Oxygen Precursor to the Reactive Intermediate in Methanol Synthesis by Cu-ZSM-5

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Abstract: The reactive oxidizing species in the selective oxidation of methane to methanol in oxygen activated Cu-ZSM-5 was recently defined to be a bent mono(μ-oxo)dicopper(II) species, $[Cu_2O]^{2+}$. In this communication we report the formation of an O_2-precursor of this reactive site with an associated absorption band at 29 000 cm^{-1}. Laser excitation into this absorption feature yields a resonance Raman (rR) spectrum characterized by $^{18}O_2$ isotope sensitive and insensitive vibrations, $\nu O-O$ and $\nu Cu-Cu$, at 736 ($\Delta^{18}O_2 = 41$ cm^{-1}) and 269 cm^{-1}, respectively. These define the precursor to be a μ-($\eta^2{:}\eta^2$) peroxo dicopper(II) species, $[Cu_2(O_2)]^{2+}$. rR experiments in combination with UV–vis absorption data show that this $[Cu_2(O_2)]^{2+}$ species transforms directly into the $[Cu_2O]^{2+}$ reactive site. Spectator Cu$^+$ sites in the zeolite ion-exchange sites provide the two electrons required to break the peroxo bond in the precursor. O_2-TPD experiments with $^{18}O_2$ show the incorporation of the second ^{18}O atom into the zeolite lattice in the transformation of $[Cu_2(O_2)]^{2+}$ into $[Cu_2O]^{2+}$. This study defines the mechanism of oxo-active site formation in Cu-ZSM-5.

Oxygen activated Cu-ZSM-5 has been recently shown to selectively oxidize methane to methanol at low temperatures[1] by means of a mono(μ-oxo)dicopper(II) species, $[Cu_2O]^{2+}$.[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 $[Cu_2O-H]^{2+}$ bond in the initial product and a frontier molecular orbital (FMO) that polarizes to an oxyl (O$^{-\bullet}$) 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 $[Cu_2O]^{2+}$ 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, $[Cu_2(O_2)]^{2+}$. Absorption and rR data show the conversion of $[Cu_2(O_2)]^{2+}$ into $[Cu_2O]^{2+}$, 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 2 h (5 °C/min, 50 mL/min), followed by a He flow overnight (50 mL/min). This treatment results in the autoreduction 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 prereduced Cu-ZSM-5 (He at 450 °C; Cu/Al = 0.5) was exposed to O$_2$ at room temperature (RT) an absorption band at ~29 000 cm^{-1} is rapidly formed (Figure 1A). After ~2 min in an 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 Figure S1A and B). After full formation of the 29 000 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 a He atmosphere resulted in the UV–vis spectral changes shown in Figure 1B. Starting at ~175 °C and higher temperatures, the formation of the 22 700 cm^{-1} band, associated with the reactive $[Cu_2O]^{2+}$ core, is observed along with the parallel disappearance of the 29 000 cm^{-1} band. This occurs with heating in either a He or O$_2$ atmosphere. The $[Cu_2O]^{2+}$ species has also been shown to form in the presence of N$_2$O at 100 °C,[1,2] and in fact, the $[Cu_2O]^{2+}$ core still forms even at RT with N$_2$O. However, unlike the case with O$_2$, when prereduced Cu-ZMS-5 is exposed to N$_2$O at RT, no 29 000 cm^{-1} band is formed, and thus there is no formation of the precursor.
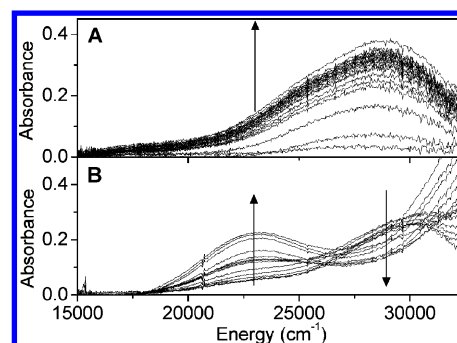

Figure 1. UV–vis absorption spectra of a prereduced Cu-ZSM-5 (in He at 450 °C) during (A) O$_2$ treatment at RT (time interval between spectra 10 s in the first 2 min, then every 50 s for 10 min and (B) subsequent heating from 25 to 375 °C in He atmosphere (temperature interval between spectra is 25 °C).

