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Sustainable Nanoporous Benzoxazole Networks as Metal-Free Catalysts for One-Pot Oxidative Self-Coupling of Amines by Air Oxygen

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The development of sustainable organocatalysts with porosity, high stability, and excellent catalytic activity offers a clean and green alternative to precious metal catalysts. Here, an efficient, nanoporous, heterogeneous benzoxazole catalyst is reported for aerobic oxidative coupling of amines. A molecular design strategy is presented to functionalize primary amines to produce valuable products under one-pot, open-air reaction conditions. Unprecedented and previously unknown, the stable imine intermediate catalyzes its own formation, also known as autocatalysis, enabling a direct and favorable access to amino acids, even if the catalysts are absent. The biomimetic benzoxazole catalysts developed here provide quantitative catalytic activity over 50 cycles with favorable kinetics with no degradation. This work also marks the first use of benzoxazoles for oxidative catalytic reactions.

1. Introduction

The majority of porous organic architectures are intrinsically catalytically active, an important characteristic that attracted great attention due to their potential applications. These are constructed solely from organic building blocks and can be classified as covalent organic frameworks (COFs) and porous organic polymers (POPs).[1] Generally, these materials are synthesized in a modular fashion with inherent suitable functional groups, which also possess high surface area, tunable pore size, and adjustable electronic structures, ultimately bringing highly promising catalytic activity.[2] Although plenty of porous materials have been developed, porous catalytic materials with requisite functionalities to carry out consecutive reaction steps in one pot are still challenging. With this in mind, we predicted that a highly stable porous organic material with mild basicity could handle oxidative coupling reactions by virtue of their in-built functionalities.

The formation and manipulation of imine derivatives is a key step for the synthesis of a range of organic intermediates,[3] which are widely applied in life sciences and the chemical industry.[4] Due to their diverse reactivity, they are used extensively in the synthesis of biologically active compounds, pharmaceuticals, agro, and fine chemicals.[5] In particular, imines act as an active intermediate for the synthesis of α-amino acids via the multicomponent Strecker reaction.[6] This, centuries-old reaction by Adolph Strecker[7] offers the way for the construction of nucleic acids, a variety of heterocycles, and natural products.[8] Complex bioactive molecules such as Manzacidin A[9] (bromopyrrole alkaloid) and (+)-lactacystin[10] (selective proteasome inhibitor) were reported following this versatile strategy, revealing that the Strecker reaction is still under active investigation. Although there are considerable developments with a wide array of effective catalytic systems,[11] the traditional synthetic route via the condensation of aldehydes and amines to form imine and subsequent hydrocyanation reaction was always the main direction to synthesize α-amino nitriles.[12] The need for activation of aldehydes led to investigations on direct oxidation of amines[13] but in contrast, imine's subsequent functionalization has been much less explored despite the huge practical promise. Recently, emerging materials such as graphene oxide and carbon nitride were shown to catalyze amine oxidative coupling to imines,[13a,14] but in each case the need for high purity oxygen gas, high pressure, high catalyst loading, and substrate limitations were prohibitive. Another crucial feature is the need for a porous catalyst since product purification and catalyst recyclability hinders feasibility.[15] These considerations lead to a need for a porous heterogeneous catalyst that could facilitate the amine to amino acid transformation while remaining unaffected by the reactive conditions.

2. Results and Discussion

Construction of functional porous materials by incorporation of heteroatoms is quite difficult because functionality and porosity must be considered together.[16] It is well known that nitrogen

