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Abstract

Methane from abundant natural gas reserves represents a valuable potential feedstock for the chemical industry, but liquefying natural gas for storage and transport renders much of the gas present in remote deposits economically inaccessible. A long-standing goal in chemistry has been the development of a catalyst capable of directly converting methane to methanol, a liquid with high energy density that can be easily stored and transported using existing infrastructure. The current industrial process for converting methane to methanol is an inefficient two-step process that results in significant greenhouse gas emissions. A direct process for converting methane to methanol would mitigate these emissions, but because of the stability of methane and the higher relative reactivity of methanol, no industrially-viable catalyst has yet been found that can convert methane to methanol with high yield.

Copper-exchanged zeolite catalysts oxidize methane to methanol with high selectivity, but a low yield per copper has prevented industrial application and hampered active site characterization. Utilizing the proton form of Cu-exchanged MOR and ZSM-5 zeolites instead of the sodium form has been shown to increase methanol productivity, which should facilitate identification of the Cu active sites, but the active site structure has not yet been unambiguously defined. Elucidating the active site structures will facilitate the design of improved catalysts.

Several Cu-exchanged MOR (Cu-MOR) and ZSM-5 (Cu-ZSM-5) catalysts were synthesized via liquid ion exchange, with varying Cu loading and co-cation (Na vs H). The effect of the co-cation on reactivity of the catalysts was investigated for both the cyclic and steady state methane-to-methanol reaction. The Cu speciation in the catalysts was investigated by X-ray absorption spectroscopy (XAS), UV-vis spectroscopy, Raman spectroscopy, and temperature-programmed reduction in H₂ (H₂-TPR).

Using a methane pressure of 35 bar, the C1 product yield during cyclic operation of a Cu-H-MOR catalyst was 0.42 mol (mol Cu)⁻¹. Linear combination fitting of the Cu K-edge X-ray absorption spectrum (XANES-LCF) of the Cu-H-MOR catalyst showed that 83% of the Cu^{II} in the fresh catalyst was reduced to Cu^I during treatment in helium at 723 K, which is assumed to be the redox-active fraction of Cu for methanol formation. Normalizing the product yield to the redoxactive fraction of Cu gave a reaction stoichiometry of 0.50 mol (mol Cu)⁻¹, which is consistent with the presence of dicopper active sites, assuming one turnover per active site in the cyclic reaction. *In situ* Raman spectroscopy of the O₂-activated Cu-H-MOR catalyst revealed no features in the peroxo stretching region, while the deep-UV Raman spectrum showed a feature at 570 cm⁻¹. This feature is consistent with the symmetric Cu-O stretch of a mono- μ -oxo dicopper(II) species, suggesting that this species, and not a μ -1,2-peroxo dicopper(II) species, is the predominant active site in the Cu-H-MOR catalyst.

Substituting Na co-cations for protons decreased the methanol selectivity and increased the CO₂ selectivity for both Cu-MOR and Cu-ZSM-5 catalysts. *In situ* UV-vis spectroscopy revealed a correlation between methanol yield and the prominence of a shoulder at 27,500 cm⁻¹ for the Cu-MOR catalysts, while a correlation between CO₂ yield and the intensity of a feature at ~22,000 cm⁻¹ was observed for the Cu-ZSM-5 and Cu-MOR catalysts. These results led to the conclusion that the presence of Na shifts the distribution of Cu from mono- μ -oxo dicopper(II) species (which promote methanol formation) to μ -1,2-peroxo dicopper(II) species (which promote CO₂ formation) in Cu-MOR and Cu-ZSM-5. This conclusion was supported by XAS results. A reaction network based on stoichiometry was proposed that describes the formation of intermediates leading to methanol, CO, and CO₂ over mono- μ -oxo dicopper(II) and μ -1,2-peroxo dicopper(II) active sites.

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1 Introduction

1.1 Background and motivation

Natural gas reserves in the United States are estimated to be 1,200 quadrillion Btu (quad), while the world's reserves of methane hydrates are estimated to be 330,000 quad. The annual energy consumption in the United States in 2011 was approximately 100 quad; methane from natural gas and hydrates therefore represents a massive natural resource for the production of both energy and chemicals.^{1,2} In recent years, the development of hydraulic fracturing technology for the recovery of natural gas from shale rock formations has greatly increased the recoverable reserves of natural gas.³ In the absence of a pipeline, natural gas must be liquefied prior to storage and transport. The liquefaction process is expensive and energy intensive, and large quantities of stored liquefied natural gas (LNG) present a safety concern.⁴ The extraction of natural gas from deposits located far from industrial infrastructure is therefore impractical. For similar reasons, much of the natural gas commonly released during oil extraction is flared, rather than being captured, releasing huge amounts of CO₂ into the atmosphere. Approximately 4 % of the world's natural gas production is currently flared.⁵ The development of a process for the on-site chemical conversion of natural gas to a liquid with higher energy density at the point of extraction is therefore highly desirable.^{6,7}

The majority of natural gas, which is typically 80-90% methane, is burned for heating and electricity generation, and thus its full potential as a feedstock for the production of chemicals and higher-value fuels has not been realized.⁸ The chemical conversion of methane falls broadly into four categories: 1) conversion to syngas (CO + H₂) via steam reforming, dry reforming, or catalytic partial oxidation (CPO); 2) direct oxidation to methanol or formaldehyde; 3) oxidative coupling to form ethylene; 4) non-oxidative conversion to aromatics and hydrogen (dehydroaromatization).⁹

Of these four routes, the indirect utilization of methane via steam reforming and syngas formation (Eqn. 1.1) is the only process currently carried out industrially, and represents the largest use of methane in the chemical industry.¹⁰

$$CH_4 + H_20 \leftrightarrow CO + 3H_2 \quad (\Delta H^0_{298\,K} = 206\,kJ\,mol^{-1})$$
 (Eqn. 1.1)

Methane steam reforming to generate syngas accounts for approximately 50 % of the world's H₂ production, with much of the H₂ being used to manufacture NH₃ via the Haber-Bosch process for use in fertilizers.⁸ Syngas can also be converted to synthetic gasoline and higher hydrocarbons over Fe, Co, or Ru catalysts in Fischer-Tropsch synthesis, as well as to methanol over Cu/ZnO/Al₂O₃ catalysts.^{9,11}

While steam reforming is the most prevalent industrial chemical process utilizing methane, it requires high temperatures and is highly endothermic, resulting in high energy costs.^{8,12,13} Furthermore, steam reforming plants must be extremely large to achieve profitability, and the capital investment required is not justified at all but the largest gas deposits. Catalysts capable of directly converting methane to oxygenates such as methanol (Eqn. 1.2) or formaldehyde under mild conditions and that avoid the expensive syngas step have therefore been intensively researched.^{9–11,14–16} The low-temperature functionalization of methane is considered to be one of the most important goals in chemistry.^{4,13} The production of methanol is particularly promising due to its versatility as a chemical feedstock and the fact that it exists as a liquid at ambient conditions. There is a large demand for methanol in the chemical industry – 45 billion kg are manufactured annually from syngas derived from natural gas.⁸ Methanol can be used directly as a

fuel, converted to gasoline via the methanol-to-gasoline process, or converted to olefins via the methanol-to-olefins process, both of which are carried out over zeolite catalysts.^{5,6,11,15}

$$CH_4 + \frac{1}{2}O_2 \to CH_3OH \qquad (\Delta H^0_{298\,K} = -126\,kJ\,mol^{-1})$$
 (Eqn. 1.2)

Despite intensive research efforts, a commercially viable catalyst for the direct low temperature oxidation of methane to methanol has not yet been developed.⁹ Much of the difficulty arises from the stability of the methane molecule and the strength of the C-H bond, resulting in a reaction that is kinetically unfavorable despite its thermodynamic favorability.¹⁸ Methane is a nonpolar molecule, has a high C-H bond strength, and a large HOMO-LUMO gap.¹⁹ Methane also has a low proton affinity and is an extremely weak acid, limiting opportunities for acid-base catalysis.¹⁰ Taken together, these factors make C-H activation in methane extremely difficult. High temperatures can be used to activate methane, but this results in the formation of highly reactive free radicals and carbocations, limiting the selectivity of the reaction.¹³ It is therefore desirable to find catalysts that activate methane at low temperature to improve selectivity. Selective partial oxidation of methane is also challenging because the C-H bonds in the partial oxidation products are weaker and therefore more reactive than those in methane, frequently resulting in low selectivity and over-oxidation to CO or CO₂.^{10,14,19,20} The C-H bond strength in methane is 440 kJ mol⁻¹, compared to 397 kJ mol⁻¹ for methanol.¹⁰ Thus, a catalyst that activates methane C-H bonds will likely activate C-H bonds in methanol as well. There is also a strong thermodynamic driving force for total oxidation to CO₂. One advantage of the indirect conversion of methane to methanol via syngas is its high selectivity. However, a significant portion of the methane used must be burned to supply the heat required for the endothermic steam reforming reaction. Taking this additional methane into consideration lowers the overall selectivity to methanol.

1.2 C-H activation and selective oxidation

Catalytic reactions in which the C-H bond of a hydrocarbon is activated fall broadly into two categories: "true" C-H activation and "fake" C-H activation.²¹ True C-H activation involves activation of the C-H bond by a metal center, and results in the formation of a metal-carbon bond. True C-H activation has the potential for higher selectivity than other activation mechanisms because the intermediates remain within the coordination sphere of the metal center throughout the course of the reaction.²² Specific mechanisms for true C-H activation include Lewis acid/base pair, electrophilic substitution, and oxidative addition.^{21,23} The Lewis acid/base pair mechanism typically involves neighboring metal Lewis acid and oxygen Lewis base pairs on a metal oxide surface that polarize the C-H bond, resulting in heterolytic abstraction of a proton and formation of M-CH₃ and O-H species. An important example of this mechanism is the oxidative coupling of methane to ethane/ethylene over Li-doped MgO catalysts, where the methane is activated at a Mg²⁺–O²⁻ Lewis acid/base pair site on the catalyst surface.²⁴

The difference between the oxidative addition and electrophilic substitution mechanisms is defined by the net direction of the transfer of electron density during the reaction. Oxidative addition involves an electron-rich metal center that activates the C-H bond by donating electron density to the C-H σ^* orbital.²⁵ In contrast, electrophilic substitution involves activation by an electron-deficient metal center, in which the C-H bond is activated by donation of bonding electrons from the C-H σ orbital to empty metal orbitals.²⁶ This mechanism has been explored extensively via homogeneous Pt-based catalysts.²⁷

In contrast to true C-H activation, "fake" C-H activation involves interaction of the alkane with metal ligands, often oxygen, rather than directly with the metal center. Many traditional oxidation catalysts used in the chemical industry, namely bulk metal oxides, operate via this principle.^{28,29} In the case of bulk oxides, the active oxygen species is a nucleophilic lattice oxygen, O²⁻, that heterolytically abstracts a proton from the alkane substrate.^{30,31} Nucleophilic oxygen typically is not transferred onto the organic substrate, but rather forms water, *e.g.* in oxidative dehydrogenation or ammoxidation reactions.³² Unfortunately, traditional metal oxide catalysts have not proven successful for the selective oxidation of methane. Many studies have been published on vanadium- and molybdenum-based oxide catalysts for the oxidation of methane to formaldehyde, but yields typically do not exceed 3%.^{10,33}

"Fake" C-H activation is also possible with electrophilic oxygen, in which the active oxygen homolytically cleaves the C-H bond via hydrogen atom abstraction (HAA), resulting in the formation of a methyl radical.²¹ This mechanism is thought to operate in Cu- (described in detail below) and Fe-exchanged zeolite catalysts.^{20,34–38}

An often under-appreciated aspect of methane selective oxidation is the activation of O_2 , with the focus usually being on activation of the strong C-H bond of methane.^{39,40} However, O_2 activation and the resulting formation of active oxygen species is critical, and in some ways more complex than C-H activation, due to the number of electrons required to cleave the O-O bond (four to form fully-reduced, closed-shell O^{2-}), and the diversity of potential partially-reduced oxygen species. Molecular O_2 has a triplet ground state, and therefore cannot directly react with singlet methane. Exciting O_2 into a singlet state allows it to react with methane, but the high temperatures required for this excitation result in unselective reactions and over-oxidation. The preferred strategy is reaction of O_2 with a metal center in the appropriate spin state, generating an active oxygen species capable of reacting with methane at lower temperatures.²¹ The extent of electron donation from the metal center(s) defines the type of activated oxygen species formed:

- 1) One electron: O_2^- (superoxo)
- 2) Two electrons: O_2^{2-} (peroxo)
- 3) Two electrons: $2O^{-}(oxyl)$
- 4) Four electrons: $2O^{2-}$ (oxo)

In selective oxidation, the oxo species is generally preferred, as peroxo species tend toward unselective reactions. Further reduction of peroxo to oxo, however, requires the involvement of additional reducing equivalents, via either a sacrificial reductant³⁰ (resulting in the second oxygen atom from O₂ being converted to water) or participation of additional metal centers, as most metals used in oxidation catalysis do not readily undergo a four-electron oxidation.⁴¹ A multinuclear metal site with sufficient reducing equivalents can convert O₂ to the fully-reduced oxo, but unless complete dissociation of the formed metal-oxo species occurs, resulting in site isolation and two equivalent metal-oxos, this results in a site containing two non-equivalent oxo species in which the reactivity of one affects the other.²¹ In the case of methane oxidation, this can result in methane reacting with the first oxygen, but because of its weak reducing power, being unable to react with the less-reactive second oxygen to fully reduce the metal, preventing activation of the next O_2 molecule and closure of the catalytic cycle. The fundamental difficulty is that the catalyst must activate both methane and the oxidant, generating intermediates of appropriate reactivity, under the same conditions. This is exceedingly difficult in the case of O_2 , as its reduction is a fourelectron process, while methane oxidation to methanol is a two-electron process.

Various strategies have been attempted to overcome the challenge of selectively oxidizing methane with O_2 . One possibility is the use of a stoichiometric oxidant, which oxidizes methane

and then is separately regenerated by O_2 . The key feature of this strategy is the spatial and mechanistic separation of methane and O_2 activation. This strategy has been successfully applied at the industrial scale in the Wacker process for the oxidation ethylene to ethylene oxide using a homogeneous Pd catalyst, with Cu^{II} acting as the stoichiometric oxidant.²² This strategy is also employed for the oxidation of methane to methanol by Cu-exchanged zeolites, in which Cu^{II} -oxo species are generated by initial treatment of the catalyst in O_2 at high temperature, typically 673–773 K.⁴² The reactor temperature is then lowered, typically to 373–473 K, O_2 is purged from the reactor, and methane is introduced, which reduces the Cu^{II} to Cu^{I} and generates surface intermediates that can subsequently be hydrolyzed to methanol.⁴³ The active Cu^{II} state of the catalyst must then be regenerated by another high-temperature treatment in O_2 .⁴⁴ The homogeneous Periana catalyst, the most successful catalyst reported to date for methane oxidation to methanol in terms of yield (>70%), uses S^{VI} in the form of H₂SO₄ as a stoichiometric oxidant.⁴⁵ The S^{VI} is reduced to S^{IV} in the form of SO₂, which can then be separately oxidized to SO₃ by O₂ and returned to the system as H₂SO₄.

The success of the Periana catalyst is due in part to its use of another strategy for achieving high methanol selectivity: product protection.^{46,47} In the Periana system, rather than being oxidized directly to methanol, methane is oxidized to methyl bisulfate (CH₃OSO₃H), which can be hydrolyzed to methanol in a separate step.⁴⁵ The electron-withdrawing bisulfate substituent reduces the electron density in the methyl C-H bonds, protecting it from further attack by the electrophilic Pt catalyst.⁴⁸ This results in a rate constant for methane oxidation to methyl bisulfate.⁴⁵

As noted above, a sacrificial reductant can be used generate a catalyst state that is capable of O_2 activation. This strategy is frequently employed by nature, *e.g.* the particulate methane monooxygenase (pMMO) enzyme in methanotrophic bacteria. This enzyme contains a Cu active site, and oxidizes methane to methanol under ambient conditions using NADH cofactor as a sacrificial reductant (Eqn. 1.3).^{49,50}

$$CH_4 + O_2 + NADH + H^+ \rightarrow CH_3OH + NAD^+ + H_2O \qquad (Eqn. 1.3)$$

Alternatively, in synthetic chemistry, H₂ can be used as the sacrificial reductant; for example, the oxidation of methane to methanol over Au-Pd nanoparticles in a H₂/O₂ gas mixture.⁵¹ The low-margin, commodity nature of methanol, however, may limit the economic viability of using a valuable co-reactant like H₂ in a commercial-scale process. In the methanotrophs that employ the pMMO enzyme, the co-reductant is regenerated, and the entire reaction cycle proceeds via an elaborate electron transfer process⁵² that would be exceedingly difficult to replicate in industrial chemistry with synthetic materials. Atomically-dispersed Rh on titania and ZSM-5 supports was shown to oxidize methane to methanol using O₂, but CO was required for the catalyst to function, possibly acting as a sacrificial reductant.⁵³

A fourth strategy involves simply bypassing the O_2 activation problem altogether and using a different oxidant. Nitrous oxide (N₂O) has been used to oxidize methane to methanol with Cu-^{54,55} and Fe-exchanged^{20,35–38,56,57} zeolites. In the case of Cu zeolites, a lower temperature is required to form the active Cu-oxo species when N₂O is used as compared to O_2 ,⁵⁵ while for Fe zeolites, it is only possible to form the active oxygen species using N₂O.³⁸ Activation of N₂O is more facile than O_2 , as it requires fewer electrons, and therefore the involvement of fewer Cu or Fe cations in forming the active species.⁵⁸ Hydrogen peroxide (H₂O₂) has been studied extensively as an oxidant for the oxidation of methane to methanol. The interaction of H₂O₂ with Fe^{II} in Fe-exchanged zeolite catalysts is thought to form hydroperoxy intermediates that are capable of selectively oxidizing methane.^{59–63} Conceptually, the use of H₂O₂ is similar to employing a sacrificial reductant to facilitate O₂ activation, the difference being that the reducing equivalents are already associated with oxygen, rather than being introduced separately to reduce the metal center. It has been speculated that reductive activation of O₂ by NADH in soluble methane monooxygenase (sMMO) enzymes, which contain Fe active sites, generates hydroperoxy species similar to those proposed for Fe-exchanged zeolites.⁵⁹ The use of H₂O₂ as an oxidant for methane oxidation to methanol is only of academic, not industrial, interest, as H₂O₂ is more expensive than methanol.

A fifth strategy for overcoming the problem of O_2 activation that has been demonstrated in the literature involves the use of electrochemistry to provide the electrons required to activate O_2 . In the presence of a Si nanowire array electrode, a Rh^{II} molecular complex catalyzed the oxidation of methane to methanol with high selectivity. The applied negative potential at the nanowire electrode generated reactive oxygen species from O_2 that oxidized the methyl group that was generated via activation of methane by the electron-rich, nucleophilic Rh^{II} center. Additionally, the electrode also provided the electrons to regenerate the active Rh^{II} catalyst after its oxidation to Rh^{III} by methane (2Rh^{II} + CH₄ \rightarrow Rh^{III}-H + Rh^{III}-CH₃).⁶⁴

1.3 Copper-exchanged zeolite catalysts for the oxidation of methane to methanol

Zeolites are crystalline, microporous aluminosilicates. Aluminum ions replace a fraction of Si ions within the silica lattice, and because Al has a +3 charge, versus +4 for Si, a charge imbalance is created that must be balanced by extra-framework cations. The charge balancing

requirement is often fulfilled by protons, but can also be fulfilled by other cations, including alkali metals, alkaline earth metals, and transition metals.

1.3.1 Active site structures in Cu-exchanged zeolites

Cu-exchanged zeolites, where Cu cations fulfill the charge-balancing requirement in the zeolite, were first studied as catalysts for NO decomposition in the 1980s by Iwamoto *et al.*^{65,66} In 2005, Cu-exchanged Na-ZSM-5 (Cu-Na-ZSM-5) and Na-mordenite (Cu-Na-MOR) zeolites were shown to be active for oxidation of methane to methanol.⁴² After activation in O_2 at 723 K, Cu-ZSM-5 exhibited a distinctive UV-vis absorption band at 22,700 cm⁻¹, which had previously been assigned to a bis- μ -oxo dicopper species.⁶⁷ Upon exposure to methane at 448 K, this band disappeared, suggesting it is associated with a Cu species that reacts with methane. Methanol was subsequently obtained via solvent extraction of the methane-treated catalyst with a water/acetonitrile mixture. Alternatively, methanol can be removed from methane-treated Cu zeolites by online steam treatment, allowing multiple cycles of O₂ activation, methane activation, and methanol desorption using the same catalyst sample.⁴⁴

A report demonstrating a linear correlation between the intensity of the UV-vis peak at 22,700 cm⁻¹ and the methanol yield for Cu-Na-ZSM-5 further supported the assignment of this peak to the active Cu species for methanol formation.⁶⁸ No correlation was observed between methanol production and the amount of CuO nanoparticles on the zeolite surface, suggesting that nanoparticles are inactive for methanol formation.⁶⁹

A more recent investigation involving site-selective resonance Raman spectroscopy was claimed to link the UV-vis peak at 22,700 cm⁻¹, and therefore the active site for methanol formation, to a mono- μ -oxo dicopper(II) species (Figure 1.1a) coordinated bidentate to oxygen

atoms of the zeolite Al tetrahedra.³⁴ Although previous extended X-ray absorption fine structure (EXAFS) analysis of Cu-Na-ZSM-5 suggested the presence of bis-μ-oxo dicopper species,⁶⁷ the active site for methanol formation was a minority species in this material, making structural assignments difficult due to the fact that the EXAFS contains an average of all species present of the metal of interest.⁷⁰ Quantum chemical calculations suggested that the mono-μ-oxo dicopper(II) active site is likely located at the intersection of the straight and sinusoidal 10 member ring (10MR) pores of ZSM-5.⁵⁴ Based on similar Raman and UV-vis spectra, Cu-Na-MOR was claimed to also contain mono-μ-oxo dicopper(II) active sites.⁷¹



Figure 1.1 Proposed active sites and active site precursors in O₂-activated Cu-exchanged zeolites for the oxidation of methane to methanol. The Cu atoms are bound to both zeolite framework oxygen (not shown), and extra-framework oxygen, which is involved in methane activation. a) mono- μ -oxo dicopper(II) ([Cu^{II}₂-O]²⁺); b) tris- μ -oxo tricopper ([Cu₃O₃]²⁺); c) μ -1,2-peroxo dicopper(II) ([Cu^{II}₂(μ -1,2-O₂)]²⁺); d) copper(II) hydroxo ([Cu^{II}OH]²⁺); e) μ -(η ²: η ²)-peroxo dicopper(II) ([Cu^{II}₂(μ -(η ²: η ²)-O₂)]²⁺).

In 2015, Grundner *et al.* showed that by exchanging Cu into the proton form of mordenite (Cu-H-MOR), where a proton fulfills the charge-balancing requirement as opposed to the previously used Na, the methanol yield per cycle increased by nearly an order of magnitude.⁷²

Based on a consistent ratio of approximately 0.33 moles of methane converted per mole of Cu for several catalysts with varying Cu loading and Si/Al ratio, it was concluded that the active site contained three Cu atoms, and that all of the Cu was contained in these sites, *i.e.* a single-site catalyst was obtained. The methanol selectivity was 75-80% (CO and CO₂ were the other products observed). Further density functional theory (DFT) and EXAFS analysis suggested the active site was a tris- μ -oxo tricopper species (Figure 1.1b), also referred to as [Cu₃O₃]²⁺. While no UV-vis peak at ~22,000 cm⁻¹ was observed, a shoulder at ~31,000 cm⁻¹ was present that decayed during interaction of the catalyst with methane, suggesting different Cu speciation in the H-form Cu-MOR compared to the Na-form.⁷² Based on Fourier transform infrared (FT-IR) spectroscopy, the active sites were claimed to be located in the 8-member ring (8MR) side pocket pores of mordenite. Sodium was found to preferentially occupy the same side pocket sites as Cu, disrupting formation of the active sites and presumably causing the lower methanol yield observed for the Na-form catalysts.⁷³

The ZSM-5 zeolite contains a three-dimensional pore network, with straight, parallel 10MR pores connected by sinusoidal 10MR pores. It also contains 5MR and 6MR pores parallel to the straight 10MR pores, but these pores are too small for reacting species to diffuse into and are therefore not of interest for catalysis.⁷⁴ Because of its more complex pore network, as well as a lack of spatial preference for Al ions, the Cu speciation is more complex in ZSM-5 than mordenite.⁷⁵ Similar to mordenite, the proton form of Cu-ZSM-5 exhibited a greater methanol yield than the sodium form, but less than the proton form of mordenite: *ca*. 1/6 of the Cu was active in Cu-H-ZSM-5 in terms of moles of methane converted per mole Cu, versus 1/3 for Cu-H-MOR. This led to the conclusion that Cu-H-ZSM still contains the [Cu₃O₃]²⁺ species that catalyzes methanol formation, but that half of the total copper in the catalyst is contained in inactive species,

due to the more heterogeneous speciation of Cu in ZSM-5.^{75,76} In addition to mordenite, zeolites omega and SSZ-13 have also shown greater methanol productivity than ZSM-5 for the cyclic methane-to-methanol reaction. These zeolites all contain 8MR pores, while ZSM-5 does not, suggesting that 8MR pores create a favorable environment for active sites that catalyze methanol formation.⁷⁷ Additional recent experimental studies have also claimed the existence of $[Cu_3O_3]^{2+}$ active sites in Cu-H-MOR,^{78,79} and several computational studies have suggested the feasibility of the formation of these sites and their ability to activate methane.^{80–82}

By optimizing the Si/Al ratio and the Cu loading of Cu-H-MOR, the methanol yield of Cu-H-MOR was increased from 0.25 to 0.47 mol (mol Cu)⁻¹. By quantifying the active Cu using multivariate curve resolution (MCR) analysis of the high energy resolution fluorescence detected X-ray absorption near edge spectra (HERFD-XANES), the active site was determined to be a dimeric Cu species, in contrast to the previously proposed trimeric species.⁸³ Based on an oxygen coordination number of *ca.* 3 for the Cu in O₂-activated Cu-H-MOR determined by EXAFS fitting,⁸⁴ Pappas *et al.* concluded that the Cu-H-MOR catalyst likely contains either mono-µ-oxo dicopper(II) (Figure 1.1a) or µ-1,2-peroxo dicopper(II) active sites (Figure 1.1c).⁸³ Both mono-µ-oxo dicopper(II) and µ-1,2-peroxo dicopper(II) species have been identified in O₂-activated Cu-exchanged chabazite zeolite (Cu-CHA) via Raman spectroscopy,^{85–87} while DFT calculations have suggested that mono-µ-oxo dicopper(II) is the thermodynamically preferred species in the 8MR side pocket of MOR,⁸⁸ where the active site for methanol formation is claimed to reside.⁷³

In addition to di- and tricopper active sites, several studies have proposed the existence of monocopper active sites in Cu-exchanged zeolites for the methane-to-methanol reaction. A DFT study of Cu-CHA calculated a methane activation barrier for a [Cu^{II}OH]⁺ species (Figure 1.1d) that was similar to the experimentally-determined activation barrier, suggesting that [Cu^{II}OH]⁺

may be the active site for methane activation in Cu-CHA.⁸⁹ A [Cu^{II}OH]⁺ species was also proposed as the active site for methane activation in Cu-CHA based on a combined reactivity and FT-IR investigation,⁹⁰ while a separate study concluded that [Cu^{II}OH]⁺ species are more likely to be the precursors to dicopper active sites.⁸⁶ Monomeric Cu species have been proposed as the active sites in Cu-Na-MOR with a high Si/Al ratio of 46 on the assumption that the Al concentration in this material is too low for the existence of proximal Al pairs that are required to host multimeric Cu species.^{91,92} Oxyl radical [Cu^{II}O]⁺ sites were predicted to have the lowest methane activation barrier among several Cu-oxygen complexes,^{89,93} but no spectroscopic evidence exists for the presence of these species in Cu-exchanged zeolites.

Based on DFT calculations, larger Cu-oxo structures containing up to five Cu atoms were predicted to be capable of activating methane in Cu-MOR, with larger clusters being more reactive than smaller clusters. The authors argued that the higher reactivity of the larger clusters was due to the weakening of Cu-O bonds in the site that occurs upon reaction with methane, and this weakening is less impactful for larger clusters.⁹⁴ Small, dehydrated copper(II) oxide clusters have also been proposed to catalyze methane oxidation to methanol in Cu-Na-MOR at elevated methane pressure.⁹⁵

As can be seen from the preceding discussion, despite years of detailed experimental and computational studies, the active site in Cu zeolites for methane activation has not been unambiguously identified. Although many studies have assumed that a single type of active site exists, it is also possible that several active site structures exist in Cu zeolites that are capable of activating methane, which may contribute to the difficulty of identifying these sites.⁷⁷

1.3.2 Activation of O₂ and formation of the Cu active site

The mechanism of the formation of Cu-oxygen species in Cu-exchanged zeolites has been the subject of several investigations. The Cu in fresh Cu zeolite catalysts is in a hydrated Cu^{II} state, and many authors have argued that the Cu^{II} must undergo "autoreduction" (*i.e.*, reduction without a reductant) to Cu^I before it can activate O₂ and form active sites.^{81,96–99} The mechanism of autoreduction has not been conclusively determined, but has been proposed to proceed through one of two possible pathways: 1) a radical-based pathway, in which hydroxyl radicals are released from [Cu^{II}OH]⁺ sites,^{86,100–102} or 2) condensation of proximal [Cu^{II}OH]⁺ sites, forming a mono- μ oxo dicopper(II) intermediate, followed by desorption of O₂ from two mono- μ -oxo dicopper(II) sites.^{98,99} The argument that autoreduction is a necessary prerequisite for active site formation was supported by the observation of a correlation between the fraction of Cu^I formed during treatment of Cu-CHA in helium at 773 K (which induces the autoreduction reaction) and the methanol yield.⁸⁶ Alternatively, the active site in Cu-MOR has also been claimed to be a Cu species that is resistant to autoreduction,⁸³ and that the oxidizing power comes from initially-present Cu^{II} rather than O₂ that is activated by Cu^{1,95,103}

When Cu-Na-ZSM-5 was subjected to thermal activation in helium at 723 K to induce autoreduction, followed by exposure to O₂ at room temperature, a UV-vis absorption band appeared at 29,000 cm⁻¹, which was attributed to a μ -(η^2 : η^2)-peroxo dicopper(II) species (Figure 1.1e).⁹⁶ Upon heating, the peak at 29,000 cm⁻¹ decayed and a peak at 22,700 cm⁻¹ appeared, suggesting that the μ -(η^2 : η^2)-peroxo dicopper(II) species is a precursor to the mono- μ -oxo dicopper(II) active site. These results suggest that paired Cu^I sites easily form peroxo species at room temperature, but higher temperatures are required to fully cleave the O-O bond to form the active oxo species via electron donation from two additional Cu^I ions. When activation of the CuNa-ZSM-5 catalyst was performed with isotopically-labeled ¹⁸O₂, followed by temperatureprogrammed desorption (TPD), ^{16,18}O₂ and ¹⁶O₂ were observed, indicating isotope scrambling with the zeolite framework. This suggests that the electron and oxygen transfer required to form the mono- μ -oxo dicopper(II) active site from the μ -(η^2 : η^2)-peroxo dicopper(II) precursor species occurs through the zeolite lattice, rather than via transport of Cu¹ ions through the zeolite pores.⁹⁶ This mechanism of O₂ activation was supported by quantum chemical calculations, where the formation of mono- μ -oxo dicopper(II) was found to proceed via the formation of a μ -(η^2 : η^2)peroxo dicopper(II) precursor by adsorption of O₂ at a pair of Cu¹ ions.⁸¹ In the first of two proposed pathways for cleavage of the peroxo, one of the oxygen atoms reversibly transfers to the zeolite lattice, forming a Si-O-O-Si species, which may explain the observed isotope scrambling during high temperature treatment of Cu-Na-ZSM-5 in ¹⁸O₂ described above. A second pathway with a lower barrier involved electron donation from two neighboring Cu¹ ions to cleave the peroxo bond and form the mono- μ -oxo dicopper(II) site.⁸¹

1.3.3 Methane activation

Numerous DFT studies have reported that mono- μ -oxo dicopper(II) species activate methane via the hydrogen atom abstraction (HAA) mechanism. Upon approach of the methane molecule, the bridging oxo ligand (O²⁻) of the mono- μ -oxo dicopper(II) species donates electron density to one of the two Cu^{II} centers, forming Cu^I and a radical-like electrophilic oxyl (O⁻). The oxyl homolytically abstracts hydrogen from methane, forming a surface hydroxyl group and a methyl radical.^{34,70,88,98,104} There is less consensus on what occurs after the HAA step. Some proposals invoke the "radical rebound" mechanism where, after hydrogen abstraction, the methyl radical rapidly reacts with the formed hydroxyl to form adsorbed methanol.^{34,88} This mechanism

is supported by the spectroscopic observation of adsorbed methanol during interaction of O_2 -activated Cu zeolites with methane.^{91,92,103,105–110}

Alternatively, HAA from methane over Cu zeolites can result in the formation of surface methoxy groups, which have been detected spectroscopically.^{91,92,103,105–112} Quantum chemical calculations have shown that the formation of methoxy groups bound to Cu is more energetically favorable than the formation of adsorbed methanol,¹⁰⁴ while more recent studies have proposed coordination of the methyl radical generated during HAA to a basic zeolite framework oxygen as a possible mechanism for methoxy formation.^{76,112} *In situ* FT-IR and nuclear magnetic resonance (NMR) spectroscopy during interaction of O₂-activated Cu zeolites with methane showed the formation of surface methoxy groups at Brønsted acid sites.^{92,105,107} Brønsted acid sites have been claimed to stabilize intermediates leading to methanol, which may in part explain the higher methanol yields of H-form Cu zeolites as compared to the Na-form.^{105,107} The lower methanol yield of Na-form catalysts has also been attributed to the ability of Na co-cations to prevent dealumination of the zeolite, as extra-framework Al species were claimed to play a role in methanol formation.¹¹³

