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Reusable Copper Catechol-based Porous Polymers for the Highly Efficient Heterogeneous Catalytic Oxidation of Secondary Alcohols

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New catechol-based porous polymers were synthesized and used as platforms for the heterogenization of molecular Cu complexes. The resulting Cu@CatMP-1 materials proved to be highly stable and performing catalysts for the oxidation of secondary alcohols with turnover numbers up to 6000, about 1 to 2 orders of magnitude higher than the current relevant state of the art, using catalyst loadings as low as 25 ppm of Cu. The solid catalyst proved to be recyclable for over 10 runs without detectable metal leaching and has been scaled to the gram scale. The coordination of Cu to catechol within the polymer has been evidenced by X-ray absorption spectroscopy.

Introduction

Heterogenization of well-defined molecular entities on a solid support is a widely used strategy to target recyclable, thus more sustainable catalytic systems compared to classical homogeneous catalysts. In this context, solid supports made by the repetition of one or several coordinating moieties, such as hybrid periodic mesoporous silica, Metal Organic Frameworks (MOF) and Porous Organic Polymers (POP) have gained increasing attention as hosts for transition-metal complexes.[1–6] Their high intrinsic porosity allows for easy access of reaction substrates to catalytic sites. These so-called porous macroligands[7–9] not only give rise to potential reusable catalysts, but they also allow for preserving the local molecular nature of the active site as well as the site isolation, which can circumvent deactivation by clustering as can happen under homogeneous conditions.[10,11] In particular, POPs are purely organic porous solids built up entirely from robust covalent bonds yielding amorphous, yet well-defined materials which can present significant stability compared to other porous macroligand materials.[12] Their versatile synthetic preparation allows for the incorporation of almost any kind of metal binding sites in the resulting polymer.[13] One particular example concerns the introduction of bipyridine units, studied in literature for a large variety of transition metal mediated reactions.[7,8,14–20] Similarly, catechols are widely used ligands in coordination chemistry, their redox "non-innocent" properties have been thoroughly explored in catalysis.[21,22] Furthermore, recent studies have shown that metal/catechol species can be efficiently immobilized onto MOF[23–29] and POP[30–35] supports, with applications in hydrogenation, hydrosilylation or catalytic degradation of toxic organophosphate compounds.[14]

Herein, we report the synthesis of novel porous macroligands made of redox-active catechol moiety as co-monomer in polymeric matrixes (namely CatMP-1) and their subsequent metalation with Cu cations. The high activity and stability of

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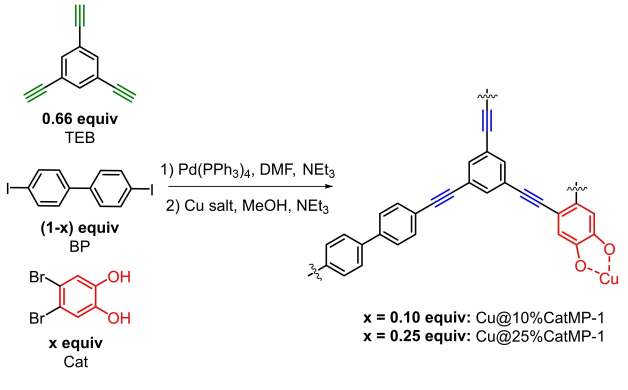
these materials are demonstrated in the catalytic oxidation of secondary alcohols.

Results and Discussion

The CatMP-1 platforms were prepared by copolymerization of 1,3,5-triethynylbenzene (TEB), 4,5-dibromocatechol (Cat) and 4,4′-diiodobiphenyl (BP) via a Pd-catalyzed Sonogashira cross-coupling reaction, according to a modified literature procedure (Scheme 1).[7] Depending on the initial amounts of co-monomers, two different materials were obtained, namely 10% CatMP-1 (molar ratio: TEB : BP : Cat = 0.66 : 0.9 : 0.1) and 25% CatMP-1 (molar ratio: TEB : BP : Cat = 0.66 : 0.75 : 0.25). Subsequent functionalization with Cu ions was performed by infiltration of copper(II) acetate in basic media (Scheme 1).

