Communication

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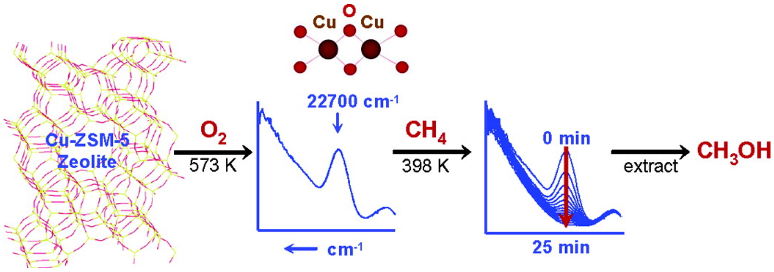

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Selective Oxidation of Methane by the Bis(μ-oxo)dicopper Core Stabilized on ZSM-5 and Mordenite Zeolites

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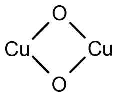
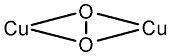
Cu-loaded zeolites have attracted wide attention for their catalytic activity in both deNO$_x$ and selective oxidation of hydrocarbons with O_2.[1−4] We have recently reported that Cu−ZSM-5, after activating in O_2 or N_2O at temperatures higher than 623 K, is characterized by an intense UV−vis band at 22 700 cm^{-1}.[5] Special interest in the origin of this band arose since a high correlation was found between the intensity of this band and the catalytic activity for direct NO decomposition of the concerning sample.[5] As evidenced by the joint characterization by EXAFS, TEM, and EPR, the 22 700 cm^{-1} band is best associated to the bis(μ-oxo)dicopper core, $[Cu_2(\mu\text{-}O)_2]^{2+}$ (**A**).[6] A subsequent combined UV−vis kinetic study led to the insight that during catalytic NO decomposition, O_2 is formed and released at this **A** core.[5] Knowing that nature selected the (μ-η^2:η^2-peroxo)dicopper center (**B**) for O_2 transport by the protein hemocyanin,[7] this functional resemblance is in further support of our spectroscopic characterization of the **A** core in Cu−ZSM-5. Indeed, comprehensive studies on synthetic model complexes in solution have shown the easy interconversion of cores **A** and **B**.[8]



A



B

Core **B** also constitutes the active site in the enzyme tyrosinase, which catalyzes the hydroxylation of phenols to *o*-diphenols and the oxidation of *o*-diphenols to *o*-quinones.[7] In view of the successful hydroxylation activities displayed by the homogeneous model complexes,[8] it was an obvious step to test whether Cu−ZSM-5 is also capable of mimicking this monooxygenase activity. In the present study, methane was chosen as substrate based on the hypothesis of the **A** core in the activated site of particulate methane monooxygenase (pMMO).[9]

Initially, the combined GC−UV−vis setup (Figure S1) was used to study the interaction of methane with the O_2-activated Cu−ZSM-5 sample. The CZ-12−0.58 sample (i.e., Cu−ZSM-5 with Si/Al = 12 and Cu/Al = 0.58) was activated at 723 K in flowing O_2, resulting in the appearance of the 22700 cm^{-1} band, assigned to a $O_{bridge} \rightarrow Cu$ charge-transfer transition in the Cu_2O_2 moiety of **A**.[10,11] After the sample was cooled to room temperature and flushed with He, CH_4 was passed over the sample while the temperature was increased. The UV−vis data displayed a prompt disappearance of the 22 700 cm^{-1} band at about 448 K, a phenomenon that was not observed when He or N_2 was applied instead of methane. Figure 1 shows the outcome of a kinetic investigation of this CH_4/CZ-12−0.58 interaction; at 448 K, the 22 700 cm^{-1} band has fully disappeared after 3 min while 25 min and 1 min are needed at 398 and 498 K, respectively (498 K: Figure S2). Analysis of the decay of the 22 700 cm^{-1} band as a function of time revealed that the reaction is first-order with respect to the **A** core (Figure S3). Although these observations are indicative for a reaction between CH_4 and the **A** core on ZSM-5, GC analysis of the outlet showed no product formation. As product desorption might be a problem, the sample was heated after reaction in a He flow, and only CO_2 was detected at around 573 K. Similar temperature-programmed desorption was also performed on the CZ-12−0.22 sample, in which no significant formation of **A** was observed. As this experiment led to only minor amounts of CO_2 desorbed between 473 and 773 K, the idea was raised that the $[Cu_2(\mu\text{-}O)_2]^{2+}$ core is indeed responsible for the product formation. However, the product(s) do not desorb and decompose at 573 K leading to CO_2.

