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Theoretical Study of Methane Activation at the Dicopper Site of pMMO

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Introduction In the present study we consider the reactivity of a dicopper species of (μ-oxo)(μ-hydroxo)$Cu^{II}Cu^{III}$, which can be derived from H-atom migration or proton-coupled electron transfer associated with the tyrosine residue in the second coordination sphere of the dicopper site of pMMO. The X-ray structure of the dicopper site is shown in Figure 1(a). In the previous studies we proposed a possible $Cu^{I}Cu^{II}$ peroxo species, shown in Figure 1(b), as a model of this active site. The $Cu^{I}Cu^{II}$ peroxo species is formed from the original reduced $Cu^{I}Cu^{I}$ state after the addition of an oxygen molecule and the transfer of one electron. We assumed that Glu35 is coordinated to one of the copper ion, as shown in Figure 1(b). Acetate is used as a model of the Glu35 residue and imidazole molecules as a model of the three His residues. In the present study we consider a peroxo species with $Cu^{II}Cu^{II}$ oxidation state containing one Tyr residue, one Glu residue, and three His residues, as shown in Figure 1(c). Here we focus on the role of the Tyr374 residue outside the first coordination sphere of the dicopper site.

Computational method We used the B3LYP* functional with 15% Hartree-Fock exchange instead of 20% in the B3LYP functional, the (16s10p6d) primitive set of Wachters-Hay supplemented with one polarization f-function (α = 1.44 for Cu) for the Cu atoms, and the D95** basis set for the H, C, and O atoms.

Results The acceptance of one electron by the Cu_2O_2 core is important to the methane activation by pMMO. The H-atom transfer discussed in the present work is equivalent of the transfer of an e^- and an H^+ to the bis(μ-oxo)$Cu^{III}Cu^{III}$ species; the (μ-oxo)(μ-hydroxo)$Cu^{II}Cu^{III}$ species as well as the bis(μ-oxo)$Cu^{II}Cu^{III}$ species shows high reactivity to methane. The H-atom transfer is responsible for the O-O bond activation and the formation of the (μ-oxo)(μ-hydroxo)$Cu^{II}Cu^{III}$ species in pMMO. DFT calculations demonstrated that the conversion of methane to methanol takes place in a two-step manner. The first transition state that leads to the C-H bond dissociation of methane requires an activation energy of 16.1 kcal/mol relative to the reactant complex.

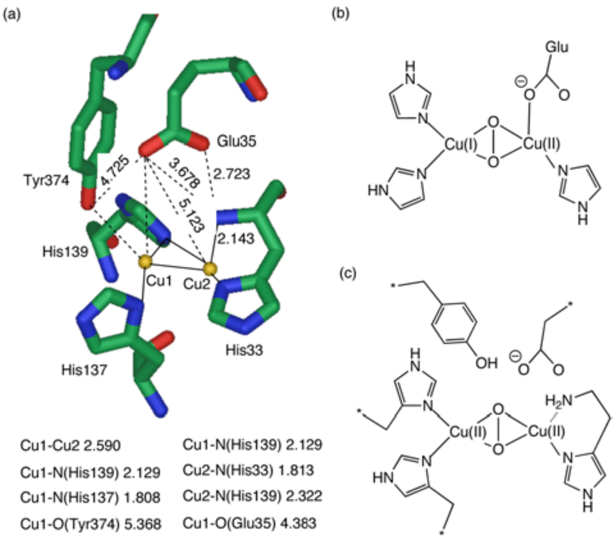

Figure 1. (a) X-ray structure and computational models of the active site: (b) a $Cu^{I}Cu^{II}$ peroxo species and (c) a $Cu^{II}Cu^{II}$ peroxo species (this work). Distances are in angstrom (Å).