The resulting Cu(II)@10%CatMP-1 and Cu(II)@25%CatMP-1 presented a Cu content of 2.0 wt% and 2.6 wt%, respectively, as determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. It was also found that approx. 0.5 wt% of Pd remained from the polymer syntheses (Table S1, Supporting Information). These metal traces have been thoroughly considered as potential active sites within the pristine 10%CatMP-1 polymer, as described below. If the Pd traces had an significant impact on the catalytic activity (see below), an extraction with however toxic KCN would allow to remove them, as reported by Marta Iglesias, Félix Sánchez and co-workers.[36]

The pristine as well as copper loaded CatMP-1 materials were further analyzed by nitrogen physisorption experiments, IR and electron paramagnetic resonance (EPR) spectroscopy. The pristine as well as the corresponding Cu-loaded materials present a permanent porosity toward N_2 (Figure S1, Supporting Information). The isotherms of the materials show a hysteresis, characteristic for the swelling behavior of porous polymers. As expected, a decrease in porosity is observed after metalation of the catechol moieties with Cu. The apparent surface area of 10%CatMP-1 (1090 $m^2 g^{-1}$) decreased to 860 $m^2 g^{-1}$ for Cu(II)-@10%CatMP-1. A similar trend is observed for 25%CatMP-1 whose apparent surface area dropped from 940 to 820 $m^2 g^{-1}$ for the corresponding Cu(II)-functionalized solid.



Scheme 1. Preparation of catechol-based microporous polymers by 1) Pd-mediated Sonagashira cross coupling in DMF/NEt_3 at 100 °C for 24 h followed by 2) Cu salt infiltration in MeOH/NEt_3 at 50 °C for 3 d to yield the corresponding Cu@CatMP-1 materials. Terminal alkyne groups (–C≡CH) are highlighted in green, medial alkyne groups (–C≡C–) in blue.

IR spectroscopy revealed successful co-polymerization of Cat and BP monomers in the final material (Figures S2–3, Supporting Information). The presence of Cat moieties is indicated by characteristic C–O stretching, C–H and C–C bending vibrations around 1250, 900 and 840 cm^{-1}, respectively.[37–39] The presence of BP is confirmed by the characteristic stretching vibration of para-polyphenylene moieties at approx. 820 cm^{-1}.[40] The disappearance of the asymmetric stretching vibration of terminal alkyne groups (–C≡CH) around 2100 cm^{-1} and the appearance of a strong band at 2200 cm^{-1}, corresponding to the asymmetric stretching vibration of medial triple bonds (–C≡C–), confirm a high degree of polymerization.[41]

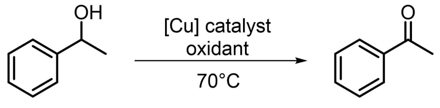
Analysis of the 10%CatMP-1 materials using EPR spectroscopy before and after functionalization with Cu^{2+} gave results comparable to those reported for MOF-supported (Cu)catecholate species.[26,29] The EPR spectrum of the non-metalated material displayed a sharp signal at $g \approx 2.007$, characteristic of a carbon centered radical, most likely a semiquinone radical (Figure S5, Supporting Information). The copper-loaded Cu(II)@10%CatMP-1 presented a much broader signal (Figure S6, Supporting Information). The shape of the EPR spectrum is similar to that observed for copper-catecholates within UiO-68 type materials.[29] It is characteristic for an isolated monomeric Cu species in a tetragonal distorted ligand environment formed by four oxygen ligand atoms (see below).[42,43] At 150 K, the EPR spectrum is composed of two components in an equal ratio. An isotropic signal centered at $g \approx 2.17$ with a high line width, indicative for a Cu atom with a dynamic ligand environment, and an anisotropic component indicative for a restricted motion of the ligand environment (Table S3).[42] These EPR data also rule out the substantial presence of dimeric copper species, since for these sites only the semiquinone radical would be observable.

