiencies were investigated (2 mol% loading and 4 atm of CO_2). Only 50% and 16% yields were obtained (Table 2, entries 7 and 10), which proved the rationality of activation mode **I**. In addition, the catalytic activity of their homogeneous counterparts (A and SIPr·HCl) were tested for comparison with the newly synthesized heterogeneous catalyst, which exhibited much lower yields (42% and 60%, respectively) than that of the heterogeneous catalysts. The heterogeneous samples' (POPs) extraordinary performance could be attributed to the combination of the gas enrichment (or storage) effect and enhanced in-pore concentrations of other substrates in the porous polymers.



Scheme 2. Three activation modes through carbene process.

A favorable feature of the catalytic system that caught our attention was the precipitation of the POP catalysts from the mixture. Thus, we investigated the possibility of recycling and reusing catalyst A_1B_1. After the reaction, the catalyst was collected by centrifugation and then reused for another round of the N-formylation reaction. To better test the stability of catalyst A_1B_1, a recycling experiment was conducted by increasing the level of the alkyne substrate to 1.0 mmol with 1 mol% of A_1B_1 to achieve an approximate ~60% yield of morpholine-4-carbaldehyde (Figure 5). Recycling catalyst A_1B_1 over four runs did not result in a loss of activity. We have supplemented the hot filtration experiment in the recyclability test. Under the same reaction condition as illustrated in Figure 5, after 24 hour's reaction (GC yield was 63%), the catalyst was filtrated off, the filtrate was continued to react for another 24 hours, and the GC yield was 65%, which indicated the heterogeneous nature of the catalyst.

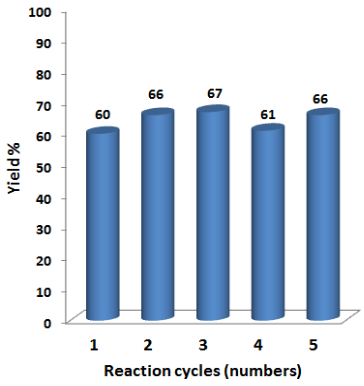


Figure 5. Recyclability test of A_1B_1 in the model reaction of the N-formylation of morpholine: morpholine (1.0 mmol), phenylsilane (1.5 mmol), A_1B_1 (1 mol%), dry THF (4 mL), room temperature, 24 h; GC yield using n-hexadecane as an internal standard.

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Subsequently, we examined the scope of this catalytic system. As shown in Figure 6, only one product was obtained for all substrates (selectivity >99%, moderate to good isolated yields) when using POP A_1B_1 as the catalyst. To further compare this unique selectivity of the POP catalysts, the homogeneous catalyst counterpart (SIPr·HCl) was tested by using the same aniline derivatives. As depicted in Figure 6, substantial amounts of the bis-formylanilines (5f'-5l') were isolated, which indicated the poor selectivity of the homogeneous counterpart. The surprising selectivity of the POP catalysts could probably be attributed to the confinement effects of the unique micropore environment in the POP catalysts, which prohibited the formation of large-size intermediates of the bis-formylanilines; it is also possible that the rigid micro-environment hindered the double-site activation mode (Figure 7), severely limiting the formation of bis-formylanilines, which easily can be realized in the homogeneous process. In addition, aliphatic secondary amines, such as morpholine, dibutylamine, 1,2,3,4-tetrahydroisoquinoline and dibenzylamine, were converted to their formamides (5a-5e) in high isolated yields after 24 h at room temperature under 4 atm of CO_2. An electron-donating group (p-methoxy, 5k, 64% yield) and an electron-withdrawing group (p-Cl, 5h, 65% yield) did not have obvious influences on the conversions observed for the aniline derivatives. Increasing the steric congestion around the phenyl ring did not deactivate the anilines, and 2,4,6-trimethylaniline was formylated in 61% yield (5i), and 2,6-diisopropylaniline was obtained with a slightly higher yield of 70% (5l). Other non-substituted anilines, phenylamine (5f, 70% yield) and naphthalen-1-amine (5g, 75% yield), all performed well under the heterogeneous catalytic system. In addition, it is worth noting that not only the compelling selectivity advantage but also the enhanced heterogeneous catalytic activity for all the investigated substrates were due to the micropore structure of our NHC-based POP catalysts, which

