



A room temperature catalyst for toluene aliphatic C–H bond oxidation: Tripodal tridentate copper complex immobilized in mesoporous silica



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ABSTRACT

A tripodal tridentate copper(II) complex, **CuImph** (**Imph** = bis(4-imidazolyl methyl)benzylamine), is synthesized to mimic the active site of copper enzymes that mediate the oxidation of aliphatic C–H bonds under mild condition. By immobilizing the model complex in the nanochannels of functionalized mesoporous silica nanoparticles (MSNs), we observe the formation of a stable bis- μ -oxo species ($[\{\text{Cu}^{\text{II}}\text{Imph}\}_2(\mu\text{-O}^2-)_2]^{2+}$) in the presence of dioxygen or air at ambient temperature. The dioxygen-activated **CuImph**@MSN samples show high reactivity and selectivity toward toluene aliphatic C–H bond oxidation, converting the toluene initially to benzyl alcohol and subsequently to benzaldehyde as the major product in a kinetic consecutive reaction. No evidence for benzoic acid is obtained, unlike the over-oxidation typically associated with present-day industrial processes operating at high temperatures. In addition, the process is self-sustaining without the requirement for a sacrificial reductant to drive the catalytic turnover. The catalyst can be fully recovered and re-used for several cycles without decay of activity.

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1. Introduction

The catalytic oxidation of C–H bonds of hydrocarbons to selective oxygenated products under mild conditions is a major challenge. Many industrial productions of feedstocks and chemical intermediates involve partial oxidation processes [1,2]. For example, the oxidation of toluene to benzaldehyde is industrially important because benzaldehyde is a versatile intermediate in the chemical industry of dyes, perfumes, and pharmaceuticals. Benzaldehyde is also routinely used as an almond flavoring in the food industry. In fact, the partial oxidation of toluene to benzaldehyde is one of the most intensively investigated case studies for the design and performance of complex oxidation reaction systems [3,4].

For greener chemistry, the selective oxidation of toluene with dioxygen to produce benzaldehyde would be very desirable [5]. A drawback of existing methods of oxidizing toluene is the propensity to over-oxidation of the benzaldehyde to benzoic acid or benzoates [4–8]. At present, the most important industrial source of benzaldehyde comes from the oxidation of toluene as a sidestream

in the production of benzoic acid using Amoco chemistry [4], and by Br-promoted radical auto-oxidation [9]. Benzaldehyde is also prepared by hydrolysis of benzyl chloride [10]; however, traces of chlorine inevitably exist in the product limiting the utility of this process. Catalysts using metal oxides (or mixed oxides) often operate at high temperatures under conditions in which it is quite difficult to control the reactivity of the lattice oxygen [6,7,11]. Recently developed bimetallic PdAu catalysts to mediate the air oxidation of toluene do give good activity at the relatively mild temperature of 160 °C [12,13]. However, good selectivity and high conversion of benzaldehyde are still not achievable due to over-oxidation. Thus, even though present-day industrial sources of benzaldehyde are sufficient to cover its demand, a room temperature process that can oxidize toluene to benzaldehyde directly without over-oxidation is still of interest from a fundamental point of view as well as to promote greener chemistry.

Many copper metalloenzymes in nature facilitate very selective oxygen insertion into the C–H bonds of hydrocarbon under mild conditions. Thus, copper complexes mimicking the active sites of metalloenzymes that catalyze oxidation reactions have attracted great interest recently [14–21]. Typically, the active site in each of these metalloenzymes comprises a copper(I) cofactor that can be activated by dioxygen to generate an intermediate capable of oxidizing various substrates. So far, numerous types of $\text{Cu}_n\text{-O}_2$

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complexes have been prepared and characterized to elucidate possible reactive intermediates and to propose reaction mechanisms that could be exploited for the oxidation of aliphatic C–H bonds [15,16,22,23]. In principle, the rational design of ligands to modulate the dioxygen chemistry and to tune steric access of the substrates could give more precise control of the catalytic activity. To date, most of the reported copper–dioxygen complexes have been handled at low temperatures (*ca.* $-80\text{ }^{\circ}\text{C}$) to perform an internal ligand hydroxylation reaction [24–28] or an exogenous substrate oxidation reaction that yields a single turnover [29–33]. Truly continuous catalytic turnover is still rare in the selective oxidation of hydrocarbons using small copper complexes. In contrast, with native enzymes, steady and selective oxidation with high stability at room temperature is the norm. Thus, in recent years, much effort has been spent to develop strategies and methodologies to enhance the catalysis by stabilizing the copper–dioxygen interactions at room temperature, but few of them are successful [34–36]. For instance, Schindler and co-workers [37] reported the air-stable dicopper(II)- μ -1,2-(end-on)-peroxo $\{\text{Cu}^{\text{II}}-(\text{O}_2^{2-})\}(\text{BPh}_4)_2$ complex, in which the cationic dicopper complex is completely shielded by sterically hindered tetraphenylboron (BPh_4^-) anions. Indeed, this copper-peroxo complex is stable at room temperature and is capable of catalyzing the toluene oxidation reaction under heterogeneous catalysis condition, but the recovery and re-use of the copper complex remain to be addressed [37]. Guillard and co-workers [38] have demonstrated that the encapsulation of the copper complex into a silica framework can facilitate the stabilization of the copper–dioxygen adduct at room temperature and allow the site to stay intact even after many O_2 binding cycles. This stable oxygenated dicopper model compound would have been an excellent system to mimic the active site of one of the copper enzymes mentioned earlier, but its utility for catalytic applications at room temperature remains to be evaluated.