1.3.4 Water-assisted product desorption

When water is introduced to Cu zeolite catalysts following methane activation, methanol is released either by hydrolysis of methoxy groups or by displacement of adsorbed methanol. Quantum chemical calculations have shown that the barrier for desorption of methanol from the Cu zeolite surface is prohibitively high in the absence of water.⁸² Additional calculations predicted that in the case of adsorbed methanol, the involvement of two water molecules is required for desorption – initial co-adsorption of the first water molecule, followed by displacement of

methanol by a second water molecule.⁸⁸ Beznis *et al.* reported that the use of more polar and protic solvents increased the amount of recovered methanol from Cu-Na-ZSM-5, suggesting that the solvent acts as a proton source during the release of methanol.¹¹⁴

In addition to methanol, CO and CO₂ are also released during methanol desorption. The formation of CO adsorbed to Cu has been observed spectroscopically during methane activation, ^{91,92,103,105,107–109} and a kinetic study comparing the rates of formation of surface intermediates leading to CO and methanol found that these intermediates form through parallel pathways, rather than CO forming via overoxidation of methanol precursors.¹⁰⁹ Formate has similarly been detected spectroscopically as a surface intermediate during methane activation, and is likely a precursor to CO₂.^{91,92,103,105,108,109} While early studies of methane oxidation over Cu zeolites reported that no gas-phase products were released during interaction of the O₂-activated catalysts with methane, two more recent studies reported the formation of gas-phase CO₂ during the methane activation step of the cyclic reaction over Cu-MOR catalysts.^{107,109}

1.3.5 Industrial viability of Cu-exchanged zeolite catalysts

Viewed in the context of the various strategies for selective methane oxidation described in section 1.2, the ability of Cu-exchanged zeolites to selectively oxidize methane using O_2 as the oxidant without a sacrificial reductant can likely be attributed to two features of the system: 1) Mechanistic separation of O_2 and methane activation via the use of a stoichiometric oxidant. This is accomplished by the step-wise reaction cycle in which Cu is first oxidized, and O_2 is subsequently removed from the reactor prior to the introduction of methane. 2) Product protection. Upon activation, methane forms methoxy or adsorbed methanol intermediates that are strongly bound to the catalyst surface, preventing further oxidation.¹¹⁵ Unfortunately, both of these aspects present significant roadblocks to the practical implementation of Cu-exchanged zeolites for methane conversion at the industrial scale. Because Cu ions interact strongly with water, the removal of methanol precursors bound strongly to the catalyst surface using water poisons the Cu sites, requiring high-temperature reactivation to remove adsorbed water.¹¹⁶ The cyclic reaction procedure and temperature adjustments between steps results in low overall methanol productivity. For Cu-CHA, assuming a cycle time of one hour and that the maximum theoretical methanol yield of 1250 μ mol g_{cat}⁻¹ (*i.e.* one methanol molecule produced per Cu atom) can be achieved, the space-time yield is two orders of magnitude lower than the commercialized Cu/Zn/Al₂O₃ catalyst used for methanol synthesis from syngas.¹¹⁵

Several attempts have been made to operate the cyclic reaction isothermally, in which O_2 activation, methane activation, and steam-assisted desorption are all carried out at 473 K, but this has resulted in either decreased methanol productivity^{95,117} or required the use of an oxidant other than O_2 ,⁵⁵ which will likely not be commercially feasible. Elevated methane pressure, however, increased the methanol yield for the isothermal cycle.^{95,117} Investigation of multiple reaction cycles using the isothermal, high methane pressure protocol for Cu-Na-MOR catalysts led to the discovery that O_2 is not required for the formation of active sites. Re-activation of the catalyst in helium at 673 K following the first reaction cycle resulted in significant methanol formation following a second methane activation step, leading to the catalyst.^{91,103,118,119} This claim, however, generated significant controversy, given the thermodynamic unfavorability of water acting as the oxidant.^{120–122}

In addition to the already-discussed Cu-MOR, Cu-ZSM-5, and Cu-CHA catalysts that have been the most extensively studied in the literature, additional Cu zeolites have also been reported

to be active for the oxidation of methane to methanol, including Cu-FER, Cu-MAZ, Cu-ERI, and Cu-FAU. Several of these catalysts exhibited comparable, and in some cases higher, methanol yields than Cu-MOR under certain conditions.^{77,108,111,123-127} The Cu-FAU material has shown particular promise for the isothermal cyclic reaction. Sushkevich et al. reported that among four Cu zeolites (Cu-FAU, Cu-ZSM-5, Cu-MOR, Cu-BEA), Cu-FAU had the lowest methanol yield using a standard reaction procedure of O₂ activation at 673 K and methane activation at 473 K. Temperature-programmed reduction in methane (CH₄-TPR) showed that Cu-FAU required the highest temperature among the four catalysts for the reduction of Cu^{II} to Cu^I by methane. Subjecting the Cu-FAU catalyst to an isothermal reaction cycle at 633 K increased the methanol yield by a factor of five, and a subsequent isothermal reaction using a Cu-FAU catalyst with higher Cu loading and elevated methane pressure (15 bar) at 633 K resulted in a methanol yield of 360 μ mol g_{cat}⁻¹ (0.25 mol (mol Cu)⁻¹).¹⁰⁸ This is the highest methanol yield for a Cu zeolite catalyst reported to date when the yield is normalized by the catalyst mass, and these findings for Cu-FAU suggest that it is possible to tune the Cu redox properties by varying the zeolite host to allow O₂ and methane activation to be carried out at the same temperature. In addition to tuning the redox properties of Cu, the zeolite framework can also potentially enhance selectivity through second sphere effects by creating a favorable environment for the adsorption of the target substrate at the active site, analogous to the role of a binding pocket in enzymes.¹²⁸

While Cu-FAU has the highest methanol yield reported to date when normalizing the yield by the catalyst mass, Cu-MOR exhibits the highest methanol yield when normalizing by the moles of Cu in the catalyst (0.58 mol (mol Cu)⁻¹).⁷⁹ In the current work, product yields for the cyclic reaction are typically normalized by the moles of Cu, as this tends to be more useful for understanding active site structure/nuclearity and reaction mechanisms. In the context of determining industrial feasibility, however, methanol productivity should be reported in terms of the cost of methanol production per reactor volume per unit time, for which product yields normalized by the catalyst mass are more relevant.¹²⁹

It is possible to operate the methane oxidation reaction over Cu zeolites under steady-state conditions by co-feeding methane, O₂, and water vapor at 473–723 K, but the rate of methanol production is extremely low, and essentially negligible methane conversion is required to retain any methanol selectivity and prevent over-oxidation to CO_2 .^{130–132} Latimer *et al.* developed a method for calculating the transition state energy, and thus the reaction rate, for C-H activation involving methyl radical-like transition states based on the hydrogen affinity of the active site.¹³³ Using this method, Kulkarni *et al.* calculated that a methane partial pressure of 10⁶ times that of methanol is required to achieve comparable rates of C-H activation for methane and methanol in the steady state reaction, resulting in a theoretical maximum methane conversion of *ca.* 0.01 %.¹¹⁵ Calculations comparing the cyclic and steady state reactions over Cu zeolites showed that the cyclic reaction is currently capable of higher overall methanol productivity than the steady state reaction), although the steady state reaction likely has more room for improvement.¹³⁴

An economic analysis of the costs associated with the construction and operation of a commercial process utilizing Cu-exchanged zeolite catalysts to covert methane to methanol showed that because of the low methanol productivity, the catalyst cost dominates the capital and raw material costs. The authors concluded that the catalyst productivity must be increased by at least two orders of magnitude before industrial use of Cu exchanged zeolites for converting methane to methanol can be considered.¹³⁵

1.4 Goals of this work

Based on the preceding discussion, three different strategies are possible for making Cuexchanged zeolite catalysts industrially viable: increasing the methanol yield per cycle for the cyclic reaction, operating the cycle isothermally without sacrificing methanol yield to increase methanol productivity, and increasing the rate of methanol formation in the steady state reaction while maintaining high selectivity. Understanding the structure of the active sites in Cu-exchanged zeolites and their reactivity toward methane are critical to realizing these goals. The objectives of this work are therefore as follows:

- Elucidate the structure of the active sites for methanol formation in the high-performing Cu-H-MOR catalyst.
- Understand the effect of H versus Na co-cations on Cu speciation in Cu-MOR and Cu-ZSM-5, and use this effect to elucidate the structure of Cu species that prevails depending on the co-cation.
- Understand the differences between the Cu active site structures in Cu-MOR and Cu-ZSM that lead to selective methanol formation versus overoxidation of methane to CO and CO₂.

The findings presented in this dissertation will facilitate the design of improved catalysts for the selective oxidation of methane to methanol by identifying properties of Cu-exchanged zeolites that lead to a high concentration of active sites that catalyze selective methanol formation.

2 Insights into the speciation of Cu in the Cu-H-mordenite catalyst for the oxidation of methane to methanol

This chapter is adapted from "Brezicki, G.; Kammert, J. D., Gunnoe, T. B.; Paolucci, C.; Davis, R. J. Insights into the Speciation of Cu in the Cu-H-MOR catalyst for the oxidation of methane to methanol. ACS Catal. 2019, 9, 5308–5319." Copyright 2019 American Chemical Society.

Abstract

The proton form of Cu-exchanged mordenite (Cu-H-MOR) was prepared via ion-exchange, and the nature of the active Cu species in the cyclic oxidation of CH₄ to CH₃OH was investigated by high-pressure reactivity testing, X-ray absorption spectroscopy (XAS), and H₂ temperature programmed reduction (TPR). Increasing the CH₄ pressure from 1 bar to 35 bar and the reaction time from 4 h to 20 h increased the product yield from 0.30 to 0.42 mol (mol Cu)⁻¹, suggesting that at lower pressures and shorter reaction times, the CH₄ activation reaction is not complete and the active site for CH₃OH formation likely contains fewer than three Cu atoms. Linear combination fitting of the Cu K-edge X-ray absorption near edge spectra showed that 83% of the Cu in freshly-prepared Cu-H-MOR can be auto-reduced in He at 723 K. Analysis of the extended X-ray absorption fine structure of Cu-H-MOR after activation in O₂ at 723 K resulted in an oxygen coordination number of 2.9. The product yield normalized by the redox-active Cu fraction was 0.50. All of these findings are consistent with a dicopper active site. The same fraction of non-reducible Cu was observed by auto-reduction in He and TPR in H₂, suggesting that redox-inert Cu is inactive toward CH₄ oxidation.

2.1 Introduction

The development of hydraulic fracturing technology for the recovery of natural gas from shale rock formations has greatly increased the recoverable reserves of natural gas.³ In the absence of a pipeline, natural gas should be liquefied prior to storage and transport. The liquefaction process is, however, expensive and energy intensive, and large quantities of stored liquefied natural gas (LNG) present a safety concern.⁴ The extraction of natural gas from deposits located far from industrial infrastructure is therefore impractical. For similar reasons, much of the natural gas commonly released during oil drilling is flared, rather than being captured, releasing huge amounts of CO₂ into the atmosphere. The development of a process for the chemical conversion of natural gas to a liquid at the point of extraction is therefore desirable.^{6,7}

Methane comprises 70-90% of natural gas by volume, and therefore represents a significant potential feedstock for chemicals and liquid fuels.^{1,2,10} Beyond natural gas, CH₄ hydrates and biogas are also potential sources of CH₄ that may be utilized in the future.¹⁰ The chemical conversion of CH₄ to CH₃OH is a promising route for the utilization of CH₄, because liquid CH₃OH can be easily stored and transported using existing infrastructure. Methanol is also an extremely versatile molecule – it is a commodity chemical with large global demand, and can be used directly as a fuel or subsequently converted to other chemicals, including formaldehyde, acetic acid, olefins, and synthetic gasoline.^{1,2,11,15}

Currently, CH₃OH is produced industrially from syngas, which is generated via steam reforming of CH₄. Steam reforming is highly endothermic, resulting in high energy costs.^{8,12,13} Due to the high temperature and pressure required, steam reforming plants are extremely capitalintensive, and most gas fields are not large enough to justify this capital expense. The direct conversion of CH₄ to CH₃OH under mild conditions would circumvent these problems and materials capable of catalyzing this reaction are therefore being intensively researched.^{9–11,14–16} Despite these efforts, a commercially viable catalyst for the direct low temperature oxidation of CH₄ to CH₃OH has not yet been developed.⁹ Much of the difficulty arises from the strength of the C-H bonds in CH₄, and the fact that CH₃OH is often much more reactive than CH₄, making it difficult to prevent over-oxidation to CO_2 .^{10,14,19,20}

In 2005, Groothaert et al. demonstrated that Cu-exchanged Na-ZSM-5 (Cu-Na-ZSM-5) and Cu-exchanged Na-mordenite (Cu-Na-MOR) zeolites are capable of oxidizing CH₄ to CH₃OH with a selectivity of > 98% in a cyclic process that temporally separates O₂ activation and CH₄ activation.⁴² After activation of the catalyst in O₂ at 723 K and treatment in CH₄ at 473 K, CH₃OH is recovered either offline via solvent extraction, or online by passing steam over the catalyst.⁴⁴ Results from a combined spectroscopic and computational study of Cu-Na-ZSM-5 led the authors to propose mono(μ -oxo) dicopper(II) species (hereafter referred to as [Cu₂O]²⁺) as the active site.³⁴ A follow-up paper from the same group proposed the same active site for Cu-Na-MOR.⁷¹ Several subsequent studies investigated the structure^{43,54,99,104} and location⁷¹ of this Cu moiety within the zeolite pores, as well as its mechanism of formation.⁹⁶

A major difficulty in characterizing the active site in early studies of Cu-zeolites was the low fraction of active Cu. For example, the moles of CH₃OH produced per mole of Cu in both Cu-Na-ZSM-5 and Cu-Na-MOR was about 5% in multiples studies.^{42,43,68,136} In 2015, however, a major breakthrough occurred when the total C1 product yield (CH₃OH + CO_x) was increased to 0.33 mol (mol Cu)⁻¹ (75-80% CH₃OH selectivity) by exchanging Cu into the proton form of mordenite (Cu-H-MOR) instead of the Na form.⁷² Based on a consistent ratio of approximately 0.33 moles of CH₄ converted per mole of Cu for numerous catalysts with varying Cu loading and Si/Al ratio (100 < μ mol Cu g_{cat}⁻¹ < 500, 5.5 < Si/Al < 21), a single active site containing three Cu
ions was proposed, with all of the Cu in the catalyst contained in these sites. Density functional theory (DFT) calculations and extended X-ray absorption fine structure (EXAFS) analysis were used to support the structure of the active site as a tris-(μ -oxo) tricopper (II) species ([Cu₃O₃]²⁺). Based on Fourier transform infrared (FT-IR) spectroscopy, these species were proposed to reside in the 8-member ring (8MR) of the side pockets of mordenite.⁷³ A recent report, however, demonstrated that optimization of the Cu loading and Si/Al ratio of Cu-H-MOR can produce a catalyst exhibiting a C1 yield of up to 0.54 mol (mol Cu)⁻¹ (~87% CH₃OH selectivity), suggesting that the active site might contain two, rather than three, Cu atoms.⁸³ In addition to [Cu₂O]²⁺ and [Cu₃O₃]²⁺, monocopper [Cu(II)OH]⁺ species,⁸⁹ dicopper peroxo [Cu₂O₂]²⁺ species,^{85,86,90} and larger Cu-oxo clusters^{94,95} have also been proposed as active sites for CH₄ to CH₃OH conversion in Cu-exchanged zeolites.

Despite the success of Cu-exchanged zeolites in oxidizing CH₄ to CH₃OH with high selectivity, these catalysts are still far from industrial viability. The cyclic nature of the reaction accounts for the high selectivity due to the temporal separation of O₂ activation and CH₄ oxy-functionalization but presents a roadblock to industrial use. Non-continuous CH₃OH production, as well as the time required for reactor temperature adjustments between each reaction step, result in low overall CH₃OH productivity. The reaction can be operated under steady-state conditions over Cu-zeolites at 473-723 K using O_2^{131} or N_2O^{130} as the oxidant, but the rate of CH₃OH production was reported to be very slow (0.001-0.1 mol CH₃OH (mol Cu)⁻¹ h⁻¹),^{130,131} and 0.02% conversion was required for CH₃OH selectivity of 40%.¹³⁰ Thus, while the reports of steady-state activity are promising, the system needs significant improvements. Several attempts have been made to operate the cyclic reaction isothermally to reduce the cycle time, but this has resulted in

either low CH_3OH productivity,⁹⁵ or required the use of an oxidant other than O_2 ,⁵⁵ which will likely not be commercially feasible.

To move the Cu-zeolite catalyst system toward industrial viability, the CH₃OH productivity must be increased either by increasing the active site density or by developing an isothermal cycle that does not sacrifice CH₃OH yield. Understanding the structure of the active sites and their mechanism of formation are critical to achieving these goals. Despite years of experimental and computational studies, the active sites in Cu-zeolites for CH₄ activation have not been unambiguously identified. The best performing catalyst to date for the cyclic CH₄ to CH₃OH reaction is Cu-H-MOR, as first reported by Grundner et al.^{72,130} and more recently optimized by Pappas et al.⁸³ Unfortunately the conditions used for the cyclic oxidation of CH₄ to CH₃OH over Cu-exchanged zeolites are not uniform throughout the literature, making direct comparisons difficult. Here we utilize conditions that are designed to maximize the CH₃OH yield from Cu-H-MOR. Results from these measurements combined with in situ X-ray absorption spectroscopy are used infer the nature of the active sites. Moreover, the influence of O₂ and H₂O impurities on the Cu speciation and reactivity is shown to be important under specific conditions.

2.2 Experimental Methods

2.2.1 Catalyst synthesis

The Cu-H-MOR catalysts were prepared using the NH_4^+ form of mordenite (MOR) (Zeolyst International, Si/Al = 10, CBV 21A). Catalysts are designated as CuX-H-MOR, where X indicates the Cu/Al ratio. MOR was ion-exchanged in an aqueous solution of Cu (II) acetate monohydrate (Sigma Aldrich, 99.99%). The pH of the ion exchange solution was adjusted to 5.7 by addition of aqueous NH₄OH (Sigma Aldrich, 28 wt. % NH₃) or nitric acid (Sigma Aldrich, 0.5

M) as required. After ion exchange, the catalyst was filtered, washed with deionized H₂O ($300 \text{ cm}^3 \text{ g}_{\text{zeolite}^{-1}}$), and dried overnight in air at approximately 393 K. Washing was performed by dispersing the filtered catalyst in $300 \text{ cm}^3 \text{ g}_{\text{zeolite}^{-1}}$ deionized H₂O and stirring. The Cu-NH₄-MOR was converted to Cu-H-MOR by thermal treatment in flowing air at 773 K (ramp rate 1 K min⁻¹) for 8 h after Cu exchange.

Two Cu-Na-MOR catalysts were prepared from NH₄-MOR (Zeolyst International, Si/Al = 10, CBV 21A). The NH₄-MOR was ion-exchanged with a 2.44 M aqueous solution of Na acetate (Sigma Aldrich, 99%) at 353 K three times with a ratio of 60 cm³ solution per gram zeolite. The Na-exchanged MOR (Na-MOR) was then filtered, washed with deionized H₂O (300 cm³ g_{zeolite}⁻¹), and dried overnight in air at approximately 393 K. The Na-MOR was ion-exchanged in an aqueous solution of Cu (II) acetate monohydrate (Sigma Aldrich, 99.99%). In one of the catalysts, the pH was adjusted to 5.7 during Cu exchange by addition of nitric acid (Sigma Aldrich, 0.5 M), whereas the other was Cu-exchanged without pH control, which resulted of a pH of approximately 6.0.

The Cu and Al concentrations of the synthesized catalysts were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) performed by Galbraith Laboratories (Knoxville, TN).

To quantify the fraction of ion-exchanged Cu (as opposed to Cu in nanoparticles) in the Cu-MOR catalysts, the used (i.e., activated in O_2 at 723 K, exposed to CH₄ at 473 K, and treated in steam at 473 K) catalysts were back-exchanged with Na based on the method of Grundner et al.⁷³ A 1.0 M solution of NaNO₃ (Sigma Aldrich, 99.99%) was prepared and heated to 333 K (200 cm³ solution per gram of catalyst). The used catalyst was added to the solution and stirred for 24 h, then filtered, washed with deionized H₂O, and dried overnight in air at approximately 393 K. The Cu concentration of the back-exchanged catalyst was measured using a Panalytical Epsilon

3x X-ray fluorescence spectrometer. The Cu Kα peak was integrated, and the Cu concentration was calculated using a calibration curve generated from Cu zeolite catalysts with known Cu concentration from ICP-OES (Figure B.1).

2.2.2 Methane oxidation reactions

Cyclic CH₄ oxidation reactions were performed in a continuous-flow fixed-bed stainless steel reactor (BTRS Jr., Autoclave Engineers). The undiluted catalyst in powder form was supported on silanized glass wool, with a thermocouple placed in the catalyst bed for temperature control. The reactor oven, sample valve, and associated tubing were heated to 393 K to prevent condensation of CH₃OH and H₂O. Helium (Praxair, Ultra-high purity, 99.999%), O₂ (Praxair, Ultra-high purity, 99.999%), and CH₄ (Praxair, 99.999%) were supplied to the reactor using Brooks mass flow controllers, and the reactor was operated at a space velocity of 80 cm³ min⁻¹ g_{cat}⁻¹. For some reactions, as noted in the main paper, a Supelco OMI-4 purifier cartridge was placed in the He line to reduce the trace O₂ concentration. The reactor heating rate was 10 K min⁻¹, unless otherwise specified.

Product quantification was performed using two online HP 5890 Series II gas chromatographs (GC), one equipped with a flame ionization detector (FID) and the other equipped with a thermal conductivity detector (TCD). The GC-FID was equipped with a Restek Rt-S-BOND column (30 m, 0.53 mm ID) and was used to quantify CH₃OH, dimethyl ether (DME), and C₂H₄ in the reactor effluent. The GC-TCD was equipped with an Agilent CarboPLOT P7 column (27.5 m, 0.53 mm ID) and was used to quantify CO and CO₂. It was assumed that DME and C₂H₄ were formed via acid-catalyzed dehydration of CH₃OH, which are well-known reactions in zeolites.¹⁷ Each DME and C₂H₄ molecule was therefore counted as originating from two CH₃OH molecules.

Unless otherwise specified, the cyclic CH₄ oxidation reaction involved three separate steps performed in sequence: activation of the catalyst in O_2 overnight at 723 K and subsequent cooling to 473 K in O_2 , reaction of the activated catalyst with CH₄ at 473 K, and desorption of CH₃OH in H₂O vapor at 473 K. The reactor was purged with 40 cm³ min⁻¹ He for 2 h between each step. Water vapor was introduced by passing He through a liquid H₂O saturator at ambient temperature. The H₂O saturator was continuously purged with He prior to the desorption step to remove trace amounts of O₂. No products were observed during the CH₄ activation step; CH₃OH, DME, C₂H₄, CO, and CO₂ were only observed after introduction of H₂O in the desorption step. After desorption was complete at 473 K, the reactor temperature was ramped to 723 K at 10 K min⁻¹, resulting in the observation of small amounts of additional CH₃OH, C₂H₄, CO, and CO₂ (< 5% of total), which were included in the calculated product yield.

Methanol, DME, CO, and CO₂ concentrations were calculated from the GC peak areas for samples collected at 10-15 minute intervals during the desorption step of the cyclic reaction using calibration curves generated from gas streams containing known concentrations of each compound. Additional details on product quantification can be found in Appendix A2.1.

2.2.3 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) of the Cu0.28-H-MOR catalyst was performed at the National Synchrotron Light Source II (beamline 8-ID) at Brookhaven National Laboratory in Upton, NY. The electron storage ring operated at 3 GeV with a beam current of 400 mA. All measurements were performed in transmission mode at the Cu K edge (8979 eV). The catalyst was pelletized to 180-425 μ m and placed in a ¹/₄" OD stainless steel tube, sealed at the ends with Kapton film. 20 mg of catalyst were loaded into the reactor tube, and all gas flow rates were 20 cm³ min⁻

¹.The catalyst bed was held in place by silanized glass wool on the upstream side of the bed, and by carbon wool on the downstream side of the bed. Reactant gases were supplied to the cell via Brooks mass flow controllers, and the reactor tube was placed inside aluminum heating blocks containing heating cartridges, with the temperature controlled via a thermocouple placed in the aluminum blocks and a temperature controller. The details of the *in situ* reactor cell can be found in James D. Kammert's doctoral thesis.¹³⁷

The catalyst was first treated in flowing He (Mattson, Ultra-high purity) at 723 K (autoreduction), followed by treatment in O_2 (Mattson, Ultra-high purity) at 723 K (O_2 activation), and finally treatment in CH₄ (Mattson, Ultra-high purity) at 473 K (CH₄ activation). Carbonaceous intermediates were then removed by treatment in O_2 at 723 K for 1 h, followed by a second treatment in He at 723 K. The cell was cooled to 323 K and purged with He between each step, and the temperature ramp rate during heating for each step was 3 K min⁻¹. Spectra were collected continuously during the temperature ramps for each step. Using a fresh catalyst sample, the Cu0.28-H-MOR catalyst was treated in H₂ (Mattson, Ultra-high purity) at 673 K with a ramp rate of 3 K min⁻¹. The beam energy was calibrated by simultaneous scanning of a Cu foil.

The XAS data were analyzed using the Demeter software package.¹³⁸ Using Athena, the spectra were first normalized to an edge jump of 1.0, and then linear combination fitting of the X-ray absorption near edge spectra (XANES-LCF) was performed to quantify the Cu speciation based on the method of Alayon et al.⁴³ The XANES-LCF was performed using standard spectra representing hydrated Cu(II), dehydrated Cu(II), and Cu(I). The standards were obtained by collecting spectra of the Cu0.28-H-MOR catalyst under the following conditions: fresh catalyst for hydrated Cu(II), after treatment in O₂ at 723 K for dehydrated Cu(II), and after treatment in He at 723 K (preceded by the following pretreatment: 1) He at 723 K, 2) O₂ at 723 K, 3) CH₄ at 473

K, 4) O_2 at 723 K), which resulted in complete reduction of Cu to Cu(I) (based on comparison of the spectrum with spectra from literature representing pure Cu(I) in similar Cu zeolite materials).^{91,139} The EXAFS fitting was performed using the Artemis software package with FEFF6.¹³⁸ Spectra were normalized and background-corrected using Athena, then k¹-, k²-, and k³weighted and Fourier-transformed to convert from k-space to R-space. Up to 7 spectra were averaged to improve the signal-to-noise ratio. The value of S₀² was fixed at 0.9 and was determined by EXAFS fitting of a Cu metal foil with path degeneracies set to the known values from crystal structure data (Figure B.4 and Table B.1). Fitting of the Cu foil yielded a S₀² value of 0.9, consistent with the value of S₀² used in several recent EXAFS fitting studies of Cu zeolites.^{72,84,86}

2.2.4 *Temperature programmed reduction*

Temperature-programmed reduction in H₂ (H₂-TPR) was performed using a Micromeritics AutoChem II 2920 analyzer. Approximately 150 mg catalyst was loaded into a quartz reaction cell on a quartz wool bed. The catalyst was pre-treated in O₂ (Praxair, Ultra-high purity) at 723 K (10 K min⁻¹) for 4 h, then cooled to 323 K in flowing O₂. The cell was purged with He (Praxair, Ultrahigh purity) for 0.5 h, then heated to 1073 K at 3 K min⁻¹ in a gas stream containing 5 vol. % H₂ in Ar (Praxair, certified mixture). All gas flow rates were 50 cm⁻³ min⁻¹. The reactor effluent was passed through a liquid nitrogen/isopropanol cold bath and then a TCD to monitor H₂ consumption.

2.3 Results and Discussion

2.3.1 Effect of CH₄ pressure and reaction time on product yield

We used catalyst synthesis and reaction conditions that were selected to mimic those previously used to study Cu-H-MOR.⁷² Cu-exchanged H-mordenite (Zeolyst International, Si/Al

= 10) catalysts are designated as CuX-H-MOR, where *X* indicates the Cu/Al ratio (synthesis details can be found in section B.1). After activation of Cu0.28-H-MOR in 1 bar O₂ (Praxair, Ultra-high purity 99.999%) at 723 K overnight and treatment in 1 bar CH₄ (Praxair, 99.999%) at 473 K for 4 h, followed by product desorption in steam at 473 K, the observed total C1 product yield (CH₃OH + CO_x) was 0.30 mol (mol Cu)⁻¹, with a CH₃OH selectivity of 84%, which is similar to the C1 product yield of 0.33 mol (mol Cu)⁻¹ and CH₃OH selectivity of 75-80% previously reported for an analogous Cu-H-MOR catalyst.⁷² In addition to CH₃OH, dimethyl ether (DME), CO, CO₂, and a trace amount of C₂H₄ were also produced over the catalyst. Both DME and C₂H₄ were likely formed via subsequent reaction of CH₃OH on the Brønsted acid sites of H-MOR. Indeed, conversion of CH₃OH to olefins over acidic zeolites is a well-known reaction.¹⁷ Thus, each DME and C₂H₄ molecule produced was included in the product yield as originating from two CH₃OH molecules: CH₃OH_{total} (mol. %) = CH₃OH_{measured} (mol. %) + 2*DME (mol. %) + 2*C₂H₄ (mol. %).

Previous work has demonstrated that increasing the CH₄ pressure from 1 bar to 36 bar during the CH₄ activation step (0.5 h at 473 K) of the cycle with a Cu-Na-MOR catalyst (Si/Al = 6, 4.7 wt. % Cu) after activation in O₂ at 723 K increases the CH₃OH yield from 0.06 to 0.14 mol (mol Cu)^{-1.95} A recent study also reported a ~20% increase in CH₃OH yield after increasing the CH₄ pressure from 1 bar to 30 bar during CH₄ treatment of an O₂-activated Cu-exchanged omega zeolite (Cu-MAZ) catalyst.¹²³ Increasing the duration of CH₄ activation at 1 bar CH₄ has also been reported to increase the product yield for Cu-CHA⁸⁶ and Cu-H-MOR¹⁴⁰ catalysts. All of these observations suggest that high pressures and long reaction times may be necessary to convert all of the active Cu sites for CH₄ oxidation.

As shown in Table 2.1, increasing the time of CH₄ exposure at 1 bar from 4 to 70 h for the O₂-activated Cu0.28-H-MOR catalyst increased the C1 yield by about 10%. Thus, exposure of the catalyst to 1 bar CH₄ at 473 K for 4 h, which is a common protocol in the literature, may not be adequate to convert all of the active Cu sites. To achieve maximum conversion of the active sites, thus ensuring a more accurate quantification based on the product yield, we exposed the O₂-activated Cu0.28-H-MOR catalyst to 35 bar CH₄ at 473 K for 20 h. This resulted in an increase of the C1 product yield to 0.42 mol (mol Cu)⁻¹, compared to 0.30 mol (mol Cu)⁻¹ for treatment in 1 bar CH₄ for 4 h (Table 2.1). An observed C1 yield > 0.33 mol (mol Cu)⁻¹ suggests that the active sites contain less than three Cu atoms, assuming a single turnover per site.

	Cu conc.	CH4 pres.	CH4 act.	C1 yield [mol	CH ₃ OH
Catalyst	[µmol g ⁻¹]	[bar]	time [h]	(mol Cu) ⁻¹]	select. [%]
Cu-H-MOR ^a	100-500	1	4	0.33	75-80
		1	4	0.30	84
		1	20	0.28	86
Cu0.28-H-MOR	371	1	70	0.33	80
		35	4	0.40	88
		35	20	0.42	90
Cu0.20-H-MOR	266	35	24	0.40	91

Table 2.1 Effect of CH_4 pressure on C1 product yield for Cu-H-MOR catalysts activated in O_2 at 723 K.

^aData from ref. ⁷² for catalysts of varying Cu concentration and Si/Al. C1 yield was similar for all catalysts with an average of approximately 0.33 mol (mol Cu⁻¹).

To test the effect of Cu loading on Cu speciation, a Cu0.20-H-MOR catalyst was prepared and tested under similar conditions as the Cu0.28-H-MOR catalyst. A similar C1 yield of 0.40 mol (mol Cu)⁻¹ was observed for a Cu0.20-H-MOR catalyst after reaction with 35 bar CH₄ for 24 h. This result suggests that Cu loading does not have a significant effect on Cu speciation over the range studied, which is consistent with previous conclusions from reaction of 1 bar CH₄ with Cu-H-MOR.⁷² Interestingly, however, Pappas et al. prepared a single Cu-H-MOR catalyst (Cu/Al = 0.18, Si/Al = 7) with higher product yields than other Cu-H-MOR catalysts in their series,⁸³ suggesting that some specific combinations of composition and synthetic route may affect Cu speciation in Cu-H-MOR.

2.3.2 In situ X-ray absorption spectroscopy of Cu0.28-H-MOR

In situ X-ray absorption spectroscopy (XAS) was performed on the Cu0.28-H-MOR catalyst to investigate the Cu speciation during the cyclic CH₄ oxidation reaction. Although the normal cyclic reaction sequence for CH₄ oxidation does not include an initial high-temperature treatment in He, we performed such a treatment during XAS to quantify the redox-active fraction of Cu in the Cu0.28-H-MOR catalyst. Thermal treatment of Cu-zeolites in inert atmosphere induces the so-called auto-reduction reaction, in which Cu(II) is reduced to Cu(I).¹⁰² Proposed mechanisms for auto-reduction include a radical-based mechanism, in which hydroxyl radicals are released from $[Cu(II)OH]^+$,^{86,100–102} as well as a condensation mechanism in which proximal $[Cu(II)OH]^+$ species condense within the zeolite pores.^{98,99}

Reduction of Cu(II) to Cu(I) is a prerequisite for O₂ activation and active site formation in Cu-zeolites.⁵⁴ Indeed, for Cu-CHA, a direct correlation between the auto-reducible fraction of Cu in the catalyst and CH₃OH yield was reported, suggesting that active sites are formed via reaction of Cu(I) with O₂.⁸⁶ The fresh catalyst initially contains hydrated Cu(II), which does not react with O₂ and therefore cannot form the active Cu sites.^{97,98} Auto-reduction can be carried out separately from O₂ activation by heating the catalyst in inert atmosphere prior to introducing O₂, or concurrently with O₂ activation simply by treating the catalyst at high temperature in O₂ (typically 723 K). In the latter case, auto-reduction and subsequent oxidation of Cu(I) by O₂ occur simultaneously.⁹⁹ A recent report demonstrating the transient formation of Cu(I) during O₂

activation for Cu-H-MOR and Cu-H-CHA observed via XAS provides experimental evidence of auto-reduction in an O₂ atmosphere.⁸⁴ Performing auto-reduction separately from O₂ activation is not necessary for the formation of active sites, but it allows for independent investigation of the redox behavior of Cu and quantification of the redox-active fraction of Cu, described below. Performing auto-reduction of Cu-H-MOR catalysts in He prior to activation in O₂ results in the same Cu speciation and subsequent product yield as directly activating the fresh catalyst in O₂ without an initial auto-reduction step.⁷⁸

Figure 2.1 shows the Cu K-edge X-ray absorption near edge spectrum (XANES) of the Cu0.28-H-MOR catalyst after each step in the reaction cycle. Spectrum 1 shows the fresh sample under He at ambient temperature, spectrum 2 was recorded after treatment in He at 723 K for 2 h (auto-reduction), spectrum 3 was obtained after subsequent treatment in 1 bar O_2 at 723 K for 4 h (O_2 activation), and spectrum 4 was recorded after cooling in O_2 , purging in He, and treatment in 1 bar CH₄ at 473 K for 1 h (CH₄ activation).



