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Oxygen precursor to the reactive intermediate in methanol synthesis by Cu-ZSM-5

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Oxygen activated Cu-ZSM-5 has been recently shown to selectively oxidize methane to methanol at low temperatures¹ by means of a mono(μ -oxo)dicopper(II) species, $[\text{Cu}_2\text{O}]^{2+}$.² The geometric and electronic structure of this reactive core was unambiguously assigned using resonance Raman (rR) spectroscopy and density functional theory (DFT) and represents a new species in inorganic chemistry. DFT calculations reproduced the low reaction barrier and kinetic isotope effect (KIE) measured experimentally and showed that the low barrier for H-atom abstraction from CH_4 reflects the strong $[\text{Cu}_2\text{O-H}]^{2+}$ bond in the initial product and a frontier molecular orbital (FMO) that polarizes to an oxyl (O^\cdot) along the reaction coordinate. Interestingly, a binuclear Cu site has recently been demonstrated to be the reactive site in particulate methane monooxygenase (pMMO), an enzyme that also oxidizes methane to methanol.³ In this study we observe an oxygen precursor to the formation of the $[\text{Cu}_2\text{O}]^{2+}$ species in Cu-ZSM-5 and, using rR spectroscopy, define its structure as a side-on bridged μ -(η^2 - η^2) peroxo dicopper(II) core, $[\text{Cu}_2(\text{O}_2)]^{2+}$. Absorption and rR data show the conversion of $[\text{Cu}_2(\text{O}_2)]^{2+}$ into $[\text{Cu}_2\text{O}]^{2+}$, while O_2 temperature programmed desorption (O_2 -TPD) experiments provide insight into how this conversion occurs upon heating.

Na-ZSM-5 (VAW, Si/Al=12) samples were ion-exchanged with aqueous solutions of varied Cu(II)-acetate concentrations.⁴ The samples were initially calcined under O_2 at 450°C for 2h (5°C/min, 50ml/min), followed by He flow overnight (50ml/min). This treatment results in the auto-reduction of the Cu sites in Cu-ZSM-5.⁵⁻⁷ Fiber optic UV-vis spectroscopy was used to monitor spectral changes of Cu-ZSM-5 at ambient and elevated temperatures, and rR measurements were performed to obtain the electronic and geometric structure information regarding the Cu/ O_2 species in Cu-ZSM-5. MS was used to monitor the O-isotope distribution in O_2 -TPD experiments.

When pre-reduced Cu-ZSM-5 (He at 450°C; Cu/Al=0.5) was exposed to O_2 at room temperature (RT) an absorption band at $\sim 29,000\text{ cm}^{-1}$ is rapidly formed (Figure 1A). After ~ 2 min in O_2 flow, the intensity increase of this absorption band levels off. This band is also observed in a Cu-ZSM-5 sample with Cu/Al=0.3 and is essentially absent in samples with Cu/Al<0.2 (see Figures S1A and B). After full formation of the $29,000\text{ cm}^{-1}$ band, the sample was flushed in He to remove excess O_2 at RT. Subsequent heating of Cu-ZSM-5 (Cu/Al=0.3) in He atmosphere resulted in the UV-vis spectral changes shown in Figure 1B.

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Supporting Information Available: Experimental procedures, UV-vis and resonance Raman spectra of formation of precursor and conversion into reactive intermediate. This material is available free of charge via the Internet at <http://pubs.acs.org>

Starting at $\sim 175^\circ\text{C}$ and higher temperatures, the formation of the $22,700\text{ cm}^{-1}$ band, associated with the reactive $[\text{Cu}_2\text{O}]^{2+}$ core, is observed along with the parallel disappearance of the $29,000\text{ cm}^{-1}$ band. This occurs with heating in either He or O_2 atmosphere. The $[\text{Cu}_2\text{O}]^{2+}$ species has also been shown to form in the presence of N_2O at 100°C ,^{1,2} and, in fact, the $[\text{Cu}_2\text{O}]^{2+}$ core still forms even at RT with N_2O . However, unlike with O_2 , when pre-reduced Cu-ZSM-5 is exposed to N_2O at RT, no $29,000\text{ cm}^{-1}$ band is formed, and thus there is no formation of the precursor.