We then investigated the catalytic properties of these copper catechol-derived POP in the oxidation of secondary alcohols. Initial experiments involved the use of 1-phenylethanol **1 a** as substrate in combination with an oxidant at 70 °C to yield acetophenone **2 a** (Table 1).[44]

While experiments with air or H_2O_2 as oxidants proved unsuccessful (entries 1 and 2), we observed a moderate yield of 26% in the presence of 1.5 equivalents of TBHP (*tert*-butyl hydroperoxide, aqueous solution) with only 36 ppm of Cu in the reaction mixture, corresponding to 0.25 mg of solid Cu(II)-@10%CatMP-1 catalyst (entry 3). Variation of the oxidant indicated that TBHP (decane solution) was best suited with a conversion of 74% (entries 1–8).

Increasing the oxidant amount from 1.5 to 2 equivalents provided almost full conversion of the starting material (entry 8). Optimal conditions were reached by decreasing the catalyst amount from 36 to 25 ppm of Cu, and the reaction time from 24 to 12 hours to obtain 94% yield, reaching a TON of 6025 and a productivity of 200 grams per gram of solid catalyst (entry 9).

Table 1. Screening of the reaction conditions.[a]



1a 2a

entry	Catalyst	Oxidant	**2a** yield [%][b]
1	Cu(II)@10% CatMP-1	air	7
2	Cu(II)@10% CatMP-1	H_2O_2	<1
3	Cu(II)@10% CatMP-1	aq. *tert*-butyl hydroperoxide (TBHP) 70%	26
4	Cu(II)@10% CatMP-1	di-*tert*-butyl peroxide	<1
5	Cu(II)@10% CatMP-1	cumyl hydroperoxide	35
6	Cu(II)@10% CatMP-1	*tert*-butyl benzoperoxoate	49
7	Cu(II)@10% CatMP-1	*tert*-butyl peracetate	60
8	Cu(II)@10% CatMP-1	TBHP^c	74/97[d]
9	Cu(II)@10% CatMP-1[e]	TBHP[c]	94[d,f]
10	Cu(I)@10% CatMP-1[e]	TBHP[c]	89[d,f]
11	Cu(II)@25% CatMP-1[e]	TBHP[c]	92[d,f]
12	10%CatMP-1[g]	TBHP[c]	12[d,f]
13	$Cu(OAc)_2$	TBHP[c]	25
14	$Cu(OAc)_2$ + catechol	TBHP[c]	38
15	none	TBHP[c]	4[d,f]
16	none	air	<1[f]

[a] Reaction conditions: 1-phenylethanol (0.5 mmol), oxidant (1.5 equiv.), Cu catalyst (36 ppm of Cu), 70 °C, 24 h. [b] Yields determined by ^1H NMR. [c] TBHP 5–6 M solution in decane. [d] 2 equiv. of oxidant are used. [e] 25 ppm of Cu are used. [f] 12 hours reaction. [g] 0.25 mg of solid are used.

A catalyst made using copper (I) triflate instead of copper (II) acetate, namely Cu(I)@10%CatMP-1 (see Supporting Information for details) showed similar activity as its analogue Cu(II)@10%CatMP-1, highlighting that the oxidation state of the copper precursor has no significant influence on the catalytic activity (89% yield, entry 10). Indeed, we can assume that copper (I) species might be oxidized to copper (II) under oxidative catalytic conditions.

The increase of density of chelating catechol sites within the polymer network from 10 mol% in Cu(II)@10%CatMP-1 to 25 mol% in Cu(II)@25%CatMP-1, thus increasing the polarity of the polymeric backbone, seemed not to impact the catalytic activity (94% vs. 92% yield, entries 9 and 11).

The non-metalated 10%CatMP-1 material was also tested and a non-negligible, yet low conversion of 12% was obtained under optimized conditions (entry 12). This low conversion most likely arise from the presence of residual Pd traces, stemming from the polymer synthesis (see Table S1). For comparison, homogeneous copper acetate with or without the addition of catechol gave rather low yields, even after 24 hours of reaction (entries 13–14). Finally, performing the reaction with no solid catalyst, with or without TBHP, only yields trace amounts of acetophenone (entries 15–16).