Figure 2.1 Normalized XANES at the Cu K edge of fresh Cu0.28-H-MOR catalyst, after heating in He at 723 K (auto-reduction) for 2 h, after treatment in O_2 at 723 K for 4 h (O_2 activation), and after reaction with 1 bar CH₄ at 473 K for 1 h (CH₄ activation).

The small pre-edge feature at 8977 eV associated with the fresh catalyst is due to the dipoleforbidden $1s \rightarrow 3d$ transition of Cu(II).¹⁴¹ The very intense white line feature centered at 8997 eV is indicative of coordination of Cu(II) to H₂O or OH ligands,¹⁰⁴ which is expected for the fresh catalyst. The XANES of fresh Cu-exchanged zeolite catalysts has been shown to be indistinguishable from aqueous Cu(II) complexes.¹⁴¹

After auto-reduction, the Cu K-edge of Cu0.28-H-MOR shifted to lower energy, indicating a decrease in the average oxidation state of Cu. A feature at 8983 eV also appeared, representative of a 1s \rightarrow 4p transition of Cu(I).^{142,143} After exposing the catalyst to O₂ at 723 K, the Cu(I) feature at 8983 eV disappeared and the Cu returned to a completely +2 state, although there were significant differences in the spectrum relative to the fresh catalyst. After O₂ activation, the white line intensity decreased compared to the fresh catalyst, likely due to the removal of H₂O ligands,^{144,145} and a shoulder at 8986 eV, associated with the 1s→4p transition of Cu(II),⁹⁹ became more prominent. Slight shifts in the edge features result from changes in the Cu coordination sphere associated with loss of H₂O ligands.^{146,147} After exposure of the O₂-activated catalyst to 1 bar CH₄ at 473 K, the feature at 8983 eV reappeared, indicating partial reduction of the Cu by CH₄, similar to previous reports for Cu-MOR.^{43,99,104}

Given the ambiguous nature of auto-reduction, we performed standard temperatureprogrammed reduction in H_2 (H_2 -TPR) to further interrogate the redox behavior of the Cu species in Cu-H-MOR. Figure 2.2 shows the H_2 -TPR profile for Cu0.28-H-MOR.



Figure 2.2 H₂-TPR of Cu0.28-H-MOR catalyst. Catalyst was pre-treated in O₂ at 723 K for 4 h, then cooled to 323 K and purged with He. Reduction was performed in 5% H₂ in Ar at a ramp rate of 3 K min⁻¹.

The low-temperature H₂ consumption in the range of approximately 323 K to 673 K, centered at approximately 473 K, represents reduction of Cu(II) to Cu(I), and the higher temperature H₂ consumption represents reduction of Cu(I) to Cu metal.¹³⁶ Based on this profile, treatment in H₂ at 673 K should result in reduction of Cu(II) to Cu(I) without formation of Cu metal. The H₂-TPR of Cu-ZSM-5 has been shown to proceed via distinct, sequential single electron reductions, in which Cu(II) is initially completely reduced to Cu(I) without formation of Cu metal, followed by reduction of Cu(I) to Cu metal at higher temperature.¹⁴⁸ The XANES of the Cu0.28-H-MOR catalyst after reduction in H₂ at 673 K (Figure 2.3), however, appeared to have a less

intense pre-edge feature at 8983 eV, representing the 1s \rightarrow 4p transition of Cu(I), than the Cu(I) standard, as well as that typically observed for pure Cu(I) in Cu-exchanged zeolites.^{91,139} Evidently, the H₂ treatment did not fully reduce all of the Cu(II) in the fresh Cu0.28-H-MOR catalyst to Cu(I).



Figure 2.3 Normalized XANES at the Cu K edge of fresh Cu0.28-H-MOR catalyst after reduction in H_2 at 673 K, auto-reduction (treatment in He at 723 K for 2 h), and Cu(I) standard. See section B.2.1 for details on Cu standards.

To gain additional insight into the nuclearity of the active site for CH_3OH formation, we estimated the fraction of active Cu in the catalyst using linear combination fitting of the X-ray absorption near edge spectra (XANES-LCF). Based on the preceding discussion of the necessity of auto-reduction of Cu(II) to Cu(I) as a prerequisite for active site formation, we assumed that the

fraction of redox-active Cu at 723 K (i.e., the fraction of Cu that undergoes auto-reduction at 723 K in He) is the fraction of Cu that participates in the CH₄ activation reaction leading to products. Normalizing the product yield to the fraction of redox-active Cu, rather than total Cu, provides more accurate insight into the nuclearity of the Cu active sites. Figure 2.4 shows the results of XANES-LCF for the Cu0.28-H-MOR catalyst after 2 h of auto-reduction in He at 723 K. Based on the results of the fit, the catalyst after auto-reduction contains 83 ± 0.3 % Cu(I), 17 ± 1.0 % dehydrated Cu(II), and 0.0 ± 0.8 % hydrated Cu(II). Thus, we conclude that 83% of the Cu in the Cu0.28-H-MOR catalyst is redox-active at 723 K, and thus capable of reacting with O₂ to form active sites. Details on the Cu standards used in XANES-LCF can be found in section B.2.1.

Buono et al. reported a Cu(I) state for an analogous Cu-H-MOR catalyst after treatment in vacuum at 773 K, with a Cu(I) $1s \rightarrow 4p$ pre-edge feature at 8983 eV slightly less intense than the white line,¹⁴⁹ which was similar to our Cu0.28-H-MOR catalyst after auto-reduction. The lower-than-expected pre-edge peak intensity was attributed by Buono et al. to a non-linear configuration of the Cu(I) species,¹⁴⁹ which is known to reduce the intensity of that feature.¹⁵⁰ For our Cu0.28-H-MOR catalyst, we attribute the lower intensity of the Cu(I) pre-edge feature of the auto-reduced catalysts compared to the Cu(I) standard to a fraction of unreduced Cu(II), rather than a difference in coordination geometry, as the Cu(I) standard was generated using the Cu0.28-H-MOR catalyst (section B.2.1).



Figure 2.4 Results of XANES-LCF for Cu0.28-H-MOR catalyst after treatment in He at 723 K for 2 h. The spectrum was fit using hydrated Cu(II), dehydrated Cu(II), and Cu(I) standards. See Appendix B for details on Cu standards.

The auto-reducibility of Cu, and therefore the fraction of potentially active Cu within the zeolite, may be affected by a number of different factors, including zeolite topology, identity of the co-cation, and the nature of the aqueous Cu(II) complexes that are introduced during ion exchange. Alayon et al. reported that for a Cu-Na-MOR catalyst, 43% of the Cu was auto-reduced at 723 K,⁹⁹ compared to 83% for our Cu0.28-H-MOR catalyst. Thus, Na may inhibit auto-reduction. However, the pH of the ion exchange solution used to synthesize the Cu-Na-MOR catalyst was not reported,⁹⁹ and is therefore assumed to have not been controlled. If the pH during

Cu exchange is greater than 5.7, Cu can exchange at surface silanols of the zeolite, resulting in weakly-adsorbed Cu species that can aggregate into non-auto-reducible CuO nanoparticles during high-temperature treatment.⁷³ During synthesis of Cu-H-MOR catalysts reported by Grundner et al., the pH was adjusted to 5.7 during Cu exchange,⁷² which was the same pH used to prepare our Cu-H-MOR catalysts. Back-exchanging the catalyst with Na removes ion-exchanged Cu, but not nanoparticles. Grundner et al. reported that for all Cu-MOR (both H and Na form) catalysts synthesized at pH < 6.0, all Cu was removed by Na back-exchange.⁷³ Similarly, we found that for both Cu-H-MOR and Cu-Na-MOR catalysts ion-exchanged at pH = 5.7, all of the Cu was removed by Na back-exchange, indicating the absence of aggregation of Cu into inactive nanoparticles. In contrast, we found that for a Cu-Na-MOR catalyst prepared without pH control, for which the pH during ion-exchange was approximately 6.0, only 60% of the Cu could be removed by Na backexchange, indicating that 40% of the Cu aggregated into non-exchangeable nanoparticles during high-temperature treatment. The O₂-activated Cu-Na-MOR catalysts prepared at $pH \le 5.7$ and subsequently treated in 1 bar CH₄ at 473 K for 4 h demonstrated higher C1 product yields (≥ 0.15 mol (mol Cu)⁻¹)^{73,113} than the yields of ~0.05 mol (mol Cu)⁻¹ previously reported for Cu-Na-MOR catalysts prepared without pH control.^{42,43} Thus, both the co-cation and pH during ion exchange may affect Cu speciation, and we hypothesize that the lack of pH control may have contributed to the lower auto-reducibility of the previously-reported Cu-Na-MOR catalyst⁹⁹ compared to our pHcontrolled Cu-H-MOR catalyst. Moreover, the high CH₃OH yield of Cu-H-MOR is likely partially related to the increased fraction of redox-active Cu compared to previous Cu-Na-MOR catalysts evaluated in the literature that were prepared without pH control. It is difficult, however, to isolate the effect of pH versus co-cation, as decreasing the pH prevents the formation of inactive

nanoparticles and also partially replaces Na^+ with H^+ , both of which increase the fraction of active Cu.⁷³

In a study that included an exploration of the auto-reducibility of Cu in Cu-CHA, Paolucci et al. found that after treatment of Cu-CHA in He at 673 K, only 55% of the initially-present $[Cu(II)OH]^+$ was auto-reduced, despite thermodynamic calculations predicting complete reduction of $[Cu(II)OH]^+$ to Cu(I).¹³⁹ As auto-reduction requires multiple Cu sites, the incomplete auto-reduction of Cu was attributed to a kinetic barrier for reaction of isolated $[Cu(II)OH]^+$. Using multivariate curve reconstruction analysis, Martini et al. showed that for Cu-CHA with optimized Si/Al and Cu/Al, nearly all the Cu(II), which was initially present as $[Cu(II)OH]^+$, was auto-reduced at 673 K.¹⁵¹ Grundner et al. reported that when Cu(II) was exchanged with H-MOR at pH = 5.7, Cu(II) was exchanged as $[Cu(II)(H_2O)_5(OH)]^+$,⁷³ which dehydrates to form framework-bound $[Cu(II)OH]^+$ upon heating.¹⁰² Our Cu0.28-H-MOR catalyst was ion-exchanged at pH = 5.7, and should therefore contain auto-reducible $[Cu(II)OH]^+$ species. Exchange of Cu complexes at lower pH forms $[Cu(II)(H_2O)_6]^{2+}$, which converts to $[Cu(II)(H_2O)_x(OH)]^+$ upon hydrolysis and then $[Cu(II)OH]^+$ during heating.^{73,152} Sushkevich et al. recently reported that Cu loading does not affect the auto-reducibility of Cu-MOR catalysts.¹⁵³

To further investigate the auto-reduction process, XANES of the Cu0.28-H-MOR catalyst was monitored during the controlled temperature ramp of the initial auto-reduction step. Figure 2.5a shows the evolution of the Cu K-edge XANES of Cu0.28-H-MOR during the initial auto-reduction in He as the temperature was increased from ambient to 723 K at 3 K min⁻¹, and Figure 2.5b shows the calculated fractions of each Cu species determined by XANES-LCF of the spectra collected at each time point during the temperature ramp.



Figure 2.5 a) XANES of the Cu0.28-H-MOR catalyst during auto-reduction (heating in He at 3 K min⁻¹ to 723 K). b) Evolution of Cu speciation of the Cu0.28-H-MOR catalyst during auto-reduction calculated by XANES-LCF of the spectra in a).

At *t*=0, dehydration of the Cu ions began as the catalyst was purged in dry He at ambient temperature. As the temperature increased, H₂O ligands continued to desorb from Cu and the previously hydrated Cu(II) ions were converted to framework-bound, dehydrated Cu(II) ions. The dehydrated Cu(II) fraction reached a maximum at approximately 493 K, concurrent with the onset of Cu(I) formation. As the temperature increased further, the Cu(I) fraction increased at the expense of the dehydrated Cu(II) fraction. This behavior is consistent with the condensation mechanism of auto-reduction in which $[Cu(H_2O)_5OH]^{2+}$ complexes are first dehydrated to framework-bound $[Cu(II)OH]^+$, followed by condensation of $[Cu(II)OH]^+$ species and subsequent desorption of O₂ and H₂O through a reduction process that is not well understood. In the XANES-LCF, both $[Cu(II)OH]^+$ and any multi-nuclear Cu-oxo species that are present are represented by the dehydrated Cu(II) standard. The transient evolution of the Cu speciation in the Cu0.28-H-MOR catalyst is similar to that reported for a Cu-Na-MOR catalyst,⁹⁹ with the exception that the Cu(I) fraction reached a significantly higher value for our Cu0.28-H-MOR catalyst (83% vs. 43%⁹⁹).

Sushkevich et al. reported that carbonaceous residues on Cu-MOR catalysts can reduce Cu(II) during thermal treatment in inert gas, potentially obscuring the fraction of Cu(I) formed by auto-reduction.¹⁵⁴ Thermally treating the catalysts in air at high temperature, however, was shown to remove carbonaceous residues, and the subsequent thermal treatment released no CO₂, indicating exclusive reduction of Cu via auto-reduction. Our Cu0.28-H-MOR catalyst was thermally treated in flowing air at 773 K for 8 h, and should therefore not contain significant carbonaceous residues that reduce Cu.

2.3.3 Active site characterization by combined XAS and reaction stoichiometry

By combining the reactivity results at elevated CH₄ pressure and the XANES-LCF results, insight can be gained into nature of the active Cu species in the Cu-H-MOR catalyst. The total C1 product yield for the Cu0.28-H-MOR catalyst after activation in 35 bar CH₄ for 20 h was 0.42 mol (mol Cu)⁻¹ with 90% selectivity to CH₃OH (0.38 mol CH₃OH (mol Cu)⁻¹, 0.031 mol CO (mol Cu)⁻ ¹, 0.010 mol CO₂ (mol Cu)⁻¹). Removing the fraction of inactive Cu (i.e., the 17% of Cu that did not auto-reduce at 723 K) from the product yield normalization provides a more accurate estimation of the nuclearity of the active site than normalizing the yield by the total Cu in the catalyst. When the total C1 product yield was calculated based on the fraction of redox-active Cu, instead of the total Cu, the ratio was 0.50 mol (mol Cu)⁻¹. The ratio of oxygen in the products (including the assumption of two H₂O molecules produced per each CO and CO₂ molecule produced) to auto-reducible Cu was 0.60 mol (mol Cu)⁻¹. These results suggest that the active sites in Cu0.28-H-MOR contain fewer than three Cu atoms, and are consistent with both [Cu₂O]²⁺ species (originally proposed as the active site for Cu-Na-ZSM-5 and Cu-Na-MOR catalysts based on resonance Raman spectroscopy,^{34,71} and more recently suggested as a possible active site in Cu-H-MOR⁸³) and [Cu₂O₂]²⁺ peroxo species (proposed as active sites in Cu-CHA,^{85,86,90} and suggested as a possible active site in Cu-H-MOR⁸³). Our maximum C1 yield of 0.50 mol (mol redox active Cu)⁻¹ is consistent with a previously proposed "radical rebound" mechanism for CH₄ activation, in which adsorbed CH₃OH is formed directly at a single dicopper active site.^{34,88}

For a Cu-MAZ catalyst, a minimum Cu loading was found to be required to obtain an active catalyst, with no CH₃OH being produced below this threshold.¹²³ Above the threshold, the CH₃OH yield was a linear function of Cu loading. The fraction of inactive Cu in Cu-MAZ was estimated from the x-intercept of the yield vs. Cu loading plot and was used to calculate a yield of 0.48 mole

CH₃OH per mole of active Cu. The authors therefore concluded that two Cu atoms were involved in the active site.¹²³ Pappas et al. also recently proposed the existence of dicopper active sites in Cu-H-MOR based on a yield of 0.47 mol CH₃OH (mol Cu)⁻¹ (87% CH₃OH selectivity; total C1 yield = 0.54 mol (mol Cu)⁻¹) obtained for a single high-performing catalyst in a series of catalysts with varying Cu loading and Si/Al.⁸³

Our observed ratio of oxygen in the products to auto-reducible Cu species being slightly greater than 0.50 may result from the small amount of CO and CO₂ produced during the reaction. The exact mechanism of CO/CO₂ formation is unknown, but we speculate that over-oxidation may be catalyzed by a minority active species with an O:Cu ratio > 0.5, such as $[Cu_2O_2]^{2+}$ (peroxo) or $[CuO_2]^+$ (superoxo). Cu-peroxo species have been observed in Cu-Na-ZSM-5 via UV-vis and Raman spectroscopy⁹⁶ and were proposed as active sites for CH₄ oxidation in Cu-CHA.^{85,86,90} Cu-superoxo species have also been observed in Cu-CHA by Raman spectroscopy.⁸⁶

The active site in Cu-H-MOR has been recently suggested to be comprised of redox-inert Cu.⁸³ This proposal, however, contradicts earlier findings of a direct correlation between the autoreducible fraction of Cu and CH₃OH yield for Cu-CHA catalysts.⁸⁶ The proposed activity of redoxinert Cu for CH₄ activation was based on an observed correlation between CH₃OH yield and the fraction of a Cu(II) species that was resistant to auto-reduction in He at 773 K identified using multivariate curve resolution analysis of Cu K-edge XANES. The authors speculated that the redox-inert Cu is $[Cu_2O]^{2+}$ that forms from condensation of $[Cu(II)OH]^+$ species. The XANES-LCF of our Cu0.28-H-MOR catalyst after reduction in H₂ at 673 K, however, gave the same Cu(I) fraction (83%) as auto-reduction (treatment in He at 723 K) (Figure B.3). Our results suggest that during both auto-reduction in He at 723 K and temperature-programmed reduction in H₂ up to 673 K, the non-reducible fraction of Cu is comprised of isolated monomeric Cu(II), rather than $[Cu_2O]^{2+}$ dimers, since $[Cu_2O]^{2+}$ should be easily reduced by H₂ at 673 K.¹⁴⁸ These isolated, redoxinert Cu(II) species may be comprised of $[Cu(II)OH]^+$ and/or bare Cu(II) ions, which can form during thermal treatment via reaction of $[Cu(II)OH]^+$ with Brønsted acid sites.¹⁵⁵ Reduction of monomeric Cu(II) to Cu(I) by H₂ likely requires two proximal Cu(II) ions to accept the two reducing equivalents of H₂. Reduction of Cu(II) to Cu(I) in Cu zeolites by CO also likely requires multiple Cu ions in close proximity.^{148,156} Thus, we conclude that for our Cu0.28-H-MOR catalyst, the redox-inert Cu likely consists of isolated monomeric Cu(II) species that are inactive toward CH₄ oxidation.

2.3.4 EXAFS fitting of the O2-activated Cu0.28-H-MOR catalyst

The Cu K-edge EXAFS can provide structural information about the active site in Cuexchanged zeolites, but because it is averaged over all Cu present, it has been of limited utility for previous low-yielding Cu zeolite catalysts where the Cu active site was a minority species.⁷⁰ For our Cu0.28-H-MOR catalyst, however, the EXAFS is more informative since the majority of Cu in our sample (83%) is involved in the catalysis. Fitting of the Fourier-transformed EXAFS (FT-EXAFS) of the Cu0.28-H-MOR catalyst after activation in O₂ at 723 K for 4 h and subsequent cooling to 473 K in O₂ was therefore performed to further investigate the nature of the active Cu species. The coordination number of oxygen to Cu in the first coordination shell may potentially distinguish between $[Cu_2O]^{2+}$, $[Cu_2O_2]^{2+}$, and $[Cu_3O_3]^{2+}$ species. The first shell oxygen coordination number of Cu in $[Cu_2O_2]^{2+}$ and $[Cu_2(\mu-1,2-O_2)]^{2+}$ species are expected to have a first shell oxygen coordination number of 3 (two framework oxygen plus one extra-framework oxygen),^{76,82,86} while $[Cu_3O_3]^{2+}$ and $[Cu_2(\mu-\eta^2:\eta^2-O_2)]^{2+}$ are expected to have a first shell oxygen coordination number of 4 (two framework oxygen plus two extra-framework oxygen).^{72,76,80,82,86} Figure 2.6a shows the magnitude of the k^2 -weighted FT-EXAFS of the activated Cu0.28-H-MOR catalyst, along with the fit and its individual contributing components, and Figure 2.6b shows the imaginary part of the k^2 -weighted FT-EXAFS with the fit. Table 2.2 shows the resulting fitted parameters.



Figure 2.6 Magnitude and b) imaginary part of k^2 -weighted FT-EXAFS of the Cu0.28-H-MOR catalyst at the Cu K edge after treatment in He at 723 K for 2 h followed by treatment in O₂ at 723 K for 4 h (and subsequent cooling to 423 K in O₂). Shown with fit and individual contributions of the first (oxygen) and second (aluminum) coordination shells of Cu. Gray dashed lines indicate the fitting range in R-space.

Table 2.2 EXAFS fitting results of the Cu0.28-H-MOR catalyst at the Cu K-edge after treatment in He at 723 K for 2 h, followed by activation in O_2 at 723 K for 4 h (and cooling to 473 K in O_2).

Scattering path	Coordination number	Distance [Å]	σ^2 [Å ²]
Cu-O	2.9 ± 0.2	1.94 ± 0.01	0.0055 ± 0.0011
Cu-Al	0.9 ± 0.3	2.69 ± 0.02	0.0051 ± 0.0042

 S_0^2 was fixed at 0.90. Fit was performed in R-space in for 2.5 < k < 13 Å⁻¹ and 1.0 < R < 2.7 Å. Combined k¹-k²-k³-weighted fit. $\Delta E_0 = -1.0 \pm 0.9$ eV. Used 7 out of 11 independent points. R-factor = 0.01. No correlations above 0.9.

The fit was performed using two single scattering paths for the absorbing Cu atom: oxygen in the first coordination shell and aluminum in the second coordination shell. The first shell oxygen coordination number of 2.9 ± 0.2 is consistent with $[Cu_2O]^{2+}$ and $[Cu_2(\mu-1,2-O_2)]^{2+}$ species, which have a first shell oxygen coordination number of 3. The fit gave a coordination number of $0.9 \pm$ 0.3 for Al at a distance of 2.69 ± 0.02 Å, which is consistent with the expected one zeolite T-site Al atom in the second coordination shell of framework-bound Cu. The coordination numbers and distances for the Cu-O and Cu-Al single scattering paths are similar to those reported by Borfecchia et al. for Cu-H-SSZ-13 and Cu-H-MOR catalysts after activation in O₂ at 773 K.⁸⁴

2.3.5 Effect of impurities on Cu speciation

In an effort to confirm that the redox-inert Cu in our Cu0.28-H-MOR catalyst was inactive for CH₄ oxidation, we performed CH₄ oxidation reactions in which the catalyst was activated by treatment in He at 723 K instead of O_2 (analogous to auto-reduction performed during XAS) followed by treatment in 35 bar CH₄ at 473 K for 20 h and product desorption in steam at 473 K. The C1 product yield under these reaction conditions was 0.40 mol (mol Cu)⁻¹, (Figure 2.7, Table B.5) which is significantly higher than expected, since the Cu(I) that predominantly exists after treatment in He at 723 K is not expected to oxidize CH₄. When cooling the Cu0.28-H-MOR catalyst after treatment in He at 723 K, the Cu(I) pre-edge peak at 8983 eV in the XANES decreased significantly in intensity, indicating oxidation of Cu(I) to Cu(II) (Figure 2.8). This may be due to the presence of trace O_2 that coordinates to Cu(I) upon cooling as a result of the shift in equilibrium of O_2 from the gas phase to the adsorbed state.



Figure 2.7 Effect of activation gas, He purification, and CH₄ treatment conditions on product yield for Cu0.28-H-MOR. Activation was performed at 723 K. Activation in 1 bar O₂ was carried out overnight with a ramp rate of 10 K min⁻¹, while activation in He was carried out for 2 h with a ramp rate of 3 K min⁻¹ to mimic auto-reduction performed during the XAS experiment. CH₄ treatment was performed at 473 K. Where specified, He was purified using a Supelco OMI-4 purifier cartridge. Selectivities for all reactions can be found in Table B.5.



Figure 2.8 Cu K-edge XANES of Cu0.28-H-MOR catalyst after treatment in He at 723 K for 2 h, with subsequent cooling in flowing He to 473 K and 323 K.

Based on the observation via XANES of re-oxidation of Cu(I) upon cooling following autoreduction, we speculate that the high yield observed for the Cu0.28-H-MOR catalyst after activation in He instead of O_2 was due to re-oxidation of Cu by trace O_2 upon cooling from 723 K to 473 K. Addition of a Supelco OMI-4 purification cartridge to reduce the O_2 concentration in the He stream decreased the C1 yield from 0.40 to 0.32 mol (mol Cu)⁻¹ under otherwise identical conditions (Figure 2.7, Table B.5), supporting the speculation that trace O_2 re-oxidized Cu during cooling. In an attempt to further reduce the amount of O_2 available to re-oxidize the Cu(I), He flow was stopped and the reactor was sealed during cooling from 723 K to 473 K following activation in He. This procedure also produced a catalyst capable of oxidizing CH_4 (Table B.5), indicating that enough oxidant is present in the reactor and within the zeolite pores to re-oxidize Cu without additional O_2 input to the reactor during cooling.

Treatment of Cu0.28-H-MOR in 1 bar CH₄ for 4 h after activation in (unpurified) He at 723 K instead of O_2 decreased the C1 product yield by 30% (Figure 2.7, Table B.5). Addition of a purification cartridge to the He stream had no effect on the yield when performing the reaction at 1 bar CH₄ (Figure 2.7, Table B.5). These results suggest that the distribution of active Cu(II) species that form via re-oxidation of Cu during cooling after auto-reduction in He is different than that formed in O_2 at high temperature. A small fraction of active sites formed during cooling after auto-reduction in He are kinetically-limited in CH₄ activation at 1 bar as they only react with CH₄ at high pressure and long reaction times. Figure 2.7 summarizes the effects of oxidant gas and He purification under the two different CH₄ treatment conditions tested.

Our results are consistent with previous studies that reported a significant amount of CH₃OH produced over Cu-Na-MOR catalysts after activation in He instead of O_2 .^{91,95,103} For example, a Cu-Na-MOR catalyst produced 0.14 mol CH₃OH (mol Cu)⁻¹ after activation in He at 673 K and subsequent treatment in 7 bar CH₄ for 0.5 h at 473 K, which increased to 0.20 mol CH₃OH (mol Cu)⁻¹ for a second reaction cycle using the same sample.¹⁰³ Based on the observation that some H₂ was produced upon introduction of steam at 473 K during the CH₃OH desorption step, which occurred concurrently with the re-oxidation of Cu observed via XAS, it was proposed that H₂O oxidized Cu(I) to form [Cu₂O]²⁺ sites that subsequently activated CH₄ in the next reaction cycle. Those reactivity results are quite similar to our finding of high CH₃OH productivity for the Cu₀.28-H-MOR catalyst after activation in He. Based on the decrease in yield after adding purification to the He stream, however, as well as the observation by XANES of re-oxidation of

Cu upon cooling in He after treatment in He at 723 K, we interpret the high CH₃OH yield from an auto-reduced sample in our study as resulting from re-oxidation of Cu by trace O₂. Indeed, a recent XAS study of Cu-H-MOR showed an increase in the Cu(II) fraction upon introduction of He following CH₄ reaction at 473 K, prior to the introduction of H₂O,¹⁴⁰ consistent with oxidation of Cu(I) (formed via reaction with CH₄) by trace O₂. Based on the observation that dehydrated Cu(II) was converted to hydrated Cu(II) rapidly upon introduction of H₂O (concurrent with CH₃OH desorption), and that oxidation of Cu(I) in the presence of H_2O occurred over a much longer time scale, the authors concluded that CH₃OH was released via hydrolysis of a Cu(II) intermediate (e.g. [Cu(II)OCH₃]), rather than H₂O-mediated re-oxidation of Cu(I).¹⁴⁰ Formate was detected by Fourier transform infrared spectroscopy of He-activated Cu-Na-MOR after CH₄ treatment,¹⁰³ which may desorb as HCOOH upon introduction of H₂O (similar to the proposed CH₃OH desorption mechanism in which H₂O hydrolyzes adsorbed methoxy species to release CH₃OH^{104,114}). Thus, the H₂ that was observed during treatment of reduced Cu in H₂O¹⁰³ may be formed via the decomposition of HCOOH over the catalyst, which is thermodynamically favorable at 473 K:

$$HCOOH \rightarrow CO_2 + H_2 \qquad (\Delta G^{473 \text{ K}} = -63 \text{ kJ mol}^{-1}) \qquad (Eqn. 2.1)$$

Apparently, the Cu0.28-H-MOR catalyst is extremely sensitive to trace oxidants that exist within the reactor and/or zeolite pores even when using ultra-high purity He with additional purification. Given the extreme sensitivity of the reduced catalyst, distinguishing between oxidation of Cu by trace O₂ versus added H₂O may be difficult in conventional reactors without quantification of H₂. Buono et al. reported that for a Cu-H-MOR catalyst treated under vacuum at

773 K in a glass reaction cell, a nearly pure Cu(I) state was maintained after cooling,¹⁴⁹ in contrast to our observation of significant re-oxidation of Cu during cooling. Thus, experimental details such as the nature of the high-temperature inert treatment (duration, temperature, inert gas vs. vacuum), additional purification, and specifics of the reactor design may have a significant effect on Cu speciation.

Similar to our observation of a significant effect of temperature on Cu speciation following auto-reduction, others have reported thermally-induced changes in Cu speciation of O₂-activated Cu zeolites. Cooling Cu-CHA⁸⁶ and Cu-MOR⁸⁴ catalysts from 773 K to 473 K in O₂ induced an increase in the first shell Cu-O peak of the FT-EXAFS (beyond what would be expected from a decrease in the Debye-Waller factor as a result of the lower temperature), as well as an increase in the white line intensity of the XANES. This change was interpreted to represent an increase in the first shell oxygen coordination number for Cu, caused by a change in the binding mode of peroxo or superoxo Cu species from end-on to side-on.^{84,86} We observed a similar increase in white line intensity of the Cu0.28-H-MOR catalyst upon cooling from 723 K to 323 K in O₂ (Figure 2.9a) as well as an increase in the FT-EXAFS first shell peak (Figure 2.9b). The EXAFS fitting of the first coordination shell of the catalyst after cooling from 473 K to 323 K resulted in an increase in the oxygen coordination number for 2.9 ± 0.2 to 3.3 ± 0.2 (Figure B.7 and Table B.4).



Figure 2.9 a) XANES and b) k^2 -weighted FT-EXAFS at the Cu K edge of the Cu0.28-H-MOR catalyst after treatment in He at 723 K for 2 h followed by treatment in O₂ at 723 K for 2 h, with subsequent cooling to 473 and 323 K in O₂.

The active Cu-oxo species in Cu-exchanged zeolites are highly reactive with H₂O,¹¹⁶ and as the temperature of Cu-exchanged zeolites decreases in the presence of H₂O, the equilibrium shifts from H₂O molecules in the gas phase to adsorbed on Cu(II) ions.¹³⁹ Thus, lowering the temperature from 723 K to 473 K (and eventually 323 K) may result in coordination of any trace H₂O present within with the reactor and/or zeolite pores to a fraction of the Cu(II) ions (similar to our observation of re-oxidation of Cu upon cooling after auto-reduction), resulting in an increased first shell oxygen coordination number. XANES-LCF of the Cu0.28-H-MOR catalyst cooled to 473 K and then 323 K in O₂ after activation in O₂ at 723 K (Figures B.8 and B.9) showed hydrated Cu(II) fractions of 0.06 and 0.15, respectively. Furthermore, the shoulder at 8986 eV (Figure 2.9a, inset), which is much more prominent for dehydrated Cu(II) compared to hydrated Cu(II), decreased in intensity upon cooling. We therefore interpret the changes in the XANES and EXAFS of our Cu0.28-H-MOR catalyst upon cooling after O₂ activation as coordination of trace H₂O molecules to a fraction of the Cu. These findings illustrate that caution should be used when interpreting spectroscopic information derived from Cu zeolite samples at low temperature following high temperature treatments.

2.4 Conclusions

The results of this study show that under many commonly employed conditions in the literature for the oxidation of CH_4 to CH_3OH over Cu-exchanged zeolites catalysts, the CH_4 activation reaction is incomplete, resulting in product yields that do not represent the active site density. Elevated CH_4 pressure and long reaction times are required for full conversion of the active sites, which is necessary for estimation of the active site nuclearity based on the product yield.

Auto-reduction in He and H₂-TPR were both shown to reduce the same fraction of Cu in Cu-H-MOR. Since both of these reactions likely require multiple Cu species in close proximity, we speculate that isolated monomeric Cu(II) sites are the redox-inert species in both cases. Normalizing the total C1 product yield by the redox-active fraction of Cu in Cu-H-MOR, instead of the total Cu, gave a ratio of 0.50 mol (mol Cu)⁻¹, which is consistent with dicopper active sites. Fitting the FT-EXAFS of the O₂-activated Cu-H-MOR catalyst gave a first-shell oxygen coordination number of 2.9 for the redox-active majority Cu species, which is consistent with both $[Cu_2O]^{2+}$ and $[Cu_2(\mu-1,2-O_2)]^{2+}$ sites.

