

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

Pieter J. Smeets,<sup>†,‡</sup> Ryan G. Hadt,<sup>†</sup> Julia S. Woertink,<sup>†</sup> Pieter Vanelderden,<sup>‡</sup>  
Robert A. Schoonheydt,<sup>\*,‡</sup> Bert F. Sels,<sup>\*,‡</sup> and Edward I. Solomon<sup>\*,†</sup>

Department of Chemistry, Stanford University, Stanford, California 94305, and Center for Surface Chemistry, Catalysis, K.U.Leuven, Kasteelpark Arenberg 23, B-3001 Leuven, Belgium

Received July 15, 2010; E-mail: robert.schoonheydt@biw.kuleuven.be; bert.sels@biw.kuleuven.be; edward.solomon@stanford.edu

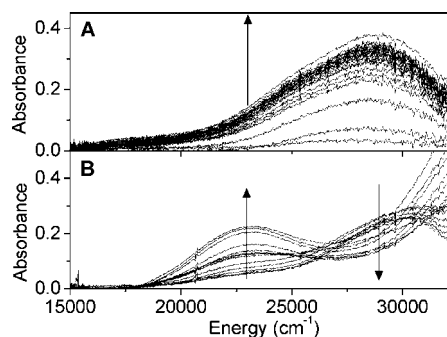
**Abstract:** The reactive oxidizing species in the selective oxidation of methane to methanol in oxygen activated Cu-ZSM-5 was recently defined to be a bent mono( $\mu$ -oxo)dicopper(II) species,  $[\text{Cu}_2\text{O}]^{2+}$ . In this communication we report the formation of an  $\text{O}_2$ -precursor of this reactive site with an associated absorption band at  $29\,000\text{ cm}^{-1}$ . Laser excitation into this absorption feature yields a resonance Raman (rR) spectrum characterized by  $^{18}\text{O}_2$  isotope sensitive and insensitive vibrations,  $\nu\text{O}-\text{O}$  and  $\nu\text{Cu}-\text{Cu}$ , at  $736$  ( $\Delta^{18}\text{O}_2 = 41\text{ cm}^{-1}$ ) and  $269\text{ cm}^{-1}$ , respectively. These define the precursor to be a  $\mu-(\eta^2-\eta^2)$  peroxo dicopper(II) species,  $[\text{Cu}_2(\text{O}_2)]^{2+}$ . rR experiments in combination with UV-vis absorption data show that this  $[\text{Cu}_2(\text{O}_2)]^{2+}$  species transforms directly into the  $[\text{Cu}_2\text{O}]^{2+}$  reactive site. Spectator  $\text{Cu}^+$  sites in the zeolite ion-exchange sites provide the two electrons required to break the peroxo bond in the precursor.  $\text{O}_2$ -TPD experiments with  $^{18}\text{O}_2$  show the incorporation of the second  $^{18}\text{O}$  atom into the zeolite lattice in the transformation of  $[\text{Cu}_2(\text{O}_2)]^{2+}$  into  $[\text{Cu}_2\text{O}]^{2+}$ . 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<sup>1</sup> by means of a mono( $\mu$ -oxo)dicopper(II) species,  $[\text{Cu}_2\text{O}]^{2+}$ .<sup>2</sup> 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  $\text{CH}_4$  reflects the strong  $[\text{Cu}_2\text{O}-\text{H}]^{2+}$  bond in the initial product and a frontier molecular orbital (FMO) that polarizes to an oxyl ( $\text{O}^{\cdot-}$ ) 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.<sup>3</sup> 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  $\mu-(\eta^2-\eta^2)$  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  $\text{O}_2$  temperature programmed desorption ( $\text{O}_2$ -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.<sup>4</sup> The samples were initially calcined under  $\text{O}_2$  at  $450\text{ }^\circ\text{C}$  for 2 h ( $5\text{ }^\circ\text{C}/$

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.<sup>5-7</sup> 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/ $\text{O}_2$  species in Cu-ZSM-5. MS was used to monitor the O-isotope distribution in  $\text{O}_2$ -TPD experiments.

