Copper-Oxygen Chemistry in Methane Oxidation

Chang Cui Literature Seminar 11/05/2013

Particulate methane monooxygenase (pMMO) and soluble methane monooxygenase (sMMO) are metalloenzymes able to activate C-H bonds (104 kcal mol^{-1}) and can affect the selective oxidation of methane into methanol[1]. sMMO is a dinuclear non-heme iron enzyme expressed at copper deficiency, and its structure and mechanism are well characterized[1]. In contrast, corresponding information about the pMMO counterpart is still being determined.

M. capsulatus (Bath) pMMO is a homotrimer and each protomer is composed of three subunits, pmoA, pmoB and pmoC. A monocopper center and a dicopper center are present in pmoB and a monozinc center is present within the transmembrane helices[2]. Not until 2010 was the active site identified based on a study of the copper dependent activity of the recombinant soluble pmoB (spmoB) subunit. Restoration of apo pMMO activity is optimized at two to three equivalents of copper. A recombinant protein containing only the undisturbed dicopper center retains catalytic activity, leading to the conclusion that the dicopper center in the pmoB subunit is the active site[3].

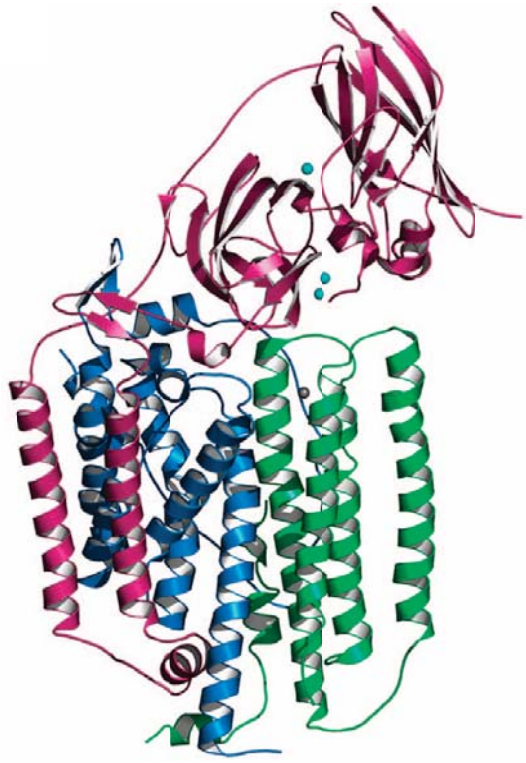


Figure 1. Structure of the *M. capsulatus* (Bath) pMMO protomer[4].

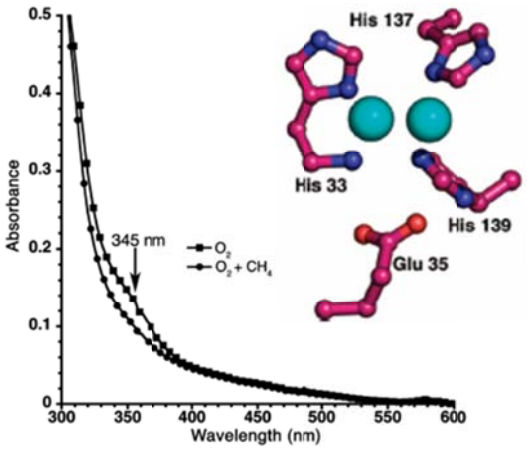
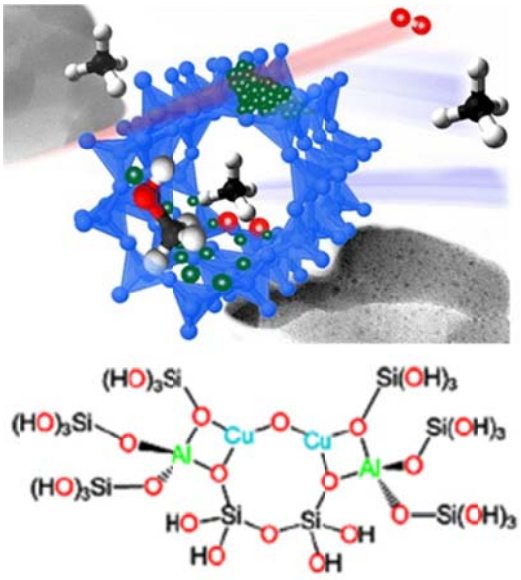


Figure 2. Reactivity of 345 nm species with methane. (Insert) Structure of the dicopper center in spmoB[5].

Spectroscopic studies of solubilized pMMO and spmoB have probed the mechanism of oxygen binding and methane activation[5]. When pMMO and spmoB are reduced and then exposed to oxygen, an absorption at 345 nm appears, which disappears after incubation with methane. This result indicates that the 345 nm species is likely to be responsible for pMMO activity. The spectroscopic resemblance with type 3 copper centers suggests a μ-(η^2:η^2) peroxo dicupric core (A).

Certain inorganic compounds are also able to oxidize methane, including Cu-ZSM-5[6]. UV visible and resonance Raman spectra suggest that a bent mono-(μ-oxo) dicupric species (B) is present. DFT calculation reproduces the spectroscopic and kinetic features and suggests that hydrogen atom abstraction is the rate determining step[6-7].



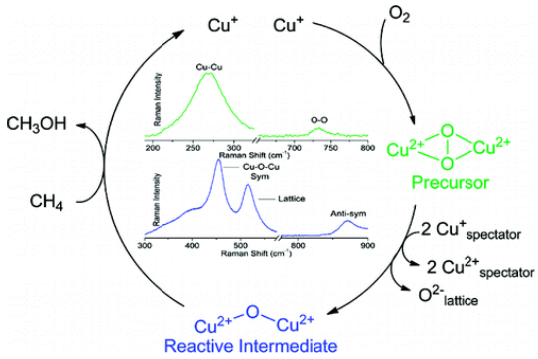


Figure 3. (uper) Selective oxidation of methane catalyzed by ZSM-5. (lower) proposed bent mono-(μ-oxo) dicupric core[6].

Figure 4. Summary of catalytic cycle[8].

However, more detailed spectroscopic and mechanistic study of Cu-ZSM-5 reveals that a μ-(η^2:η^2) peroxo dicupric core related to species A in pMMO is a precursor for the reactive intermediate B, although the latter has never been captured in biological system[8]. A catalytic cycle for Cu-ZSM-5 is proposed as following: a dicuprous center reduces oxygen forming A, which is subsequentially reduced by spectator cuprous ions, converted to B, which oxidizes methane regenerating dicuprous states[8].

In summary, the active site of pMMO and Cu-ZSM-5 have been identified as dicupric centers, and preliminary assessments of the mechanism have been made based on investigations in both protein and inorganic complex. The active site in pMMO is conclusively demonstrated to be a dicopper center in pmoB subunit. In Cu-ZSM-5, a μ-(η^2:η^2) peroxo dicupric core is presumably a precursor to a bent mono-(μ-oxo) dicupric

species, the latter of which abstracts a hydrogen atom from methane leading to a selective conversion to methanol.

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