We showed that O₂ and H₂O impurities contributed to observed changes in Cu oxidation state and first shell oxygen coordination number for Cu-H-MOR when cooling the catalyst following high-temperature treatment. These effects can potentially complicate the interpretation of both spectroscopy and reactivity results for Cu-exchanged zeolites under certain conditions.

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3 Effect of the co-cation on Cu speciation in Cu-exchanged mordenite and ZSM-5 catalysts for the oxidation of methane to methanol

Abstract

Cu-exchanged zeolites are promising catalysts for the direct methane to methanol reaction, but the design of improved catalysts has been hampered by limited understanding of the active site structures. Here, we show that the identity of the co-cation (H vs. Na) in Cu-MOR and Cu-ZSM-5 catalysts significantly affects Cu speciation and the resulting reactivity of the catalysts in the cyclic methane to methanol reaction. Combining reactivity results with spectroscopy and DFT calculations allows identification of the prevailing active site structure depending on the identity co-cation. The H-form of the catalysts contain a high concentration of mono-µ-oxo dicopper(II) species, which are selective for methanol formation, whereas the presence of Na shifts the Cu distribution toward μ -1,2-peroxo dicopper(II) species, which promote overoxidation of methane to carbon oxides. Results from DFT calculations indicate Cu preferentially forms mono-µ-oxo dicopper(II) species in the 8MR side pockets of MOR, whereas the μ -1,2-peroxo dicopper(II) species is favored in the 12MR main channels of MOR for some Al pair configurations. Competition between Na and Cu for ion exchange sites in the 8MR side pockets results in displacement of some Cu into the 12MR main channels, thus affecting Cu speciation and catalyst selectivity. These findings suggest the choice of co-cation can be used to control active site structure in transition metal ion exchanged zeolites.

3.1 Introduction

Natural gas is an abundant natural resource that has been made more accessible in recent years by hydraulic fracturing technology.³ Methane is the primary component of natural gas, and has received increased attention as a more environmentally-friendly alternative to oil as a source of carbon for the production of energy and chemicals.^{157,158} Most methane sources, however, are far from industrial infrastructure. It is therefore desirable to convert methane to higher-value, more energy-dense compounds at the point of extraction.¹⁵⁸ For example, methanol is an easily-transportable liquid under ambient conditions that can be easily converted into many other chemicals, including olefins, formaldehyde, acetic acid, and synthetic gasoline.^{1,2,11,15}

Methanol is currently produced indirectly from methane by first converting CH_4 to syngas $(CO + H_2)$ via steam reforming. The high endothermicity of steam reforming results in high processing costs and significant greenhouse gas emissions.^{8,12,13} The direct conversion of methane to methanol under mild conditions would mitigate much of these undesirable emissions and allow the recovery of methane from small, dispersed sources that are not suitable for the construction of capital-intensive steam reforming plants, such as remote oil fields where the methane released during oil extraction is often flared. Although many catalysts capable of directly oxidizing methane to methanol have been intensively researched, the high stability of the methane molecule coupled with the higher relative reactivity of the product methanol have thus far prevented the development of a selective catalytic process that converts methane to methanol with industrially-relevant yields.^{9–11,14–16}

In 2005, Cu-exchanged Na-ZSM-5 and Na-MOR zeolites were shown to activate methane at 448 K after a pre-treatment in O₂ at 723 K, forming surface intermediates that could subsequently be extracted as methanol in a water/acetonitrile solvent.⁴² The Cu active site was

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claimed to be associated with a UV-vis peak at 22,700 cm⁻¹ in the O₂-activated material,^{42,68} which was later shown to exhibit a linear correlation with the methanol yield,¹¹⁴ supporting its assignment as representing the active Cu species. The low concentration of active sites in the catalysts initially hampered their characterization, but site-selective resonance Raman spectroscopy was claimed to identify the structure of the active site in Cu-Na-ZSM-5 and Cu-Na-MOR as a mono-µ-oxo dicopper(II) species.^{34,71}

While Cu zeolites have yet to achieve industrial application in the direct methane to methanol reaction, many advancements have been made over the last 15 years in terms of the practical viability of the Cu zeolite system and the fundamental understanding of the active site structure and reaction mechanism. In contrast to offline solvent extraction, methanol can also be removed from a methane-treated Cu zeolite catalyst via online steam extraction, providing an opportunity to continuously cycle the reaction through repeated steps of O₂ activation, methane activation, and methanol desorption.⁴⁴ Operating the methane activation step at elevated methane pressure increased the methanol yield per cycle, as well as enabled isothermal operation of the three-step cycle at 473 K (as opposed to performing the O₂ activation step at high temperature, typically 723-773 K).⁹⁵ Isothermal operation, however, resulted in a lower methanol yield as compared to high temperature O₂ activation for Cu-MOR catalysts.

A significant advancement was made in 2015, when it was shown that using the H-form of Cu-MOR (as opposed to the Na form) increased the methanol yield per cycle by nearly an order of magnitude for the traditional cyclic reaction (i.e., O₂ activation at 723 K, followed by treatment in 1 bar methane at 473 K).⁷² Based on fitting of the extended X-ray absorption fine structure (EXAFS) and an average C1 product yield of 0.33 mol (mol Cu)⁻¹, a tris-µ-oxo tricopper active site was proposed. Importantly, all of the Cu in the catalyst was claimed to be active, greatly

facilitating characterization of the active site in the Cu-H-MOR catalyst. The tricopper active site was also later proposed to exist in Cu-H-ZSM-5, albeit at a lower concentration than in Cu-H-MOR.^{75,76} Pappas *et al.* were able to increase the methanol yield per cycle to 0.47 mol (mol Cu)⁻¹ for the Cu-H-MOR catalyst by optimizing the Cu loading and Si/Al ratio.⁸³ Additional characterization of the Cu-H-MOR catalyst suggested the presence of either mono-µ-oxo dicopper(II) or μ -1,2-peroxo dicopper(II) active sites.^{83,84} We undertook a further study of the active site structure in Cu-H-MOR, applying the high methane pressure reaction protocol previously demonstrated for Cu-Na-MOR,⁹⁵ which increased the C1 product yield from 0.30 to 0.42 mol (mol Cu)^{-1,159} X-ray absorption spectroscopy (XAS) and temperature programmed reduction in H₂ (H₂-TPR) suggested the existence of mono- μ -oxo dicopper(II) or μ -1,2-peroxo dicopper(II) active sites, consistent with the results of Pappas et al.⁸³ Recently, Zheng et al. reported a methanol yield of 0.58 mol (mol Cu)⁻¹ for Cu-H-MOR using a methane pressure of 40 bar.⁷⁹ This increase in yield was interpreted as the participation of a second oxygen atom in the tris- μ -oxo tricopper site that becomes reactive when the methane chemical potential is sufficiently high.

In addition to di- and tricopper active sites, monocopper species have also been proposed as active sites in Cu-exchanged zeolites for the methane to methanol reaction.^{89,91,92} Interestingly, the debate among mono-, di-, and tricopper active sites in Cu-exchanged zeolites mirrors the debate regarding the active site nuclearity in the pMMO enzyme, in which mono-, di-, and tricopper active sites have also been proposed.^{50,150,160–163}

Evidently, despite many detailed studies, the active site structure in Cu-exchanged zeolites for the methane to methanol reaction has not been unambiguously determined. Here, we report an investigation on the effect of Cu loading and the zeolitic co-cation (H vs Na) on the speciation and resulting reactivity of Cu in MOR and ZSM-5 zeolites. These effects facilitate the elucidation of the structure of active Cu species depending on the zeolite properties. Both Cu-Na-MOR and Cu-Na-ZSM exhibit a greater propensity for overoxidation of methane to CO₂ than the corresponding H-form catalysts. This effect has been observed previously and was explained as a stabilization of surface intermediates leading to methanol by Brønsted acid sites in the H-form Cu zeolites.^{105,107} Alternatively, Dyballa *et al.* reported that Na co-cations prevented dealumination of the zeolite in MOR, and suggested that extra-framework Al plays a role in the higher methanol productivity of Cu-H-MOR compared to Cu-Na-MOR.¹¹³ Based on spectroscopic evidence, we find that the cocation also affects the speciation of Cu in the O₂-activated catalysts, independent of its role in the methane activation reaction. Combining results from reactivity and spectroscopy experiments, we propose that zeolitic protons promote the formation of mono- μ -oxo dicopper(II) species, which are selective for methanol formation, while the presence of Na cations shifts the Cu distribution toward μ -1,2-peroxo dicopper(II) species, which promote overoxidation of methane to CO₂.

3.2 Experimental Methods

3.2.1 Catalyst synthesis

Catalysts are designated as Cu*x-y-zeo*, where *x* is the Cu/Al ratio, *y* is the co-cation (Na or H) and *zeo* is the zeolite (MOR or ZSM-5). Catalysts were prepared via liquid ion exchange using NH₄-ZSM-5 (CBV 2314, Si/Al = 11.5, Zeolyst International) and NH₄-MOR (CBV 21A, Si/Al = 10, Zeolyst International) zeolites. The Na-form catalysts were first ion exchanged three times in a 2.44 M aqueous solution of sodium acetate (Sigma Aldrich, 99 %) at 353 K for 4 h and washed with deionized (DI) water. The Cu0.26-H/Na-MOR catalyst was ion exchanged in a 0.2 M solution of sodium acetate at 353 K for 4 h prior to Cu exchange. In contrast to the other H-form catalysts,

which were Cu-exchanged in the NH₄-form, the Cu0.45-H-ZSM-5 catalyst was converted to the proton form prior to Cu exchange by thermal treatment of NH₄-ZSM-5 in medical air (Praxair) at 773 K (1 K min⁻¹) for 8 h. The zeolites were Cu exchanged in an aqueous solution of Cu^{II} acetate monohydrate (0.0025–0.1 M, Sigma Aldrich, 99.9 %) at room temperature for 24 h. The pH of the ion exchange solution was adjusted to 5.2–5.7 by addition of aqueous ammonium hydroxide (Sigma Aldrich, 28 wt. % NH₃) or nitric acid (Sigma Aldrich, 0.5 M) as required, with the exception of the Cu0.43-Na-ZSM-5(6.2) catalyst. This catalyst was Cu-exchanged without pH control to mimic earlier syntheses from the literature,^{34,42,71,96} and had a measured pH of 6.2 during Cu exchange. After Cu exchange, the catalysts were filtered, washed with DI water, dried overnight in air at ~383 K, and subjected to a thermal treatment in medical air at 773 K (1 K min⁻¹) for 8 h to convert residual ammonium ions to protons and to remove any carbonaceous residues leftover from ion exchange. The elemental composition of the catalysts was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) performed by Galbraith Laboratories in Knoxville, TN (Table C.1).

3.2.2 Methane oxidation reactions

Cyclic methane oxidation reactions were performed as described in our previous publication.¹⁵⁹ Briefly, 0.5 g catalyst was loaded into a gas-phase flow reactor (supported on a glass wool bed) and activated in flowing O₂ (Praxair, 99.999 %) overnight at 723 K (10 K min⁻¹). The reactor was then cooled to 473 K in flowing O₂, purged with helium at 473 K for 2 h, treated in 35 bar methane (Praxair, 99.999 %) at 473 K for 20 h, purged with helium (Praxair, 99.999 %) at 473 K for 2 h, and finally subjected to steam-assisted desorption in a gas stream comprised of 2.5 % water / balance helium. The helium was purified using a Supelco OMI-4 purifier. Water was

introduced by passing the helium stream through a water saturator. The saturator was continuously purged with helium prior to starting desorption. All gas flow rates were 40 cm³ min⁻¹. Once desorption was complete at 473 K, the reactor temperature was ramped to 723 K at 3 K min⁻¹. Some CO₂ was produced during the methane reaction over several of the catalysts, and introduction of water vapor resulted in desorption of methanol, dimethyl ether (DME), CO, CO₂, and a small amount of ethylene that made a negligible contribution to the overall product yield. It was assumed that DME and ethylene were produced via dehydration of methanol, and each DME and ethylene molecule was therefore counted as two methanol molecules. Reaction products were measured using online gas chromatography, and product yields were calculated by integrating the concentration of each product over time. Calibration curves were generated using gas streams of known concentration.

Steady state methane oxidation reactions were carried out at a total pressure of 1 bar and a space velocity of 40 cm³ min⁻¹ g_{cat}⁻¹. The catalysts were used as loose powders and not pelletized, to mimic the cyclic reactions. The catalysts were pre-treated in 40 cm³ min⁻¹ O₂ at 723 K (10 K min⁻¹) for 4 h, then cooled to 483 K and purged with 40 cm³ min⁻¹ helium for 0.5 h. The reactant gas mixture was comprised of 72.5 vol. % methane, 2.5 vol. % H₂O, 1.0 vol. % O₂, and balance helium. Water vapor was introduced by passing the gas stream through a saturator. After introducing the reactant gas mixture at 483 K following pre-treatment, we waited approximately 20 h for steady state to be reached. The conversion was subsequently increased by increasing the reactor temperature in 30 K increments at 10 K min⁻¹. After each temperature change, we waited at least 2 h for a new steady state to be reached. The detected products (methanol, CO, CO₂) were quantified via online gas chromatography, as in the cyclic reactions. The overall rate and the

methane and O_2 conversions were calculated based on the measured methanol, CO, and CO₂ concentrations (assuming two water molecules produced per CO/CO₂ molecule).

3.2.3 UV-vis spectroscopy

UV-vis spectra were measured in the diffuse reflectance mode using a Cary 5000 spectrometer (Agilent) equipped with a Harrick Praying Mantis *in situ* reactor cell (model DRP-P72). The H-ZSM-5 or H-MOR (generated from the NH₄-form by thermal treatment in air at 773 K for 8 h) samples were used as references, and the reflectance data were transformed using the Kubelka-Munk function (F(R)). The gas flow rates were 30 cm³ min⁻¹ and the temperature ramp rate was 10 K min⁻¹. Spectra were measured in the range of 12,500–45,000 cm⁻¹ with a step size of 10 cm⁻¹.

3.2.4 Raman spectroscopy

In a typical Raman measurement, the sample was either compressed on a glass slide for *ex situ* measurements or placed in the sample holder of a Harrick Raman chamber for *in situ* measurements. As shown in Figure C.5, the spectra were measured by a customized Raman spectrometer (TriVista CRS spectrometer, S&I GmbH, Germany) using a microscope focusing the beam with a 10× objective lens (Olympus) on the sample.¹⁶⁴ Seven different lasers were used for excitation including one solid state laser from Coherent (488 nm), four diode-pumped solid-state lasers from Cobolt (532 nm, 457 nm, and 355 nm) and CryLas (266 nm, FQCW 266), and a dual wavelength He-Cd laser from Kimmon Koha (442 nm and 325 nm). Laser powers were tuned by neutral density filters (0.9-1.0 mW) to prevent sample damage. Exposure times (30 min for the 266 nm laser and 3 min or 10 min for the other lasers) were optimized accordingly with regard to

a high signal-to-noise ratio. The entrance slit was set to 100 µm for all measurements. The primary laser lines were cut off by corresponding edge filters. The scattered light was dispersed on 600 or 2400 grooves/mm gratings depending on laser wavelength and resolution requirement, and monitored by liquid-nitrogen-cooled CCD detectors (PyLoN:2K, Princeton Instruments).

For the *in situ* measurements, ~25 mg Cu zeolite samples were placed in the Harrick Raman chamber and heated from room temperature to 723 K under 5 cm³ min⁻¹ pure O₂ (central gas supply) at a heating rate of 10 K min⁻¹. After reaching the desired temperature, the sample was activated by pure O₂ for at least two hours followed by multi-wavelength Raman spectroscopy measurements. If required, the sample was then cooled to room temperature under O₂ and measured with the 266 nm excitation laser. The sample was then heated to 473 K at 10 K min⁻¹ in O₂ and then purged with pure helium (50 cm³ min⁻¹, central gas supply) to remove the remaining O₂ in the chamber. Methane was then introduced (5 cm³ min⁻¹, 99.9995%, Westfalen) at 473 K for 2.5 h, followed by cooling to room temperature in methane for spectrum measurement.

3.2.5 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) was performed at beamline 8-ID of the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory in Upton, NY, according to our previously described methods.¹⁵⁹ Briefly, the catalyst samples were loaded into a home-built *in situ* reactor cell¹⁶⁵ and held in place by plugs of glass wool on the upstream side and carbon wool on the downstream side. Up to three catalysts were measured simultaneously under identical conditions by utilizing the multi-sample-holder design of the reactor cell and the moveable, programmable sample stage at beamline 8-ID of NSLS-II. Spectra were measured in transmission mode at the Cu K edge (8979 eV), and the energy was calibrated by simultaneous scanning of a Cu foil. All temperature ramp rates were 3 K min⁻¹, and gases (O₂, helium, H₂, Mattson Ultra-high purity) were supplied to the reactor cell using Brooks mass flow controllers. The XAS data were analyzed using the Demeter software package.¹³⁸ Linear combination fitting of the X-ray absorption near edge spectra (XANES-LCF) was performed in Athena using standard spectra representing dehydrated Cu^{II}, hydrated Cu^{II}, Cu^I, and Cu metal, as previously described.¹⁵⁹ Fitting of the extended X-ray absorption fine structure (EXAFS) was performed using Artemis with FEFF6, with S₀² set to 0.90, as previously described.¹⁵⁹

3.3 Results and Discussion

3.3.1 Reactivity of Cu-MOR and Cu-ZSM-5 catalysts

We previously reported results suggesting that the active sites in a Cu0.28-H-MOR catalyst were either mono- μ -oxo dicopper(II) or μ -1,2-peroxo dicopper(II) species.¹⁵⁹ To further explore the nature of Cu species in zeolite hosts, we tested two additional Cu-MOR catalysts with the same Si/Al ratio of the parent MOR (10), varying the Cu loading and co-cation (H vs. Na). We also tested four Cu-ZSM-5 catalysts with similar Si/Al ratio of the parent ZSM-5 (11.5), again varying the Cu loading and co-cation. Catalysts are designated at Cu*x*-*y*-*zeo*, where *x* is the Cu/Al ratio, *y* is the co-cation (Na or H), and *zeo* is the zeolite (MOR or ZSM-5). Table 3.1 shows the results of the cyclic methane oxidation reaction for each catalyst activated in 1 bar O₂ at 723 K overnight and subsequently treated in 35 methane at 473 K for 20 h.

Catalyst	CH4 conversion	Yield [mol (mol Cu) ⁻¹]			Selectivity [%]		
Catalyst	[mol (mol Cu) ⁻¹]	CH ₃ OH	СО	<i>CO</i> ₂	CH ₃ OH	CO	<i>CO</i> ₂
Cu0.28-H-MOR	0.43	0.39	0.036	0.005	90	8.4	1.2
Cu0.28-Na-MOR	0.36	0.25	0.043	0.068	69	12	19
Cu0.41-Na-MOR	0.31	0.15	0.038	0.12	49	12	39
Cu0.26-H-ZSM-5	0.32	0.27	0.048	0.005	83	15	1.6
Cu0.45-H-ZSM-5	0.33	0.19	0.072	0.066	58	22	20
Cu0.45-Na-ZSM-5	0.25	0.10	0.043	0.11	41	17	42
Cu0.54-Na-ZSM-5	0.27	0.059	0.047	0.16	22	17	61

Table 3.1 Cyclic methane oxidation reaction results for Cu-MOR and Cu-ZSM-5 catalysts activated in O₂ at 723 K. CH₄ activation step was performed in 35 bar CH₄ at 473 K for 20 h.

Both the presence of Na and higher Cu loading decreased the selectivity toward methanol and increased the selectivity toward CO₂. The H-form catalysts also had approximately 25 % higher overall methane conversion when comparing the two pairs of Cu-MOR and Cu-ZSM-5 catalysts with the same Cu loading. For all of the catalysts except Cu0.28-H-MOR and Cu0.26-H-ZSM-5 (*i.e.*, the two most selective catalysts), some formation of gaseous CO₂ was observed during the methane activation reaction, up to a maximum of 0.086 mol (mol Cu)⁻¹ for the Cu0.54-Na-ZSM catalyst (the yield for each product during each reaction step for all of the catalysts is listed in Table C.2). This is in contrast to the original report on a Cu-Na-ZSM-5 catalyst of similar composition, where no gas-phase products were reported during interaction of the O₂-activated catalysts with methane.⁴²

Alayon *et al.* reported that one-half to two-thirds of the Cu in Cu-Na-MOR was reduced from Cu^{II} to Cu^I during interaction with methane at 473 K, despite only ~0.04 mol methanol (mol Cu)⁻¹ being formed.^{43,104} This discrepancy in the large fraction of Cu reduced by methane and the comparatively small fraction of methanol formed could potentially be explained by the complete

combustion of some methane upon exposure to the O₂-activated catalyst, resulting in the formation of CO₂, as we observed for several of our catalysts, and reduction of Cu without methanol formation. Interaction with methane also resulted in the formation of 22 % hydrated Cu^{II},¹⁰⁴ possibly due to the formation of water during combustion, which interacts strongly with Cu^{II} and would likely be observed as an increase in the hydrated Cu^{II} fraction. Similar to our results, the detection of CO₂ during the methane activation step over Cu-MOR catalysts has recently been reported.^{107,109}

After the methane activation step at 473 K, the reactor was purged with helium and then a gas stream containing 2.5 vol. % H₂O balanced by helium was introduced, resulting in desorption of methanol, dimethyl ether (DME), CO, and CO_2 . We assumed that DME was formed via dehydration of methanol, and each DME molecule was counted as two methanol molecules.²⁷ Sushkevich and van Bokhoven reported that following product desorption of Cu-MOR treated in 7 bar methane, a temperature ramp resulted in the desorption of some additional CO_2 .¹⁰⁵ For each catalyst listed in Table 3.1, after desorption was complete, the reactor temperature was therefore increased to 723 K at 3 K min⁻¹ while continuing the gas flow of water-saturated helium. During this temperature ramp, a small amount (ca. 5-10 % of the total C1 yield) of additional CO and CO_2 desorbed from the catalyst (the CO and CO_2 yields for each catalyst during the post-desorption temperature ramp, along with the other reaction steps, are shown in Table C.2). We decided, however, not to include this small amount of additional CO_x in the final yield and selectivity calculations in Table 3.1, for reasons detailed in Section C.2. Table C.3 is an alternate version of Table 3.1 which includes the CO_x formed during the post-desorption temperature ramp in the overall yield and selectivity calculations. The overall trends in Table 3.1 and Table C.3 show the same influences of Cu loading and the co-cation on the activity and selectivity of the catalysts.

In contrast to the cyclic methane-to-methanol reaction over Cu zeolites, very few studies on the steady state reaction exist in the literature.^{130–132} Narsimhan *et al.* reported a higher steady state methanol productivity for Cu-H-ZSM-5 than Cu-Na-ZSM-5,¹³¹ and Dinh *et al.* observed lower methanol selectivity for the Na form of Cu-CHA compared to the H form.¹³² Similarly, we observed a higher methanol productivity and selectivity in the steady state reaction for the Cu0.28-H-MOR catalyst compared to the Cu0.28-Na-MOR catalyst (Table 3.2).

Table 3.2 Steady state methane oxidation reaction results for two Cu-MOR catalysts. Catalysts were pre-treated in O₂ at 723 K for 4 h. Gas feed = 72.5 % methane, 2.5 % water, 1.0 % O₂, balance helium. Total pressure = 1 atm. Space velocity = 40 cm³ min⁻¹ g_{cat}⁻¹.

	Cu0.28-H-MOR				Cu0.28-Na-MOR				
Temp.	Rate	CH4	O 2	CH ₃ OH	Rate	CH4	O 2	CH ₃ OH	
[K]	[mol (mol	conv.	conv.	select.	[mol (mol	conv.	conv.	select.	
	Cu) ⁻¹ h ⁻¹]	[%]	[%]	[%]	Cu) ⁻¹ h ⁻¹]	[%]	[%]	[%]	
483	0.0019	0.0009	0.034	100	0.0012	0.0007	0.035	74	
513	0.032	0.023	1.6	37	0.034	0.028	2.2	5.7	
543	0.36	0.30	23	5.5	0.31	0.26	21	0.75	

For the Cu0.28-H-MOR catalyst at 483 K, the methane oxidation rate $(0.0019 \text{ mol } (\text{mol } \text{Cu})^{-1} \text{ h}^{-1})$ was similar to that reported by Narsimhan *et al.* $(0.0046 \text{ mol } (\text{mol } \text{Cu})^{-1} \text{ h}^{-1})$ for a similar Cu0.14-H-MOR catalyst.¹³¹ The slightly lower observed rate in our case might be related to the higher Cu loading and the lower methane partial pressure (73 vs. 98 kPa) in the present work, for which the reaction was shown to be first order.¹³¹

3.3.2 In situ UV-vis spectroscopy of Cu-MOR and Cu-ZSM-5

The results in Table 3.1 show significant variations in the reactivity of the tested catalysts, which may be related to differences in Cu speciation. We therefore used UV-vis spectroscopy, which has been used extensively to characterize Cu-exchanged zeolites, to investigate the Cu

speciation in our catalysts. The state of Cu in O₂-activated Cu zeolites is primarily Cu^{II}, which exhibits two distinct regions of UV-vis absorption: the d-d transition region with absorption bands centered between 12,000 and 20,000 cm⁻¹, and the ligand to metal charge transfer (LMCT) region above 20,000 cm⁻¹.^{87,166} Absorption bands between 20,000 – 30,000 cm⁻¹ are typically assigned to LMCT bands involving electron transfer from extra-framework oxygen ligands to Cu (O_{ef} \rightarrow Cu), while bands above 30,000 cm⁻¹ are typically assigned to charge transfer from zeolite framework oxygen ligands (O_{fw} \rightarrow Cu).^{87,166,167}

A UV-vis absorption band at 22,000–23,000 cm⁻¹ was assigned as the LMCT of a mono- μ -oxo dicopper(II) species in O₂-activated Cu-Na-ZSM-5³⁴ and Cu-Na-MOR.⁷¹ In contrast, Cu-H-MOR had no absorption features in this region, instead exhibiting a weak, broad shoulder at ~31,000 cm⁻¹ assigned to a tris- μ -oxo tricopper species.⁷² Park *et al.* similarly found that Cu-Na-MOR exhibited a UV-vis peak at ~22,000, cm⁻¹, while Cu-H-MOR did not.⁷⁷ Apparently, the zeolite co-cation (Na vs. H) affects the Cu speciation, as evidenced by the differing UV-vis spectra. The Cu-H-MOR catalyst that exhibited the shoulder at ~31,000 cm⁻¹ in its UV-vis spectrum, however, was ion-exchanged at pH 5.7 to prevent Cu exchange at silanols and precipitation of Cu^{II}(OH)₂ that occurs at pH > 6.^{72,73} To rule out variations in the UV-vis spectra of Cu-MOR and Cu-ZSM-5 being related to high pH during ion exchange, all of the catalysts listed in Table 3.1 were exchanged at pH 5.2–5.7. Figures 3.1 and 3.2 show the UV-vis spectra of Cu-MOR and Cu-ZSM-5 catalysts, respectively, in O₂ at 723 K. The spectra are normalized to the d-d transition band at ~13,000 cm⁻¹.



Figure 3.1 UV-vis spectra of Cu-MOR catalysts in O_2 at 723 K. Spectra are normalized to the d-d transition band at ~13,000 cm⁻¹.



Figure 3.2 UV-vis spectra of Cu-ZSM-5 catalysts in O_2 at 723 K. Spectra are normalized to the d-d transition band at ~13,000 cm⁻¹.

In Figure 3.1, the Cu0.28-H-MOR catalyst shows no distinct feature at ~22,000 cm⁻¹ but a weak, broad shoulder at 27,500 cm⁻¹, similar to that previously reported for Cu-H-MOR.⁷² The analogous Na-form catalyst with identical Cu loading, Cu0.28-Na-MOR, appears to have a weaker shoulder at 27,500 cm⁻¹ than Cu0.28-H-MOR. As described above, Cu-Na-MOR catalysts typically exhibit a UV-vis peak at ~22,000 cm⁻¹. The baseline of the spectrum for Cu0.28-Na-MOR is more intense than Cu0.28-H-MOR at 22,000 cm⁻¹, although no peak is discernable. The Cu0.41-Na-MOR catalyst has a weak but evident feature at 21,600 cm⁻¹, suggesting that both the presence of Na and higher Cu loading are associated with the formation of this feature. The absence

of a distinct peak at ~22,000 cm⁻¹ for the Cu0.28-Na-MOR catalyst may be due to the fact that its ion-exchange pH was decreased to 5.7, which results in the replacement of some Na ions by protons. While the overall intensity of the spectra at ~27,500 cm⁻¹ for the Cu0.41-Na-MOR and Cu0.28-H-MOR catalysts are similar, the prominence, or relative intensity, of the shoulder is significantly greater for the Cu0.28-H-MOR catalyst. Similar to the results reported by Grundner *et al.*,⁷² the shoulder at 27,500, cm⁻¹ decayed during exposure to methane at 473 K (Figure C.1), suggesting that it is associated with a reactive Cu species.

Figure 3.2 clearly shows that for Cu-ZSM-5, the intensity of the lower-energy peak at 22,300 cm⁻¹ is correlated with both the presence of Na and higher Cu loading. For both the H and Na form samples, the catalyst with higher Cu loading exhibited a more intense peak at 22,300 cm⁻¹.

Figures 3.1 and 3.2 reveal that for both Cu-MOR and Cu-ZSM-5, the peak at ~22,000 cm⁻¹ is associated with the presence of Na and high Cu loading, rather than high pH during ion exchange, since all catalysts were ion exchanged at pH \leq 5.7. Comparing the UV-vis spectra with the reaction results in Table 3.1, it is evident that the lower-energy feature at ~22,000 cm⁻¹ correlates with CO₂ selectivity, rather than methanol selectivity. The distinctive peaks observed for the Cu-ZSM-5 catalysts, exhibiting a wide range of intensity, allowed us to plot the product yields as a function of the intensity of the 22,300 cm⁻¹ peak (Figure 3.3) for these catalysts. Figure C.2 shows similar plots for the Cu-MOR catalysts, although due to the much less distinctive features at ~22,000 cm⁻¹ (Figure 3.1) the horizontal axis is better described as the background intensity of the spectrum, as opposed to a peak intensity.



Figure 3.3 Product yields in the cyclic methane to methanol reaction for a) methanol b) CO and CO₂ vs. intensity of the UV-vis peak at 22,300 cm⁻¹ for the four Cu-ZSM-5 catalysts in Figure 3.2. Trend lines were added for methanol and CO₂.

Figure 3.3 shows a clear negative correlation between the intensity of the 22,300 cm⁻¹ peak and methanol yield, and a positive correlation with the CO₂ yield, suggesting that the Cu species associated with this peak participates in the formation of CO₂. In earlier work, a positive correlation between the methanol yield and the intensity of a UV-vis peak at 22,700 cm⁻¹ was reported for Cu-ZSM-5 catalysts (nominal Si/Al ratio = 17.5, compared to 11.5 for our Cu-ZSM- 5 catalysts).¹¹⁴ The product yields in that study, however, were all < 0.005 mol (mol Cu)⁻¹, *i.e.* nearly two orders of magnitude lower than in the present case, which casts doubt on the previous attribution of reported spectral features to the very small fraction of the active Cu species in the samples.

Comparison of the Cu-MOR UV-vis spectra in Figure 3.1 and the reactivity results in Table 3.1 might indicate a correlation between the prominence of the shoulder at 27,500 cm⁻¹ and methanol productivity. The Cu0.28-H-MOR catalyst has both the highest methanol yield and the most prominent shoulder at 27,500 cm⁻¹, suggesting that this feature is associated with the active site for methanol formation. None of the Cu-ZSM-5 catalysts, however, exhibited a feature near 27,500 cm⁻¹. This may be related to a lower concentration of Cu species associated with this feature in Cu-ZSM-5, as the catalyst with the highest methanol yield (Cu0.28-H-MOR) exhibited only a weak, broad shoulder at 27,500 cm⁻¹. The Of_w→Cu LMCT band at ~42,000 cm⁻¹ was also more intense for the Cu-ZSM-5 catalysts than Cu-MOR, which may further obscure weak features near 27,500 cm⁻¹ for Cu-ZSM-5. It is also possible that the structure of the Cu species associated with the shoulder at 27,500 cm⁻¹ is slightly different in ZSM-5 than in MOR due to the different pore structures, potentially resulting in a lower extinction coefficient for this species in Cu-ZSM-5.