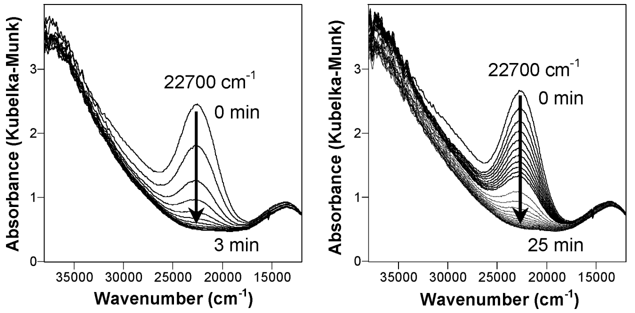


Figure 1. Fiber-optic UV−vis spectra of O_2-activated CZ-12−0.58 during reaction with CH_4 (5% in N_2; 25 mL min^{-1}) at 448 K (left) and at 398 K (right). Time interval between two spectra in full line = 25 s; time interval between two spectra in dashed line = 125 s. Kubelka−Munk = $f(R) = (1 - R)^2/2R$ with R the absolute reflectance of the sample.

To gather more information on the nature of the adsorbed product, the CZ-12−0.58 sample was extracted in a 1:1 water/acetonitrile mixture (4.25 mL/g zeolite) after reaction with CH_4 at 448 K.[12] An amount of 8.2 μmol CH_3OH per gram of CZ-12−0.58 was extracted. The identification of methanol as the only product was confirmed by GC, GC−MS, ^{13}C NMR, and ^1H NMR (Figures S7−13). Reaction with ^{18}O-labeled O_2 and ^{13}C-labeled CH_4 yielded ^{18}O- and ^{13}C-labeled CH_3OH, respectively (Figures S11−13). Taking into account the absence of CO_2 in the online GC analysis during reaction, this implies a selectivity[13] of at least 98% with respect to methanol. Furthermore, upon interaction of CZ-12−0.58 with CH_4 at room temperature, no significant decrease of the 22 700 cm^{-1} band was found and only 0.81 μmol/g methanol was extracted. These observations offer a first indication of the key role of the **A** core in this selective oxidation of methane.

In Figure 2, parts A and B, respectively, the amount of extracted methanol and the UV−vis spectra are plotted as a function of the Cu/Al ratio for a series of Cu−ZSM-5 samples with increasing copper loading. From the spectra, the appearance of the 22 700 cm^{-1} band in the sample with Cu/Al = 0.25 and its gradual increase with copper loading is clearly distinguished. As for the NO decomposition, for the oxidation of methane a sharp increase of activity is also found at Cu/Al $\geq$ 0.25. This strong match of the appearance of the 22 700 cm^{-1} band and the sharp increase in activity in the 0.2 < Cu/Al < 0.3 region enclose a second line of evidence for the key role of the **A** core in the oxidation of methane

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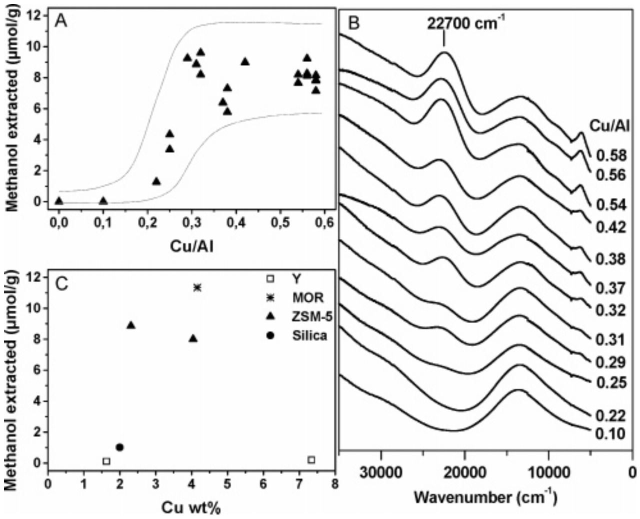