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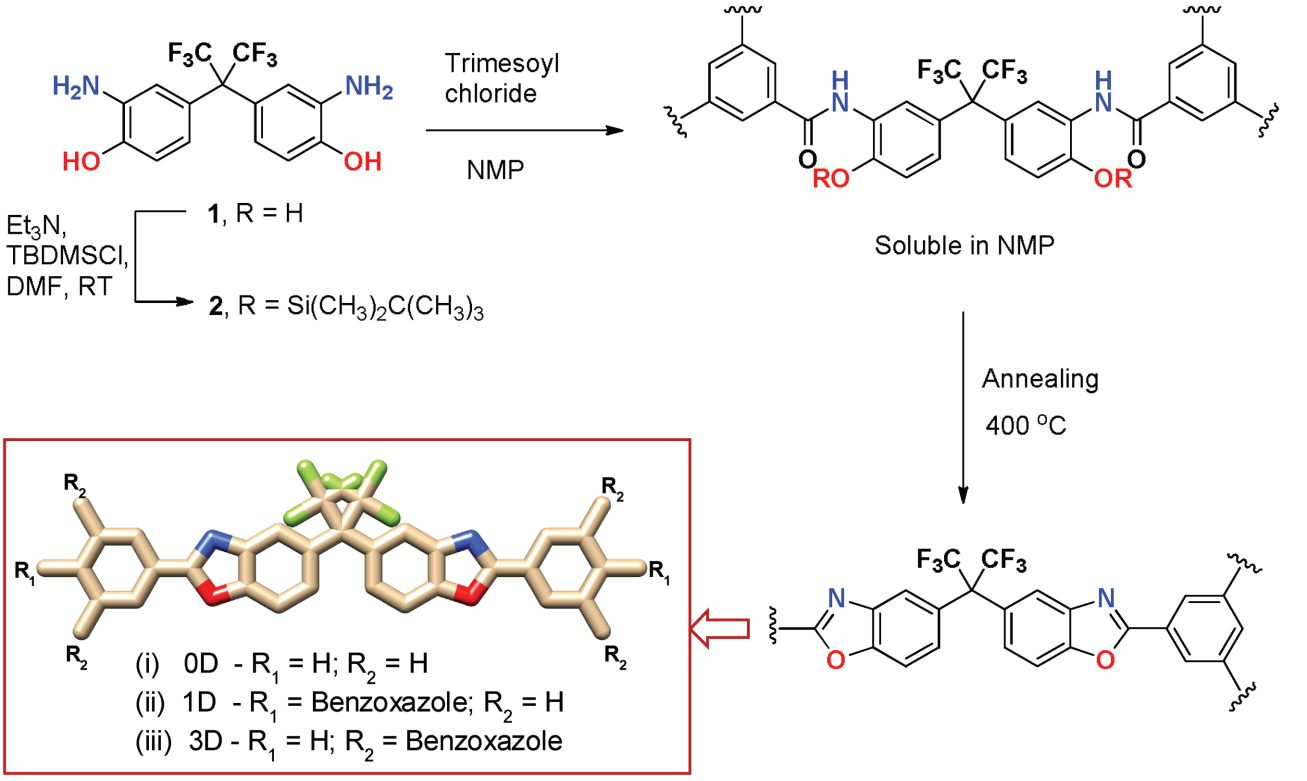

Scheme 1. Synthesis of 0D, 1D, and 3D benzoxazole catalysts.

incorporated porous materials are effective for the gas adsorption properties and emerged as an effective approach. In order to find a better and more effective Strecker catalyst that could work in ambient conditions, we identified that an optimal catalyst should contain basic heteroatoms and a stable aromatic ring to survive all conditions and repetitive cycles under oxidative conditions. Graphitic equivalent of oxazoles are known as benzoxazoles,[17] and we chose them to be best candidates for the oxidative amine couplings since (1) they are thermally very stable, especially under reactive (e.g., oxygen) gas flow[18] and (2) basic enough to carry out the reaction but not too strong to not allow continuous cycles. We then synthesized molecular (0D), linear (1D) and network (3D) structures of benzoxazoles (**Scheme 1**) using a silylation method we recently developed[17] (see the Supporting Information for detailed experimental methods). Typically, we first synthesized a silylated monomer, which on further treatment with trimesoyl chloride forms amide prepolymer. The prepolymer is soluble in polar solvents such as *N*-methyl-2-pyrrolidone (NMP). This allows film making, a feature that is not common for network polymers. Finally, annealing at 400 °C results in porous covalent organic polymer (COP-95, the code is only for indexing purposes, no chemical information is intended) 3D benzoxazole. The porous polymer network is chemically stable, completely insoluble in solvents with high thermal stability.