The rR spectrum of the oxygen precursor species formed at RT obtained with laser excitation at 363.8 nm ($27,473\text{ cm}^{-1}$) is shown in Figure 2A. Vibrational features are observed at 269 and 736 cm^{-1} that are not present using laser excitation outside of the $29,000\text{ cm}^{-1}$ band, proving that they are resonance enhanced by the species responsible for this absorption feature. When the RT treatment of the auto-reduced Cu-ZSM-5 sample is performed with isotope labeled $^{18}\text{O}_2$, the 736 cm^{-1} feature shifts to 695 cm^{-1} ($\Delta^{18}\text{O}_2=41\text{ cm}^{-1}$) while the 269 cm^{-1} feature is isotope insensitive. These vibrational frequencies and isotope perturbation pattern are characteristic of those of μ - $(\eta^2\text{-}\eta^2)$ peroxo dicopper(II) species.⁸ Thus, we assign the 736 and 269 cm^{-1} features to the O-O stretch ($\nu\text{O-O}$) and the Cu-Cu stretch ($\nu\text{Cu-Cu}$) of the μ - $(\eta^2\text{-}\eta^2)$ peroxo dicopper(II) moiety, respectively. The $29,000\text{ cm}^{-1}$ absorption band is thus assigned as a peroxo $\pi^*\sigma$ to Cu(II) charge transfer (CT) transition. Upon heating the rR sample, the 363.8 nm rR μ - $(\eta^2\text{-}\eta^2)$ peroxo dicopper(II) precursor features go away (Figure S3). In parallel, excitation at 457.9 nm ($21,834\text{ cm}^{-1}$) leads to the enhancement of the vibrational features in Figure 2B (see Figure S4 for comparison of 457.9 nm rR spectra of the RT precursor and the $[\text{Cu}_2\text{O}]^{2+}$ species). These have been assigned in reference 2 as the isotope sensitive, intense symmetric (456 cm^{-1}) and weak antisymmetric (870 cm^{-1}) stretching vibrations characteristic of the μ -oxo-bridged $[\text{Cu}_2\text{O}]^{2+}$ species. These results parallel the absorption changes and show that the side-on bridged peroxo dicopper(II) species converts to the $[\text{Cu}_2\text{O}]^{2+}$ species reactive in the selective oxidation of methane to methanol.

An important issue in this conversion is the fate of the second O atom as only one O atom remains in the reactive $[\text{Cu}_2\text{O}]^{2+}$ intermediate. The treatment of the reactive intermediate at temperatures above 350°C results in the disappearance of its characteristic $22,700\text{ cm}^{-1}$ absorption feature with release of O_2 . Thus, a second O atom recombines with the bridging O atom from the reactive intermediate, and through microscopic reversibility, the desorbing O_2 can contain information on the conversion of $[\text{Cu}_2(\text{O}_2)]^{2+}$ into $[\text{Cu}_2\text{O}]^{2+}$.

An O_2 -TPD study in He flow was performed after treatment of Cu-ZSM-5 with $^{18}\text{O}_2$ at 240°C . From our previous study, reaction of Cu-ZSM-5 and $^{18}\text{O}_2$ at 240°C results in formation of pure ^{18}O labeled reactive sites (i.e. $[\text{Cu}^{\text{II}}\text{-}^{18}\text{O}\text{-Cu}^{\text{II}}]^{2+}$).² Figure 3 follows the desorbing O_2 isotopes, $^{16}\text{O}_2$, $^{16,18}\text{O}_2$ and $^{18}\text{O}_2$, upon subsequent heating in He flow. Although the site was formed with pure $^{18}\text{O}_2$, little $^{18}\text{O}_2$ desorbs. In the temperature range where the $22,700\text{ cm}^{-1}$ band disappears (between 350°C and 420°C), corresponding to the loss of the $[\text{Cu}^{\text{II}}\text{-}^{18}\text{O}\text{-Cu}^{\text{II}}]^{2+}$ species, the ratio of $^{16,18}\text{O}_2/^{18}\text{O}_2$ released is greater than 10. This shows that the second ^{18}O atom initially present in the peroxo precursor does not recombine with the bridging ^{18}O atom of $[\text{Cu}_2\text{O}]^{2+}$ upon O_2 desorption. As shown in Figure 3, the majority of bridging ^{18}O recombines with ^{16}O , which originates from the zeolite lattice, resulting in dominantly $^{16,18}\text{O}_2$ desorption. This also indicates that the second ^{18}O atom does not form a second $[\text{Cu}^{\text{II}}\text{-}^{18}\text{O}\text{-Cu}^{\text{II}}]^{2+}$ species as this would result in desorption of $^{18}\text{O}_2$. A reference TPD experiment without the initial O_2 treatment at 240°C showed no O_2 desorption in this temperature region. The large fraction of $^{16}\text{O}_2$ observed in Figure 3 is thus not the result of destruction of the zeolite lattice. At higher temperature the fraction of desorbing $^{16,18}\text{O}_2$ atoms decreases and mainly $^{16}\text{O}_2$ desorbs. This represents migration-recombination through the zeolite lattice of abundantly present O atoms deposited on other