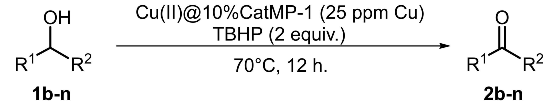
The substrates scope for the oxidation of secondary alcohols catalyzed by Cu(II)@10%CatMP-1 was then explored. As summarized in Table 2, various aromatic and aliphatic alcohols were evaluated under the optimized reaction conditions (25 ppm Cu, 2 equiv. TBHP, 70 °C, 12 h). The 1-phenylethanol derivatives functionalized at the *para*-position with either electron-rich (CH_3, **1b**; OMe, **1c**) or -poor functions (Br, **1d**) led to the formation of the corresponding ketones **2b**–**d** in excellent yields. Similarly, the oxidation of 1-phenyl-1-propanol (**1e**) and diphenylmethanol (**1f**) proceeded smoothly to ketones **2e** and **2f**, with yields of with 93% and 92% respectively. In contrast, the heterogeneous Cu catalyst performed less productively in the presence of aliphatic alcohols, giving moderate to good yields of the corresponding oxidized products **2g**–**m**. For instance, the oxidation of cyclic aliphatic alcohols such as cyclopentanol (**1g**), 2-methylcyclohexanol (**1h**) or cycloheptanol (**1i**) occurred with formation of the ketones **2g**–**i** with 68%, 72% and 62% yield, respectively. Acyclic alcohols gave moderate to good yields of **2j**–**m** (59–77%). It is worth noting that the reaction seems not to be substantially limited here by the diffusion of reactants within the polymeric network as far as sterically congested substrates like the 3,3-dimethylbutan-2-ol (**1m**) gave a good yield (69%). The applicability of Cu(II)@10% CatMP-1 was then demonstrated for the oxidation of a more complex alcohol like 5α-cholestan-3β-ol. The resulting 5α-cholestanone (**2n**) is a steroid involved in mammalian metabolism and can be used as platform for the synthesis of cholestane heterocyclic derivatives.[45,46]

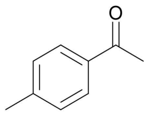
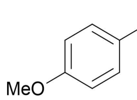
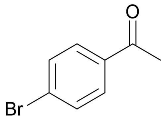
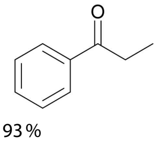
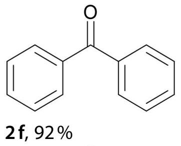
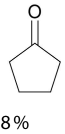
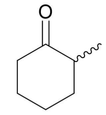
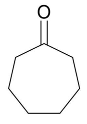
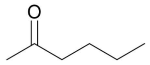
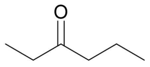
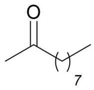
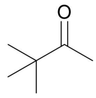
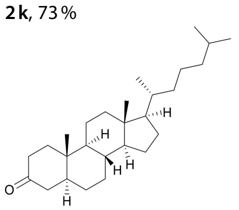
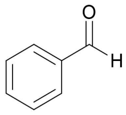
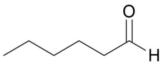
An initial attempt under the above-mentioned optimized conditions proved rather unsuccessful due to the poor solubility of the starting material, as only 12% of **2n** was isolated after reaction. Nevertheless, addition of toluene increased the yield up to 46%. A couple of primary alcohols were also tested, namely benzyl alcohol (**1o**) and 1-hexanol (**1p**). However, very low formation of the corresponding aldehyde products **2o**–**p** was observed in both cases.

With a TON up to 6025, the Cu(II)@10%CatMP-1 reached an activity higher than that reported for an highly active molecular diphenoxo-bridged dicopper catalyst for the same reaction but under microwave irradiation (TON up to 2500).[47] The activity of Cu(II)@10%CatMP-1 is also more than one order of magnitude higher than those previously reported for heterogenized Cu-based molecular systems, either copper biscarbene complexes grafted on mesoporous silica (TON up to 194)[48] or copper phthalocyanine immobilized on graphene (TON up to 245) or on mesoporous silica (TON up to 203).[49] Note that all systems gave rise to comparable yields above 90%.