The synthesized 3D-benzoxazole catalyst was characterized with ^{13}C cross polarisation magic-angle-spinning (CP/MAS) solid state NMR and Fourier transform infrared (FT-IR) spectroscopic methods. The ^{13}C CP-MAS NMR spectra show the peak at 168.3 (−C=N−), 157.0, 147.4, 134.4, and 116.4 ppm corresponds to the aromatic ring of benzoxazole units and linkers, 70.67 and 56.4 ppm confirm the presence of $-CF_3$ and attached quaternary carbon. The chemical connectivity and the benzoxazole ring were also confirmed by the presence of stretching band at 1658 cm^{-1} (−C=N−), 1526, and 1190 cm^{-1} (benzoxazole ring) in FT-IR spectra (Figures S2 and S3, Supporting Information). Porosity of 3D-benzoxazole was studied from the Ar adsorption–desorption isotherms measured at 87 K showing typical type I reversible isotherms and the rapid Ar uptake at very low pressures displays the characteristics of permanent micropores. The specific surface area was determined by the Brunauer–Emmett–Teller method and found to be 754 $m^2\ g^{-1}$ (**Figure 1**a), at the level or better than many commercial zeolite catalysts.[19] Thermogravimetric analysis (TGA) shows exceptional thermal stability in air for an organic polymer (up to 384 °C, Figure 1b), covering well above the catalytic reaction temperatures and regeneration wash/dry cycles.

In addition to the chemical requirements, substrate diffusion through a heterogeneous catalyst becomes critical for designing an optimum catalyst. Generally, materials with intrinsic porosity have high surface area and tunable pore sizes that can act as a better catalyst because of the effective mass transfer.[4d,15b,20] It is important to note that among the synthesized catalysts, 3D porous benzoxazole exhibited excellent catalytic activity (**Figure 2**a) and to the added advantage it can be readily made in scalable quantities and can be cast into films despite its network structure that is heterogeneous in nature and insoluble in all tested solvents. In order to develop the best working benzoxazole catalyst, we screened catalyst choice, loading, temperature,

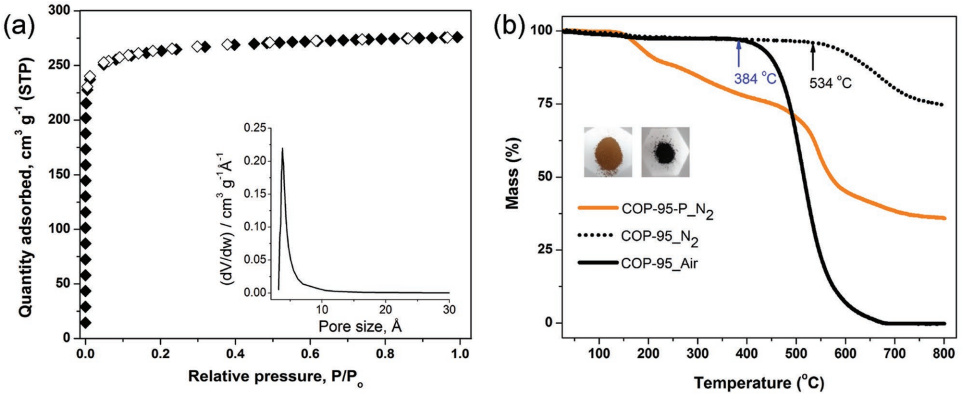

Figure 1. a) Ar adsorption–desorption isotherms. Inset: Non-local density functional theory (NL-DFT) pore size distribution (argon 87 K, slit pore, aspect ratio 4). b) Thermogravimetric analysis of prepolymer and COP-95 under N_2 and air.

and solvent (Figure 2 and Figure S9, Supporting Information) in the oxidative self-coupling of benzyl amine (**Table 1**).