remote Cu sites in Cu-ZSM-5,^{4,9} resulting in isotope scrambling of the $^{16}\text{O}_{\text{lattice}}$ and ^{18}O .¹⁰⁻¹²

The high incorporation of lattice ^{16}O into O_2 desorbed from $[\text{Cu}_2^{18}\text{O}]^{2+}$ ($T < 420^\circ\text{C}$) indicates that the reverse occurs upon formation of the $[\text{Cu}_2\text{O}]^{2+}$ reactive species from the $[\text{Cu}_2(\text{O}_2)]^{2+}$ precursor. Thus, the high $^{16,18}\text{O}_2/^{18}\text{O}_2$ desorption ratio reflects the competition between newly formed ^{18}O lattice sites and equivalent and more prevalent ^{16}O lattice sites.

Two additional electrons are required to cleave the O-O bond of $[\text{Cu}_2(\text{O}_2)]^{2+}$. Experimental and computational data showed that the Cu's of the reactive intermediate are Cu^{2+} and not Cu^{3+} , and DFT calculations of an initial $[\text{Cu}_2\text{O}]^{4+}$ resulted in delocalization of the additional holes into the lattice, creating $[\text{Cu}_2\text{O}]^{2+}$ and an electron deficient lattice.² Also, the electron donor and acceptor capabilities of zeolite lattices have been demonstrated experimentally,¹³⁻¹⁵ indicating that spectator Cu^+ ions in ion-exchange sites can donate the electrons required to reduce the precursor and form the $[\text{Cu}_2\text{O}]^{2+}$ reactive species.