Recent experimental findings for the Cu-H-MOR catalyst have suggested the existence primarily of either mono- μ -oxo dicopper(II) or μ -1,2-peroxo dicopper(II) active sites.^{83,159} The mono- μ -oxo dicopper(II) species in Cu-Na-ZSM-5 and Cu-Na-MOR has previously been assigned to a UV-vis peak ~22,000 cm⁻¹.^{34,71} The Cu-H-MOR catalyst exhibited a UV-vis feature at 27,500 cm⁻¹, and not at ~22,000 cm⁻¹, suggesting that the shoulder at 27,500 cm⁻¹ is associated with a μ -1,2-peroxo dicopper(II) species. The selectivity pattern of the catalysts shown in Table 3.1, however, casts doubt on this assignment. The tendency of the catalysts toward overoxidation

should be strongly influenced by the amount of available oxygen in the active sites. The ratio of oxygen to Cu in the μ -1,2-peroxo dicopper(II) species is twice that of the mono- μ -oxo dicopper(II) species (1.0 vs. 0.5), suggesting that the μ -1,2-peroxo dicopper species should be more likely to overoxidize methane. In general, peroxo species tend to promote unselective oxidation.²¹ Table 3.4 lists the molar ratio of oxygen in the reaction products (calculated assuming that two water molecules are formed for each CO and CO₂ molecule) to Cu for each catalyst. The values range from 0.52 for the most selective catalyst (Cu0.28-H-MOR) to 0.85 for the least selective catalyst (Cu0.54-Na-ZSM-5). The oxygen:Cu ratios indicate a greater amount of active oxygen in the catalysts with a more intense UV-vis peak at ~22,000 cm⁻¹ (i.e., the Na-form and high Cu-loading catalysts). The Cu0.54-Na-ZSM-5 catalyst (with the most intense UV-vis band at ~22,000 cm⁻¹) has an oxygen: Cu ratio close to the expected value for μ -1,2-peroxo dicopper(II) species, while the Cu0.28-H-MOR catalyst (with the most prominent shoulder at 27,500 cm⁻¹ and no absorption band at ~22,000 cm⁻¹) has a value close to that expected for the mono- μ -oxo dicopper species. We therefore consider the possibility that the UV-vis peak at ~22,000 cm⁻¹ is actually associated with a μ -1,2-peroxo dicopper(II) species, and that the shoulder at 27,500 cm⁻¹ is associated with a monoμ-oxo dicopper(II) species. Cu-Na-MOR was found to have a higher methanol yield with respect to the intensity of the UV-vis peak at ~22,000 cm⁻¹ compared to Cu-Na-ZSM-5, further suggesting that this peak may not represent the active site for methanol formation.⁶⁸

Recent work reporting simulated UV-vis spectra of various Cu-oxygen complexes in Cu-CHA supports our assignment of the higher-energy shoulder at 27,500 cm⁻¹ to a mono- μ -oxo dicopper(II) species and the lower energy peak at ~22,000 cm⁻¹ to a μ -1,2-peroxo dicopper(II) species.¹⁵⁶ The spectra of three different mono- μ -oxo dicopper(II) species coordinated within the 8MR of CHA all had absorption bands centered near 30,000 cm⁻¹, while a μ -1,2-peroxo dicopper(II) species had an absorption band at a lower energy of *ca.* 23,000 cm⁻¹. Haack and Limberg summarized the UV-vis absorption features of molecular mono- μ -oxo dicopper(II) complexes from literature, finding that the O→Cu LMCT band for these complexes ranged from 20,000–43,000 cm⁻¹, with an average energy of 31,000 cm⁻¹.¹⁶⁸ Elwell *et al.* performed a similar analysis of molecular μ -1,2-peroxo dicopper(II) complexes and found that the reported O→Cu LMCT bands of these complexes all had energies of < 23,000 cm⁻¹.¹⁶⁹ These results from the literature on molecular Cu-oxygen complexes are consistent with our assignment of the lower-energy absorption band at ~22,000 cm⁻¹ in our UV-vis spectra to the LMCT of a μ -1,2-peroxo dicopper(II) species and the higher-energy shoulder at 27,500 cm⁻¹ to the LMCT of a mono- μ -oxo dicopper(II) species.

Understanding the role of the co-cation in affecting the Cu speciation can assist in elucidating the structure of the different Cu species present in our Cu-ZSM-5 and Cu-MOR catalysts. As seen in Table 3.1, the catalysts with Na co-cations had a lower overall methane conversion than the catalysts with H co-cations. Sushkevich and van Bokhoven reported a similar effect for reactions of Cu-MOR under elevated methane pressure, with Cu-Na-MOR catalysts exhibiting both a lower methanol yield and lower methanol selectivity.¹⁰⁵ Grundner *et al.* observed that for O₂-activated Cu-MOR catalysts treated in methane at atmospheric pressure, the presence of Na decreased the methane conversion, although no effect on selectivity was reported.⁷³ Complementary FT-IR experiments with spectral deconvolution revealed that both Cu and Na cations preferentially occupy the 8MR side pocket pores of MOR. Thus, when Na is present, it disrupts the formation of the active sites in the 8MR side pocket and forces Cu into the larger 12MR main channels of MOR.⁷³

Based on our findings of lower methanol selectivity for Na-form catalysts, and our proposal of more prevalent μ -1,2-peroxo dicopper(II) species in the Na-form catalysts, we propose the following extension of the findings of Grundner *et al.*⁷³ regarding the effect of Na: in the absence of Na, Cu preferentially forms mono- μ -oxo dicopper(II) active sites in the 8MR side pocket pores of MOR. In the presence of Na, however, some of the Cu is displaced from the side pockets and into the larger 12MR main channel pores, which results in the formation of the larger μ -1,2-peroxo dicopper(II) species, with two bridging oxygen atoms instead of one. This proposed scenario is consistent with our observation of lower methanol selectivity with higher Cu loading. The Cu initially populates the thermodynamically-preferred smaller 8MR side pockets and forms the smaller mono- μ -oxo species with a single bridging oxygen ligand that selectively catalyzes methanol formation, while at higher Cu loadings, the Cu populates less stable sites in the larger 12MR main channels that form the larger μ -1,2-peroxo species that promote overoxidation. This effect of the co-cation on Cu location and speciation may occur in addition to previously proposed effects of the co-cation on the methane activation reaction in Cu zeolites.^{105,107,112}

In a DFT study of the energetics of several Cu-oxygen complexes coordinated within zeolite pores of varying size (including the 8MR of CHA and the 12MR of MOR), Vilella and Studt found that the most stable location for the mono- μ -oxo dicopper(II) species was the 8MR.¹⁷⁰ The most stable configuration of the μ -1,2-peroxo dicopper(II) species in the 12MR of MOR was significantly more stable than any of the configurations calculated for the 8MR, suggesting that the larger μ -1,2-peroxo dicopper species is better suited to the larger 12MR main channels of MOR. Engedahl *et al.* calculated that a [Cu-O-Cu] structure in the 8MR of CHA was more stable than any structures containing > 1 oxygen atom under the conditions of O₂ activation.¹⁷¹ These computational results are supported by an experimental investigation of the methane-to-methanol

reaction over several different types of Cu-exchanged zeolites.⁷⁷ Cu-loaded zeolite hosts that contain 8MR pores (MOR, SSZ-13, omega) had higher methanol yields than other zeolites that do not contain 8MR pores (including ZSM-5 and zeolites Y and L), indicating that 8MR pores provide a favorable environment for Cu species that selectively oxidize methane to methanol. We similarly observed lower methanol yields for the Cu-ZSM-5 catalysts (Table 3.1), whose accessible pores include only 10MR channels, than the Cu-MOR catalysts.

While less information is available regarding the siting of the Cu active sites for methanol formation in ZSM-5, a similar effect of Na regarding both the UV-vis spectra and the selectivity for Cu-MOR and Cu-ZSM-5 catalysts suggests that Na affects the Cu speciation similarly in both zeolites. The framework Al is known to preferentially occupy the 8MR side pockets of MOR, creating a high concentration of Al pairs⁷² that can host +2-charged mono-µ-oxo dicopper(II) species that selectively oxidize methane to methanol. The Al distribution in ZSM-5 is more complex, but similar to MOR, it was found that Al pairs in close proximity were required to form the active sites that selectively oxidize methane to methanol in Cu-ZSM-5.⁷⁵

As discussed in section 3.1, we found that the Cu0.28-Na-MOR catalyst had a lower methanol selectivity than the Cu0.28-H-MOR catalyst in the steady state methane oxidation reaction, mirroring the selectivity pattern observed in the cyclic reaction. Taken together, these results suggest that it may be generally true that Na blocks the formation of active sites that catalyze selective methanol formation in Cu zeolites.

Our proposal of the lower energy UV-vis peak at ~22,000 cm⁻¹ being associated with a μ -1,2peroxo dicopper(II) species, rather than a mono- μ -oxo dicopper(II) species, is an alternative explanation for the origin of this feature as compared to previous literature on this topic. In particular, a combined UV-vis and resonance Raman spectroscopic study of Cu-Na-ZSM-5 linked a UV-vis peak at 22,700 cm⁻¹ to the mono- μ -oxo dicopper(II) species.³⁴ We therefore explored the Raman spectra of our Cu zeolite catalysts in an attempt to reconcile those observations with the results of the current work.

3.3.3 Raman spectroscopy of Cu-MOR and Cu-ZSM-5

As described in section 3.2, previous experimental results have suggested the existence of either mono- μ -oxo dicopper(II) or μ -1,2-peroxo dicopper(II) active sites in Cu-H-MOR.^{83,159} Based on UV-vis spectroscopy and reactivity results, we argued that the Cu-H-MOR contains primarily mono- μ -oxo dicopper(II) species. In order to further distinguish between these two active site structures in Cu-H-MOR, we employed Raman spectroscopy, which has previously been used to characterize mono- μ -oxo dicopper(II) and μ -1,2-peroxo dicopper(II) species in Cu-exchanged zeolites.^{34,71,85,86} While both species should exhibit Raman bands in the Cu-O stretching region (*ca.* 450–650 cm⁻¹), only the μ -1,2-peroxo dicopper species should have a band in the peroxo stretching region (*ca.* 800–1100 cm⁻¹).^{85,169,170} Figure 3.4 shows Raman spectra of the Cu0.28-H-MOR catalyst in O₂ at 723 K, measured with several different visible and UV excitation lasers in an attempt to capture any resonance enhancement effects¹⁷² that may be present.



Figure 3.4 Raman spectra of the Cu0.28-H-MOR catalyst in O_2 at 723 K. The black spectrum is Cu-free H-MOR zeolite (Si/Al = 10), shown for comparison.

The spectra for the Cu0.28-H-MOR catalyst do not show any new features in the peroxo stretching region that are not present in the Cu-free H-MOR (black spectrum), suggesting that peroxo species are not the predominant Cu species in this catalyst in its activated state. In fact, the spectra of the catalyst do not exhibit any new features in any region, including the Cu-O stretching region, that are not present for H-MOR. The Cu-O stretching region, however, appears more likely to be obscured by features associated with the MOR vibrational modes, based on the presence of several features in this region for the H-MOR (Figure 3.4, black spectrum). Interestingly, features at 456 and 512 cm⁻¹ are observed for H-MOR, which are nearly identical in energy to features reported for Cu-Na-ZSM-5 and Cu-Na-MOR (456 and 514 cm⁻¹) that were attributed to symmetric Cu-O stretching modes of the mono- μ -oxo dicopper(II) species.^{34,71}

Figure 3.5 shows the Raman spectrum of the Cu0.41-Na-MOR catalyst in O₂ at 723 K and after cooling to 473 K, as well as the parent Na-MOR measured *ex situ* with a deep-UV 266 nm

excitation laser. The spectrum of Cu0.41-Na-MOR at 723 K shows peaks at 456 and 512 cm⁻¹ (in addition to features from the MOR) consistent with peaks previously reported by Vanelderen *et al.* for Cu-Na-MOR that were assigned to a mono- μ -oxo dicopper(II) species.⁷¹ The relative intensity of these peaks, however, is significantly less compared to the results of Vanelderen *et al.*⁷¹ Our results are consistent with the lower intensity of the UV-vis peak at ~22,000 cm⁻¹ for the Cu0.41-Na-MOR catalyst compared to previously reported UV-vis spectra of Cu-Na-MOR catalysts in the literature,⁷¹ as the intensity of the two Raman peaks at 456 and 514 cm⁻¹ is resonance-enhanced by the UV-vis-active Cu species with an absorption band at ~22,000 cm⁻¹.³⁴



Figure 3.5 Raman spectra of the Cu0.41-Na-MOR catalyst in O_2 at 723 K, followed by cooling to 473 K (442 nm excitation laser), and the parent Na-MOR measured *ex situ* (266 nm excitation laser).

When the temperature of the sample cell was decreased from 723 K to 473 K, the relative intensity of the peaks at 456 and 512 cm⁻¹ decreased (Figure 3.5, blue spectrum). We attribute this behavior to coordination of trace water molecules in the cell to Cu as the temperature is lowered, which hydrolyzes the dehydrated Cu^{II}-oxygen species associated with the UV-vis absorption band at ~22,000 cm⁻¹ that is responsible for enhancement of features in the Raman spectrum. The UV-vis absorption band at ~22,000 cm⁻¹ also decayed during cooling from 723 K to 473 K (Figure

C.3). We previously reported an increase in the hydrated Cu^{II} fraction in Cu-H-MOR, observed via XANES-LCF, during cooling of the catalyst following activation in O₂ at 723 K.¹⁵⁹ The decay of Raman bands assigned to Cu-oxygen complexes in O₂-activated Cu-CHA has also been attributed to the presence of trace water impurities.⁸⁵

Interestingly, the spectrum of the Cu0.41-Na-MOR catalyst cooled to 473 K (Figure 3.5, blue spectrum) appears very similar to the Cu-free H-MOR spectrum (Figure 3.4, black spectrum), as well as the parent Na-MOR spectrum measured ex situ with a 266 nm excitation laser (Figure 3.5, black spectrum). In particular, the peaks at 456 and 512 cm⁻¹ in the Raman spectrum of the Cu0.41-Na-MOR catalyst in O₂ at 723 K (Figure 3.5, red spectrum) that were attributed to a mono-µ-oxo dicopper(II) species^{34,71} are also present in the parent Na-MOR (Figure 3.5, black spectrum). Raman peaks at similar energies have previously been assigned to vibrations of the 4MR and 5MR of MOR.^{173–175} Inspection of the peak at 456 cm⁻¹ in the Na-MOR spectrum measured using a 266 nm laser (Figure 3.5, black spectrum) reveals that it is actually a composite of two overlapping peaks centered at 450 and 464 cm⁻¹. Figures C.8 and C.9 contain additional Raman spectra of two Na-MOR samples (Si/Al = 10 and Si/Al = 6.5) measured *ex situ* with several different excitation lasers, several of which also show clear evidence of two overlapping peaks centered near 450 and 464 cm⁻¹. These observations for the parent Na-MOR are remarkably similar to results reported for Cu-Na-MOR, where a broad Raman peak centered at ~456 cm⁻¹ was resolved via spectral subtraction into two peaks centered at 450 and 465 cm⁻¹.⁷¹ These peaks were attributed to the symmetric Cu-O stretch of two mono-µ-oxo dicopper(II) species with slightly different geometries. Figures 3.5, C.8, and C.9, however, show that these peaks are present in the Cu-free MOR.

The presence of Raman peaks in the Cu-free MOR that were previously attributed to a mono- μ -oxo dicopper(II) species leads us to the consider the alternative possibility that these peaks are associated with MOR vibrational modes, and that they can potentially be enhanced by the presence of a UV-vis-active Cu species. However, energy shifts in the Raman bands of Cu-Na-ZSM-5 attributed to vibrational modes involving the extra-framework oxygen atom of the mono-µ-oxo dicopper(II) species when the catalyst was activated in ¹⁸O₂ seemingly provided conclusive evidence that these peaks were associated with the vibrations of a Cu species.^{34,96} We attempted to reproduce these experiments, the results of which are detailed in Section C.5. Our results suggest that activation in ¹⁸O₂ at 723 K can induce shifts in the position of Raman features associated with zeolite vibrational modes, likely via incorporation of ¹⁸O into the zeolite lattice. This is not surprising, given that isotopic scrambling of ¹⁸O₂ with zeolite lattice oxygen of Cu-exchanged zeolites has previously been reported.⁹⁶ The shift of zeolite Raman peaks after activation in ¹⁸O₂ due to isotopic scrambling, combined with the apparent enhancement of some zeolite Raman features by UV-vis-active Cu species and the significant overlap between zeolite vibrations and symmetric Cu-O stretching modes of Cu-oxygen species, makes the definitive assignment of Raman bands for Cu-exchanged zeolites difficult. Our results suggest, however, that the UV-vis peak at ~22,000 cm⁻¹ may not be associated with a mono-µ-oxo dicopper(II) species, as the corresponding resonance-enhanced Raman bands at 456 and 514 cm⁻¹ that were assigned to this species³⁴ appear to be associated instead with zeolite vibrational modes. These results support our proposal in section 3.2 that the UV-vis band at ~22,000 cm⁻¹ is associated with a μ -1,2-peroxo dicopper(II) species rather than a mono-µ-oxo dicopper(II) species, as the UV-vis band at ~22,000 cm⁻¹ was originally assigned to a mono-µ-oxo dicopper(II) species based on Raman features³⁴ that appear to be associated with zeolite vibrational modes.

Quantum chemical calculations showed that the most likely location for the mono- μ -oxo dicopper(II) species in ZSM-5 is the γ site located at the intersection of the straight and sinusoidal 10MR channels.^{54,76} This site has a similar 8MR geometry as the sites that likely host the mono- μ -oxo dicopper(II) species in MOR and CHA.^{72,73,88,170} The Cu-O-Cu angle of the mono- μ -oxo dicopper(II) species at this site was calculated to be 115°,⁷⁶ significantly less than the angle of 139° determined based on the position of the Raman band at 456 cm⁻¹ that was claimed to represent the symmetric Cu-O stretch of the mono- μ -oxo dicopper(II) species.³⁴ The smaller Cu-O-Cu angle of 115° would result in an energy of 554–609 cm⁻¹ for the symmetric Cu-O stretch of the mono- μ -oxo dicopper(II) species,³⁴ which is in line with more recent reports for the energy of this vibration of the mono- μ -oxo dicopper(II) species in both molecular complexes and Cu-exchanged zeolites.^{85,86,116,176}



Figure 3.6 Raman spectra of three Cu-MOR catalysts in O_2 at 723 K. Excitation laser wavelength = 442 nm. Spectra were scaled so that the MOR peak at 630 cm⁻¹ was of similar intensity for all three catalysts.

Figure 3.6 shows the Raman spectra of the Cu0.41-Na-MOR, Cu0.28-Na-MOR, and Cu0.28-H-MOR catalysts in O₂ at 723 K measured with a 442 nm excitation laser. The spectra were scaled so that the MOR peak at 630 cm⁻¹ was of similar intensity for all three catalysts, as this peak does not appear to be significantly affected by the presence of UV-vis-active Cu species. The enhancement of the MOR peaks at 456 and 512 cm⁻¹ in Figure 3.6 correlates with the intensity of the UV-vis spectrum at ~22,000 cm⁻¹ for each catalyst in Figure 3.1. The small peak at 972 cm⁻¹ may be associated with a peroxo O-O stretch,^{85,86,169,177} or alternatively with the Cu^{II}-shifted v_{asym} (T-O-T) vibration of MOR.^{178,179} As discussed previously, the apparent enhancement of

Raman bands associated with zeolite vibrational modes by UV-vis-active Cu species hampers the definitive assignment of the Raman bands.

The absence of any features associated with Cu species in the Raman spectra of Cu0.28-H-MOR in Figure 3.4 limits their ability to provide information regarding Cu speciation in this catalyst. In an attempt to elucidate features associated with Cu in H-form Cu-MOR, we synthesized a catalyst with higher Cu loading (Cu0.44-H-MOR), and measured its Raman spectrum using a deep-UV excitation laser (266 nm) and a long measurement time (30 minutes). This method has previously been used to characterize highly dispersed CuO_x supported on KIT-6 silica, where typical UV and visible lasers were unable to detect vibrations of Cu species above the background silica vibrations.¹⁸⁰ Using a deep-UV laser, however, revealed a feature at 560 cm⁻¹ that was not present in the silica support, and based on complementary EXAFS and DFT calculations was assigned to the symmetric Cu-O stretching mode of a mono-µ-oxo dicopper(II) species on the silica surface. Figure 3.7 shows Raman spectra of our Cu0.44-H-MOR catalyst measured with a deep-UV 266 nm excitation laser after activation in O_2 at 723 K (red spectrum), and after reaction with methane at 473 K (blue spectrum). The catalyst was cooled to room temperature prior to measurement of each spectrum to further aid in identifying any features originating from Cu species.



Figure 3.7 Deep-UV Raman spectra of the Cu0.44-H-MOR catalyst after activation in O₂ at 723 K (red spectrum) and after reaction with methane at 473 K (blue spectrum). Catalyst was cooled to room temperature prior to measurement. Spectra were measured using a 266 nm excitation laser.

The spectrum of the O₂-activated catalyst shows a distinctive feature at 570 cm⁻¹ that is not present in the parent MOR and that decays after reaction with methane, indicating that it is associated with a reactive Cu species. The feature at 570 cm⁻¹ is very similar to the feature at 560 cm⁻¹ that was attributed to a mono- μ -oxo dicopper(II) species for CuO_x/KIT-6, supporting assignment of mono- μ -oxo dicopper(II) as the majority species in Cu-H-MOR, as well as assignment of this species to the UV-vis shoulder at 27,500 cm⁻¹. Raman bands at a similar energy of 617 cm⁻¹ have been assigned to the symmetric Cu-O stretch of mono- μ -oxo dicopper(II) species in Cu-CHA.^{85,86} A review of Raman spectroscopic data of molecular mono- μ -oxo dicopper(II) complexes reported that the energy of the symmetric Cu-O stretch ranged from 555–640 cm⁻¹ for all of the complexes for which data were available,¹⁸¹ consistent with the assignment of the band at 570 cm⁻¹ in our deep-UV Raman spectrum to a mono- μ -oxo dicopper(II) species.

Interestingly, the Raman band at 570 cm⁻¹ attributed to a mono-µ-oxo dicopper(II) species in the Cu-0.44-H-MOR catalyst was stable even after cooling the sample cell to room temperature, while spectroscopic features we assigned to the μ -1,2-peroxo dicopper(II) species decayed after cooling from 723 to 473 K (Figures C.3 and C.7), which we attribute to coordination of trace water impurities in the cell to Cu^{II} at lower temperature, as described above. Evidently, the mono-µ-oxo dicopper(II) species is more stable toward water than the μ -1,2-peroxo dicopper(II) species, which is similar to results reported by Ipek et al. for Cu-CHA, in which a Cu-CHA sample was activated in O₂ at 723 K and sealed in a glass capillary.⁸⁵ At room temperature, a Raman band at 617 cm⁻¹ that was assigned to a mono-µ-oxo dicopper(II) species was stable, while bands that were assigned to a μ -1,2-peroxo dicopper(II) species decayed over several days. The authors attributed this decay to a trace amount of water leaking into the system.⁸⁵ Figure C.1 shows the UV-vis spectrum of Cu0.28-H-MOR in O₂ at 723 K, and after cooling to 473 K. While the overall intensity of the spectrum decreases due to the lower temperature, at 473 K the shoulder at 27,500 cm⁻¹ (which we are assigning to the mono-µ-oxo dicopper(II) species) is still clearly present, in contrast to the peak at ~22,000 cm⁻¹ (Figure C.3, assigned to μ -1,2-peroxo dicopper(II)), which disappeared after cooling to 473 K.

3.3.4 X-ray absorption spectroscopy of Cu-MOR and Cu-ZSM-5

To further investigate the effects of the co-cation on Cu speciation, we performed X-ray absorption spectroscopy on several Cu-MOR and Cu-ZSM-5 catalysts. Figure 3.8a shows the XANES at the Cu K edge for the Cu0.28-H-MOR, Cu0.28-Na-MOR, Cu0.45-H-ZSM-5, and

Cu0.45-Na-ZSM-5 catalysts in O₂ at 723 K. The spectra are similar for all catalysts and are characteristic of dehydrated Cu^{II}. The small pre-edge peak at 8977 eV is from the Cu^{II} dipole-forbidden 1s \rightarrow 3d transition,¹⁴¹ and the shoulder at 8986 eV is from the Cu^{II} 1s \rightarrow 4p transition.⁹⁹



Figure 3.8 Cu K edge XANES (a) and phase-uncorrected FT-EXAFS (b) of four Cu-MOR and Cu-ZSM-5 catalysts in O_2 at 723 K.

Figure 3.8b shows the corresponding magnitude of the Fourier-transformed EXAFS (FT-EXAFS) for each catalyst in O₂ at 723 K. The first shell peak centered at ~1.4 Å (phaseuncorrected) is due to backscattering from both zeolite framework and extra-framework oxygen. The second coordination shell in the range of *ca*. 2 – 3 Å (phase-uncorrected) is more complex and has variously been attributed to backscattering from Cu, Al, and Si.^{67,72,75,78,79,83,84,86,159,182} Table 3.3 shows the results of EXAFS fitting for the four catalysts. All four catalysts have a first shell oxygen coordination number of approximately 3. This coordination number is consistent with both mono- μ -oxo dicopper(II) and μ -1,2,-peroxo dicopper(II) species. An oxygen coordination number of 3 is inconsistent with the catalysts containing a majority of either μ -(η^2 : η^2)-peroxo dicopper(II) or tris- μ -oxo tricopper(II) species, which have an oxygen coordination number of 4. Figures C.17 – C.20 show plots of each fit compared to the measured FT-EXAFS.

Catalyst	Coord. number	Distance [Å]	σ² [Ų]	ΔE0 [eV]	R-factor
Cu0.28-H-MOR	3.1 ± 0.4	1.92 ± 0.02	$\begin{array}{c} 0.0091 \pm \\ 0.0028 \end{array}$	-3.2 ± 1.4	0.010
Cu0.28-Na-MOR	2.6 ± 0.4	1.93 ± 0.02	$\begin{array}{c} 0.0053 \pm \\ 0.0023 \end{array}$	-2.8 ± 1.5	0.013
Cu0.45-H-ZSM-5	3.1 ± 0.4	1.92 ± 0.01	$\begin{array}{c} 0.0072 \pm \\ 0.0019 \end{array}$	-4.2 ± -1.2	0.006
Cu0.45-Na-ZSM-5	3.0 ± 0.4	1.93 ± 0.02	$\begin{array}{c} 0.0070 \pm \\ 0.0025 \end{array}$	-2.9 ± 1.4	0.013

Table 3.3 EXAFS fitting results at the Cu K edge of four Cu-MOR and Cu-ZSM-5 catalysts treated in O₂ at 723 K.^a Fits were performed using a single oxygen scattering path.

 ${}^{a}S_{0}{}^{2}$ was set to 0.90. Fits were performed in R space with ranges of 2 < k < 11 Å⁻¹ and 1 < R < 2 Å. A combined k¹-k²-k³-weighted fit was performed. Each fit used 4 out of 5.6 independent points. None of the fits had any correlations above 0.90.

While we previously modeled an Al backscatterer at 2.69 Å (coordination number = 0.9 ± 0.3) for the Cu0.28-H-MOR catalyst,¹⁵⁹ in the present case the high temperature (723 K) and complexity of the second coordination shell (especially for the Na-form catalysts, as seen in Figure 3.8b) prevented us from obtaining satisfactory fits when this shell was included. While we conclude that the Cu0.28-H-MOR catalyst contains mostly mono- μ -oxo dicopper(II) species due to its high methanol yield and corresponding spectroscopic characterization described in the previous sections, the other three catalysts, especially in the Na form, likely contain a higher fraction of μ -1,2,-peroxo dicopper(II) species, which would result in the Cu EXAFS having significant contributions from oxygen in the second coordination shell, further complicating the fitting of the EXAFS.

Treatment of Cu zeolites in an inert atmosphere at high temperature induces the autoreduction reaction, in which Cu^{II} is reduced to Cu^{I} without a reductant via desorption of

O₂.^{98,101,102,183} To investigate the effect of the co-cation on the autoreducibility of Cu, we first pretreated the Cu0.28-H-MOR and Cu0.28-Na-MOR catalysts in O₂ at 723 K, then changed the gas flow to helium while maintaining a temperature of 723 K. Figure 3.9 shows the resulting Cu K edge XANES of both catalysts in helium at 723 K. The appearance of a feature at 8983 eV is indicative of the formation of Cu^{I,142,143} Linear combination fitting of the XANES (XANES-LCF) using Cu^I and dehydrated Cu^{II} standards (Figures C.21 and C.22) showed that for the Cu0.28-Na-MOR catalyst, 20 % of the initially-present Cu^{II} was reduced to Cu^I, while for Cu0.28-H-MOR, only 7 % of the Cu^{II} was reduced to Cu^I. Evidently, the presence of Na increases the fraction of Cu that undergoes autoreduction in helium at 723 K. This behavior is consistent with our hypothesis of Na shifting the Cu distribution from mono-µ-oxo dicopper(II) toward µ-1,2-peroxo dicopper(II) species. We expect the μ -1,2-peroxo dicopper(II) species to be more susceptible to autoreduction, as the O₂ moeity is already present, making desorption of O₂ mechanistically simple (Scheme 3.1a). In contrast, autoreduction and O₂ desorption from mono-µ-oxo dicopper(II) (the probable active site for methanol formation) is more complex, requiring the involvement of at least two sites and likely involving a higher activation barrier (Scheme 3.1b). Sushkevich *et al.* similarly suggested that the presence of a second oxygen atom should facilitate release of O₂ from Cuoxygen species during heating of Cu zeolites.¹⁵³ The greater extent of autoreduction of Cu0.28-Na-MOR vs. Cu0.28-H-MOR observed via XANES-LCF is consistent with the results of analogous UV-vis experiments, in which the peak at ~22,000 cm⁻¹ disappeared in helium at 723 K, while the shoulder at 27,500 cm⁻¹ was mostly unaffected (Figure C.4), supporting assignment of the peak at ~22,000 cm⁻¹ to a μ -1,2-peroxo dicopper(II) species and the shoulder at 27,500

cm⁻¹ to a mono- μ -oxo dicopper(II) species. Pappas *et al.* have similarly reported that the active site responsible for methanol formation in Cu-H-MOR is a redox-inert (*i.e.*, resistant to autoreduction) Cu^{II} species.⁸³



Figure 3.9 Cu K edge XANES of the Cu0.28-Na-MOR and Cu0.28-H-MOR catalysts in helium at 723 K. Catalysts were pre-treated in O_2 at 723 K for 3 h. The feature at 8983 eV is a fingerprint of Cu^I.


Scheme 3.1. Autoreduction reaction for (a) *trans*-µ-1,2,-peroxo dicopper(II) and (b) mono-µ-oxo dicopper(II) species.

We previously reported that of 83 % of the Cu in the fresh Cu0.28-H-MOR catalyst was autoreduced during treatment in helium at 723 K (compared to 7 % when the catalyst is subjected to an *in situ* pre-treatment in O_2 at 723 K). The greater extent of autoreduction for the fresh catalyst is likely due to the presence of water and trace hydrocarbon impurities, which are removed by the oxidative pre-treatment. Water mobilizes Cu^{II} ions in the zeolite pores,^{89,139,184–186} which may facilitate autoreduction, and hydrocarbon impurities can reduce Cu^{II} to Cu^I during heating in an inert atmosphere.¹⁵⁴

To further investigate the effect of the co-cation on the redox properties of Cu in Cu-MOR, we performed H₂-TPR (3 K min⁻¹) of the Cu0.28-H-MOR and Cu0.28-Na-MOR catalysts following activation in O₂ at 723 K, as well as a catalyst with intermediate Na loading. It should be noted that the Na-form catalysts also contain some protons, as the Cu ion exchange solution during synthesis is slightly acidic. The extent of reduction of Cu^{II} during H₂-TPR was measured by XANES-LCF at the Cu K edge using standards for dehydrated Cu^{II}, hydrated Cu^{II}, Cu^I, and Cu metal. The Cu^I and Cu metal fractions are plotted vs. temperature during H₂-TPR in Figure 3.10. Each data set is labelled with the ratio of Na to Al in the catalyst.



Figure 3.10 Cu(I) (a) and Cu metal (b) fractions calculated by XANES-LCF during H₂-TPR at the Cu K edge of the Cu0.28-H-MOR (Na/Al = 0.00, black), Cu0.26-H/Na-MOR (Na/Al = 0.17, red), and Cu0.28-Na-MOR (Na/Al = 0.41, blue) catalysts. Catalysts were pre-treated in O₂ at 723 K for 4 h. Ramp rate = 3 K min⁻¹.

Figure 3.10 shows that the presence of Na promotes the reduction of Cu by H₂. Initially, the rate of Cu^I formation increased with Na concentration, while at higher temperature, the Cu^I fraction decreased for the Cu0.28-Na-MOR and Cu0.26-H/Na-MOR catalysts as the Cu^I was reduced to Cu metal. At 723 K, approximately 70 % of the Cu in the Cu0.28-H-MOR catalyst was Cu^I, while for the Cu0.28-Na-MOR catalyst, nearly all of the Cu was reduced to metal. We interpret these results as a manifestation of the effect of Na on the location of Cu ions in the MOR pores described in section 3.2. Sodium preferentially occupies the 8MR side pockets of MOR,

displacing some of the Cu from its thermodynamically preferred location in the 8MRs into the 12MR main channels. The Cu in the larger 12MRs is less stable and therefore more susceptible to reduction by H₂. Similar results have been reported for Cu-CHA, where Cu^{II} ions in the larger 8MRs are reduced by H₂ at a lower temperature than Cu^{II} in the smaller 6MRs.¹⁸⁷

3.3.5 Proposed reaction network for CH₄ activation

In the preceding sections we have argued that mono-µ-oxo dicopper(II) species in Cu-MOR and Cu-ZSM-5 effect selective oxidation of methane to methanol, while µ-1,2-peroxo dicopper(II) species promote overoxidation. Figure 3.3b shows that for Cu-ZSM-5, the CO yield is maximized at an intermediate intensity of the UV-vis peak at ~22,000 cm⁻¹, which we are assigning to the μ -1,2-peroxo dicopper(II) species. Similarly, the Cu0.28-Na-MOR catalyst had the highest CO yield among the three Cu-MOR catalysts (Table 3.1), and exhibited an intermediate intensity of its UVvis spectrum at ~22,000 cm⁻¹ compared to the other Cu-MOR catalysts (although it did not exhibit an actual peak at this energy). For both Cu-MOR and Cu-ZSM-5, the catalyst with the most intense UV-vis peak at ~22,000 cm⁻¹ had the highest CO₂ yield. These results suggest that μ -1,2-peroxo dicopper(II) species are responsible for CO_2 formation, and that both μ -1,2-peroxo dicopper(II) and mono-µ-oxo dicopper(II) species are involved in CO formation. Over the last several years, a number of studies have revealed the nature of the surface intermediates formed during the methane activation reaction over Cu zeolites via in situ IR and NMR spectroscopy, which include methoxy, adsorbed methanol, CO, and formate.^{91,92,103,105–112} Combining these results with the results we have presented in the preceding sections, along with the knowledge that methanol formation requires one oxygen atom, CO formation requires three oxygen atoms, and CO₂ formation requires four oxygen atoms, allows us to propose a reaction network based on stoichiometry for the

activation of methane and the formation of surface intermediates leading to methanol, CO, and CO_2 (Scheme 3.2). The spectroscopic evidence from the literature for the formation of each intermediate in Scheme 3.2 is discussed below.