Our catalytic investigation began with stirring a colloidal mixture of benzyl amine (5 mmol) and 3D benzoxazole catalyst (25 mg) open to air and without solvent at 80 °C (Figure 2). Within 10 h, we observed over 90% conversion with 99% selectivity. A comparative study with lower surface area 3D benzoxazoles (COP-93 and COP-94) revealed that diffusive

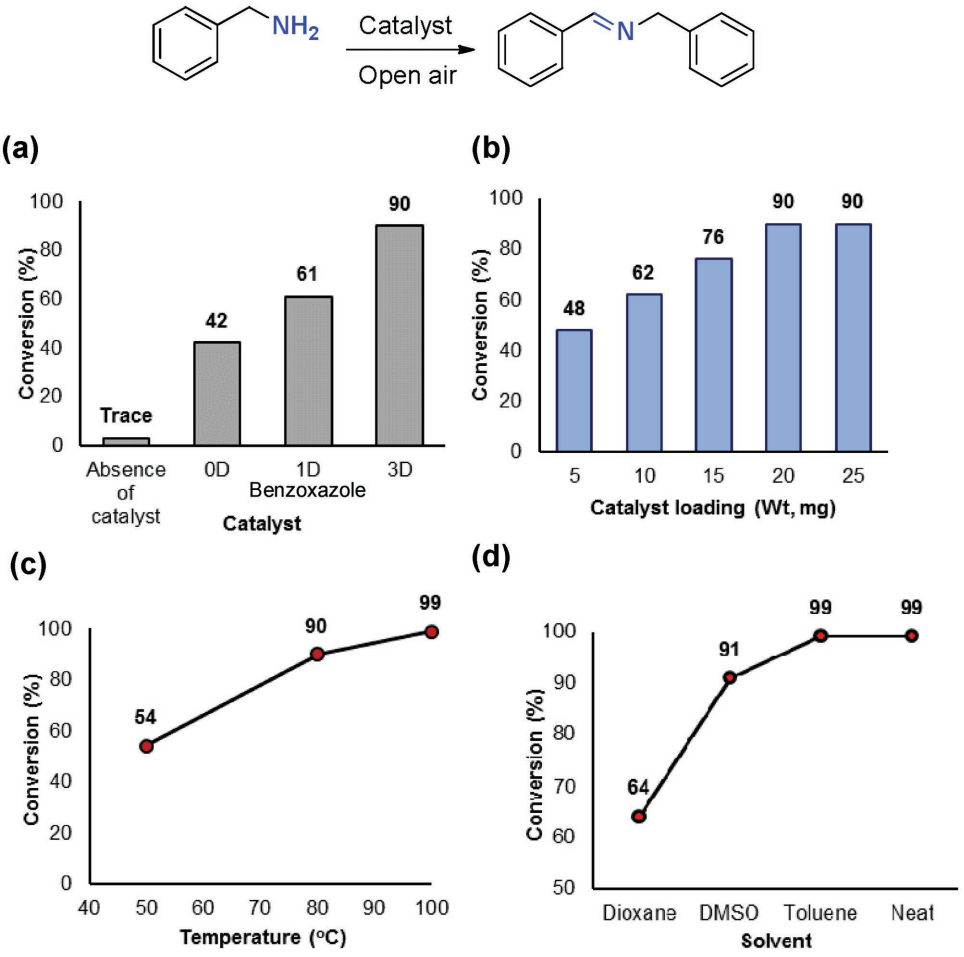

Figure 2. Optimization of reaction conditions for the oxidation of benzyl amine to imine. The reaction was carried out by using benzyl amine as model substrate (5 mmol) under open air at specified conditions. a) Screening of catalyst type at 80 °C using 20 mg of catalyst. b) Screening for catalyst loading (3D benzoxazole) at 80 °C, reaction time 8 h. c) Optimization for reaction temperature using 20 mg of 3D benzoxazole catalyst, reaction time 8 h. d) Optimization for solvent using 20 mg of 3D benzoxazole catalyst.