Figure 2. (A) Amount of methanol extracted per gram of Cu−ZSM-5 sample, as a function of the Cu/Al ratio of the CZ-12 samples. (B) Stacked UV−vis−NIR absorption spectra (in au) of the of CZ-12 samples activated in O_2 at 723 K. (C) Amount of methanol extracted per gram of Cu sample, as a function of the Cu wt % of the sample.

into methanol. However, unlike the activity profile obtained for NO decomposition, the amount of methanol extracted does not further increase for samples with $0.32 < Cu/Al < 0.58$, while the 22 700 cm^{-1} band intensity still increases. This asymptotic behavior might tentatively be explained by a hampered methanol extraction for the samples with higher Cu loadings due to pore blocking by the excess of copper species in these overexchanged samples. This interpretation is corroborated by the quantification of the CO_2 evolving during methanol decomposition at 573 K. For CZ-12−0.31, 6.7 μmol/g CO_2 was desorbed, which is in acceptable agreement with 8.9 μmol/g extracted methanol. In contrast, for CZ-12−0.58, 21.7 μmol/g CO_2 was desorbed, which highly exceeds the amount of 8.2 μmol/g extracted methanol. Assuming a Cu:CH_3OH stoichiometry of 2:1, one can calculate that 4.6% of the Cu atoms in the CZ-12−0.31 sample participates in this stoichiometric methane to methanol conversion.

To study the importance of the zeolite structure, a comparative study was made with the following Cu-exchanged materials: zeolite Y (Si/Al = 2.7, Cu/Al = 0.05 and 0.29), zeolite mordenite (Si/Al = 8.8, Cu/Al = 0.43), and amorphous silica (Si/Al = 141, 2 wt % Cu). Figure 2C shows very low methanol yields, i.e., below 1 μmol/g, for Cu−Y and Cu−silica, while for Cu−mordenite an even higher yield (11.34 μmol/g) than that for Cu−ZSM-5 is extracted. The UV−vis spectra of Cu−Y and Cu−silica display no significant absorption around 22 700 cm^{-1}, while a clear band at 22 200 cm^{-1} is observed for Cu−mordenite (Figures S4−6). These results show that the relation between stabilization of **A** and methane oxidation can be extended from ZSM-5 to other zeolite topologies with comparable Si/Al ratios and embodies the third line of evidence of this study.

In addition to methane, the interaction of ethane with Cu−ZSM-5 was briefly studied. A full disappearance of the 22 700 cm^{-1} band is observed within 2 min already at room temperature, which is in line with the decreased strength of the C−H bond in ethane compared to methane. Extraction yielded both ethanol and acetaldehyde in a ratio close to 4:1.

In summary, the capability of the presented Cu−zeolite systems to convert methane selectively into methanol at 398 K clearly indicates that they contain highly activated oxygen species. These low-temperature routes are presently of high interest since the many C−H activation routes require high temperature and are thus far not successful.[14] The strong resemblances between Cu−ZSM-5 and the bioinorganic bis(μ-oxo)dicopper complexes, both on spectroscopic (UV−vis/EXAFS) and on functional grounds (O_2 transport and monooxygenase activity), firmly support that this interesting copper-oxo dimer is successfully anchored in ZSM-5. While the selective oxidation capacity of the homogeneous model complexes in solution is frequently confined to intramolecular ligand hydroxylations,[8] the present gas-phase oxidation of methane and ethane by this heterogeneous bis(μ-oxo)dicopper system marks an important step forward. In this context, it is noteworthy that, in the soluble methane monooxygenase (sMMO), the active site of the hydroxylase is identified as a bis(μ-oxo)diiron core.[15] Moreover, Fe−ZSM-5 was found to convert methane to methanol and benzene to phenol at low temperature.[16] As a consequence, the present results raise the notion that the specific microporous structure and Si/Al ratio of pentasil zeolites such as ZSM-5 and mordenite might be especially suited to stabilize bis(μ-oxo)bridged bimetallic species. This insight is the entrance to a wide range of possibilities since a number of bis(μ-oxo)bimetallic (e.g., Ni, Cu, Ti, V, Fe, Co) cores have thus far been identified in solution and have interesting catalytic properties.[17−20]

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Supporting Information Available: Details of the procedures for (i) sample preparation, (ii) UV−vis analysis, (iii) extraction, and (iv) GC, MS, and NMR analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) The calculation of the selectivity is documented in the Supporting Information.
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