Even though there have been numerous model inorganic complexes prepared to mimic natural enzymes for the oxidation of hydrocarbons [34–36], few works have attempted to integrate a scaffold similar to the protein backbone to sequester the complex in the design of the catalyst for the reaction in a homogeneous solution. It is well known that the protein backbone in enzymes plays important roles in site-isolation, nanoconfinement and substrate channel(s) to facilitate a specific catalytic action. We believe that this design feature is essential if the model system is to mimic the structure and reactivity of a metalloenzyme. In this work, we use the nanopores of mesoporous silica to play the role of the scaffold.

Mesoporous silica nanoparticles (MSNs) possess a rigid framework that can provide a protective shield to stabilize the oxygenated reactive species. The MSNs are endowed with certain unique properties that are particularly suitable for immobilizing small biomimetic model compounds for chemical catalysis, including large surface area, controllable geometric parameters, and a modifiable surface, to accommodate the types and sizes of molecules that can penetrate them [39–41]. With a particle size of $\sim 100\text{ nm}$, MSNs can be suspended in solution very well without strong light scattering so that solution spectroscopic methods can be applied to interrogate the MSNs. Further, we can exploit these properties to internally decorate the mesopores [42] encompassing the biomimetic inorganic complex with the desired enzymatic functionality [39–41,43]. The deployment of MSNs also facilitates their separation from the liquid phase (by centrifugation) and re-use of the metal complexes in the catalytic processes. Therefore, model compounds immobilized on MSNs may provide a feasible route to perform efficient catalytic reactions mimicking native enzymes.

In this study, we report the design and synthesis of a tripodal tridentate histidine-like copper(II) complex **Culmph** (**Imph** = bis(4-imidazolyl methyl)benzylamine) to mimic the active

site of a native copper enzyme in performing the aliphatic C–H bond activation under mild conditions. The model complex exhibits a four-coordinate distorted square-planar geometry with the N3 donor set provided by the ligand and a coordinated acetonitrile molecule. In a preliminary study applying **Culmph** to the oxidation of toluene in a homogeneous solution, we found that the catalysis is limited to low temperatures ($-80\text{ }^{\circ}\text{C}$) and gives low product yields (8% benzaldehyde), and moreover, the catalyst could not be recovered due to the decomposition of the copper complex [15,44,45]. Herein we show that the **Culmph** can be efficiently loaded on to the nanochannels of functionalized MSNs to develop a heterogeneous catalyst for toluene oxidation. The MSN-immobilized copper complex is transformed into a stable dicopper(III)-bis- μ -oxo species upon activation of the **Culmph** by dioxygen, and the copper–oxygen adduct mediates the catalytic conversion of toluene into benzyl alcohol and benzaldehyde at room temperature. We have studied the process in two solvent systems: tetrahydrofuran (THF) and neat toluene. In-depth characterization of the functionalized MSNs and the **Culmph**@MSNs (**Culmph** complex immobilized in the mesoporous silica nanoparticles) has been undertaken, and studies of the catalytic properties of the **Culmph**@MSNs are performed on a dilute solution of toluene in THF solvent. To evaluate the efficacy of the system for possible industrial applications, its catalytic activities have been also investigated in neat toluene. Finally, we have prepared aluminum-substituted mesoporous silica nanoparticles (Al-MSNs) to promote the surface acidity of the MSNs [46,47]. We find that the acidity facilitates the selectivity of the oxidation reaction and optimizes the total yield of the final product benzaldehyde.

2. Experimental

2.1. Materials

All solvents and chemicals used in the studies were of commercially available analytical grade, if not mentioned otherwise. Solvents for air-sensitive reactions were distilled under argon.

2.2. Synthesis of the ligand **Imph**

$\text{NaBH}(\text{OAc})_3$ (34.97 g, 165 mmol) was added to a THF solution (100 ml) containing imidazole-4-carboxaldehyde (**Im-CHO**, 5.29 g, 55.0 mmol) and benzylamine (5.89 g, 55.0 mmol). The suspension was stirred overnight; then acetic acid (3.30 g, 55.0 mmol) and additional **Im-CHO** (5.29 g, 55.0 mmol) were added to the solution. After 10 h of further stirring, the solution was adjusted to basic by adding NaOH solution, and the THF was removed under reduced pressure. A saturated NaCl aqueous solution (50 ml) was added to the residue, and the oily layer was separated and extracted twice with dichloromethane (100 ml). The combined chloroform extracts were dried over MgSO_4 . After filtration, the dichloromethane was evaporated under reduced pressure to give a colorless oil that was dissolved in an ethyl acetate/diethyl ether mixture. The solution was allowed to stand overnight to give a colorless powder. The calculated reaction yield was 75% (10.2 g). The characteristic ^1H NMR (CDCl_3 , 400 MHz) spectra gave δ (ppm) = 3.50 (2H, s, CH_2 of benzyl), 6.92 (2H, s, 5-H of imidazole), 7.20 (1H, t, *p*-H of benzyl), 7.30 (2H, t, *m*-H of benzyl), 7.40 (2H, d, *o*-H of benzyl), and 7.57 (2H, s, 3-H of imidazole).

2.3. Synthesis of **Culmph**

A portion of Et_3N (1.67 ml, 12.0 mmol) was added to an THF/ CH_3CN mixture solution (20 ml) containing **Imph** (2.27 g, 4.1 mmol) and $\text{Cu}^{\text{II}}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.49 g, 4.1 mmol) with stirring

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