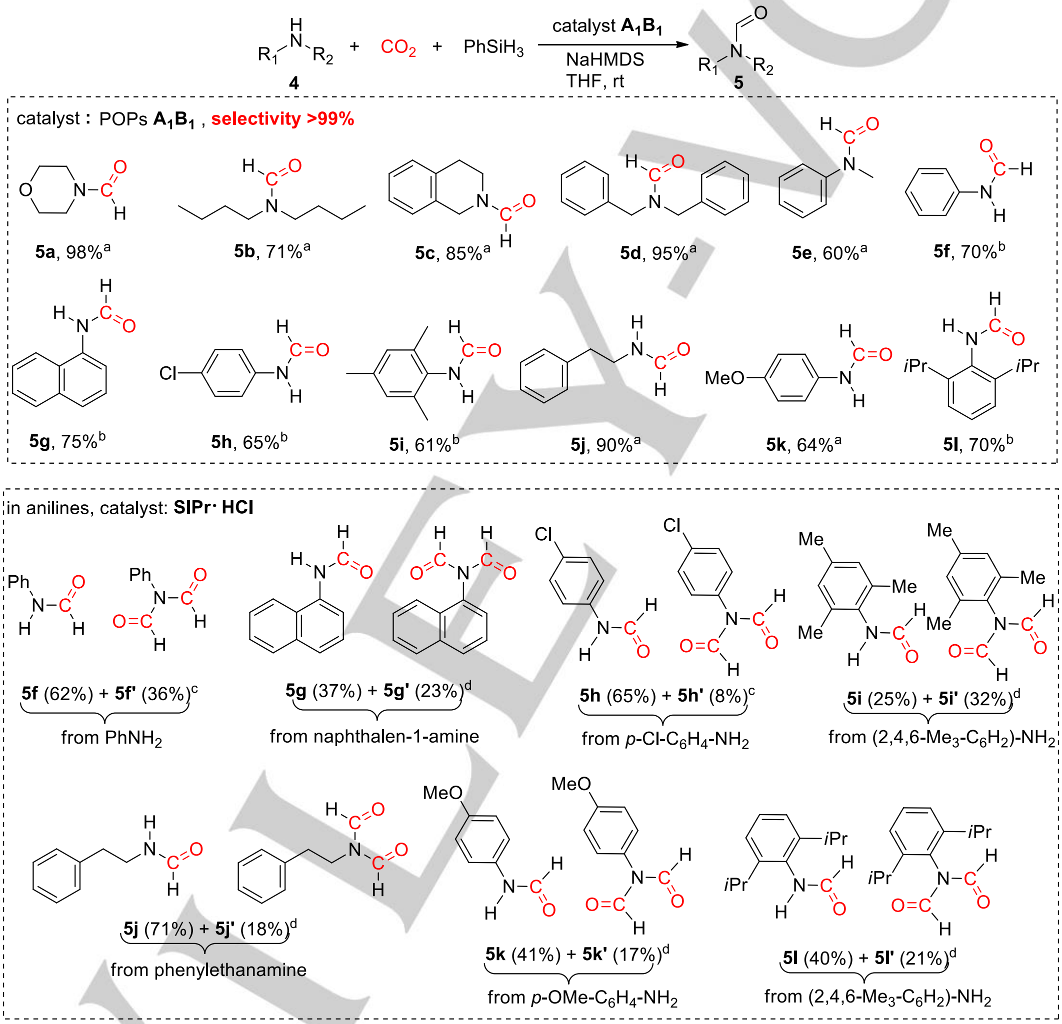

Figure 6. Scope of the catalytic formylation of N-H bonds using CO_2 and $PhSiH_3$. Reaction conditions: amine substrate 0.5 mmol, CO_2 4 atm, $PhSiH_3$ 0.75 mmol, catalyst 2-20 mol%, NaHMDS 2-20 mol%, THF 2 mL, room temperature, 24 h. [a]10 mg of polymeric catalyst (equivalent to 2 mol% of the imidazolium salts), 2 mol% NaHMDS. [b] 25 mg of polymeric catalyst (equivalent to 5 mol% of the imidazolium salts), 5 mol% NaHMDS. [c] 20 mol% catalyst. [d]10 mol% catalyst. All yields are isolated yields and are the average of two runs, except for 5a and 5b, which were analyzed by GC.