The rR spectrum of the oxygen precursor species formed at RT obtained with laser excitation at 363.8 nm (27 473 cm^{-1}) is shown in Figure 2A. Vibrational features are observed at 269 and 736

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cm^{-1} that are not present using laser excitation outside of the 29 000 cm^{-1} band, proving that they are resonance enhanced by the species responsible for this absorption feature. When the RT treatment of the autoreduced Cu-ZSM-5 sample is performed with isotope labeled $^{18}O_2$, the 736 cm^{-1} feature shifts to 695 cm^{-1} ($\Delta^{18}O_2 = 41$ cm^{-1}) while the 269 cm^{-1} feature is isotope insensitive. These vibrational frequencies and isotope perturbation pattern are characteristic of those of μ-(η^2-η^2) peroxo dicopper(II) species.[8] Thus, we assign the 736 and 269 cm^{-1} features to the O−O stretch (νO−O) and the Cu−Cu stretch (νCu−Cu) of the μ-(η^2-η^2) peroxo dicopper(II) moiety, respectively. The 29 000 cm^{-1} absorption band is thus assigned as a peroxo π^*_σ to Cu(II) charge transfer (CT) transition. Upon heating the rR sample, the 363.8 nm rR μ-(η^2:η^2) peroxo dicopper(II) precursor features go away (Figure S3). In parallel, excitation at 457.9 nm (21 834 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 [Cu$_2$O]$^{2+}$ species). These have been assigned in ref 2 as the isotope sensitive, intense symmetric (456 cm^{-1}) and weak antisymmetric (870 cm^{-1}) stretching vibrations characteristic of the μ-oxo-bridged [Cu$_2$O]$^{2+}$ species. These results parallel the absorption changes and show that the side-on bridged peroxo dicopper(II) species converts to the [Cu$_2$O]$^{2+}$ species reactive in the selective oxidation of methane to methanol.

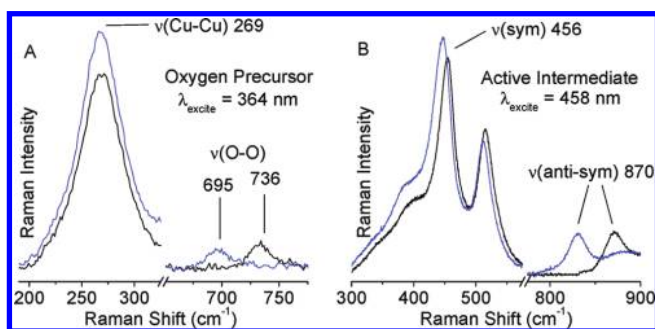**Figure 2.** (A) rR spectra (363.8 nm) of $^{16}O_2$ (black) and $^{18}O_2$ (blue) precursor formed at RT and (B) rR spectra (457.9 nm) of reactive site formed by heating the O$_2$ precursor rR samples.

An important issue in this conversion is the fate of the second O atom as only one O atom remains in the reactive [Cu$_2$O]$^{2+}$ intermediate. He treatment of the reactive intermediate at temperatures above 350 °C results in the disappearance of its characteristic 22 700 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 [Cu$_2$(O$_2$)]$^{2+}$ into [Cu$_2$O]$^{2+}$.

An O$_2$-TPD study in a He flow was performed after treatment of Cu-ZSM-5 with $^{18}O_2$ at 240 °C. From our previous study, reaction of Cu-ZSM-5 and $^{18}O_2$ at 240 °C results in formation of pure ^{18}O labeled reactive sites (i.e., [Cu^{II}−^{18}O−Cu^{II}]$^{2+}$).[2] Figure 3 follows the desorbing O$_2$ isotopes, $^{16}O_2$, $^{16,18}O_2$, and $^{18}O_2$, upon subsequent heating in a He flow. Although the site was formed with pure $^{18}O_2$, little $^{18}O_2$ desorbs. In the temperature range where the 22 700 cm^{-1} band disappears (between 350 and 420 °C), corresponding to the loss of the [Cu^{II}−^{18}O−Cu^{II}]$^{2+}$ species, the ratio of $^{16,18}O_2/^{18}O_2$ 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 [Cu$_2$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 $^{16,18}O_2$

desorption. This also indicates that the second ^{18}O atom does not form a second [Cu^{II}−^{18}O−Cu^{II}]$^{2+}$ species as this would result in desorption of $^{18}O_2$. 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 $^{16}O_2$ observed in Figure 3 is thus not the result of destruction of the zeolite lattice. At higher temperature the fraction of desorbing $^{16,18}O_2$ atoms decreases and mainly $^{16}O_2$ 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 $^{16}O_{lattice}$ and ^{18}O.[10−12]