Adsorbed methanol:	$[CuIIOCuII]2+ + CH4 \rightarrow [CuI(CH3OH)CuI/II]2+$	(1)
Methoxy:	$[Cu^{ }OCu^{ }]^{2+} + Z + CH_4 \longrightarrow [Cu^{ }(OCH_3)Cu^{ / }]^{2+} + ZH$	(2)
Adsorbed CO:	$[Cu^{ }OCu^{ }]^{2+} + [Cu^{ }OOCu^{ }]^{2+} + CH_4 \rightarrow [Cu^{ }(CO)]^+ + 3Cu^{ } + 2H_2O$	(3)
Formate:	$2[Cu^{II}OOCu^{II}]^{2+} + CH_4 \rightarrow [Cu^{II}(HCOO)]^+ + [Cu^{II}(OH)]^+ + 2Cu^{I} + H_2O$	(4)
CO ₂ :	$2[Cu^{II}OOCu^{II}]^{2+} + CH_4 \rightarrow 4Cu^{I} + CO_2 + 2H_2O$	(5)

Scheme 3.2. Proposed reaction network based on stoichiometry for the formation of surface intermediates during the methane activation reaction over O₂-activated Cu zeolite catalysts involving mono- μ -oxo dicopper(II) ([Cu^{II}OCu^{II}]²⁺) and μ -1,2-peroxo dicopper(II) ([Cu^{II}OOCu^{II}]²⁺) species. Z in reaction 2 represents the zeolite surface.

Reaction 1 depicts the formation of adsorbed methanol at a single mono- μ -oxo dicopper(II) site, which has been described extensively in the literature.^{34,76,82,93,106,188,189} The reaction proceeds via the "radical rebound" mechanism, in which the bridging extra-framework oxygen of the mono- μ -oxo dicopper(II) site abstracts a hydrogen atom from methane, forming a surface hydroxyl and a methyl radical. The methyl radical then reacts with the surface hydroxyl to form adsorbed methanol, which is subsequently displaced by water in the desorption step of the reaction and released into the vapor phase. The formation of adsorbed methanol during the methane activation reaction over Cu zeolites has been directly observed via *in situ* IR and NMR spectroscopy.^{91,92,103,105–110,190}

Reaction 2 shows the formation of surface methoxy effected by a single mono-µ-oxo dicopper(II) site, which is released as methanol via hydrolysis in the desorption step.¹⁰⁴ Similar to adsorbed methanol, methoxy formation has been directly observed via *in situ* IR and NMR

spectroscopy.^{91,92,103,105–112} There is some debate as to the location of the methoxy species on the Cu zeolite surface. Alayon et al. proposed that for Cu-MOR, methane activation proceeds via the formation of hydroxy and methoxy species at two neighboring dicopper sites,¹⁰⁴ but the higher methanol yields reported in recent years have effectively ruled out the involvement of four Cu atoms to produce one methanol molecule.^{72,78,79,83,159} Based on ¹³C MAS NMR spectra, Narsimhan et al. reported the formation of methoxy bound to Cu over Cu-Na-MOR, while for Cu-H-MOR, methoxy groups bound to both Cu and Brønsted acid sites were observed.¹¹² More recent studies have similarly reported the formation of surface methoxy groups bound both to Cu (concurrent with the formation of a Brønsted acid site),^{103,106} as well as to the zeolite surface¹⁹⁰ at Brønsted acid sites.^{92,105,107}. Sushkevich et al. proposed a mechanism in which methane activation at a monoμ-oxo dicopper(II) site proceeds via the initial formation of methoxy bound to Cu, along with the formation of a Brønsted acid site on the zeolite surface, followed by migration of the methoxy group to the Brønsted acid site.⁹² Alternatively, already-present Brønsted acid sites have been claimed to stabilize surface methoxy groups and prevent their overoxidation, explaining the higher methanol selectivity for H-form Cu zeolites.^{105,107} The higher methanol yields for our H-form Cu-MOR and Cu-ZSM-5 catalysts, however, cannot be explained solely by higher methanol selectivity, as the H-form catalysts also exhibit significantly higher overall methane conversion, in addition to higher methanol selectivity, which we attribute to differences in Cu speciation. It is entirely possible that that the co-cation (Na vs. H) affects both the active site structure and the methane activation reaction.

In reaction 2 of Scheme 3.2, we have written the methoxy group as being bonded to Cu, along with the formation of a Brønsted acid site on the zeolite surface (ZH). As the preceding discussion indicates, however, the reverse situation is also possible, with the methoxy group bound

to the zeolite surface. In either case, introduction of water during the desorption step should result in hydrolysis of the methoxy and release of methanol.

In both reactions 1 and 2 of Scheme 3.2, we have written the oxidation state of the second Cu ion as either +1 or +2, as there is some debate as to the extent of reduction of Cu during the formation of adsorbed methanol and methoxy. Several attempts have been made to correlate the methanol yield to the amount of Cu^I formed during methane activation (measured by analysis of the Cu XANES), but no consensus has yet been reached regarding the number of Cu¹ ions formed per methanol molecule. A value of approximately two Cu^I ions formed per methanol (indicating the reduction of both Cu^{II} ions in a presumed dicopper active site) has been reported for Cu-MOR and Cu-MAZ catalysts.^{117,123} Newton et al. tabulated the Cu^I/methanol ratio for a number of studies in the literature for which data were available, finding that in many cases the ratio was close to 2, although in some cases it was much higher, which was attributed to both experimental factors and low methanol selectivity.¹⁹¹ Conversely, Lomachenko et al. plotted the measured methanol yield vs. the amount of Cu¹ formed (both on the basis of total Cu in the catalyst) for several Cu-H-MOR catalysts and found a linear correlation with a slope of 0.9. This was interpreted as the reduction of a single Cu^{II} ion by methane in a presumed mono-µ-oxo dicopper(II) active site, forming a mixed-valent [Cu^{II}(OCH₃)Cu^I] intermediate.¹⁴⁰

Reaction 3 in Scheme 3.2 depicts the formation of adsorbed CO over neighboring mono- μ -oxo dicopper(II) and μ -1,2-peroxo dicopper(II) sites. Both water and Cu^I-CO have been detected spectroscopically during the methane activation reaction over Cu zeolites.^{91,92,103,105,107–109} We propose that both a mono- μ -oxo dicopper(II) and a μ -1,2-peroxo dicopper(II) site are involved in CO formation based on the fact that three oxygen atoms are required to oxidize methane to CO (assuming the concurrent formation of two water molecules), and also based on the observation

that the maximum CO yield for Cu-ZSM-5 occurred for a catalyst with an intermediate intensity of the UV-vis peak at ~22,000 cm⁻¹ (Figure 3.3), which we are assigning to the μ -1,2-peroxo dicopper(II) species. Similarly, the Cu0.28-Na-MOR catalyst had the highest CO yield among the Cu-MOR catalysts (Table 3.1), and exhibited an intermediate intensity of its UV-vis spectrum at ~22,000 cm⁻¹ compared to the other Cu-MOR catalysts (although no actual peak is visible). We have argued that the effect of the co-cation and Cu loading is to shift the distribution of Cu between mono- μ -oxo dicopper(II) and μ -1,2-peroxo dicopper(II) species; an intermediate concentration of the μ -1,2-peroxo dicopper(II) species therefore implies an intermediate concentration of the mono- μ -oxo dicopper(II) species. The observation that CO formation is maximized when both of these species are presumably present in appreciable quantities, rather than when one dominates over the other, leads to the conclusion that both are likely involved in CO formation. In a kinetic study of the formation of surface intermediates during the methane activation reaction over Cu-MOR, Sushkevich and van Bokhoven found that Cu^I-CO forms in a parallel pathway to surface methanol/methoxy, rather than via overoxidation of these species in a series reaction,¹⁰⁹ consistent with our proposed reaction network.

Reaction 4 depicts the formation of surface formate over two neighboring μ -1,2-peroxo dicopper(II) species. Similar to methoxy, adsorbed CO, and adsorbed methanol, surface formate has been detected via *in situ* IR and NMR spectroscopy over Cu zeolites during the methane activation reaction.^{91,92,103,105,108,109} We have drawn the formate species as being bound monodentate to a single Cu atom, although a bidentate coordination to two Cu atoms is also possible. Sushkevich *et al.* observed both monodentate and bidentate formate during methane activation over Cu-Na-MOR, with the prevailing coordination mode depending on the Si/Al ratio of the MOR.⁹²

Formate has been reported to be a precursor to CO₂, and the intensity of formate IR bands was inversely correlated with methanol selectivity for Cu-Na-MOR catalysts.^{91,92,103,105} We have previously proposed that surface formate species are hydrolyzed to formic acid upon introduction of water to methane-treated Cu-MOR, which then exergonically decomposes to H₂ and CO₂.¹⁵⁹ This was proposed as a possible alternative explanation for the detection of H₂ during waterassisted desorption, which Sushkevich *et al.* have proposed is due to oxidation of Cu by water.^{91,103} We propose that two μ -1,2-peroxo dicopper(II) species are involved in the formation of formate based on the correlation between the UV-vis peak at ~22,000 cm⁻¹ (assigned to the μ -1,2-peroxo dicopper(II) species) and the CO₂ yield during desorption (of which formate is likely a precursor, and which trended with the overall CO₂ yield for each catalyst, Table 3.1).

Reaction 5 in Scheme 3.2 shows the formation of gas-phase CO₂ over two neighboring μ -1,2-peroxo dicopper(II) species. While the original paper demonstrating the stepwise oxidation of methane to methanol over O₂-activated Cu-Na-ZSM-5 and Cu-Na-MOR catalysts reported that no gas-phase products were formed during the methane activation step,⁴² we observed CO₂ formation during this step at 473 K for all but the two most methanol-selective catalysts (Cu0.28-H-MOR and Cu0.26-H-ZSM-5), up to a maximum value of 0.086 mol (mol Cu)⁻¹ for the Cu0.54-Na-ZSM-5 catalyst (Table C.2). More recent studies have also reported the formation of CO₂ during methane activation over Cu-MOR.^{107,109} Similar to formate, we propose that two proximal μ -1,2-peroxo dicopper(II) sites are involved in CO₂ formation based on the fact that four oxygen are required to oxidize methane to CO₂, and that the catalysts with a greater concentration of μ -1,2-peroxo dicopper(II) sites (based on the intensity of the UV-vis peak at ~22,000 cm⁻¹) produced more CO₂ during the methane activation step (which trended with the overall CO₂ yield for each catalyst, Table 3.1 and Table C.2). Reactions 1 and 2, as well as reactions 4 and 5, depict the formation of different products from the same reactants. In the case of methanol/methoxy formation over mono- μ -oxo dicopper(II) sites, differing reactivity may result from slight variations in the geometry of the mono- μ -oxo dicopper(II) species depending on the number of Si tetrahedra separating the Al pairs that host these species, which in turn affects their electronic structure.¹⁵⁶ Alternatively, the nature of the surrounding zeolite framework can also impact the reactivity of Cu species in different locations in the zeolite through second-sphere effects.¹²⁸ In the case of formate vs. CO₂ formation over neighboring μ -1,2-peroxo dicopper(II) sites, we speculate that the reactivity may also be affected by the proximity of the two sites.

As a check on the compatibility of the proposed reaction network in Scheme 3.2 with our reactivity data in Table 3.1, we calculated the hypothetical total amount of Cu involved in the reaction for each catalyst assuming that the reaction proceeds via Scheme 3.2 (Table 3.4). The fraction of active Cu is obtained by multiplying the methanol yield by two (based on a single mono- μ -oxo dicopper(II) site catalyzing methoxy/methanol formation in Reactions 1 and 2 in Scheme 3.2), the CO yield by four (based on a mono- μ -oxo dicopper(II) and a μ -1,2-peroxo dicopper(II) site effecting CO formation in Reaction 3 of Scheme 3.2), the CO₂ yield by four (based on two μ -1,2-peroxo dicopper(II) sites effecting formate and CO₂ formation in Reactions 4 and 5 of Scheme 3.2, respectively, and assuming that formate is a precursor to CO₂), and summing the values. All the yields in the calculation are normalized to the total Cu in each catalyst on a mole basis. A value of unity for the sum would therefore imply that 100 % of the Cu in the catalyst participates in the reaction, assuming the reaction network is correct. A value of less than unity would imply that some fraction of the Cu is inactive (again assuming that the reaction network is correct), while a value significantly greater than unity would imply that the reaction network is

likely incorrect, as not enough Cu is available in the catalyst for the reaction to proceed as described in Scheme 3.2. Table C.4 shows an alternate version of Table 3.4 in which the small amounts of CO_x produced during the post-desorption temperature ramp were included in the calculations.

Catalyst	Total oxygen in products ^a [mol (mol Cu) ⁻¹]	Fraction of active Cu ^b	Molar ratio of oxygen to active Cu ^c
Cu0.28-H-MOR	0.52	0.94	0.55
Cu0.28-Na-MOR	0.65	0.95	0.69
Cu0.41-Na-MOR	0.75	0.94	0.80
Cu0.26-H-ZSM-5	0.43	0.75	0.58
Cu0.45-H-ZSM-5	0.67	0.94	0.72
Cu0.45-Na-ZSM-5	0.66	0.80	0.82
Cu0.54-Na-ZSM-5	0.85	0.96	0.89

Table 3.4 Calculations of the fraction of active Cu and O/Cu molar ratio based on the reactivity results in Table 3.1 and the proposed reaction network in Scheme 3.2.

^aCalculated assuming that three oxygen atoms are required for CO formation and four oxygen atoms are required for CO₂ formation

^b = $2 * CH_3OH$ yield + 4 * CO yield + $4 * CO_2$ yield (normalized to total Cu in catalyst)

^c = Total oxygen in products / fraction of active Cu

Table 3.4 shows that the fraction of active Cu in each catalyst based on the proposed reaction network is between 0.75 and 0.96, implying that the majority of Cu is participating in the reaction for all of the catalysts. While these values cannot prove the validity of the reaction network in Scheme 3.2, they do not force us to rule it out based on the product yields. The molar ratio of oxygen to active Cu is obtained by dividing the total amount of oxygen in the reaction products for each catalyst (on a mole basis, and assuming that three oxygen atoms are required for CO

formation and four oxygen atoms are required for CO₂ formation) by the fraction of active Cu. This value would be 0.5 for a hypothetical catalyst with only mono- μ -oxo dicopper(II) active sites, and 1 for a hypothetical catalyst with only μ -1,2-peroxo dicopper(II) active sites. As expected, the ratio is between 0.5 and 1 for each catalyst, consistent with a distribution of Cu between mono- μ -oxo dicopper(II) and μ -1,2-peroxo dicopper(II) species. The Cu0.28-H-MOR catalyst has a ratio of 0.55, implying a majority of mono- μ -oxo dicopper(II) active sites that is consistent with its high methanol selectivity of 90 %. In contrast, the Cu0.54-Na-ZSM-5 catalyst has a ratio of 0.89, implying the existence of mostly μ -1,2-peroxo dicopper(II) active sites that is consistent with its low methanol selectivity of 22 %. The remaining catalysts have both intermediate ratios and intermediate corresponding methanol selectivities.

3.4 Conclusions

This study elucidates the effect of the zeolitic co-cation (H vs. Na) on Cu speciation in Cuexchanged zeolite catalysts, and the resulting consequences for reactivity of the catalysts in the cyclic methane to methanol reaction. While Cu-MOR and Cu-ZSM-5 catalysts containing only H co-cations exhibited a high methanol selectivity, introducing Na into the catalysts decreased the methanol selectivity and increased the propensity of the catalysts toward overoxidation of methane. A similar effect of the co-cation on selectivity was observed in the steady state methane to methanol reaction, suggesting that the identity of the co-cation may affect Cu speciation in similar ways under different conditions.

The Cu-MOR and Cu-ZSM-5 catalysts in the Na and H form exhibited variations in their UV-vis spectra that correlated with the selectivity pattern observed for the cyclic methane to methanol reaction. High methanol selectivity for the H-form catalysts was associated with an

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absorption band assigned to a mono- μ -oxo dicopper(II) species, while high CO₂ selectivity for the Na-form catalysts was associated with an absorption band assigned to a μ -1,2-peroxo dicopper(II) species. *In situ* Raman spectroscopy revealed that UV-vis-active Cu species are potentially capable of enhancing the Raman bands of the zeolite host, indicating that great care must be taken when assigning the Raman bands of Cu zeolites based on resonance enhancement effects.

We propose that the effect of the co-cation on Cu speciation in MOR involves competition between Cu and Na cations for energetically-preferred sites in the MOR 8MR side pockets. In the absence of Na, Cu selectively populates the side pockets, which preferentially form mono- μ -oxo dicopper(II) species for all possible Al pair configurations, according to quantum chemical calculations. In the presence of Na, some Cu is displaced into less-stable locations in the larger 12MR main channels of MOR. Results from DTF calculations indicate the μ -1,2-peroxo dicopper(II) species are more stable than mono- μ -oxo dicopper(II) species for several Al pair configurations in the 12MR main channels, which explains the greater prevalence of these species in the Na-form catalysts.

The results of this study reveal the ability of the zeolitic co-cation to act as a powerful tool in tuning the speciation of Cu by controlling its location within the zeolite, which will likely have relevance in a wide range of reactions catalyzed by transition metal ion exchanged zeolites. In the context of the methane to methanol reaction, our findings demonstrate the importance of controlling the zeolite environment surrounding Cu for maximizing the concentration of active sites that are selective for methanol formation. Based on the findings of this study, future work should focus on optimizing the combination of co-cation, zeolite topology, and Al distribution to maximize the methanol yield of Cu zeolite catalysts.

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4 Conclusions

4.1 Summary of findings

In this work, Cu speciation and reactivity in Cu-exchanged MOR and ZSM-5 zeolite catalysts for the oxidation of methane to methanol were investigated. For the cyclic methane-to-methanol reaction over a Cu0.28-H-MOR catalyst, increasing the methane pressure and reaction time increased the C1 product yield from 0.30 to 0.42 mol (mol Cu)⁻¹, indicating that under conditions previously reported in the literature, the methane activation reaction is not complete over Cu-H-MOR catalysts, and that at low methane pressure the yield likely does not represent the active site density.

Heating the fresh Cu0.28-H-MOR catalyst in helium at 723 K resulted in reduction of 83 % of the initially-present Cu^{II} to Cu^I, as measured by *in situ* XANES-LCF. Normalizing the C1 product yield under conditions that were shown to result in nearly complete conversion of the active sites by this redox-active fraction of Cu gave a stoichiometry of 0.50 mol (mol Cu)⁻¹, which is consistent with the existence of predominantly dimeric Cu active sites (assuming one turnover per active site in the cyclic reaction). Fitting of the EXAFS of the O₂-activated Cu0.28-H-MOR catalyst resulted in an oxygen coordination number of 2.9, which is consistent with two different dimeric Cu^{II} species: mono- μ -oxo dicopper(II) and μ -1,2-peroxo dicopper(II).

Trace O_2 and H_2O impurities were found to have a significant effect on Cu speciation in Cu zeolite catalysts. *In situ* XAS showed an increase in the hydrated Cu^{II} fraction during cooling of the Cu0.28-H-MOR catalyst following activation in O_2 at 723 K, likely due to coordination of trace H_2O molecules to Cu^{II} at lower temperature. Similarly, a conversion from Cu^I to Cu^{II} was observed while cooling the catalyst after treatment in helium at 723 K, which was attributed to

coordination of trace O_2 molecules to Cu as the temperature decreased. Similar effects were observed in the UV-vis and Raman spectra of Cu zeolite catalysts.

In situ Raman spectroscopy was used to distinguish between mono- μ -oxo dicopper(II) and μ -1,2-peroxo dicopper(II) species in the Cu-H-MOR catalyst. A Cu0.28-H-MOR catalyst exhibited no features in the peroxo stretching region, suggesting that μ -1,2-peroxo dicopper(II) is not the predominant Cu species in this catalyst. No features in the Cu-O stretching region were observed, possibly due to this region being obscured by features from MOR vibrational modes. Deep-UV Raman of a catalyst with higher Cu loading (Cu0.44-H-MOR) revealed the presence of a new feature at 570 cm⁻¹, which is in the expected range for the symmetric Cu-O stretch of a mono- μ -oxo dicopper(II) species, suggesting that this may be the predominant Cu species in the Cu-H-MOR catalyst.

The effect of the zeolite co-cation (H vs. Na) on Cu speciation and reactivity of Cu-MOR and Cu-ZSM-5 catalysts was also investigated. For both Cu-MOR and Cu-ZSM-5 catalysts, introducing Na co-cations, as well as increasing the Cu loading, decreased the methanol selectivity and increased the CO₂ selectivity in the cyclic methane-to-methanol reaction. The Na-form of Cu-MOR also exhibited lower methanol selectivity in the steady state methane-to-methanol reaction than the corresponding H-form catalyst.

In situ UV-vis spectroscopy of three O₂-activated Cu-MOR catalysts with varying cocation (H vs. Na) and Cu loading showed that the H-form catalyst (Cu0.28-H-MOR) exhibited the most prominent shoulder at 27,500 cm⁻¹ among the three catalysts, while the Na-form catalyst with high Cu loading (Cu0.41-Na-MOR) exhibited the most intense feature at ~22,000 cm⁻¹. The prominence of the shoulder at 27,500 cm⁻¹ correlated with the methanol yield in the cyclic methane-to-methanol reaction, while the intensity of the spectra at ~22,000 cm⁻¹ correlated with CO₂ yield. Four Cu-ZSM-5 catalysts exhibited a similar effect of the co-cation and Cu loading on their UV-vis spectra, with catalysts in the Na form and with high Cu loading exhibiting more intense UV-vis peaks at ~22,000 cm⁻¹. The CO₂ yield of the Cu-ZSM-5 catalysts showed a strong positive correlation with the intensity of a UV-vis peak at ~22,000 cm⁻¹. Based on these selectivity patterns, corresponding deep-UV Raman spectroscopy of Cu-H-MOR, and simulated UV-vis spectra from the literature,¹⁵⁶ the UV-vis peak at ~22,000 cm⁻¹ was assigned to a μ -1,2-peroxo dicopper(II) species, and the shoulder at 27,500 cm⁻¹ was assigned to a mono- μ -oxo dicopper(II) species.

The results of additional *in situ* Raman spectroscopy experiments of Cu-Na-ZSM-5 and Cu-Na-MOR catalysts suggested that UV-vis-active Cu species can potentially enhance the intensity of Raman features associated with zeolite vibrational modes, and that high-temperature treatment of Cu zeolites in ¹⁸O₂ can shift the energy of zeolite Raman bands due to isotopic scrambling of oxygen with the zeolite lattice. These effects make the definitive assignment of Raman bands in Cu zeolites difficult.

Building on previous results from the literature,⁷³ Na ions were proposed to displace a fraction of Cu from the thermodynamically-preferred 8MR side pockets of MOR (that likely host the active sites for methanol formation) into the larger 12MR main channel pores. The larger main channel pores promote the formation of the larger μ -1,2-peroxo dicopper(II) species, with an additional bridging oxygen ligand, instead of the smaller mono- μ -oxo dicopper(II) species that is favored in the 8MR side pocket.

Fitting of the EXAFS of four O₂-activated Cu-MOR and Cu-ZSM-5 catalysts gave oxygen coordination numbers of *ca*. 3 for the Cu, which is consistent with the existence of both mono- μ -oxo dicopper(II) and μ -1,2-peroxo dicopper(II) species in which the Cu is bound to two zeolite

framework oxygens and one extra-framework oxygen. Results of XANES-LCF showed that the Cu in Na-form Cu-MOR is more susceptible to autoreduction following O_2 activation than the corresponding H-form catalyst, which is consistent with the Na-form catalyst containing a greater fraction of μ -1,2-peroxo dicopper(II) species. Additional XANES-LCF analysis of three Cu-MOR catalysts with varying H/Na ratios showed that increasing the Na content resulted in more extensive reduction of Cu during H₂-TPR, consistent with Na ions displacing Cu from more-stable sites in the 8MR side pocket into less-stable sites in the 12MR main channel of MOR.

Combining the reactivity and spectroscopy results of the current work with spectroscopic results from the literature detailing the nature of surface intermediates formed during methane activation, along with the known stoichiometry for the formation of methane oxidation products, a reaction network was proposed for methane activation over O₂-activated Cu-MOR and Cu-ZSM-5 catalysts. This network involves formation of surface intermediates leading to methanol at single mono- μ -oxo dicopper(II) active sites, formation of CO at neighboring mono- μ -oxo dicopper(II) sites, and formation of surface intermediates leading to CO₂ at two neighboring μ -1,2-peroxo dicopper(II) sites.

The results in this dissertation present a comprehensive understanding of the Cu active site structures in Cu-MOR and Cu-ZSM-5 catalysts, the factors that affect the formation of these structures, and the resulting reactivity of the structures toward methane. These findings will facilitate the design of improved catalysts for the important direct methane-to-methanol reaction.

4.2 Future work

4.2.1 *Temperature-programmed reactions to quantify extra-framework oxygen*

In this work, the nature of the Cu active sites in Cu-MOR and Cu-ZSM-5 catalysts was investigated based on observed product yields in the cyclic methane oxidation reaction, as well as by various spectroscopic methods, including UV-vis, Raman, and XAS. Quantification of extraframework oxygen present in the O_2 -activated catalysts would allow further insight into the structure of the active sites, and could be accomplished via temperature-programmed reactions. Temperature-programmed reduction in H₂ (H₂-TPR) should be performed on the Cu-MOR and Cu-ZSM-5 catalysts discussed in Chapters 2 and 3, with the extra-framework oxygen quantified by measuring H₂ consumption, as the H₂ should react with extra-framework oxygen to form water. The H₂-TPR should be started at below-ambient temperature to allow an accurate quantification of H₂ consumption, as the reaction begins already at 323 K as shown in Figure 2.2. The H₂-TPR results should be correlated to XANES-LCF (performed under the same conditions, *i.e.* the same catalyst pre-treatment, H₂ concentration, and temperature ramp rate), similar to the experiment shown in Figure 3.10. During H₂-TPR, some H₂ will reduce Cu^I (which does not have extraframework oxygen ligands) to Cu metal, and will thus not be consumed by reaction with extraframework oxygen. The amount of Cu^I reduced to Cu metal must therefore be determined by XANES-LCF in order to accurately quantify the amount of H₂ consumed by reaction with extraframework oxygen.

Temperature-programmed reduction in CO (CO-TPR) of the O₂-activated catalysts should be performed to complement H₂-TPR. Extra-framework oxygen should react with CO to form CO₂; extra-framework oxygen can therefore be quantified by measuring both CO consumption and CO₂ production. A detector with > 1 measurement channels (*e.g.* mass spectrometry, Fourier transform infrared spectroscopy) should be used to simultaneously measure CO and CO₂ concentrations in the reactor effluent. Preliminary CO-TPR experiments have suggested that the O/Cu ratio in the Cu0.28-H-MOR catalyst is close to 0.5, which is consistent with this catalyst containing a majority of mono- μ -oxo dicopper(II) sites.

As discussed in Chapter 3, μ -1,2-peroxo dicopper(II) species are expected to be more susceptible to autoreduction (*i.e.* desorption of O₂) than mono- μ -oxo dicopper(II) species. Temperature-programmed desorption of O₂ (O₂-TPD) of O₂-activated Cu-MOR and Cu-ZSM-5 catalysts in the Na and H form should therefore be performed to quantify the amount of O₂ evolved during heating in inert atmosphere, which should then be correlated to the amount of Cu^I formed under the same conditions measured by XANES-LCF. The amount of O₂ evolved is expected to be higher for the Na-form catalysts, as the results in Chapter 3 suggest that these catalysts contain a greater proportion of μ -1,2-peroxo dicopper(II) species than the corresponding H-form catalysts.

4.2.2 Correlation of product yields to Cu reduction during methane activation

Scheme 3.2 depicts a proposed reaction network for the reaction of methane with mono- μ -oxo dicopper(II) and μ -1,2-peroxo dicopper(II) active sites. To further investigate this proposed network, the product yields for Cu-MOR and Cu-ZSM-5 catalysts in the Na and H form should be correlated to the amount of Cu^I formed during the methane activation reaction, measured by XANES-LCF. The proposed network involves varying extents of reduction of Cu^{II} to Cu^I by methane depending on the products formed, *e.g.* CO formation is accompanied by the reduction of four Cu ions, while formate formation involves reduction of two Cu ions. The methane oxidation reactions and XANES-LCF experiments should be carried out under identical conditions, or,

ideally, XANES-LCF should be performed *operando* to simultaneously measure product yields and the extent of Cu reduction.

Scheme 3.2 shows that the formation of methanol precursors involves the reduction of either one or two Cu ions, which would result in some ambiguity when analyzing the proposed reaction network based on correlating product formation to the extent of Cu reduction. In the literature, the reduction of both one and two Cu ions has been proposed to accompany methanol formation.^{117,140,191} The evidence for the reduction of one Cu ion during methanol formation, however, is more convincing, as it involved analysis over a series of measured ratios of Cu¹ formed to methanol yield for different catalysts reacting under different conditions, instead of a single data point, and also considered the effect of selectivity on the molar ratio of methanol yield to Cu¹ formed.¹⁴⁰ For experiments analyzing the proposed reaction network in Scheme 3.2 by correlating the extent of Cu reduction to product yields, it should therefore initially be assumed that methanol formation involves the reduction of one Cu ion.

Formate is likely a precursor to CO_2 ,⁹² and in Chapter 2, formate was proposed to be hydrolyzed to formic acid during steam-assisted desorption, followed by exergonic decomposition of formic acid to CO_2 and H_2 . To further investigate this proposal, and to confirm whether CO_2 produced during steam-assisted desorption should be used to quantify surface formate during *operando* XANES-LCF, the H_2 evolved during desorption (previously observed, but not quantified¹⁰³) should be measured and correlated to the CO_2 evolved.

4.2.3 Characterization of Cu in Cu-FAU

The Cu-FAU material exhibited the highest methanol yield reported to date on a catalyst mass basis (360 μ mol g_{cat}⁻¹, 0.25 mol (mol Cu)⁻¹) for the cyclic methane to methanol reaction.¹⁰⁸

The reaction was performed isothermally at 633 K, and the methane pressure applied during the methane activation step of the cyclic reaction was 15 bar. When the methane activation reaction was performed at 473 K (the standard temperature used in the literature), Cu-FAU exhibited the *lowest* methanol yield among four different Cu zeolites, including Cu-MOR and Cu-ZSM-5. It therefore appears that Cu-FAU is capable of forming a uniquely high density of active sites, but that a higher temperature is required during methane activation as compared to other Cu zeolites to maximize the methanol yield. This high density of active sites should greatly facilitate their spectroscopic characterization. The Cu-FAU catalyst should therefore be synthesized and similar UV-vis, Raman, and EXAFS measurements to those described in Chapter 3 should be performed. These experiments should reveal whether Cu-FAU contains similar active sites to those in Cu-MOR and Cu-ZSM-5, or, more likely based on the higher temperature required for maximizing the methanol yield, different types of active sites.

Additionally, the methanol yield should be measured for the Cu-FAU catalyst at an increased O₂ activation temperature and higher methane pressure, which have been shown to increase the active site density and methanol yield.⁸⁶ While the longer cycle time imposed by these modifications may not be worth the increased methanol yield from an industrial perspective, maximizing the active site density and product yield should facilitate elucidation of the active site structure(s).

A. Methane oxidation over supported Pt-based catalysts

A.1 Introduction

Pt-based catalysts have been extensively studied for C-H bond activation. Shilov et al. were the first to describe C-H activation and alkane conversion to alcohols by homogeneous Pt complexes,¹⁹² but these systems had low yields and poor catalyst stability.¹⁹³ Building on the early work of Shilov, Periana et al. developed a homogeneous Pt catalyst that oxidizes methane to methyl bisulfate (which can by hydrolyzed to methanol in a separate step) in sulfuric acid solvent with 81% selectivity at 90% methane conversion.⁴⁵ The catalyst is a (bpym)PtCl₂ complex that activates methane via electrophilic substitution at the electrophilic Pt^{II} center. After C-H activation and formation of a Pt-C bond, the Pt center is oxidized to Pt^{IV} by H₂SO₄. Methyl bisulfate (CH₃OSO₃H) is then released in a reductive functionalization step that regenerates the Pt^{II} active site.¹³ As described above, the success of the Periana catalyst is derived in part from its use of a stoichiometric oxidant (H₂SO₄) and product protection to prevent over-oxidation. Despite its high activity and stability, the industrial viability of the Periana catalyst is limited by its maximum possible product concentration in solution of < 1 M, which would result in prohibitively high separation costs.¹⁹⁴ As the methanol concentration increases, it stabilizes the ground state of the catalyst, increasing the C-H activation barrier.²²

Palkovits *et al.* developed a Pt-based solid catalyst for the low temperature conversion of methane to methanol based on the homogeneous Periana catalyst.^{195,196} The catalyst was synthesized by coordinating PtCl₂ to a covalent triazine-based framework (CTF), which acts as a solid ligand. The final product was a solid material containing single-atom Pt sites with a coordination environment that mimics that of the Periana catalyst. The Pt-CTF catalyst performed similarly to the Periana catalyst, but also has limited industrial potential due to the low maximum

methanol concentration. The Pt-CTF catalyst, however, represents the first example of a heterogeneous catalyst that oxidizes methane to methanol at low temperature with an industrially-relevant yield.¹⁰ A similar catalyst consisting of Pt coordinated to nitrogen-doped carbon showed even better activity than the Pt-CTF catalyst was also recently reported.¹⁹⁷

Platinum nanoparticle surfaces are well-known to activate the C-H bonds in methane.^{198–} ²⁰⁰ Wei et al. studied methane steam reforming over Group VIII metal nanoparticles, and found that Pt is the most active Group VIII metal for C-H bond activation.²⁰¹ Methane completely dissociates on the Pt surface to form chemisorbed carbon and hydrogen, and the reaction rate increased with increasing dispersion, indicating that coordinatively unsaturated Pt atoms are more active for CH₄ dissociation.²⁰¹ In a study of catalytic partial oxidation (CH₄ + $\frac{1}{2}O_2 \rightarrow CO + 2H_2$) over Pt nanoparticles supported on silica and γ -alumina, Chin et al. discovered the presence of several kinetic regimes depending on the coverage of chemisorbed oxygen on the Pt surface.²⁰² Oxygen coverage in turn depends on the O₂ pressure when O₂ dissociation is equilibrated, and on the CH₄/O₂ ratio when the ratio is large enough that O₂ dissociation is not equilibrated due to fast consumption of chemisorbed oxygen by CH₄-derived species on the Pt surface. Depending on the kinetic regime, C-H activation primarily occurred on two adjacent Pt atoms, adjacent Pt and chemisorbed oxygen atoms, or two adjacent chemisorbed oxygen atoms. Chemisorbed oxygen is effective for H atom abstraction from CH₄ and Pt atoms are effective for CH₃ stabilization, making adjacent Pt – chemisorbed oxygen sites the most active for C-H activation. The addition of an oxophilic metal like Re to Pt may increase the prevalence of adjacent Pt–O sites on the catalyst surface, facilitating C-H bond activation in methane.