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possessed both the substrate enrichment and confinement effects.

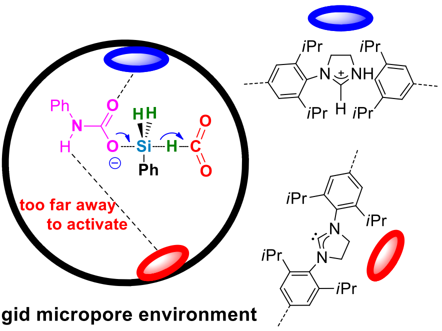


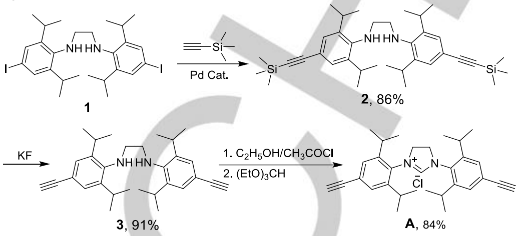
Figure 7. Proposed rigid micropore environment.

Conclusions

In summary, POPs materials based on NHC building blocks with tunable surface areas and pore volumes have been prepared via the $Co_2(CO)_8$-catalyzed trimerization reaction of terminal alkyne groups. Notably, compared with their homogeneous counterparts, the heterogeneous POP catalyst A_1B_1 displayed enhanced activity and extremely high selectivity. This improved activity could be attributed to the enrichment of reactants, and the extremely high selectivity (> 99%) could probably be attributed to the confinement effect that was posed to occur in the favorable micropore environments, which prohibited the formation of the large-size intermediates of bis-formylanilines or hindered the double site activation mode. In addition, the POPs catalyst A_1B_1 has good substrates tolerance and could be reused at least four times without a loss of activity. These unique characteristics clearly indicate that this kind of POP catalyst with built-in NHCs could provide a new platform for the exploration of catalytic transformation of CO_2 and other poorly selective catalytic reactions.[14h, 20]

Experimental Section

Synthesis of Acetylene-Functionalized SIPr·HCl. The synthetic route for the preparation of the acetylene-functionalized N-heterocyclic carbene precursor building block, ac-SIPr·HCl (A), is shown in Scheme 3. Diiododiamine 1 (4.47 g, 7.0 mmol) was reacted with trimethylsilylacetylene via a Pd-catalyzed Sonogashira coupling and subsequent treated with KF to give alkyne-functionalized diamine 3 (2.34 g, 5.46 mmol) in 78% yield over two steps. Intermediate 3 (2.34 g, 5.46 mmol) was treated with excess of ethanolic HCl (approximately 3 equiv, freshly prepared by the cautious addition of 1.6 mL of acetyl chloride to 15 mL of absolute ethanol). After 30 min of vigorous stirring, the solution was filtrated, and the solid was washed with cold ethanol to give double chlorhydrate 3·2HCl, which was then refluxed in 70 mL of a 1/1 $HC(OEt)_3$/EtOH mixture for 2 h. After the reaction mixture was cooled to room temperature and evaporated, the residue was triturated with 50 mL of Et_2O and then recrystallized from CH_2Cl_2/n-pentane to give 2.25 g of white solid A (84% yield based on 3). Its molecular structure was confirmed by Single-crystal X-ray diffraction analysis, which showed the expected structural motif with terminal alkyne substituents (Figure 8, CCDC 1469334).



Scheme 3. Synthesis of acetylene-functionalized SIPr·HCl

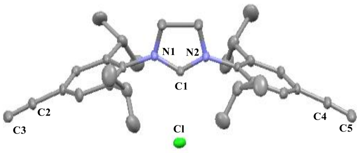


Figure 8. Crystal structure of monomer **A**. Displacement ellipsoids are set at 30% probability, and H atoms have been omitted for clarity.