Table 1. Substrate scope for the catalytic oxidative coupling of benzylamines and their one-pot conversion into α-amino nitriles.

Entry[a)]	Substrate R	Time [h]	Imine, yield[b)] [%], (selectivity[c)], %)	Time [h]	α-Amino nitrile, yield[b)] [%], (selectivity[c)], %)
1	H (1a)	5	2a, 99 (>99)	4	3a, 99 (99)[d)]
2	H (1a)	5	2a, 99 (>99)	10	3a, 46 (99)[e)]
3	H (1a)	5	2a, 99 (>99)	10	3a, 63 (99)[f)]
4	4-Me (1b)	8	2b, 99 (>99)	4	3b, 99 (99)[d)]
5	4-MeO (1c)	8	2c, 96 (99)	4	3c, 98 (99)[d)]
6	3-MeO (1d)	8	2d, 95 (99)	6	3d, 94 (99)[d)]
7	2-MeO (1e)	8	2e, 97 (99)	6	3e, 96 (99)[d)]
8	4-F (1f)	8	2f, 96 (99)	6	3f, 95 (99)[d)]
9	4-Cl (1g)	8	2g, 91 (99)	8	3g, 94 (99)[d)]
10	2-Cl (1h)	8	2h, 96 (99)	8	3h, 93 (99)[d)]
11	4-Br (1i)	8	2i, 93 (99)	8	3i, 91 (99)[d)]
12	4-CN (1j)	10	2j, 91 (99)	12	3j, 90 (99)[d)]

[a)]Reaction conditions: Catalyst (20 mg), substrate (5 mmol), toluene (0.5 mL); [b)]Isolated yield; [c)]Determined by ^{1}H NMR using $CDCl_3$ as a solvent; [d)]Using TMSCN (1.2 equiv.); [e)]Using EtOCOCN (1.2 equiv.) as a source of cyanide; [f)]Using EtOCOCN (1.2 equiv.) at 60 °C.

enhancement from high surface area and pore volume facilitates better conversions (Figure S9 and Table S1, Supporting Information). Surprisingly, model benzoxazole compound (0D) fared the least catalytic activity (42%) in the longer, 16 h of testing, leading to a conviction that space requirements for effective substrate interactions are not negotiable. Linear benzoxazole polymer (1D) suffered from the same fate, although slightly enhanced conversions (61%) in 10 h, perhaps because of the rigid backbone allowing more residential time with the substrate-catalytic interaction. It is noteworthy that in the absence of catalyst, only very trace amount of product was formed even after 16 h (Figure 2). Next, we studied the amount of catalyst loading required for the oxidative self-coupling of benzyl amine. By ranging from 5 to 25 mg, we found that 20 mg was enough for complete conversion (Figure 2). We also screened temperature for the ideal reaction conditions. At 50 °C, the reaction proceeds with low conversions (54%) but when raised to 100 °C excellent conversion (99%) and selectivity (>99%) was observed. Toluene was found the best among the solvents tested (1,4-dioxane, dimethyl sulfoxide (DMSO)), although 3D benzoxazole catalyst did not need one.