In summary, we have characterized a RT O_2 precursor in the formation of $[\text{Cu}_2\text{O}]^{2+}$, a reactive site capable of the low temperature, selective oxidation of methane to methanol in oxygen activated Cu-ZSM-5. In combination, UV-vis absorption and rR data show the precursor is a μ -($\eta^2:\eta^2$) peroxo dicopper(II) core (with an absorption band at $29,000\text{ cm}^{-1}$) and that this species converts directly into the $[\text{Cu}_2\text{O}]^{2+}$ reactive intermediate (with an absorption band at $22,700\text{ cm}^{-1}$). Scheme 1 presents a summary of this process. We propose that the spectator Cu^+ ions in the ion-exchange sites provide the required electrons to cleave the bridging peroxo O-O bond. $^{18}\text{O}_2$ -TPD experiments showed incorporation of the second ^{18}O atom into the zeolite lattice upon formation of the $[\text{Cu}_2\text{O}]^{2+}$ reactive intermediate. This study defines the mechanism of oxo-reactive site formation in Cu-ZSM-5. While the $[\text{Cu}_2\text{O}]^{2+}$ core has been shown to be highly reactive in methane oxidation, we are actively pursuing other reactive Cu/ O_2 species in oxygen activated Cu-ZSM-5, and are currently investigating the relative reactivity of the precursor and the $[\text{Cu}_2\text{O}]^{2+}$ intermediate.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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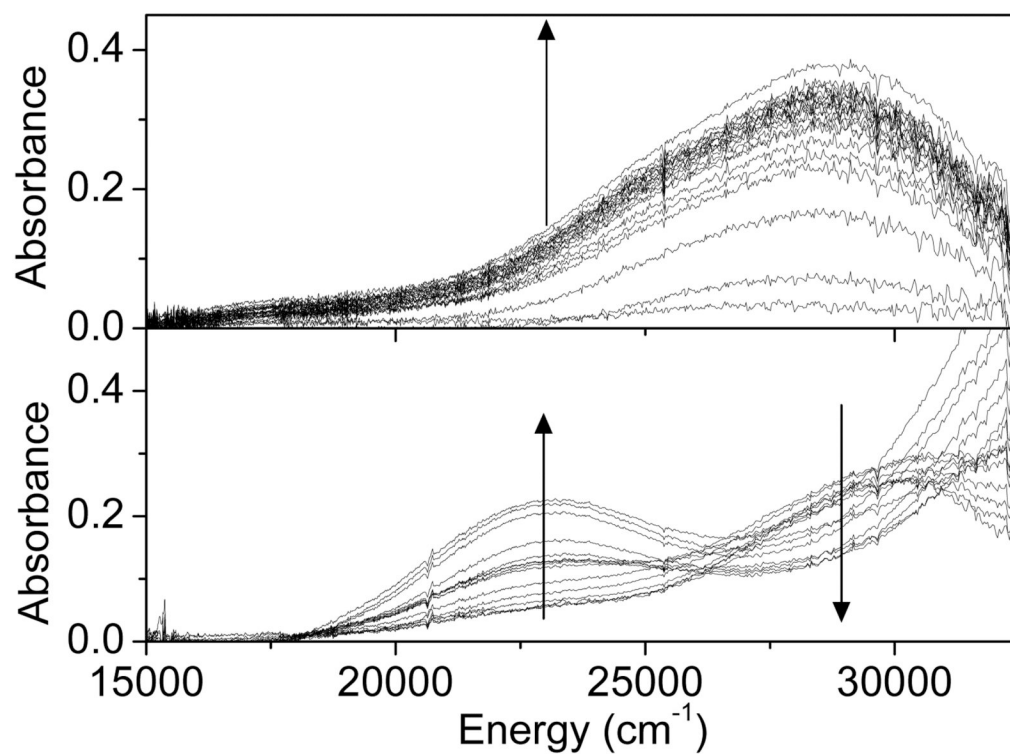
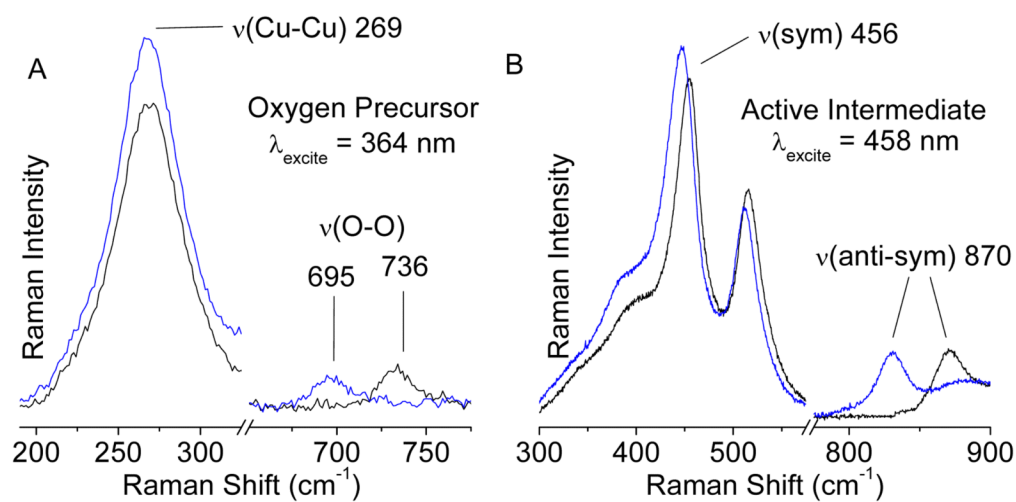


Figure 1. UV-vis absorption spectra of a pre-reduced Cu-ZSM-5 (in He at 450°C) during A) O₂ treatment at RT. Time interval between spectra 10 sec in the first 2 min, then every 50 sec for 10 min B) subsequent heating from 25°C to 375°C in He atmosphere (temperature interval between spectra is 25°C).

**Figure 2.**

A) rR spectra (363.8 nm) of ¹⁶O₂ (black) and ¹⁸O₂ (blue) precursor formed at RT and B) rR spectra (457.9 nm) of reactive site formed by heating the O₂ precursor rR samples.