Synthesis of SIPr-Built-in POP catalysts. The SIPr·HCl-built-in polymeric organic polymer catalyst could be readily prepared from the Co-catalyzed intermolecular alkyne trimerization of ac-SIPr·HCl (A) and 1,3,5,7-tetrakis(4-ethynylphenyl)adamantine (B). Monomer B was selected as a three-dimensional connector and synthesized according to the reported procedures.[21] To tune the physical properties of these POPs, different monomer ratios (A:B = 1:1, 2:1 and 3:1) were selected for the co-polymerization to provide the corresponding SIPr-built-in POP catalysts, which were named A_xB_y according to the monomer ratio (Scheme 1). The following is a typical procedure for the preparation of A_1B_1: in an argon-filled glovebox, a 20 mL vial equipped with a magnetic stir bar was charged with monomers A (80 mg, 0.17 mmol) and B (90 mg, 0.17 mmol). This mixture was dissolved in dry 1,4-dioxane (6 mL), and then, $Co_2(CO)_8$ (30 mg, 0.09 mmol) was added. The solution was stirred for 5 min prior to being sealed. The reaction mixture was then stirred at 115 ℃ for 3 h, during which a black precipitate was generated. After cooling the reaction mixture to room temperature, the vial was opened, and the precipitate was isolated by filtration, washed with H_2O (50 mL), and stirred in concentrated aqueous HCl (15 mL) for 1 h. The remaining black polymer was isolated by filtration, washed with H_2O (50 mL) and MeOH (50 mL), and then refluxed in CH_2Cl_2 in a Soxhlet extractor for 3 days. The resultant material (167 mg, 98% yield based on all monomers mass) was dried under a dynamic vacuum for 24 h at 60 °C. The A_2B_1 and A_3B_1 POP catalysts could be prepared in near quantitative yields following the above procedure by changing the corresponding A/B ratio.

Representative Procedure for the Catalytic Formylation of an Amine with CO_2. In a typical experiment, morpholine (0.5 mmol, 44 mg), phenylsilane (0.75 mmol, 81 mg), catalyst A_1B_1 (2 mol%, 10 mg), NaHMDS (2 mol%, 9 mg) and 2 mL of dry THF were loaded in a 5 mL ampoule vial equipped with a magnetic stir bar under an argon atmosphere. Then, the vial was transferred to a 100 mL stainless steel autoclave, sealed and pressurized with 4.0 atm of CO_2 after being purged three times with pure CO_2. Then, the reactor was stirred at room temperature for 24 h. After the reaction, the excess CO_2 was discharged, and the reaction mixture was analyzed by gas chromatography (GC), which indicated a 98% yield of N-formylmorpholine (n-hexadecane was used as an internal standard).

Keywords: N-heterocyclic carbene • porous organic polymer • carbon dioxide • formylation • heterogenized catalyst

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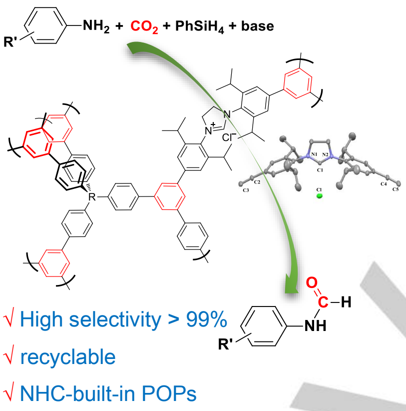
Table of Contents

FULL PAPER

Porous organic polymers with built-in N-heterocyclic carbenes were prepared and used as a selective and efficient heterogeneous catalyst for the reductive N-formylation of amine with CO_2. The improved performance could be attributed to the unique micropore structure of the POPs catalysts.



√ High selectivity > 99%

√ recyclable

√ NHC-built-in POPs

Hui Lv, Wenlong Wang, Fuwei Li**

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Porous Organic Polymers with Built-in N-Heterocyclic Carbenes: Selective and Efficient Heterogeneous Catalyst for the Reductive N-formylation of Amines with CO_2