In a progressive catalytic experiment with successive additions of amines but not removing the product, we observed an unusually sustainable catalytic activity (Figure 4a). Commonly, the increase in product formation negates the forward transformation, leading to lower conversions and catalytic deactivation. Suspecting an autocatalytic pathway, we removed the catalyst and continued adding substrates. The catalytic activity persisted, although with lesser yields (up to 46%), proving that the imine product can catalyze its own formation, also known as autocatalysis. Our control experiments with a small amount of imine to be present in the reagent mixture verified autocatalysis (**Figure 3**a), in that the reaction was catalyzed through an S shape isotherm. This indicates more catalytic activity is observed (hence the positive slope) once more of the catalyst is formed, leading to a final stabilization when no more substrates are around. These findings also shed light into other previous unusual observations on oxidative amine couplings. For example, imine autocatalysis may have been the reason why amine oxidative coupling under 1 atm pure oxygen (without any catalysts) was moderately successful (49%) resembling the autocatalytic yields we have observed without the catalyst.[21]

To demonstrate the general applicability of 3D benzoxazole catalyst and scope of the process, we attempted to carry out further functionalization in one pot without purification of the imine intermediates (Table 1) since it offers advantages in atom economy and process simplification. In such strategies, one particular challenge is the reactivity of the reactants and the catalysts toward the nucleophiles. Benzoxazoles, the robust heterocyclic basic catalysts, proved to be inert toward a wide range of nucleophiles (here three representatives are chosen, Figure 3b) and since the imine conversion is quantitative, there is no worry about the side reactions of the nucleophilic substitution. We have shown that each of cyanide (aromatic amino acid precursor), phosphite (amino phosphonate precursors), and nitroalkane (aliphatic amino acid precursor)-based nucleophiles yield near perfect selectivity and very high conversions. For the cyanide addition, we varied the source by employing less toxic trimethyl silyl cyanide (TMSCN) and ethyl cyanoformate (EtOCOCN), to show that alternatives are also feasible (Table 1). The TMSCN is more labile and requires less strong base to release cyanide, therefore higher yields are achieved. One can also introduce chiral CN^- as a nucleophile.[22] In the light of these, this method has immediate impact on the viability of oxidative amine coupling in today's amino acid production pathways.

To study whether the coupling reaction can be generalized, we evaluated the substrate scope of 3D benzoxazole catalyst with different electron donating and withdrawing groups on the aromatic ring (Table 1). In general, we observed that irrespective of the electronic effects, almost all the substrates worked well with the 3D benzoxazole catalyst and resulted in good to excellent conversions (90–99%) with the added advantage of excellent selectivity (99%) in the overall time of 9–22 h (Table 1). Taking all the findings into perspective, we can now conclude that the wide scope and single component nature of the oxidative amine coupling reaction could also infer hints for the prebiotic chemistry steps of forming complex biomolecules.

Mechanism of the catalytic transformation is also studied by monitoring the reaction by a time resolved liquid NMR using a molecular (0D) benzoxazole catalyst (Figure 3c). It is generally accepted that there are two major pathways for the oxidative amine coupling reactions.[11k,23] Popular choice is the aldehyde pathway, perhaps being in line with traditional Strecker concepts, but the NMR studies clearly ruled out any formation of aldehyde, the key intermediate for the conventional mechanism (Figure 3d). It is therefore safe to say that an attack by primary amine into the initial reactive imine (pathway I) leads to the more stable coupling product. Air oxygen produces the first imine (in both mechanisms) through hydroxylamine dehydration. This is why oxygen presence is required, no reaction observed without it.

Lastly, we evaluated the recyclability of the heterogeneous catalyst (**Figure 4**) since leaching and degradation could prevent