The stability and recyclability of the Cu(II)@10%CatMP-1 catalyst were assessed under the optimized conditions using 1-phenylethanol as substrate. The catalyst was recovered after reaction for consecutive uses and no significant decay of activity was observed over 10 reuses (Figure 1a). Over 10 consecutive catalytic cycles stable yields between 88 and 94 % of acetophenone were observed, corresponding to TON per cycle between approx. 5640 and 6025. To confirm the high

Table 2. Scope of the oxidation of various secondary alcohols.[a,b]



 **2 b**, 92 %	 **2 c**, 88 %	 **2 d**, 94 %
 **2 e**, 93 %	 **2 f**, 92 %	 **2 g**, 68 %
 **2 h**, 72 %	 **2 i**, 62 %	 **2 j**, 77 %
 **2 k**, 73 %	 **2 l**, 59 %	 **2 m**, 69 %
 **2 n**, 12 %/46 %[c]	 **2 o**, 6 %	 **2 p**, < 1 %

[a] Reaction conditions: alcohol **1 b**–**p** (0.5 mmol), TBHP (2 equiv.), Cu(II)@10 %CatMP-1 (25 ppm Cu; ca. 0.016 mol % Cu), 70 °C, 12 h. [b] Isolated yield.
[c] Toluene (0.5 mL) was added.

stability of the catalyst, we also performed recycling experiments for a much shorter reaction time of one hour. Again, stable, albeit lower yields between 38 and 43 % were observed over 4 consecutive cycles (Figure S9). The yields correspond to TOF at the initial period of the reaction (≤ 1 h) of 2.4–$2.8 \cdot 10^3\,h^{-1}$, comparable to the activities for homogeneous complexes 1.2–$7.6 \cdot 10^3\,h^{-1}$.[47]

ICP-OES analysis also showed no detectable leaching of Cu in solution during all runs. In parallel, a hot filtration test was performed after 1 hour of reaction at 45 % yield, and no additional acetophenone was formed by the end of the reaction (Figure 1b). This demonstrates the truly heterogeneous nature of the polymer-based copper catalyst.

X-ray absorption near-edge structure (XANES) spectra, collected for Cu(II)@10 %CatMP-1 before reaction and after one and ten runs, evidenced Cu(II) species with square planar coordination in the fresh as well as the two spent samples (Figure 2a and Figure S7). The precise position of the absorption edge is slightly shifted to lower energy for the Cu(II)@10 % CatMP-1 samples in comparison to $Cu(OAc)_2$, indicating a slightly lower effective charge.[50] No changes occur after one cycle of reaction (dashed blue line in Figure 2a), but after 10 cycles, a very slight shift of the edge towards higher energies and the growth of first resonance occur while copper remains at Cu(II) oxidation state. The Cu(II) oxidation state is further confirmed by XPS spectroscopy. XPS spectra recorded on fresh and spent catalyst only show signals for Cu(II) at approx. 935 eV ($2p_{3/2}$) and 954 eV ($2p_{1/2}$) together with their characteristic and pronounced satellite peaks (Figure S8, for further discussion see SI).[51–54] Cu(I) or Cu(0) species with their close shell d^{10} configuration, will not give rise to those satellites which are assumed to involve a ligand-to-metal electron transfer, requiring partially occupied metal *d* orbitals.[53]

In Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) data, a small increase of intensity of the first-shell contribution is visible (Figure 2b) for the reacted catalyst, which corresponds to the change in the number of oxygen neighbors, $N_{Cu\text{-}O}$ from 3.6 to 3.9 (see Table S4). In summary, the combination of XANES, EXAFS and XPS spectra demonstrate that there are no Cu containing clusters or nanoparticles (Cu^0, Cu_2O, CuO), the Cu remains in the oxidation state +II and remains atomically dispersed in a square planar coordination by four ligand atoms,[55] even after 10 catalytic cycles.