In this work, supported Pt and Pt-Re bimetallic catalysts were studied for the partial oxidation of methane to methanol. In homogeneous catalysis, one possible strategy for producing

alcohols from alkanes involves the insertion of an oxygen atom into a metal–alkyl bond, but there are few examples of this reaction in the literature.²⁰³ The oxygen insertion reaction for metal– methyl bonds has been demonstrated for oxidized Re complexes.^{203,204} The reaction forms a metal methoxide, which decomposes to methanol in aqueous solution. The reaction is stoichiometric rather than catalytic, with the Re complex acting as the substrate, but nonetheless represents an example of oxidative functionalization of a methyl group coordinated to an oxidized Re species, potentially similar to the Re species present in Pt-Re bimetallic heterogeneous catalysts. Thus, the envisioned function of the Pt-Re catalyst includes activation of CH₄ by Pt, generating a methyl fragment, followed by transfer of the methyl fragment to Re and subsequent oxy-functionalization. In terms of the various strategies for selective methane oxidation described in section 1.2, the goal of the Pt-Re catalyst is to generate a surface capable of both methane and oxidant activation to create intermediates of appropriate reactivity under the same conditions, and to use nano-structuring to place these functionalities in sufficiently close proximity to allow the intermediates to interact.

In this work, N₂O was used as an oxidant instead of O₂. One of the most difficult aspects of partial oxidation of hydrocarbons is the requirement that the catalyst perform two functions: activation of the C-H bond in the hydrocarbon, and activation of O₂ to generate a surface oxygen species of the appropriate reactivity.²⁰⁵ These two functions cannot be tuned independently by altering the catalyst composition. The use of a different oxidant, such as N₂O, therefore represents an opportunity to alter the reactivity of the surface oxygen without affecting the C-H activation function of the catalyst.²⁰⁵ The use of N₂O for the partial oxidation of methane to methanol over Fe-exchanged zeolite catalysts is an example of this principle.^{20,35–38} The unique " α -oxygen"

species that forms upon exposure of the catalyst to N_2O cannot be formed from O_2 , demonstrating the unique reactivity of N_2O and its ability to form surface oxygen species not accessible to O_2 .

A.2 Experimental methods

A.2.1 Catalyst synthesis

The Pt and Pt-Re catalysts were supported on SBA-15, a mesoporous silica material first synthesized by Zhao et al.²⁰⁶ To synthesize the SBA-15, 75 g of deionized (DI) water was mixed with 300 g of 2.0 N HCl solution (Sigma-Aldrich) and heated to 308 K while stirring. After the solution reached 308 K, 10 g of Pluronic P123 surfactant (Sigma-Aldrich) was added to the solution. After the surfactant was dissolved, 21.25 g of tetraethylorthosilicate (TEOS) (Sigma-Aldrich, 99.999%) was added as the silica source. The solution was stirred for 20 h at 308 K. After 20 h, the solution was transferred to an autoclave and heated in an oven for 24 h at approximately 373 K. After the hydrothermal treatment, the solid precipitate was filtered, washed with DI water, and dried in air at room temperature. The dried precipitate was thermally treated in medical air (Praxair) at 773 K for 6 h with a temperature ramp rate of 1 K min⁻¹.

The Pt and Pt-Re catalysts were prepared using the incipient wetness impregnation technique. For the pure Pt catalyst, tetraamineplatinum(II) nitrate (Sigma-Aldrich, 99.995%) was dissolved in DI water and then slowly added to SBA-15 with stirring. Additional DI water was then added until the incipient wetness point was reached. The catalyst was dried overnight in an oven at approximately 373 K and then reduced in flowing dihydrogen (Praxair, 99.999%) at 723 K for 3 h with a temperature ramp rate of 0.5 K min⁻¹.

The 8Pt-7.6Re/SBA-15 catalyst was prepared using the same method as the pure Pt catalyst, except an additional impregnation step with ammonium perrhenate (Sigma-Aldrich, \geq 99%) was performed after the initial addition of Pt and drying.

The Pt/CeO₂ catalyst was prepared via incipient wetness impregnation based on the method of Fu et al.²⁰⁷ First, 0.159 g tetraammineplatinum(II) nitrate (Sigma-Aldrich) was dissolved in approximately 2.0 g DI water. The Pt solution was then slowly added to 7.60 g CeO₂ powder (Sigma Aldrich, <25 nm particle size) with stirring until the incipient wetness point was reached. The catalyst was then dried overnight in air at approximately 383 K and then thermally treated in medical air at 673 K for 10 h (ramp rate = 1 K min⁻¹).

To remove Pt nanoparticles and generate a catalyst with only isolated Pt(II) ions, the Pt/CeO₂ catalyst was leached in an aqueous sodium cyanide solution. The pH of 100 g of DI water was adjusted 11.9 by addition of sodium hydroxide. Next, 2.0 g sodium cyanide (Sigma Aldrich) was dissolved in the solution, followed by addition of 3.0 g of the Pt/CeO₂ catalyst. The mixture was stirred for 3.5 h, then filtered, washed with DI water, dried overnight in air at 383 K, and thermally treated in medical air at 673 K for 2 h (ramp rate = 1 K min⁻¹).

A.2.2 Reactivity testing

Methane oxidation reactions were carried out in a continuous-flow fixed-bed stainless steel reactor (BTRS Jr., Autoclave Engineers). For all reactions, the catalyst was diluted with 1.5 g SiC (Sigma-Aldrich, 400 mesh). Unless otherwise specified, the reaction conditions were: $50 \text{ cm}^3 \text{ min}^{-1}$ total gas flow rate, 1 vol. % N₂O (Praxair, 4 vol. % N₂O / balance He), 20 vol. % CH₄ (Praxair, 99.999%), balance He (Praxair, 99.999%), temperature = 373-573 K, total pressure = 1 atm. When

required, *in situ* reduction of the catalyst was performed for 1 h using flowing H_2 (Praxair, 99.999%), followed by flushing pure He through the reactor for at least 15 min.

Analysis of the reactor effluent was performed periodically using two Hewlett Packard 5890 series II gas chromatographs – one equipped with a thermal conductivity detector (TCD), used for analyzing light gases including CH₄, N₂, N₂O, CO, CO₂, and O₂, and the other equipped with a flame ionization detector (FID), used for analyzing CH₄ and other combustible organics. The GC-TCD was equipped with an Alltech 6 ft. CTR-1 column, and the GC-FID was equipped with an Agilent 30 m DB-WAX column.

Catalyst performance was characterized by the conversion of N₂O. Methane was treated as an internal standard, assuming that its concentration remained constant at 20 %, since at 100 % N₂O conversion the CH₄ concentration would only decrease by at most 1 % due to the excess CH₄ relative to N₂O in the reactor feed. Product concentrations were calculated using the following formula, which is derived by assuming that the ratio of the concentration of two components is equal to the ratio of their normalized peak areas:

$$product \ concentration = \frac{normalized \ product \ peak \ area}{normalized \ CH_4 \ peak \ area} * 20\%$$
(Eqn. A.1)

The normalized peak area was calculated by dividing the actual peak area by the TCD response factor for each component. The N_2O conversion was calculated from the effluent N_2O concentration:

$$N_2 0 \ conversion = \frac{(feed \ N_2 0 \ concentration) - (effluent \ N_2 0 \ concentration)}{(feed \ N_2 0 \ concentration)} * 100\%$$
(Eqn. A.2)

A.2.2 Catalyst characterization

The surface area of the Pt and Pt-Re catalysts was determined using N₂ physisorption. Physisorption experiments were performed using a Micromeritics ASAP 2020 automated adsorption analyzer. The samples were first degassed at 723 K for 4 h, and the analysis was performed at 77 K. Surface area was calculated using the Brunauer-Emmett-Teller (BET) adsorption model.

X-ray diffraction (XRD) was used to characterize the crystal structure of the Pt and Pt-Re particles. XRD patterns were obtained using a Panalytical X'Pert Pro MPD Diffractometer with Cu K α radiation in a 2 θ range of 10⁰ to 120⁰.

Transmission electron microscopy (TEM) was performed using a JEOL 2000FX microscope operating at 200 kV equipped with Gatan slow-scan and wide-angle TV-rate cameras. Scanning transmission electron microscopy – high-angle annular dark field imaging (STEM-HAADF) and energy dispersive spectroscopy (EDS) were performed with a FEI Titan microscope operating at 300 kV, equipped with a Gatan 794 multi-scan camera. Catalyst samples were dispersed in cyclohexane and deposited on 400 mesh Cu grids (Ted Pella).

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of the 8Pt-7.6Re/SBA-15 catalyst was performed using a Bio-Rad (FTS-60A) FT-IR spectrometer equipped with a liquid nitrogen cooled MCT detector. The *in situ* cell consisted of a high temperature gas reaction chamber (Harrick Scientific) placed on a Praying Mantis diffuse reflectance sample accessory. Spectra were obtained by averaging 100 scans collected at a resolution of 4 cm⁻¹. The catalyst sample was diluted by 50 wt. % with KBr. A background was collected by scanning the sample after pre-treatment in helium at 473 K. After background collection the catalyst was exposed to a gas stream containing 1.0 vol. % N₂O, 20. vol. % CH₄, and balance He at 473 K. The cell was then purged with He at 473 K prior to spectrum collection.

A.3 Results and discussion

A.3.1 Catalyst characterization

Mesoporous silica SBA-15 was prepared as a support for Pt and Pt-Re nanoparticles. The surface area of the SBA-15 support determined from N₂ physisorption using the BET method was 718 m² g⁻¹, while the BET surface area of the 8Pt-7.6Re/SBA-15 catalyst was 502 m²/g. The decreased surface area of the Pt-Re catalyst relative to the SBA-15 is likely due to blockage of some the mesopores by metal nanoparticles, reducing the available area for N₂ adsorption, as well as an increase in mass of the sample due to the presence of the metals.²⁰⁸

The 8Pt/SBA-15 (8 wt. % Pt) catalyst had XRD peak positions consistent with metallic Pt.²⁰⁹ The Pt-Re XRD pattern closely matched the pattern observed by Anderson *et al.* for Pt-Re nanoparticles supported on Vulcan carbon, which the authors concluded represented a Pt-Re alloy.²¹⁰

Figure A.1 shows TEM images of metal nanoparticles in the 8Pt-7.6Re/SBA-15 (8 wt. % Pt, 7.6 wt. % Re, 1:1 Pt:Re molar ratio) catalyst. A statistical particle size analysis was not performed, but the particles shown appear to be approximately 5 nm or less in diameter. This is consistent with the reduced surface area and pore volume of the SBA-15 after deposition of metal particles being due to blockage of the some of the pores by the particles, since the particles are of similar size to the pores. Figure A.2 shows metal nanoparticles in the 8Pt/SBA-15 catalyst. The particles appear larger than those in the Pt-Re catalyst, with some up to 20 nm in diameter. EDS analysis of the Pt-Re catalyst showed the presence of Pt and Re, but the presence of alloyed

particles could not be confirmed due to the difficulty of analyzing individual particles. Based on the combind XRD and TEM results, we concluded that the Pt and Pt-Re catalysts consists of welldispersed nanoparticles, and that the Pt-Re catalyst likely contains alloyed Pt-Re nanoparticles.



Figure A.1. TEM images of 8Pt-7.6Re/SBA-15 catalyst



Figure A.2. TEM images of 8Pt/SBA-catalyst

A.3.2 Catalyst reactivity

The activity of the Pt-Re and pure Pt catalysts was tested in a flow reactor at 473 K and atmospheric pressure. Gas was fed to the reactor at 50 cm³ min⁻¹ with a composition of 1% N₂O, 20% CH₄, and balance helium, unless otherwise specified. The only observed products were N₂ and CO₂ – no methanol, or other selective oxidation products, were detected. Catalyst activity was measured in terms of N₂O conversion due to the significant excess of CH₄. The unreduced Pt-Re catalyst showed essentially no activity, while performing an *in situ* reduction in H₂ at 473 K

drastically increased the activity, although there was significant deactivation over time. When CH_4 was replaced with N_2 in the gas feed, significant N_2O conversion was still observed, likely due to oxidation of oxophilic Re and/or deposition of N_2O or oxygen from N_2O on the catalyst surface. However, the N_2O conversion was higher when CH_4 was present, indicating that some of the consumed N_2O reacted with species derived from CH_4 .

Figure A.3a shows the concentrations of O_2 and N_2 in the reactor effluent for reactions of N_2O and CH_4 over the Pt-Re catalyst at 473 K, as well as the corresponding N_2O conversion on the opposite axis. The N_2 concentration in the reactor effluent correlated with the N_2O conversion, while very little O_2 production was observed. This indicates that oxygen from N_2O participates in reactions with methane and/or is consumed by the catalyst, rather than desorbing as O_2 .

Figure A.3b compares the N₂O conversion over time of the Pt-Re bimetallic catalyst to the pure Pt catalyst at 473 K. The Pt-Re catalyst was pre-reduced in the reactor with H₂ at 473 K, while the Pt catalyst was not subjected to an *in situ* reduction. The pure Pt catalyst is expected to remain in a metallic state upon exposure to air after the initial reduction performed at 723 K as part of the catalyst synthesis, unlike the Pt-Re catalyst in which the oxophilic Re oxidizes upon exposure to air.²¹¹ Similar to the Pt-Re catalyst, some of the N₂O conversion over the pure Pt catalyst was due to oxygen consumption by the catalyst, but to a lesser extent than the Pt-Re catalyst.

Figure A.4a shows the N₂O conversion for the pure Pt catalyst at 473 K both with and without CH₄ present in the reactor feed. The conversion was higher when CH₄ was present, suggesting that some of the consumed N₂O participated in reactions with CH₄. For reactions where CH₄ was not co-fed, the N₂O conversion for the Pt catalyst was higher at all time points than the Pt-Re catalyst, suggesting that the pure Pt has higher activity for N₂O dissociation than Pt-Re.

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Figure A.3. a) Concentrations of O_2 and N_2 in reactor effluent compared to N_2O conversion for the Pt-Re catalyst. b) Comparison of N_2O conversion for Pt-Re and pure Pt catalysts (same amount of Pt in reactor for both reactions). T = 473 K, pressure = 1 atm, 50 cm³ min⁻¹ flow rate, feed composition 1% N_2O , 20% CH₄, balance He.



Figure A.4. a) N₂O conversion for pure Pt catalyst with and without CH₄ present in the reactor feed. b) N₂O conversion with no CH₄ in reactor feed subtracted from N₂O conversion with CH₄ in the reactor feed (same amount of Pt in reactor for both reactions). T = 473 K, pressure = 1 atm, 50 cm³ min⁻¹ flow rate, feed composition 1% N₂O, 20% CH₄, balance He. CH₄ was replaced with N₂ for the reaction without CH₄.

Burch *et al.* showed that N_2O decomposes to N_2 and chemisorbed oxygen at room temperature over Pt nanoparticles, and that addition of Bi to the Pt surface drastically decreased the N_2O decomposition activity.²¹² Addition of Re may similarly disrupt the Pt active sites for N_2O decomposition.

The difference between the N₂O conversion with and without CH₄ in the reactor feed was taken as an approximate measure of the N₂O conversion due to reaction with CH₄ or surface intermediates derived from CH₄. The difference in N₂O conversion between reactions with and without a CH₄ co-feed for the Pt and Pt-Re catalysts is shown in Figure A.4b. The greater difference for Pt suggests that the pure Pt catalyst has a higher activity than Pt-Re for reactions involving N₂O and CH₄. Figure A.4b also shows that the difference in N₂O conversion increased over time for the pure Pt catalyst, but decreased over time for the Pt-Re catalyst. This suggests that the rate of reactions involving CH₄-derived species increased over time for the pure Pt catalyst and decreased over time for the Pt-Re catalyst.

Falcone *et al.* showed that without any pre-treatment, the majority of Re in a Pt-Re bimetallic catalyst supported on silica was in a +7 oxidation state (as measured by X-ray photoelectron spectroscopy), while after reduction in H₂ at 473 K, Re existed primarily as Re(0) and Re(II). Furthermore, after reduction, the surface of the nanoparticles became enriched in Pt relative to the unreduced catalyst.²¹¹ Under oxidizing conditions, Re diffuses to the surface of Pt-Re bimetallic nanoparticles.²¹³ We therefore conclude that the deactivation observed for the Pt-Re catalyst is due to migration of Re to the surface of the Pt-Re nanoparticles, resulting in blocking of the active Pt sites. After the initial reduction, the surface of the nanoparticles is enriched in metallic Pt, which is active for CH₄ oxidation. Upon exposure to an oxidant, however, Re diffuses to the surface and forms an oxide layer, resulting in the observed decrease in activity. A pure Re catalyst showed no activity for methane oxidation (after reduction in H₂ at 473 K), as measured by the difference in N₂O conversion with and without CH₄ in the reactor feed. The observed increase in activity over time for the pure Pt catalyst is likely due to an increase in the concentration of

reactive surface intermediates; *i.e.*, the reaction has not yet reached steady state and transient behavior is being observed.

The Pt-Re catalyst was evidently not capable of converting CH_4 to CH_3OH under the conditions tested. It is not clear, however, which step or steps in a potential reaction sequence are inhibited. One possibility is that methoxy species coordinated to Re do form as initially envisioned, but that no pathway for desorption of methanol is available. To test this hypothesis, CH_4 oxidation reactions were performed in which water vapor was co-fed to the reactor, which could potentially hydrolyze methoxy species to methanol.⁴⁴ Co-feeding water vapor, however, did not result in methanol production. Furthermore, DRIFTS experiments showed no evidence of methoxy species on the catalyst surface after reduction in H_2 at 473 K and subsequent exposure to CH_4 and N_2O at 473 K.

As described above, Pt nanoparticle surfaces completely dissociate CH₄, resulting in the oxidation of chemisorbed carbon and hydrogen to CO₂ and H₂O, respectively. Isolated Pt atoms or ions, however, may be able to activate a single C-H bond in CH₄, preserving an intact methyl fragment that could potentially react to form methanol. To test this hypothesis, a catalyst consisting of isolated Pt(II) ions coordinated to CeO₂ was prepared according to the method of Fu *et al.*²⁰⁷ Under the same reaction conditions as the Pt-Re and pure Pt catalysts supported on SBA-15, however, both with and without co-feeding water, CO₂ was the only observed methane oxidation product for the Pt/CeO₂ catalyst.

A.4 Conclusions

Methane oxidation with N_2O over supported Pt and Pt-Re bimetallic catalysts did not produce methanol, and CO_2 was the only methane oxidation product observed. After accounting for N₂O consumed by oxidation of Re and formation of surface oxygen species on the catalysts, the 8Pt/SBA-15 catalyst exhibited a higher activity than the 8Pt-7.6Re/SBA-15 catalyst. The Re in the Pt-Re catalyst likely inhibited methane combustion by blocking active Pt sites. Co-feeding water vapor did not result in the observation of selective methane oxidation products. A catalyst designed to generate atomically-dispersed Pt supported on CeO_2 also exhibited only combustion activity.

B. Supporting Information for Chapter 2



B.1. Additional details on experimental methods

Figure B.1. Calibration curve for calculating Cu wt. % of Cu-mordenite catalysts based on the Cu K α peak area obtained from X-ray fluorescence spectroscopy (XRF). Cu wt. % was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) performed by Galbraith Laboratories in Knoxville, TN.

The C₂H₄ concentration was calculated using the published FID response factor²¹⁴ with

CH₃OH as an external standard:

$$C_{C2H4} = \frac{MW_{CH3OH} * RF_{CH3OH} * C_{CH3OH} * A_{C2H4}}{MW_{C2H4} * RF_{C2H4} * A_{CH3OH}}$$
(Eqn. B. 1)

where MW = molecular weight, RF = FID response factor, C = concentration in mol. %, and A =

GC peak area.

The total CH₃OH concentration was calculated from the DME, C₂H₄, and measured

CH₃OH concentrations:

$$C_{total CH30H} = C_{measured CH30H} + 2 * C_{DME} + 2 * C_{C2H4}$$
(Eqn. B.2)

where concentrations are in mol. %.
The yield for each product was calculated by integrating its concentration in the reactor effluent over time during the desorption step of the cyclic reaction:

yield
$$[mol \ (mol \ Cu^{-1})] = \frac{\int_0^T C(t)dt \ [mol. \ \% \ min] * gas \ flow \ rate \ [L \ min^{-1}]}{100 \ [\%] * 22.4 \ [L \ mol^{-1}] * \ catalyst \ mass \ [g_{cat}] * \ Cu \ conc. \ [mol \ g_{cat}^{-1}]} (Eqn. B. 3)$$

where C is product concentration in mol. % and T is the total duration of the desorption step in minutes.

The total C1 product yield was calculated as the sum of total CH₃OH, CO, and CO₂ yield during step 3 (desorption) of the cyclic CH₄ oxidation reaction:

$$yield_{C1} = yield_{total CH30H} + yield_{C0} + yield_{C02}$$
(Eqn. B. 4)

where yields are in moles of product per mole of Cu in the catalyst. Methane conversion is determined from overall C1 product yield.

Example product yield calculation:

 $C_{total CH3OH} = C_{measured CH3OH} + 2 * C_{DME} + 2 * C_{C2H4}$

 $C_{total CH3OH} = 0.30 \ mol \ CH_3OH \ (mol \ Cu)^{-1} + 2 * 0.040 \ mol \ DME \ (mol \ Cu)^{-1} + 2$

 $* 0.0010 mol C_2 H_4 (mol Cu)^{-1}$

 $C_{total CH30H} = 0.38 mol CH_30H (mol Cu)^{-1}$

 $yield_{C1} = yield_{total CH30H} + yield_{C0} + yield_{C02}$

 $yield_{C1} = 0.38 \ mol \ CH_3 OH \ (mol \ Cu)^{-1} + 0.031 \ mol \ CO \ (mol \ Cu)^{-1}$

 $+ 0.010 mol CO_2 (mol Cu)^{-1}$

 $yield_{C1} = 0.42 \ mol \ (mol \ Cu)^{-1}$

B.2. Additional X-ray absorption spectroscopy results

B.2.1. X-ray absorption near edge spectroscopy linear combination fitting (XANES-LCF)

Linear combination fitting of the XANES (XANES-LCF) of the Cu0.28-H-MOR catalyst was performed based on the method of Alayon et al.⁴³ The experimental spectrum of the Cu0.28-H-MOR catalyst after auto-reduction in He was fitted using a linear combination of standard spectra representing hydrated Cu^{II}, dehydrated Cu^{II}, and Cu^I as shown in Figure B.2. These three standard spectra represent the three types of copper species that likely exist in the catalyst. The fresh Cu0.28-H-MOR catalyst, which contains hydrated Cu^{II} complexes,¹⁰⁴ was used as the hydrated Cu^{II} standard, while the Cu0.28-H-MOR catalyst after activation in O₂ at 723 K, which contains fully dehydrated, framework-bound Cu^{II} ions,⁴³ was the standard for dehydrated Cu^{II}.

Previous reports have shown that for Cu-MOR samples subjected to multiple reaction cycles, the CH₃OH yield increased after the first cycle.^{91,103,215} In order to investigate the effect of multiple reaction cycles on the redox behavior of Cu in the Cu0.28-H-MOR catalyst, we performed a second auto-reduction in He at 723 K following the initial reaction cycle (i.e. auto-reduction in He at 723 K, activation in O₂ at 723 K, and reaction with CH₄ at 473 K). Prior to the second auto-reduction, the catalyst was treated in O₂ at 723 K to remove carbonaceous species deposited during the CH₄ treatment. The second auto-reduction in He at 723 K resulted in XANES that was consistent with solely Cu(I) in the sample, with a pre-edge peak at 8983 eV slightly more intense than the white line.^{91,139} The spectrum collected after the second auto-reduction was therefore used as the Cu¹ standard in XANES-LCF.



Figure B.2. Cu standards used in XANES-LCF (Cu K edge). The hydrated Cu(II) standard is the fresh Cu0.28-H-MOR catalyst, the dehydrated Cu(II) standard is the Cu0.28-H-MOR catalyst after activation in O_2 at 723 K for 4 h, and the Cu(I) standard is the Cu0.28-H-MOR catalyst in He at 723 K with the following pre-treatment: He at 723 K for 2 h, O_2 at 723 K for 4 h, CH₄ at 473 K for 1 h, and O_2 at 723 K for 1 h. In between steps, the reactor was cooled to 323 K, and also purged with He between the O_2 and CH₄ treatments.



B.2.2. XANES-LCF of the Cu0.28-H-MOR catalyst after reduction in H₂ at 673 K

Figure B.3. XANES-LCF of the Cu0.28-H-MOR catalyst after reduction in H₂ at 673 K. Fitting was performed to emphasize the 8983 eV region (representing the Cu(I) $1s \rightarrow 4p$ transition), rather than the entire XANES, in order to quantify the Cu(I) fraction as accurately as possible.



Figure B.4. Magnitude (a) and imaginary part (b) of the k^2 -weighted FT-EXAFS and fit of Cu metal foil at the Cu K-edge to determine S_0^2 . Path degeneracies were fixed to known values from crystal structure data. Additional fitting results in Table B.1.

Degeneracies we	ie inkeu to known van	ies nom erystal situ	ciule uata.	
Backscatterer	Path type	Degeneracy	Distance [Å]	σ² [Ų]
Cu	Single scattering	12	2.54 ± 0.00	0.0089 ± 0.0002
Cu	Single scattering	6	3.59 ± 0.01	0.0134 ± 0.0012
Cu	Acute triangle	48	3.83 ± 0.03	0.023 ± 0.006
Cu	Double scattering	48	4.41 ± 0.02	0.0056 ± 0.0045
Cu	Single scattering	24	4.39 ± 0.01	0.0090 ± 0.0017
Cu	Obtuse triangle	96	4.70 ± 0.01	0.0021 ± 0.0021
Cu	Obtuse triangle	48	4.75 ± 0.00	0.00002 ± 0.0020

Table B.1. EXAFS fitting results of Cu metal foil at the Cu K-edge used to determine S_0^2 . Degeneracies were fixed to known values from crystal structure data.

Fit was performed in R-space in for 2.5 < k < 15 Å⁻¹ and 1.0 < R < 4.4 Å. Combined k¹-k²-k³-weighted fit. $S_0^2 = 0.90 \pm 0.02$. $\Delta E_0 = 2.1 \pm 0.3$ eV. Used 16 out of 27 independent points. R-factor = 0.001.

B.2.4. Comparison of EXAFS fitting of the Cu0.28-H-MOR catalyst with N_{oxygen} *fixed at 3 and 4* To directly compare the compatibility of the EXAFS data with dicopper versus tricopper active site models, fits of the first coordination shell were performed with the coordination number of the oxygen scattering path fixed to both 3 and 4 (Figures B.5–B.6 and Table B.2). Fixing the oxygen coordination number to 3 resulted in an order of magnitude decrease in the R-factor compared to 4 (R-factor = 0.006 for N_{oxygen} = 3, versus R-factor = 0.06 for N_{oxygen} = 4), indicating a much better fit for N_{oxygen} = 3 than for N_{oxygen} = 4.



Figure B.5. a) Magnitude and b) imaginary part of k^2 -weighted FT-EXAFS of the Cu0.28-H-MOR catalyst at the Cu K edge after treatment in He at 723 K for 2 h followed by treatment in O₂ at 723 K for 4 h (and subsequent cooling to 473 K in O₂). The first shell oxygen coordination number was fixed at 3. Additional fitting results in Table B.2.



Figure B.6. a) Magnitude and b) imaginary part of k^2 -weighted FT-EXAFS of the Cu0.28-H-MOR catalyst at the Cu K edge after treatment in He at 723 K for 2 h followed by treatment in O₂ at 723 K for 4 h (and subsequent cooling to 473 K in O₂). The first shell oxygen coordination number was fixed at 4. Additional fitting results in Table B.2.

Table B.2. EXAFS fitting results of the first coordination shell of the Cu0.28-H-MOR catalyst at the Cu K-edge after treatment in He at 723 K for 2 h, followed by activation in O₂ at 723 K for 4 h (spectrum collected after cooling to 473 K in O₂). Two fits were performed, with the first shell oxygen coordination number set to both 3 and 4 to compare the $[Cu_2O]^{2+}$ (N_{oxygen} = 3) and $[Cu_3O_3]^{2+}$ (N_{oxygen} = 4) structural models.

Scattering path	Coordination number (fixed)	Distance [Å]	σ^2 [Å ²]	ΔE0[eV]	R-factor
Cu-O	3	1.92 ± 0.01	0.0061 ± 0.0049	$\textbf{-3.9}\pm0.8$	0.006
Cu-O	4	1.92 ± 0.03	0.011 ± 0.002	-4.8 ± 2.8	0.06

 S_0^2 was fixed at 0.9. Fits were performed in R-space in for 2.5 < k < 13 Å⁻¹ and 1.0 < R < 2.0 Å. Combined k¹-k²-k³-weighted fits. Used 6 out of 11 independent points. No correlations above 0.9.

B.2.5. EXAFS fitting of the O₂-activated Cu0.28-H-MOR catalyst with a Cu-Cu scattering path included

Borfecchia et al. reported that for a Cu-H-MOR catalyst, inclusion of a Cu-Cu single scattering path in the second coordination shell of Cu resulted in high correlations (> 0.95) between several parameters and unphysical values of the structural parameters of the Cu-Al and Cu-Cu paths. As a result, if a contribution from Cu-Cu scattering in the second coordination shell of the central Cu atoms existed, it was unable to be identified.⁸⁴ Similarly, when attempting to add a Cu-Cu single scattering path in the second coordination shell of Cu for the O₂-activated Cu0.28-H-MOR catalyst, we obtained unphysical values and high correlations for several structural parameters (Table B.3). It was therefore not possible to use Cu-Cu scattering to verify the dicopper structural model.

Table B.3. EXAFS fitting results of the Cu0.28-H-MOR catalyst at the Cu K-edge after treatment in He at 723 K for 2 h followed by activation in O_2 at 723 K for 4 h (spectrum collected after cooling to 473 K) with a Cu-Cu scattering path included.

Scattering path	Coordination number	Distance (Å)	σ^2 (Å ²)
Cu-O	2.5 ± 0.4	1.93 ± 0.01	0.0043 ± 0.0011
Cu-Al	2.8 ± 5.6	2.68 ± 0.10	0.045 ± 0.001
Cu-Cu	-0.8 ± 0.6	2.62 ± 0.02	0.0087 ± 0.0050

 S_0^2 was fixed at 0.9. Fit was performed in R-space in for 2.5 < k < 13 Å⁻¹ and 1.0 < R < 3.0 Å. Combined k¹-k²-k³-weighted fit. $\Delta E_0 = -2.1 \pm 1.4$ eV. Used 10 out of 13 independent points. R-factor = 0.003. Correlation between σ^2_{AI} and $N_{AI} = 0.98$.

B.2.6. Effect on the EXAFS of cooling the Cu0.28-H-MOR catalyst after activation in O_2 at 723 K



Figure B.7. a) Magnitude and b) imaginary part of k^2 -weighted FT-EXAFS of the Cu0.28-H-MOR catalyst at the Cu K edge after treatment in He at 723 K for 2 h followed by treatment in O₂ at 723 K for 4 h (and subsequent cooling to 323 K in O₂), shown with fit. Gray dashed lines indicate the fitting range in R space. Additional fitting details can be found in Table B.4.

Table B.4. Comparison of EXAFS fitting results for the first coordination shell of the Cu0.28-H-MOR catalyst at the Cu K-edge in O_2 after cooling to 473 K and subsequently to 323 K (after treatment in He at 723 K for 2 h and activation in O_2 at 723 K for 4 h).

Temp. [K]	Scattering path	Coord. number	Distance [Å]	$\sigma^2 [\text{\AA}^2]$	ΔE0[eV]	R-factor
473	Cu-O	2.9 ± 0.2	$\begin{array}{c} 1.92 \pm \\ 0.01 \end{array}$	$\begin{array}{c} 0.0051 \pm \\ 0.0008 \end{array}$	-3.7 ± 0.8	0.003
323	Cu-O	3.3 ± 0.2	$\begin{array}{c} 1.93 \pm \\ 0.01 \end{array}$	$\begin{array}{c} 0.0064 \pm \\ 0.00092 \end{array}$	-3.0 ± 0.7	0.007

 S_0^2 was fixed at 0.9. Fits were performed in R-space in for 2.5 < k < 13 Å⁻¹ and 1.0 < R < 2.0 Å. Combined k¹-k²-k³-weighted fits. Used 4 out of 7 independent points. No correlations above 0.9.

B.2.7. Effect on the XANES of cooling the Cu0.28-H-MOR catalyst after activation in O_2 at 723 K



Figure B.8. XANES-LCF of the Cu0.28-H-MOR catalyst after treatment in He at 723 K for 2 h followed by activation in O_2 at 723 K for 4 h and subsequent cooling to 473 K in O_2 . Data and fit are plotted with the weighted components and residual.



Figure B.9. XANES-LCF of the Cu0.28-H-MOR catalyst after treatment in He at 723 K for 2 h followed by activation in O_2 at 723 K for 4 h and subsequent cooling to 323 K in O_2 . Data and fit are plotted with the weighted components and residual.



B.2.8. XANES-LCF of the Cu0.28-H-MOR catalyst after cooling following auto-reduction

Figure B.10. XANES-LCF of the Cu0.28-H-MOR catalyst after treatment in He at 723 K for 2 h, then cooled to 473 K in He. Data and fit are plotted with the weighted components and residual.



Figure B.11. XANES-LCF of the Cu0.28-H-MOR catalyst after treatment in He at 723 K for 2 h, then cooled to 323 K in He. Data and fit are plotted with the weighted components and residual.

B.3. Effect of gas impurities on product yields for Cu0.28-H-MOR

			C1 product yield	CH ₃ OH
Activation ^a	CH4 treatment ^b	He purification	[mol (mol Cu) ⁻¹]	selectivity [%]
O.º	35 bar, 20 h	N/A	0.42	90
O_2^*	1 bar, 4 h	N/A	0.30	84
	35 bar, 20 h	None	0.40	89
	35 bar, 20 h	Supelco OMI-4	0.32	81
He ^d	35 bar, 20 h ^e	Supelco OMI-4	0.34	90
	1 bar, 4 h	None	0.21	85
	1 bar, 4 h	Supelco OMI-4	0.23	77

Table B.5. Effect of activation gas, CH₄ treatment, and purification on product yield for Cu0.28-H-MOR.