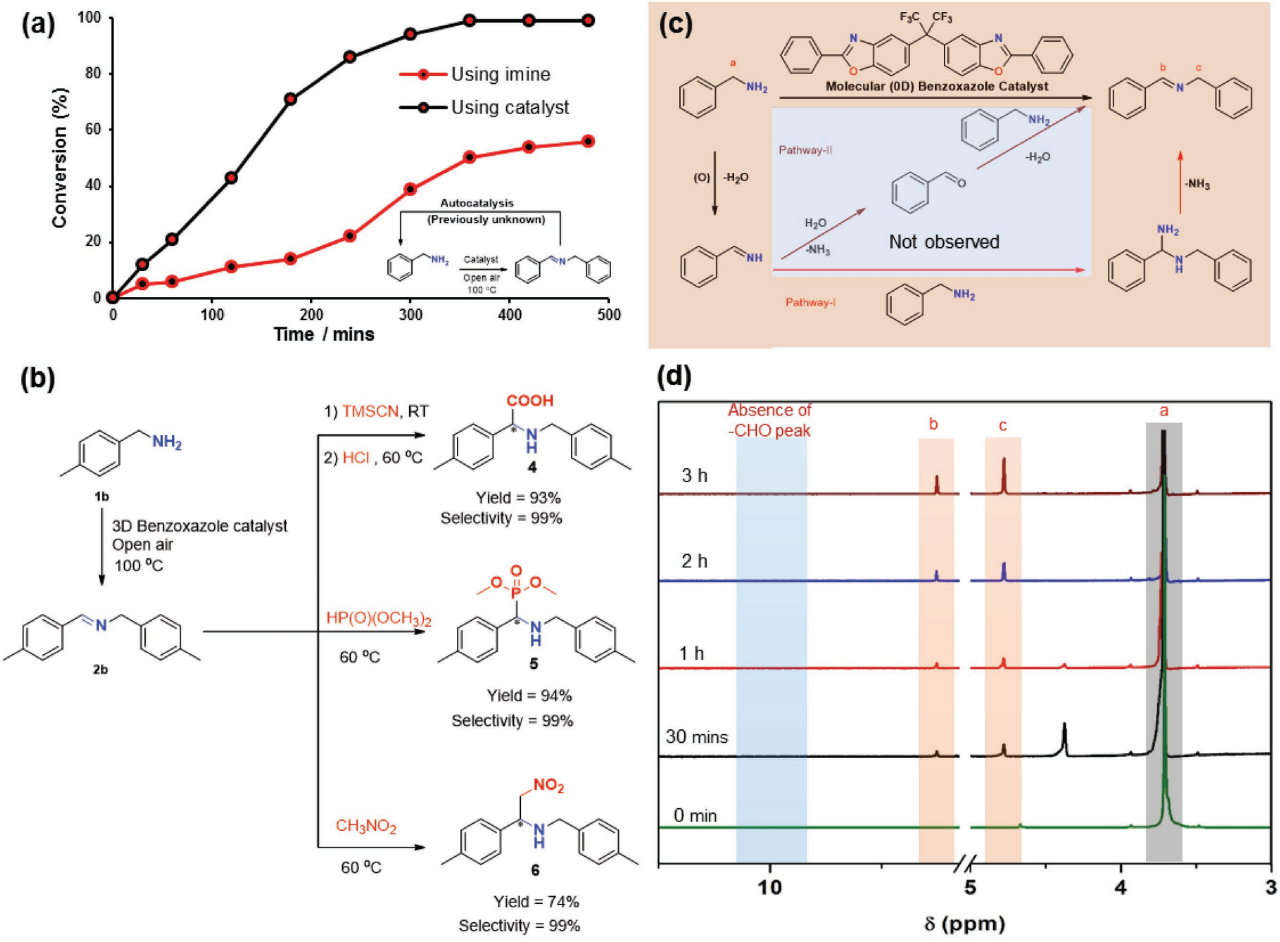

Figure 3. Discovery of imine autocatalysis and suggested mechanism. a) Kinetics and autocatalytic evidence for imine formation from the plot for the time versus conversion for the oxidation reaction carried out with catalyst (20 mg), and with imine (30 µL). b) Nucleophile variation for the one-pot conversion of amines into value added products at specified reaction conditions. c) Probable mechanism for the preparation of imine from benzyl amine. d) ^{1}H NMR recorded using $CDCl_3$ as a solvent in different time interval. Reaction was conducted with 0D benzoxazole as a catalyst (20 mg) and benzyl amine as a substrate (5 mmol) at 100 °C.