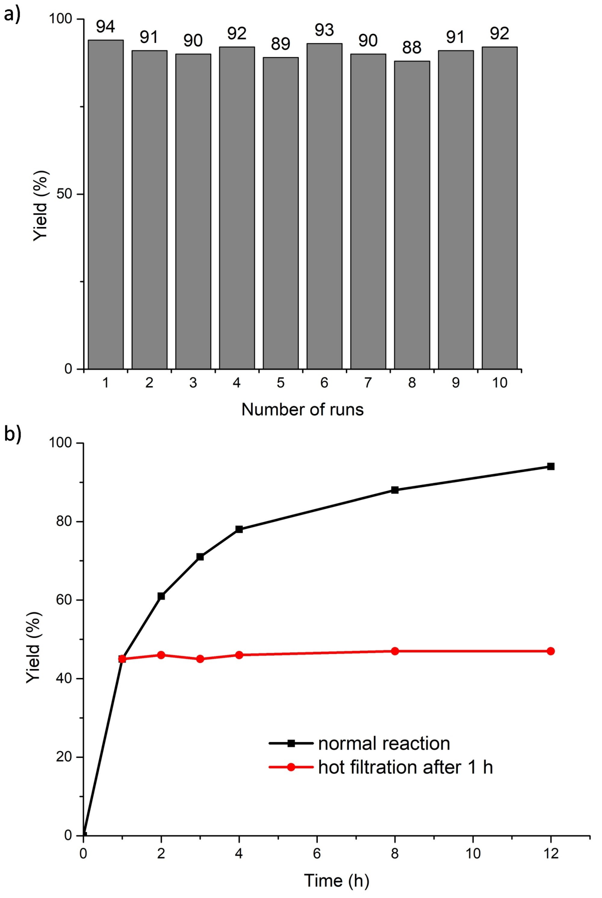
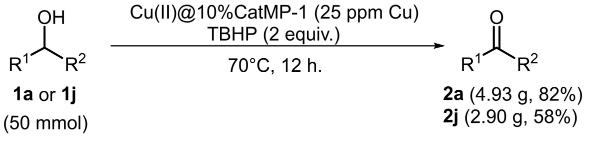


Figure 1. (a) Catalytic activity of Cu(II)@10 %CatMP-1 (25 ppm) in 1-phenylethanol oxidation to acetophenone over 10 runs. (b) Comparison between the model reaction under optimal conditions (black) and with the catalyst removed after 1 h (red).

Finally, we demonstrated that this heterogeneous catalytic system was also easily applicable to larger scales for the conversion of 1-phenylethanol **1 a** and 2-hexanol **1 j** (Scheme 2).

When employing 50 mmol of starting material, Cu(II)@10% CatMP-1 performed as well as under standard testing conditions (see Tables 1 and 2) with respectively 82% and 58% yield, giving access to 4.9 g of acetophenone **2 a** and 2.9 g of 2-hexanone **2 j** corresponding to productivities of 192 (**2 a**) and 112 g (**2 j**) product per g of solid catalyst. ICP-OES analysis of the supernatant after the large-scale reactions also showed no detectable Cu leaching into the liquid phase.



Scheme 2. Gram-scale oxidation of **1 a** and **1 j**.

