Direct oxygen insertion to C-H bond by enzyme-mimic copper complexes

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Abstract:

In this presentation, I will discuss the use of enzyme mimic copper complexes which was confined in mesoporous silica as a nanoreactor. The catalytic system has the advantages of (1) controlled C-H activation by O2, (2) concentrated substrate and reactants such that reaction rate at room temperatures are accelerated. Two examples will be shown in detailed catalytic mechanism studies, (1) methane oxidation to methanol, and (2) selective oxidation of toluene to benzyl alcohol and benzaldehyde.

Keywords: Metahne, Toluene, Oxidation, Copper complex, Mesoporous

1. Introduction

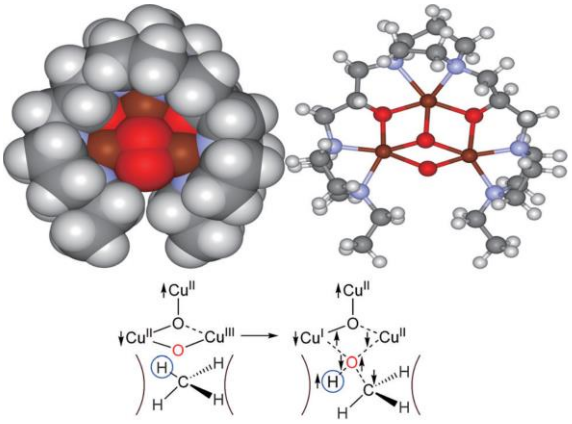
The exquisite selectivity and excellent activity of oxidative transformation performed by copper enzymes have been sources of inspiration for chemists trying to emulate their catalytic functions. Synthesis of model compounds to mimic the active site of copper enzyme has been an active area of research. However, in these model compounds in homogeneous solution the necessary function of the protein backbone is usually not considered. Protein backbone plays important roles in site-isolation, nanoconfinement, and substrate duct to facilitate a specific catalytic action. A smart combination of enzyme mimetic complex and a nanostructured media, for mimicking protein skeleton, to optimize enzymatic functions would be most desirable.

A di-copper complex was used in direct oxidation of toluene to benzyl alcohol and benzaldehyde by oxygen at room temperature. The 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. Various functionalized Mesoporous silica nanoparticles were used as scaffold to encapsulate the complex. No additional sacrificial reductant is needed. This heterogeneous formulation of the dicopper cluster is capable of converting toluene into benzaldehyde with high catalytic efficiency and excellent product yields without over-oxidation at room temperature. The heterogeneous catalyst is also robust and re-usable. Detailed mechanistic study was performed to understand the catalytic steps.

A tri-coper catalyst is assembled by immobilizing into mesoporous silica nanoparticles the tricopper complex [CuICuICuI(7-N-Etppz)]1+, where 7-N-Etppz stands for the organic ligand 3,30-(1,4-diazepane-1,4-diyl)bis[1-(4-ethylpiperazine-1-yl)propan-2-ol] which is a biomimic complex of the enzyme monooxygenase. The tricopper cluster complex has been shown to mediate efficient methane oxidation without over-oxidation in homogeneous solution when the catalytic turnover is driven by hydrogen peroxide in acetonitrile. The turnover mechanism of the catalyst is similar between the two complexes in which molecular oxygen was directly involved in the oxidation.

2. Results and discussion

A tricopper complex was designed and synthesized to mimic monooxygenase, its catalytic turnover at room temperature is very high(TON > 150) and it can be reused without much change of catalytic activity.



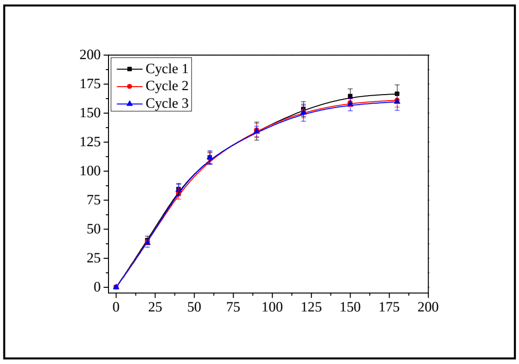
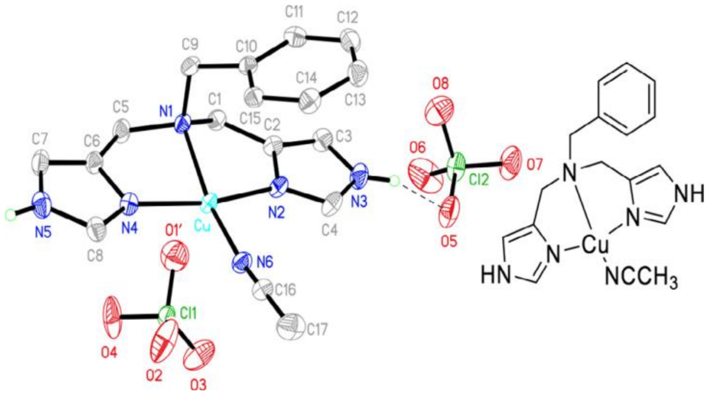


Fig. 1 Tricopper cluster for the oxidation of methane **Fig. 2** Turn overall of methane to methanol

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



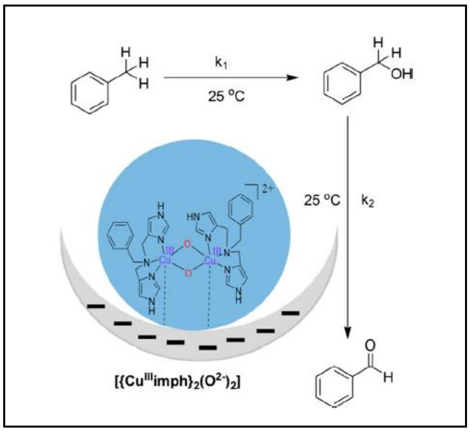


Fig. 3 The cationic part of [CuII(Imph)(CH3CN)](ClO4)2, **Fig. 4** Dimerization of CuIIImph with oxygen bridge as catalyst

CuIIImph

3. Conclusions

The heterogeneous formulation exhibits dramatically higher catalytic efficiencies and turnover numbers as compared to the homogeneous counterpart offering the most proficient catalyst for (1) selective conversion of methane into methanol at room temperature developed to date. (2) selective conversion of toluene to benzyl alcohol and then to benzaldehyde in a two-step mechanism. The terminal oxidant is O2.

References

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