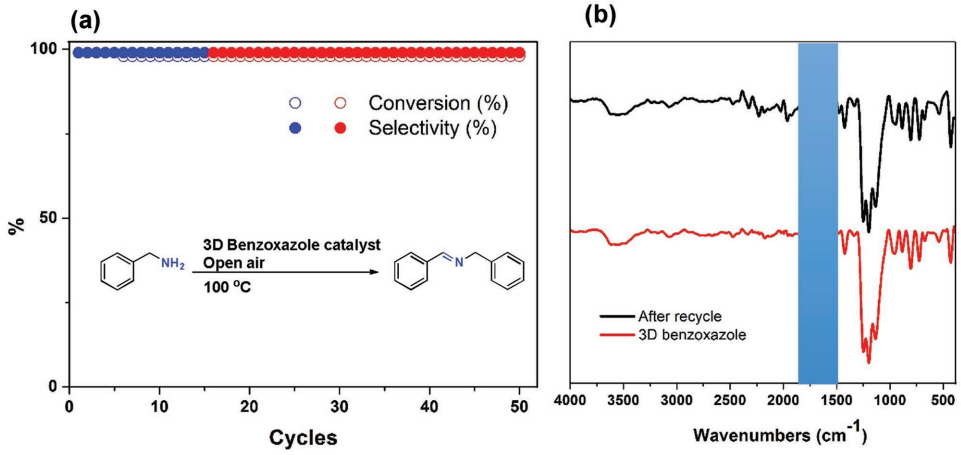

Figure 4. a) Recyclability of 3D benzoxazole catalyst using benzyl amine as substrate under optimized reaction conditions: 3D benzoxazole catalyst (20 mg) using benzyl amine as a substrate (5 mmol) at 100 °C. b) FT-IR of 3D benoxazole fresh and recycled catalyst.

consecutive uses. After each cycle, the catalyst was removed by centrifugation and washed repeatedly with acetone and ethanol, and dried under vacuum at 100 °C for the subsequent catalytic runs (up to 15 cycles). The recovered catalyst worked well and retained its catalytic activity, from then we keep on adding 1 mmol of benzyl amine as substrate and checked for its activity up to 50 mmol and the results indicated that there is no noticeable change in the conversion and nature of the catalyst (Figure 4b). It is also important to note that we have even reused the same batch of the catalyst (after washing and drying) in different substrate conversions, another sign for its wide spread potential in chemical industries.

3. Conclusions

In conclusion, we reported a new, metal-free 3D benzoxazole porous polymer network with excellent catalytic activity for the oxidative coupling of primary amines into imines. The imines are readily converted into derivatives such as α-amino nitriles with excellent conversions (90–99%) and selectivity (99%). Mechanism studies on model compounds ruled out aldehyde intermediates. Unprecedentedly, imines were also found to catalyze their formation for a previously unknown autocatalytic behavior. These findings provide new means and understanding for producing a range of organic building blocks, most notably amino acids.

4. Experimental Section

General Procedure for the One Pot Conversion of Amine to α-Amino Nitrile: In a typical reaction, catalyst (20 mg) and benzylamine (5 mmol) were mixed in an oven dried round bottom flask. To the heterogeneous mixture, solvent (if used, e.g., toluene, 0.5 mL) was added and these mixtures were stirred together at 100 °C under open air. The reaction was monitored by thin layer chromatography (TLC) and upon the completion of the reaction the mixture was cooled to room temperature. To the cooled reaction mixture, TMSCN (1.2 equiv.) was added and allowed the reaction mixture to stir at room temperature. Upon completion of the reaction, the catalyst was filtered and the solvent was evaporated under reduced pressure. The filtered catalyst was washed with acetone and methanol. The resulted product was characterized with ^{1}H NMR.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

benzoxazole, covalent organic polymers, heterogeneous catalysts, microporous polymers, nanoporous materials

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