When prerduced Cu-ZSM-5 (He at  $450\text{ }^\circ\text{C}$ ; Cu/Al = 0.5) was exposed to  $\text{O}_2$  at room temperature (RT) an absorption band at  $\sim 29\,000\text{ cm}^{-1}$  is rapidly formed (Figure 1A). After  $\sim 2$  min in an  $\text{O}_2$  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  $29\,000\text{ cm}^{-1}$  band, the sample was flushed in He to remove excess  $\text{O}_2$  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  $\sim 175\text{ }^\circ\text{C}$  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 a He or  $\text{O}_2$  atmosphere. The  $[\text{Cu}_2\text{O}]^{2+}$  species has also been shown to form in the presence of  $\text{N}_2\text{O}$  at  $100\text{ }^\circ\text{C}$ ,<sup>1,2</sup> and in fact, the  $[\text{Cu}_2\text{O}]^{2+}$  core still forms even at RT with  $\text{N}_2\text{O}$ . However, unlike the case with  $\text{O}_2$ , when prerduced Cu-ZSM-5 is exposed to  $\text{N}_2\text{O}$  at RT, no  $29\,000\text{ cm}^{-1}$  band is formed, and thus there is no formation of the precursor.

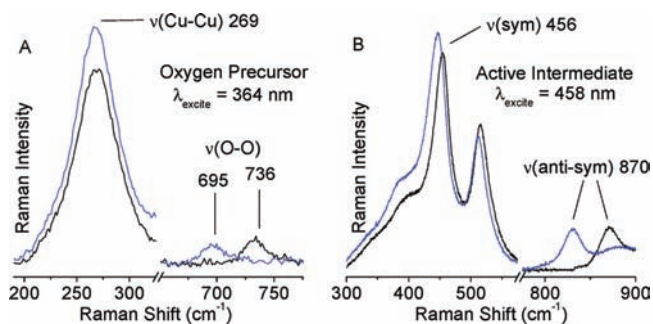


**Figure 1.** UV-vis absorption spectra of a prerduced Cu-ZSM-5 (in He at  $450\text{ }^\circ\text{C}$ ) during (A)  $\text{O}_2$  treatment at RT (time interval between spectra 10 s in the first 2 min, then every 50 s for 10 min) and (B) subsequent heating from 25 to  $375\text{ }^\circ\text{C}$  in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

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

<sup>†</sup> Stanford University.  
<sup>‡</sup> K.U.Leuven.

$\text{cm}^{-1}$  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 autoreduced Cu-ZSM-5 sample is performed with isotope labeled  $^{18}\text{O}_2$ , the 736  $\text{cm}^{-1}$  feature shifts to 695  $\text{cm}^{-1}$  ( $\Delta^{18}\text{O}_2 = 41 \text{ cm}^{-1}$ ) while the 269  $\text{cm}^{-1}$  feature is isotope insensitive. These vibrational frequencies and isotope perturbation pattern are characteristic of those of  $\mu$ -( $\eta^2$ - $\eta^2$ ) peroxo dicopper(II) species.<sup>8</sup> Thus, we assign the 736 and 269  $\text{cm}^{-1}$  features to the O–O stretch ( $\nu$ O–O) and the Cu–Cu stretch ( $\nu$ Cu–Cu) of the  $\mu$ -( $\eta^2$ - $\eta^2$ ) 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  $\mu$ -( $\eta^2$ - $\eta^2$ ) 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 ref 2 as the isotope sensitive, intense symmetric (456  $\text{cm}^{-1}$ ) and weak anti-symmetric (870  $\text{cm}^{-1}$ ) stretching vibrations characteristic of the  $\mu$ -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.



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

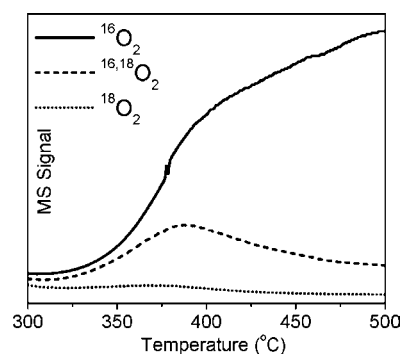
An important issue in this conversion is the fate of the second O atom as only one O atom remains in the reactive  $[\text{Cu}_2\text{O}]^{2+}$  intermediate. The treatment of the reactive intermediate at temperatures above 350  $^{\circ}\text{C}$  results in the disappearance of its characteristic 22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