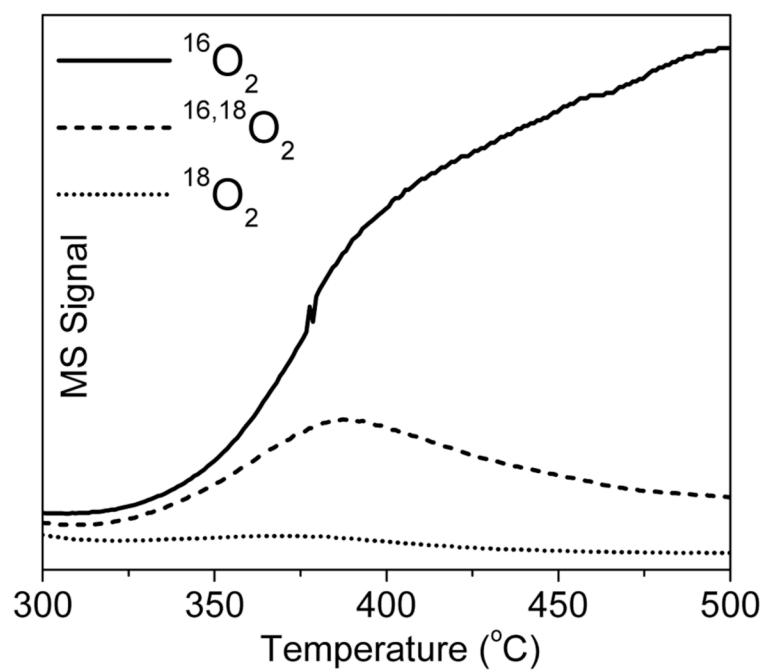
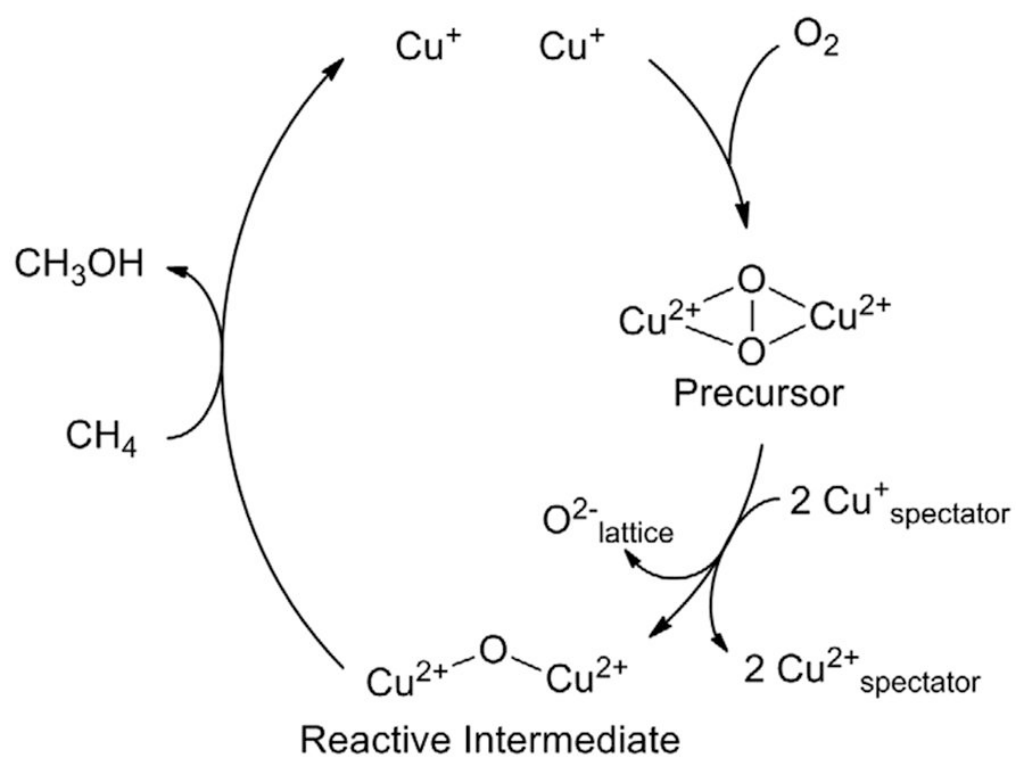


Figure 3. MS signal of $^{16}\text{O}_2$, $^{16,18}\text{O}_2$ and $^{18}\text{O}_2$ as a function of temperature during O_2 -TPD ($2^\circ\text{C}/\text{min}$ in He) of activated Cu-ZSM-5 (Cu/Al=0.5, Si/Al=12). Note that the peak in the $^{16,18}\text{O}_2$ desorption profile corresponds to loss of the $22,700\text{ cm}^{-1}$ absorption feature.



Scheme 1.