The Development of Cu^I Complexes for Controlled Oxidation of Hydrocarbons by Dioxygen at Room Temperature: Harnessing the Second "O" Atom for Catalytic Turnover

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Abstract: Here we show the first example of a dicopper complex $Cu^{III}(\mu\text{-}O)_2Cu^{III}$ immobilized in mesoporous silica nanoparticles capable of functioning like a "dioxygenase" in hydrocarbon oxidation. We have undertaken a mechanistic study to clarify how this catalytic conversion is accomplished without the input of sacrificial reductants. We show that a second molecule of dioxygen (O_2) is involved, forming an O_2 complex with the $Cu^{II}(\mu\text{-}O)Cu^{II}$ intermediate to give a species with the $[Cu_2O_3]^{2+}$ core, which then mediates the transfer of the remaining O atom of the original O_2 molecule to the organic substrate to complete the catalytic turnover.

Keywords: aliphatic C−H bond activation, single-turnover experiments, copper dioxygenase model, mesoporous silica nanoparticle

1. Introduction

The rich chemistry of copper complexes with O_2 is often exploited to develop oxidation catalysts for controlled oxidation of hydrocarbons and other organics. Typically, these systems mimic the behavior of copper monooxygenases in their oxidation chemistry. For instance, a tricopper cluster complex mimic the active site of the particulate methane monooxygenase, which can catalyze the conversion of methane into methanol efficiently under ambient conditions.[1-3] Recently, we have reported on a dicopper system[4] (a $Cu^{III}(\mu\text{-}O)_2Cu^{III}$@MSN-TP-3) that can mediate the catalytic conversion of toluene into benzaldehyde by O_2, in which the oxidizing power of both O atoms is harnessed for catalytic turnover. Here, we describe a kinetic and mechanistic study on the toluene oxidation in order to develop an understanding of how this dicopper system carries out this interesting and unique chemistry. These findings are augmented by insights garnered from density functional theory (DFT) modeling.

2. Experimental

All the preparations of the materials (including **CuImph** complex, MSN-TP-3) have been previously reported.[4] The MSN-TP-3 was synthesized using tetraethylorthosilicate as a precursor under basic conditions. In order to facilitate anchoring of the positively charged tricopper complexes, the MSN were functionalized by 5% anionic 3-(trihydroxysilyl)-propylmethyl-phosphonate (TP) to generate a negatively charged surface within the MSN channels. The **CuImph** complex was immobilized in the nanochannels of silica by the ion-exchange method via electrostatic coulomb attraction. The loading of the copper complex in the nanoparticles was determined by measuring the copper content by ICP-MS and C, N elemental analysis. Single turnover experiments were performed to prepare the dicopper-oxo intermediate **1**, **2**, and **3** for spectroscopic characterization.

3. Results and discussion

The reaction scheme for the catalytic turnover of toluene oxidation is shown in Figure 1. Two of the immobilized **Cu^{II}Imph** are reduced by sodium ascorbate and follow by O_2 activation to generate the Cu^{III}(μ-

$O)_2Cu^{III}$ species **1** in the nanochannels of the MSN-TP-3. The single turnover experiments demonstrate that the $Cu^{III}(\mu\text{-}O)_2Cu^{III}$ species **1** can catalyze the oxidation of toluene to benzyl alcohol *via* O-atom transfer and then convert into the relatively inert $Cu^{II}(\mu\text{-}O)Cu^{II}$ species **2**. In the presence of excess O_2, however, the latter is rapidly activated to give the significantly more reactive $Cu^{III}(\mu\text{-}O)((\mu\text{-}1,2)\text{-peroxo})Cu^{III}$ species **3,** which can oxidize the benzyl alcohol to benzaldehyde, and produce a stoichiometric amount of H_2O. After that, dicopper catalyst has reverted back to the $Cu^{III}(\mu\text{-}O)_2Cu^{III}$ species **1** upon completion of the turnover cycle, as confirmed by UV-Visible spectrum.

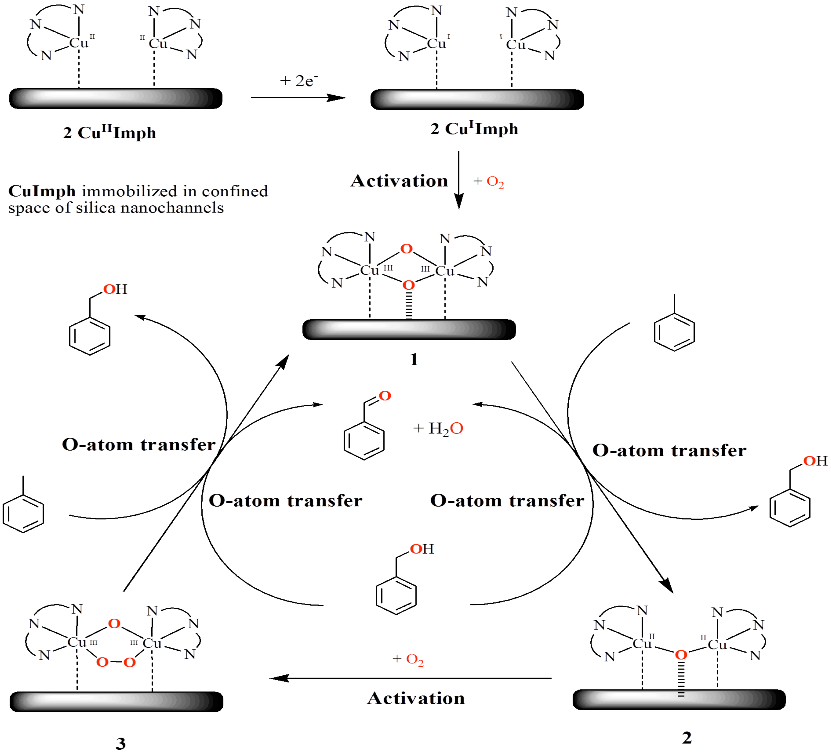

Figure 1. The reaction scheme for the toluene oxidation reaction mediated by the **CuImph**@MSN-TP-3 catalytic system.

4. Conclusions

In summary, we have used a catalytic system consisting of a mesopore-immobilized dicopper complex activated and bridged by O_2 for room temperature conversion of toluene into benzaldehyde to illustrate how it is possible to harness both O atoms for hydrocarbon oxidation. Through the pore-confinement effect, various stages of the oxygen-bridged dicopper complex can be stabilized and identified. These single-turnover experiments have allowed us to examine the details of the catalyst during turnover and to clarify how the "O" equivalents are being transferred from the activated dicopper cluster to the toluene substrate in the two kinetic steps. We have performed UV-Visible spectral measurements and EXAFS analysis, as well as EPR redox titrations, on the intermediates in the catalytic cycle during the turnover to link the chemistry occurring at each step of the cycle to the structure of the dicopper-oxo species. By way of this kinetic/mechanistic study, we have shown how it is possible to convert the $Cu^{III}(\mu\text{-}O)_2Cu^{III}$ catalytic system from a "monoxygenase" into a "dioxygenase". Insights into this chemistry have been provided by DFT modeling.

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