An  $\text{O}_2$ -TPD study in a He flow was performed after treatment of Cu-ZSM-5 with  $^{18}\text{O}_2$  at 240  $^{\circ}\text{C}$ . From our previous study, reaction of Cu-ZSM-5 and  $^{18}\text{O}_2$  at 240  $^{\circ}\text{C}$  results in formation of pure  $^{18}\text{O}$  labeled reactive sites (i.e.,  $[\text{Cu}^{\text{II}}-^{18}\text{O}-\text{Cu}^{\text{II}}]^{2+}$ ).<sup>2</sup> Figure 3 follows the desorbing  $\text{O}_2$  isotopes,  $^{16}\text{O}_2$ ,  $^{16,18}\text{O}_2$ , and  $^{18}\text{O}_2$ , upon subsequent heating in a 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 and 420  $^{\circ}\text{C}$ ), corresponding to the loss of the  $[\text{Cu}^{\text{II}}-^{18}\text{O}-\text{Cu}^{\text{II}}]^{2+}$  species, the ratio of  $^{16,18}\text{O}_2/^{18}\text{O}_2$  released is greater than 10. This shows that the second  $^{18}\text{O}$  atom initially present in the peroxo precursor does not recombine with the bridging  $^{18}\text{O}$  atom of  $[\text{Cu}_2\text{O}]^{2+}$  upon  $\text{O}_2$  desorption. As shown in Figure 3, the majority of bridging  $^{18}\text{O}$  recombines with  $^{16}\text{O}$ , which originates from the zeolite lattice, resulting in dominantly  $^{16,18}\text{O}_2$

desorption. This also indicates that the second  $^{18}\text{O}$  atom does not form a second  $[\text{Cu}^{\text{II}}-^{18}\text{O}-\text{Cu}^{\text{II}}]^{2+}$  species as this would result in desorption of  $^{18}\text{O}_2$ . A reference TPD experiment without the initial  $\text{O}_2$  treatment at 240  $^{\circ}\text{C}$  showed no  $\text{O}_2$  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,<sup>4,9</sup> resulting in isotope scrambling of the  $^{16}\text{O}_{\text{lattice}}$  and  $^{18}\text{O}$ .<sup>10–12</sup>

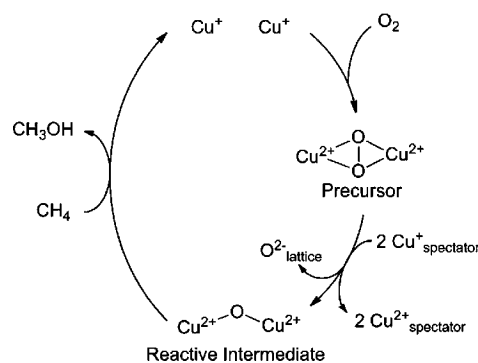
The high incorporation of lattice  $^{16}\text{O}$  into  $\text{O}_2$  desorbed from  $[\text{Cu}_2^{18}\text{O}]^{2+}$  ( $T < 420 \text{ }^{\circ}\text{C}$ ) indicates that the reverse occurs upon formation of the  $[\text{Cu}_2\text{O}]^{2+}$  reactive species from the  $[\text{Cu}_2(\text{O}_2)]^{2+}$  precursor. Thus, the high  $^{16,18}\text{O}_2/^{18}\text{O}_2$  desorption ratio reflects the competition between newly formed  $^{18}\text{O}$  lattice sites and equivalent and more prevalent  $^{16}\text{O}$  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  $\text{Cu}^{2+}$  and not  $\text{Cu}^{3+}$ , 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.<sup>2</sup> Also, the electron donor and acceptor capabilities of zeolite lattices have been demonstrated experimentally,<sup>13–15</sup> indicating that spectator  $\text{Cu}^+$  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.



**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  $\text{O}_2$ -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



In summary, we have characterized a RT  $\text{O}_2$  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  $\mu$ -( $\eta^2$ : $\eta^2$ ) 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  $\text{Cu}^+$  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  $^{18}\text{O}$  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<sub>2</sub> 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.

**Acknowledgment.** P.J.S. acknowledges the IWT, FWO, and K.U.Leuven for graduate and postdoctoral fellowships, and J.S.W. acknowledges the NIH for a traineeship. R.G.H. is a Gerhard Casper Stanford Graduate Fellow. This research was supported by the GOA and the Long Term Structural Funding-Methusalem Funding by the Flemish Government (R.A.S., B.F.S.) and by NIH Grant DK-31450 (E.I.S.).

**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