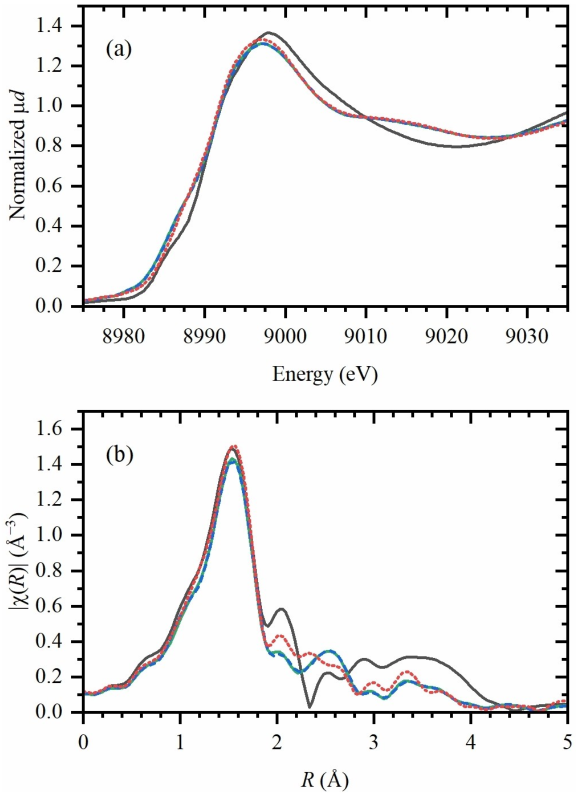


Figure 2. XANES (a) and FT-EXAFS (b) data for copper (II) acetate (solid black), fresh Cu(II)@10 %CatMP-1 (solid green), Cu(II)@10 %CatMP-1 after 1 cycle (dashed blue), and Cu(II)@10 %CatMP-1 after 10 catalytic runs (dotted red).

Conclusion

In conclusion, we have designed novel catechol-based porous polymers as porous macroligands for the heterogenization of molecular Cu complexes. The resulting materials showed outstanding stability and activity for the catalytic oxidation of secondary alcohols in the presence of TBHP as oxidant, with Cu loading down to the ppm level to reach TONs up to 6025. The truly heterogeneous Cu(II)@10 %CatMP-1 catalyst was recycled over 10 runs without notable loss of activity or Cu leaching. The well-defined Cu-catechol coordination has been evidenced by EPR and X-ray absorption spectroscopies, confirming the single-site character of the Cu active sites within the porous polymer even after recycling. Finally, the scalability of this novel heterogeneous catalytic system has been demonstrated with the gram-scale preparation of a couple of substrates keeping its high productivity. Together these results further evidence the wide applicability of heterogenous catalysts based on porous solid macroligands.

Experimental Section

10 %CatMP-1 catalysts synthesis: For a typical synthesis, 100.0 mg (0.67 mmol) 1,3,5-triethynylbenzene, 26.8 mg (0.10 mmol) 4,5-dibromobenzene-1,2-diol, 372.4 mg (0.90 mmol) 4,4′-diiodobiphenyl and 15.5 mg (13 μmol) Pd(PPh$_3$)$_4$ were added to a flame dried Schlenk tube inside a glovebox. The Schlenk tube was sealed with a silicone septum. Outside the glovebox, 12 mL of anhydrous DMF and 6 mL of anhydrous NEt$_3$ were added and the Schlenk tube was placed in an oil bath preheated to 100 °C. The reaction mixture was stirred at 100 °C for 24 h. After the mixture had been cooled to room temperature the yellow solid was subjected to purification by Soxhlet extraction using CHCl$_3$ for 6 h and using MeOH overnight. The yellow solid was dried at 80 °C under vacuum. Then, 56 mg of 10%CatMP-1 and 1.7 mg (9 μmol) of copper(II) acetate were added to a glass vial under inter atmosphere. To the mixture 3.5 mL of degassed methanol and 0.5 mL of degassed triethylamine were added and the suspension was stirred for 3 d at 50 °C. The supernatant was removed by centrifugation and the solid washed with anhydrous MeOH for 2 days (exchange of MeOH every 12 h). The solid was dried under reduced pressure first at room temperature, then at 80 °C. Typical yield: 240 mg.

Catalysis: A 10 mL crimp-cap vial was loaded with the secondary alcohol (0.50 mmol), TBHP (5–6 M in decane, 1.00 mmol) and Cu(II)@10%CatMP-1 (25 ppm) under air. The mixture was heated at 70 °C for 12 h. After cooling to room temperature, the reaction media was centrifuged and the liquid supernatant was isolated for purification over column chromatography. For the recycling experiments, the solid was simply recovered after centrifugation, washed with 4×2 mL EtOH and dried overnight at 80 °C under vacuum before being used again for the next run.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: alcohol oxidation · catechol · copper · heterogeneous catalysis · porous polymer

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