The high incorporation of lattice ^{16}O into O$_2$ desorbed from [Cu$_2^{18}$O]$^{2+}$ ($T < 420$ °C) indicates that the reverse occurs upon formation of the [Cu$_2$O]$^{2+}$ reactive species from the [Cu$_2$(O$_2$)]$^{2+}$ precursor. Thus, the high $^{16,18}O_2/^{18}O_2$ 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 [Cu$_2$(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 [Cu$_2$O]$^{4+}$ resulted in delocalization of the additional holes into the lattice, creating [Cu$_2$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 [Cu$_2$O]$^{2+}$ reactive species.
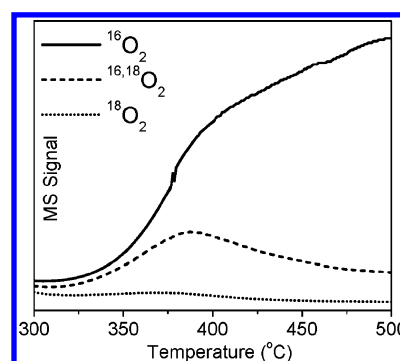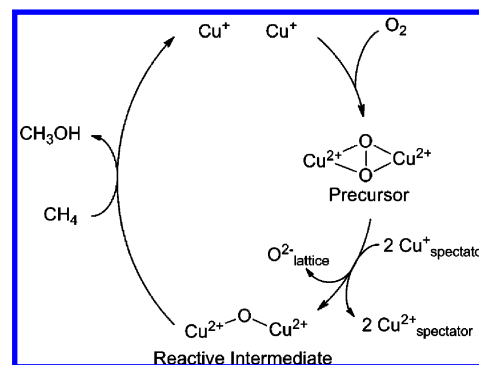

Figure 3. MS signal of $^{16}O_2$, $^{16,18}O_2$, and $^{18}O_2$ as a function of temperature during O$_2$-TPD (2 °C/min in He) of activated Cu-ZSM-5 (Cu/Al = 0.5, Si/Al = 12). Note that the peak in the $^{16,18}O_2$ desorption profile corresponds to loss of the 22 700 cm^{-1} absorption feature.

Scheme 1

In summary, we have characterized a RT O$_2$ precursor in the formation of [Cu$_2$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 cm^{-1}) and that this species converts directly into the $[Cu_2O]^{2+}$ reactive intermediate (with an absorption band at 22 700 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. $^{18}O_2$-TPD experiments showed incorporation of the second ^{18}O atom into the zeolite lattice upon formation of the $[Cu_2O]^{2+}$ reactive intermediate. This study defines the mechanism of oxo-reactive site formation in Cu-ZSM-5. While the $[Cu_2O]^{2+}$ 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 $[Cu_2O]^{2+}$ intermediate.

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.

References

(1) Groothaert, M. H.; Smeets, P. J.; Sels, B. F.; Jacobs, P. A.; Schoonheydt, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 1394–1395.
(2) Woertink, J. S.; Smeets, P. J.; Groothaert, M. H.; Vance, M. A.; Sels, B. F.; Schoonheydt, R. A.; Solomon, E. I. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 18908–18913.
(3) Balasubramanian, R.; Smith, S. M.; Rawat, S.; Yatsunyk, L. A.; Stemmler, T. L.; Rosenzweig, A. C. *Nature* **2010**, *465*, 115–119.
(4) Smeets, P. J.; Groothaert, M. H.; van Teeffelen, R. M.; Leeman, H.; Hensen, E. J. M.; Schoonheydt, R. A. *J. Catal.* **2007**, *245*, 358–368.
(5) Iwamoto, M.; Furukawa, H.; Mine, Y.; Uemura, F.; Mikuriya, S. I.; Kagawa, S. *J. Am. Chem. Soc.* **1986**, 1272–1273.
(6) Da Costa, P.; Moden, B.; Meitzner, G. D.; Lee, D. K.; Iglesia, E. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4590–4601.
(7) Smeets, P. J.; Woertink, J. S.; Sels, B. F.; Solomon, E. I.; Schoonheydt, R. A. *Inorg. Chem.* **2010**, *49*, 3573–3583.
(8) Baldwin, M. J.; Root, D. E.; Pate, J. E.; Fujisawa, K.; Kitajima, N.; Solomon, E. I. *J. Am. Chem. Soc.* **1992**, *114*, 10421–10431.
(9) Pirngruber, G. D.; Pieterse, J. A. Z. *J. Catal.* **2006**, *237*, 237–247.
(10) Fu, C. M.; Korchak, V. N.; Hall, W. K. *J. Catal.* **1981**, *68*, 166–171.
(11) Pirngruber, G. D.; Roy, P. K.; Prins, R. *J. Catal.* **2007**, *246*, 147–157.
(12) Novakova, J.; Schwarze, M.; Sobalik, Z. *Catal. Lett.* **2005**, *104*, 157–162.
(13) Corma, A.; Garcia, H. *Chem. Rev.* **2002**, *102*, 3837–3892.
(14) Garcia, H.; Roth, H. D. *Chem. Rev.* **2002**, *102*, 3947–4007.
(15) Yoon, K. B. *Chem. Rev.* **1993**, *93*, 321–339.

JA106283U