^aPerformed at 723 K

^bPerformed at 473 K

^cReproduced from Table 2.1 for comparison with He activation.

^dFor activation in He, the activation time was 2 h (compared to overnight for O_2) and the ramp rate was 3 K min⁻¹ (compared to 10 K min⁻¹ for O_2), to mimic auto-reduction in the XAS experiment.

^eHe flow stopped and valves on both upstream and downstream side of reactor closed during cooling from 723 K to 473 K following activation.

C. Supporting Information for Chapter 3

C.1. Catalyst information

Catalyst	Si/Al (nominal)	pH during Cu exchange	Cu conc. (wt. %)	Na conc. (wt. %)	Al conc. (wt. %)
Cu0.28-H-MOR	10	5.7	2.20	Not measured	3.70
Cu0.28-Na-MOR	10	5.7	2.36	1.26	3.61
Cu0.41-Na-MOR	10	5.6	3.39	1.08	3.53
Cu0.26-H-ZSM-5	11.5	5.7	2.03	Not measured	3.29
Cu0.45-H-ZSM-5	11.5	5.2	3.24	Not measured	3.07
Cu0.45-Na-ZSM-5	11.5	5.7	3.55	0.392	3.37
Cu0.54-Na-ZSM-5	11.5	5.6	3.91	0.221	3.09
Cu0.43-Na-ZSM- 5(6.2)	11.5	6.2	3.16	Not measured	Not measured
Cu0.44-H-MOR	10	5.7	3.24	Not measured	3.37
Cu0.26-H/Na-MOR	10	5.7	2.18	0.504	3.56

C.2. Additional methane oxidation reaction results

Catalyst	Yield during CH4 activationalyst[mol (mol Cu) ⁻¹]		Yield during desorption [mol (mol Cu) ⁻¹]			Yield during temperature ramp [mol (mol Cu) ⁻¹]			
	СН ₃ ОН	CO	CO_2	СН ₃ ОН	СО	<i>CO</i> ₂	CH ₃ OH	СО	CO_2
Cu0.28-H- MOR	-	-	-	0.39	0.036	0.005	-	0.015	0.039
Cu0.28-Na- MOR	-	-	0.051	0.25	0.043	0.017	-	0.006	0.036
Cu0.41-Na- MOR	-	-	0.056	0.15	0.038	0.064	-	0.003	0.019
Cu0.26-H- ZSM-5	-	-	-	0.27	0.048	0.005	-	0.009	0.032
Cu0.45-H- ZSM-5	-	-	0.011	0.19	0.072	0.055	-	0.020	0.022
Cu0.45-Na- ZSM-5	-	-	0.042	0.10	0.043	0.064	-	0.001	0.016
Cu0.54-Na- ZSM-5	-	-	0.086	0.059	0.047	0.077	-	-	0.016

Table C.2. Product yields during each step of the cyclic methane-to-methanol reaction.

As stated in section 3.3.1, after desorption was complete, the reactor temperature was increased to 723 K at 3 K min⁻¹. During this temperature ramp, some additional CO and CO₂ desorbed from the catalyst: on average, 0.008 mol CO (mol Cu)⁻¹ and 0.031 mol CO₂ (mol Cu)⁻¹). Sushkevich and van Bokhoven also reported desorption of CO₂ during temperature-programmed desorption (TPD) of Cu-MOR catalysts following treatment in 7 bar methane.¹⁰⁵ We did not include this additional CO_x in the yield and selectivity calculations in Table 3.1, mainly due to the observation of desorption of a small amount of methane (along with the CO and CO₂) during the temperature ramp. This desorbing methane may participate in side reactions with O₂ (which also may desorb from confined locations in the zeolite pores during the

temperature ramp) that form CO_x at higher temperature. Some methane is likely forced into highly confined locations within the zeolite pores during exposure of the catalysts to elevated methane pressure over a period of 20 h at 473 K, which subsequently desorbs when methane is removed from the reactor and the temperature is increased. This hypothesis is supported by the observation that the amount of CO_x that desorbed during the temperature ramp is approximately 50 % higher for the Cu-MOR catalysts than the Cu-ZSM-5 catalysts. This difference may be realted to the greater availability of highly confined locations within the pore network of MOR (containing compressed 8 member ring (8MR) side pockets) compared to ZSM-5 (an accessible pore network comprised entirely of 10MR channels). Moreover, a post-desorption thermal ramp of Cu-Na-MOR following exposure to methane at atmospheric pressure (as opposed to elevated methane pressure) did not result in the observation of any additional CO_x.^{44,166} Table C.2 contains the products yields during each step of the reaction (methane activation, desorption, post-desorption thermal ramp), and Table C.3 is an alternate version of Table 3.1 which includes the CO_x formed during the post-desorption temperature ramp in the overall yield and selectivity calculations.

Catalwat	CH4 conversion	Yield [mol (mol Cu) ⁻¹]			Selectivity [%]		
Catalyst	[mol (mol Cu) ⁻¹]	CH ₃ OH	СО	CO ₂	CH ₃ OH	СО	CO ₂
Cu0.28-H-MOR	0.49	0.39	0.051	0.044	80	11	9
Cu0.28-Na-MOR	0.40	0.25	0.049	0.10	62	12	26
Cu0.41-Na-MOR	0.33	0.15	0.041	0.14	46	12	42
Cu0.26-H-ZSM-5	0.36	0.27	0.057	0.037	74	16	10
Cu0.45-H-ZSM-5	0.37	0.19	0.092	0.088	52	25	24
Cu0.45-Na-ZSM-5	0.27	0.10	0.044	0.12	38	16	45
Cu0.54-Na-ZSM-5	0.29	0.059	0.047	0.18	21	16	63

Table C.3. Alternate version of Table 3.1 that includes CO_x produced during post-desorption temperature ramp in methane conversion and selectivity calculations.

Table C.4. Alternate version of Table 3.4 that includes CO_x produced during post-desorption temperature ramp in the calculations.

Catalyst	Total oxygen in products ^a [mol (mol Cu) ⁻¹]	Fraction of active Cu ^b	Molar ratio of oxygen to active Cu ^c
Cu0.28-H-MOR	0.72	1.16	0.62
Cu0.28-Na-MOR	0.81	1.11	0.73
Cu0.41-Na-MOR	0.83	1.03	0.81
Cu0.26-H-ZSM-5	0.59	0.91	0.64
Cu0.45-H-ZSM-5	0.82	1.11	0.74
Cu0.45-Na-ZSM-5	0.72	0.87	0.83
Cu0.54-Na-ZSM-5	0.92	1.02	0.90

^aCalculated assuming that three oxygen atoms are required for CO formation and four oxygen atoms are required for CO₂ formation

^b = $2 * CH_3OH$ yield + 4 * CO yield + $4 * CO_2$ yield (normalized to total Cu in catalyst)

^c = Total oxygen in products / fraction of active Cu

C.3. Additional UV-vis spectra



Figure C.1. UV-vis spectra of Cu0.28-H-MOR catalyst during O_2 activation (1–2) and subsequent treatment in methane (3).



Figure C.2. Product yields in the cyclic methane to methanol reaction for a) methanol b) CO and CO₂ vs. intensity of the UV-vis spectrum at 21,600 cm⁻¹ for Cu-MOR catalysts. Trend lines were added for methanol and CO₂.



Figure C.3. UV-vis spectra of the Cu0.43-Na-ZSM-5(6.2) catalyst in O_2 at 723 K (blue) and after cooling to 473 K (green). The Cu0.43-Na-ZSM-5(6.2) catalyst was prepared to mimic earlier Cu-Na-ZSM-5 catalysts reported in the literature that were synthesized without pH control during Cu exchange.^{34,42,68,96} The "6.2" in the catalyst name indicates the measured pH during Cu exchange.



Figure C.4. UV-vis spectra of Cu0.28-H-MOR (a) and Cu0.54-Na-ZSM-5 (b) catalysts after activation in O₂ at 723 K (red) and after switching gas flow to helium (blue).



C.4. Raman experimental setup and additional Raman spectra

Figure C.5. Representation of customized Raman spectroscopy and Harrick Raman chamber.¹⁶⁴



Figure C.6. Raman spectra of the Cu0.43-Na-ZSM-5(6.2) catalyst in O₂ at 723 K, measured with several excitation lasers. The Cu0.43-Na-ZSM-5(6.2) catalyst was prepared to mimic earlier Cu-Na-ZSM-5 catalysts reported in the literature that were synthesized without pH control during Cu exchange.^{34,42,68,96} The "6.2" in the catalyst name indicates the measured pH during Cu exchange.



Figure C.7. Raman spectra of the Cu0.43-Na-ZSM-5(6.2) catalyst in O_2 at 723 K, followed by cooling in O_2 to 473 K. Measured using a 442 nm excitation laser. The decay of features upon cooling from 723 K to 473 K is attributed to hydrolysis of dehydrated Cu^{II}-oxygen complexes that are responsible for enhancement of the Raman features by trace O_2 in the cell, consistent with the decay of the UV-vis band at ~22,000 cm⁻¹ observed during cooling (Figure C.3).



Figure C.8. Raman spectra of Na-MOR (Si/Al = 10) measured *ex situ* with several excitation lasers.



Figure C.9. Raman spectra of Na-MOR (Si/Al = 6.5) measured *ex situ* with several excitation lasers.

Raman spectroscopy of the Cu0.43-Na-ZSM-5(6.2) catalyst treated in ¹⁶O₂ vs. ¹⁸O₂

As discussed in section 3.3.3, we attempted to reproduce prior Raman experiments performed by Smeets *et al.* using the Cu0.43-Na-ZSM-5(6.2) catalyst involving autoreduction in helium at 723 K, followed by cooling to 323 K and treatment in either ¹⁶O₂ or ¹⁸O₂ (with subsequent heating to 723 K).⁹⁶ Heating Cu-exchanged zeolites in an inert atmosphere induces the autoreduction reaction, where Cu^{II} is reduced to Cu^I, which is highly reactive toward O₂.^{98,101,102,183} The Cu0.43-Na-ZSM-5(6.2) catalyst was Cu-exchanged without pH control to mimic earlier syntheses from the literature,^{34,42,71,96} and had a measured pH of 6.2 during Cu exchange. Raman spectra of the Cu0.43-Na-ZSM-5(6.2) catalyst (Figure C.6) were consistent with those previously reported in the

literature.³⁴ Smeets *et al.* found that exposure of an autoreduced Cu-Na-ZSM-5 catalyst to O₂ at room temperature resulted in the formation of Raman features that were consistent with μ -(η^2 : η^2)peroxo dicopper(II) species; namely, peaks at 269 and 736 cm⁻¹ that were attributed to Cu-Cu and O-O stretching modes, respectively. The Cu-Na-ZSM-5 catalyst treated in O₂ at room temperature also exhibited a UV-vis absorption band at 29,000 cm⁻¹ that was assigned to a μ -(η^2 : η^2)-peroxo dicopper(II) species. Upon heating, these Raman and UV-vis features disappeared, and the same features that were assigned to the mono-µ-oxo dicopper(II) species were observed, leading to the conclusion that the μ -(η^2 : η^2)-peroxo dicopper(II) species is a precursor to the mono- μ -oxo dicopper(II) species. The transformation between these two species was explained based on neighboring Cu^I ions providing the two additional electrons required to cleave the peroxo bond and form the oxo. The Raman spectrum at 723 K was measured with a 458 nm excitation laser to induce resonance enhancement associated with the UV-vis peak at 22,700 cm⁻¹, while the spectrum at room temperature was measured with a 364 nm laser to match the frequency of the UV-vis band at 29,000 cm^{-1.96} Exposure of the autoreduced Cu-Na-ZSM-5 catalyst to ¹⁸O₂ at room temperature shifted the Raman peak at 736 cm⁻¹ to lower energy, consistent with its assignment as the O-O stretch of a peroxo species.⁹⁶

We performed similar experiments with the Cu0.43-Na-ZSM-5(6.2) catalyst, where it was first subjected to autoreduction in helium at 723 K, followed by cooling to 323 K and treatment in ${}^{16}O_2$, with subsequent heating to 723 K. Similar to the work of Smeets *et al.*,⁹⁶ we measured Raman spectra with both 355 nm and 457 nm excitation lasers.

Figures C.10 and C.11 show the spectra at each step in the ${}^{16}O_2$ experiment measured with the 355 nm and 457 nm lasers, respectively. The peaks at 269 and 736 cm⁻¹ are visible at 323 K in ${}^{16}O_2$ when using the 355 nm laser, although they appear somewhat less intense than in the spectra

reported by Smeets *et al.*⁹⁶ Several additional peaks are present in the ranges of 300–600 cm⁻¹ and 900–1200 cm⁻¹. The peak at 1146 cm⁻¹ is most likely from the O-O stretch of a Cu-superoxo species,⁸⁶ which can form at low temperature via interaction of an O₂ molecule with a single Cu^I ion generated during autoreduction.¹⁶⁹ It is not clear whether this peak was observed in the prior work of Smeets *et al.*, as it is outside the range of the reported spectra.⁹⁶ The superoxo peak is present at low intensity in helium at 323 K following autoreduction at 723 K, possibly due to trace O₂ impurity in the cell. It is not initially clear whether the other peaks are from zeolite vibrational modes or Cu species, as it appears that the presence of UV-vis-active Cu species can enhance the Raman vibrations of the zeolite, as described in section 3.3.3.

Superoxo species have also been detected via Raman spectroscopy in O₂-activated Cu-CHA, although they were claimed not to play a role in methane oxidation.^{86,177} We found no clear evidence of superoxo species in the Cu0.43-Na-ZSM-5(6.2) or Cu-MOR catalysts directly activated in O₂ at 723 K. Moreover, based on the formation of superoxo species during interaction of O₂ with Cu¹ at 323 K, microscopic reversibility implies that superoxo adducts should desorb as O₂ during the 2 h post-activation helium purge at 473 K. Additionally, the O/Cu ratio calculated based on the product yields was < 1 for all catalysts (Table 3.1, Table 3.4), suggesting that Cu-superoxo species (which have a O/Cu ratio of 2) do not play a major role in methane oxidation. A DFT study investigating methane activation over several Cu-oxygen complexes in Cu-CHA found that Cu-superoxo had the highest barrier among the investigated complexes,⁸⁹ further suggesting that Cu-superoxo species do not play a significant role in methane activation.



Figure C.10. Raman spectra of the Cu0.43-Na-ZSM-5(6.2) catalyst measured with a 355 nm excitation laser. Catalyst was pre-treated in helium at 723 K.



Figure C.11. Raman spectra of the Cu0.43-Na-ZSM-5(6.2) catalyst measured with a 457 nm excitation laser. Catalyst was pre-treated in helium at 723 K.

The corresponding spectra measured with the 457 nm laser are shown in Figure C.11, and are mostly consistent with the results of Smeets *et al.*⁹⁶ Peaks at 448 and 508 cm⁻¹ are visible already at 323 K in ¹⁶O₂, and increase in intensity as the temperature is increased to 723 K. Also at 723 K, features appear at 850, 903, and 961 cm⁻¹, which were previously assigned as the anti-symmetric Cu-O stretch of mono- μ -oxo dicopper(II), the first overtone of the symmetric Cu-O stretch of mono- μ -oxo dicopper(II), and the combination band of the bands at 448 and 508 cm⁻¹.³⁴ The major difference between our spectrum in ¹⁶O₂ at 723 K and that of Smeets *et al.*⁹⁶ is the energy of the band at 850 cm⁻¹, which was previously reported at somewhat higher energy (874 cm⁻¹).^{34,96}

Figures C.12 and C.13 show a similar experiment to Figures C.10 and C.11, except that ¹⁸O₂ was used instead of ¹⁶O₂. Additional spectra were collected for this experiment after cooling the catalyst to 323 K following treatment at 723 K in ¹⁸O₂. The superoxo peak is again visible with the 355 nm laser in helium at 323 K with low intensity. Upon exposure to ¹⁸O₂, the superoxo peak increases in intensity and shifts to 1082 cm⁻¹, supporting its assignment as the O-O stretch of a superoxo species. The peak at 736 cm⁻¹ attributed to the O-O stretch of the μ -(η^2 : η^2)-peroxo dicopper(II) species also appears shifted to lower energy (*ca.* 695 cm⁻¹), consistent with the results of Smeets *et al.*⁹⁶



Figure C.12. Raman spectra of the Cu0.43-Na-ZSM-5(6.2) catalyst measured with a 355 nm excitation laser. Catalyst was pre-treated in helium at 723 K and treated in ${}^{18}O_2$. Bold labels indicate peak that shift either after introduction of ${}^{18}O_2$ at 323 K or after heating to 723 K.



Figure C.13. Raman spectra of the Cu0.43-Na-ZSM-5(6.2) catalyst measured with a 457 nm excitation laser. Catalyst was pre-treated in helium at 723 K and treated in ${}^{18}O_2$.

The behavior of the other peaks in ¹⁸O₂ provide some information regarding their assignment as vibrational modes of the zeolite vs. a Cu species. The bolded labels indicate peaks that shift after treatment in ¹⁸O₂, either before or after heating to 723 K. The peak at 993 cm⁻¹ shifts to lower energy, but only after the catalyst has been heated to 723 K in ¹⁸O₂. This behavior suggests that this peak is associated with a zeolite vibrational mode, and that it is shifted after high-temperature treatment in ¹⁸O₂ due to incorporation of ¹⁸O into the zeolite lattice. This phenomenon has been previously observed for Cu-exchanged zeolites, evidenced by desorption of ^{16,18}O₂ and ¹⁶O₂ during TPD after activation of Cu-Na-ZSM-5 in ¹⁸O₂ at 723 K – indicative of isotope scrambling with the zeolite lattice oxygen.⁹⁶ The peak at 993 cm⁻¹ is within the expected range for the Cu^{II}-shifted zeolite T-O-T vibration.^{178,179,216} Similarly, the peak at 593 cm⁻¹ shifted to lower energy after hightemperature treatment in ¹⁸O₂, suggesting that it is also associated with a zeolite vibrational mode. There appear to be two or more overlapping peaks in the 450–500 cm⁻¹ region, which may be associated with vibrations of the 4MR/6MR units of ZSM-5,²¹⁶ but are also in the expected energy range of symmetric Cu-O stretches of Cu-oxygen complexes.

The peak at 372 cm⁻¹ in Figure C.12 that is present with a relatively weak intensity in the autoreduced Cu0.43-Na-ZSM-5(6.2) catalyst becomes more intense and shifts to lower energy upon introduction of ${}^{18}O_2$ at 323 K. This behavior suggests that it is associated with a Cu species, rather than the zeolite, since 323 K is likely too low of a temperature for isotope scrambling to occur with the zeolite lattice oxygen. Similar to the weak superoxo peak at 1146 cm⁻¹ that is present in the autoreduced catalyst prior to introducing O₂, the peak at 372 cm⁻¹ may be associated with a Cu-oxygen complex that forms due to interaction of trace O₂ in the cell with Cu^I upon cooling. A

Raman band of similar energy at 360 cm⁻¹ has previously been assigned to the Cu-O bending mode of a *trans*-µ-1,2-peroxo dicopper(II) species in Cu-CHA.⁸⁵

After introduction of ¹⁸O₂ to the autoreduced catalyst at 323 K, the peak observed at 269 cm⁻¹ in ¹⁶O₂ shifted to 260 cm⁻¹, and remained at this energy after heating to 723 K in ¹⁸O₂ and subsequent cooling back to 323 K (Figure C.12). As described above, this behavior is consistent with this peak representing a vibrational mode of a Cu species, rather than the zeolite. Smeets *et al.* assigned this peak to the Cu-Cu stretching mode of the μ -(η^2 : η^2)-peroxo dicopper(II) species, although a shift when using ¹⁸O₂ was not observed,⁹⁶ in contrast to the present case.

The spectra measured with the 457 nm laser (Figure C.13) are again broadly consistent with the results of Smeets *et al.*⁹⁶ The peak at 448 cm⁻¹ in ¹⁶O₂ shifts to 442 cm⁻¹, while no shift in the peak at 508 cm⁻¹ is observed.

Figure C.14 directly compares the spectra of Cu0.43-Na-ZSM-5(6.2) measured with the 355 nm laser in ${}^{16}O_2$ and ${}^{18}O_2$ at 323 K, prior to heating to 723 K. The peaks labelled in bold indicate peaks that are shifted for ${}^{18}O_2$ relative to ${}^{16}O_2$. These spectra reveal that the peak at 524 cm⁻¹ in ${}^{16}O_2$ is shifted to lower wavenumber for ${}^{18}O_2$, indicating that it is associated with a Cu species. The energy of this peak is consistent with the symmetric Cu-O stretch of both η^2 -superoxo dicopper(II) and μ -1,2-peroxo dicopper(II) complexes.^{85,169,217–219} Formation of superoxo and μ -1,2-peroxo adducts from single Cu^I and paired Cu^I ions, respectively, is feasible at 323 K, as no extra electrons to cleave the O-O bond are required from additional Cu^I ions.



Figure C.14. Comparison of Raman spectra of the Cu0.43-Na-ZSM-5(6.2) catalyst following autoreduction in helium at 723 K and subsequent treatment in either ¹⁶O₂ or ¹⁸O₂ at 323 K. Spectra measured using a 355 nm excitation laser. Bold labels indicate peaks that shifted in ¹⁸O₂ relative to ¹⁶O₂.

Similar to Figure C.14, Figure C.15 directly compares the spectra of Cu0.43-Na-ZSM-5(6.2) measured with the 457 nm laser in ${}^{16}O_2$ and ${}^{18}O_2$ at 723 K. As noted above, the peak at 448 cm⁻¹ shifted to lower wavenumber in ${}^{18}O_2$, while the peak at 508 cm⁻¹ did not shift. The peak at 225 cm⁻¹ is similar in energy to a peak at 237 cm⁻¹ that was attributed to the Cu-O bending mode of monoµ-oxo dicopper(II) in Cu-Na-ZSM-5.³⁴ It is also similar in energy, however, to the reported Cu-O bending mode of a *trans*-µ-1,2-peroxo dicopper(II) species in Cu-CHA.⁸⁵ Although there was no apparent shift of this peak in ${}^{18}O_2$ as compared to ${}^{16}O_2$, the previously reported shift was only 3 cm⁻¹,³⁴ which is too small to detect in our spectra.



Figure C.15. Comparison of Raman spectra of the Cu0.43-Na-ZSM-5(6.2) catalyst following autoreduction in helium at 723 K and subsequent treatment in either ¹⁶O₂ or ¹⁸O₂ at 323 K, followed by heating to 723 K. Spectra were measured using a 457 nm excitation laser. Bold labels indicate peaks that shifted in ¹⁸O₂ relative to ¹⁶O₂.

While the peaks at 903 and 961 cm⁻¹ are too broad to make definitive determinations regarding shift, the peak at 850 cm⁻¹ clearly shifts to lower wavenumber by approximately 35 cm⁻¹, consistent with previous literature.^{34,96} The energy and isotopic shift of this peak are consistent with the O-O stretch of a μ -1,2-peroxo dicopper(II) species.^{85,169,170} Activation of a Cu-Na-ZSM-5 catalyst in a mixture of ¹⁶O₂ + ¹⁶O¹⁸O + ¹⁸O₂ in a 1:2:1 molar ratio at 723 K produced Raman peaks at 830 cm⁻¹ and 870 cm⁻¹, without a peak at intermediate wavenumber that would be expected for the ¹⁶O-¹⁸O stretch of the peroxo, suggesting that the peak at 870 cm⁻¹ (850 cm⁻¹ in our case) is not from a peroxo O-O stretch (it was instead assigned as the first overtone of the symmetric Cu-O stretch of mono- μ -oxo dicopper(II)).³⁴ The expected formation of a third peak of intermediate wavenumber, however, assumes that isotopic exchange between surface species and the gas phase is negligible.²²⁰ Significant isotopic exchange of oxygen has been reported for Cu zeolites, observed

by the desorption of ${}^{16}O_2$ and ${}^{16}O^{18}O$ during TPD of Cu-Na-MOR pre-treated in ${}^{18}O_2$ at 723 K.⁹⁶ We therefore cannot rule out assignment of this peak as the O-O stretch of a μ -1,2-peroxo dicopper(II) species, which may also be associated with peaks at 225 and 524 cm⁻¹, as described above. Table C.5 summarizes the assignment of Raman bands to vibrational modes of either the zeolite or a Cu-oxygen species that we were able to propose on the basis of the behavior of the bands in ${}^{16}O_2$ vs. ${}^{18}O_2$.

Deals negition in 160. (am:1)	Aggignmont
Feak position in (O2 (Cin)	Assignment
269	Cu-oxygen species
372	Cu-oxygen species
448	zeolite
508	zeolite
524	Cu-oxygen species
593	zeolite
736	Cu-oxygen species
993	zeolite
1146	Cu-oxygen species

Table C.5. Proposed assignments Raman bands in Figures C.10–C.15.

Figure C.16 shows the Raman spectra of the parent Na-ZSM-5 measured with different excitation lasers. Similar to MOR, it appears that the bands that were previously assigned as symmetric Cu-O stretching modes of mono- μ -oxo dicopper(II) (456 and 514 cm⁻¹)³⁴ are also present in the parent Na-ZSM-5. The intense band at 383 cm⁻¹ has been assigned as a vibration of the 5MR of ZSM-5, while the bands at 439, 456, and 474 cm⁻¹ were assigned as vibrations of the 4/6MR units.²¹⁶ A weak, broad band also appears to be present in the vicinity of 514 cm⁻¹ in the spectra measured using the 266 and 442 nm excitation lasers.


Figure C.16. Raman spectra of Na-ZSM-5 (Si/Al = 11.5) measured *ex situ* with several excitation lasers.

C.5. EXAFS fitting and XANES-LCF



Figure C.17. (a) Magnitude and (b) imaginary part of k²-weighted FT- EXAFS of the Cu0.28-H-MOR catalyst at the Cu K edge after activation in O₂ at 723 K. S₀² was set to 0.90, based on fitting of Cu standards as described in our previous publication.¹⁵⁹ Fits were performed in R space with ranges of $2 < k < 11 \text{ Å}^{-1}$ and 1 < R < 2 Å. A combined k¹-k²-k³-weighted fit was performed.



Figure C.18. (a) Magnitude and (b) imaginary part of k²-weighted FT- EXAFS of the Cu0.28-Na-MOR catalyst at the Cu K edge after activation in O₂ at 723 K. S₀² was set to 0.90, based on fitting of Cu standards as described in our previous publication.¹⁵⁹ Fits were performed in R space with ranges of 2 < k < 11 Å⁻¹ and 1 < R < 2 Å. A combined k¹-k²-k³-weighted fit was performed.



Figure C.19. (a) Magnitude and (b) imaginary part of k²-weighted FT- EXAFS of the Cu0.45-H-ZSM-5 catalyst at the Cu K edge after activation in O₂ at 723 K. S₀² was set to 0.90, based on fitting of Cu standards as described in our previous publication.¹⁵⁹ Fits were performed in R space with ranges of 2 < k < 11 Å⁻¹ and 1 < R < 2 Å. A combined k¹-k²-k³-weighted fit was performed.



Figure C.20. (a) Magnitude and (b) imaginary part of k²-weighted FT- EXAFS of the Cu0.45-Na-ZSM-5 catalyst at the Cu K edge after activation in O₂ at 723 K. S₀² was set to 0.90, based on fitting of Cu standards as described in our previous publication.¹⁵⁹ Fits were performed in R space with ranges of 2 < k < 11 Å⁻¹ and 1 < R < 2 Å. A combined k¹-k²-k³-weighted fit was performed.



Figure C.21. XANES-LCF for Cu0.28-H-MOR catalyst after treatment in O₂ at 723 K followed by helium at 723 K. The spectrum was fit using Cu(I) and dehydrated Cu(II) standards, as described in our previous publication.¹⁵⁹ R-factor = 0.0004.



Figure C.22. XANES-LCF for Cu0.28-Na-MOR catalyst after treatment in O₂ at 723 K followed by helium at 723 K. The spectrum was fit using Cu(I) and dehydrated Cu(II) standards, as described in our previous publication.¹⁵⁹ R-factor = 0.0005.

D. Co-authored work

D.1. Reduction of Propionic Acid over Pd-promoted Supported WOx Catalysts

This work was previously published as: Kammert, J. D.; Brezicki, G.; Miyake, N.; Stavitski, E.; Davis, R. J. Reduction of Propionic Acid over Pd-promoted Supported WO_x Catalysts. ChemCatChem. 2019, 12, 314–325.

Abstract

Silica-, titania-, and zirconia-supported tungsten oxide catalysts were synthesized by wetness impregnation techniques. When promoted with Pd, these materials catalyzed the reduction of propanoic acid to 1-propanol at 433 K with a selectivity of up to 92 % (13.5 % conversion) in atmospheric pressure of H₂. Over Pd-promoted WO_x/TiO₂, the observed orders of reaction were 0.2 in H₂ and 0.7 in propanoic acid, and the apparent activation energy was 54 kJ mol⁻¹. In situ X-ray absorption spectroscopy of Pd-promoted WO_x/SiO₂ revealed a slight reduction of the W from +6 to an average oxidation state of about +5 during H₂ treatment above 473 K. In situ infrared spectroscopy indicated the catalyst surface was covered mostly by propanoate species during reaction. For comparison, supported phosphotungstic acid was also evaluated as a catalyst under identical conditions, but the resulting high acidity of the catalyst was deleterious to alcohol selectivity.

D.2. Steam reforming of ethylene over manganese-chromium spinel oxides

This work was previously published as: Yang, L., Bukhovko, M. P., Brezicki, G., Malek, A., Li, L., Jones, C. W., Agrawal, P. K., Davis, R. J. Steam reforming of ethylene over manganese-chromium spinel oxides. J. Catal. 2019, 380, 224–235.

Abstract

A series of Mn-Cr-O spinel catalysts of different stoichiometry was synthesized using a sol-gel method and characterized using X-ray diffraction, X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, N₂ and H₂O adsorption, and H₂-temperature programmed reduction. The introduction of extra Mn to stoichiometric MnCr₂O₄ led to Mn³⁺ substitution in the spinel lattice of Mn_{1.5}Cr_{1.5}O₄ whereas excess Cr in Mn_{0.5}Cr_{2.5}O₄ formed Cr₂O₃. Ethylene steam reforming at atmospheric total pressure and 873 K over the Mn-Cr-O spinel catalysts was nearly first order in ethylene, negative order in water and zero order in excess dihydrogen. The reaction kinetics were consistent with a Mars-van Krevelen type mechanism. Whereas Cr₂O₃ was nearly inactive for ethylene steam reforming, Mn₃O₄ was substantially more active than the spinel catalysts, but Mn₃O₄ deactivated significantly upon in situ reduction to MnO. The spinel catalysts were therefore more active and structurally stable for ethylene steam reforming than either of the pure metal oxides.

D.3. High-Throughput Operando-Ready X-Ray Absorption Spectroscopy Flow Reactor Cell for Powder Samples

This work was previously published as: Kammert, J. D., Brezicki, G., Acevedo-Esteves, R., Stavitski, E., Davis, R. J. High-Throughput Operando-Ready X-Ray Absorption Spectroscopy Flow Reactor Cell for Powder Samples. Rev. Sci. Instrum. 2020, 91, 013107.

Abstract

A high-throughput, *operando*-ready X-ray absorption spectroscopy catalytic reaction cell consisting of 4 parallel reactors was designed to collect X-ray absorption near edge structure and extended fine structure spectra under reaction conditions. The cell is capable of operating at temperatures from ambient conditions up to 773 K and pressures from ambient to 2 MPa in a variety of gas environments. The cell design is mechanically simple, and programmable operation at beamline 8-ID (NSLS-II, Brookhaven National Laboratory) makes it straightforward to use. Reactor tube parts were available as-fabricated from commercial sources, while the heating jacket and cell mounting required custom machining.

References

- (1) Stringer, J. Basic Research Needs To Assure A Secure Energy Future; 2003.
- (2) EIA Annual Energy Reviewhttp://www.eia.gov/totalenergy/data/annual/showtext.cfm?t=ptb0105.
- (3) Kerr, R. A. Natural Gas From Shale Bursts Onto the Scene. *Science* (80-.). 2010, 328, 1624–1626.
- Olah, G. A.; Goeppert, A.; Prakash, G. K. S. *Beyond Oil and Gas: The Methanol Economy*, 1st ed.; Wiley-VCH: Los Angeles, 2006.
- (5) Emam, E. A. Gas Flaring in Industry: An Overview. *Pet. Coal* 2015, 57, 532–555.
- (6) Foster, N. R. Direct Catalytic Oxidation of Methane to Methanol a Review. *Appl. Catal.* 1985, *19*, 1–11.
- (7) Brown, M. J.; Parkyns, N. D. Progress in The Partial Oxidation of Methane To Methanol and Formaldehyde. *Catal. Today* **1991**, *8*, 305–335.
- (8) McFarland, E. Unconventional Chemistry for Unconventional Natural Gas. *Science (80-.*). 2012, *338*, 340–342.
- Lunsford, J. H. Catalytic Conversion of Methane to More Useful Chemicals and Fuels: A Challenge for the 21st Century. *Catal. Today* 2000, *63*, 165–174.
- (10) Horn, R.; Schlögl, R. Methane Activation by Heterogeneous Catalysis. *Catal. Letters* 2015, 145, 23–39.
- (11) Tang, P.; Zhu, Q.; Wu, Z.; Ma, D. Methane Conversion: The Past and Future. *Energy Environ. Sci.* 2014, 7, 2580–2591.
- (12) Schiffer, Z. J.; Manthiram, K. Electrification and Decarbonization of the Chemical Industry. *Joule* 2017, *1*, 10–14.

- (13) Hashiguchi, B. G.; Bischof, S. M.; Konnick, M. M.; Periana, R. A. Designing Catalysts for Functionalization of Unactivated C-H Bonds Based on the CH Activation Reaction. *Acc. Chem. Res.* 2012, 45, 885–898.
- (14) Otsuka, K.; Wang, Y. Direct Conversion of Methane into Oxygenates. *Appl. Catal. A Gen.* **2001**, 222, 145–161.
- (15) Holmen, A. Direct Conversion of Methane to Fuels and Chemicals. *Catal. Today* 2009, 142, 2–8.
- (16) Alvarez-Galvan, M. C.; Mota, N.; Ojeda, M.; Rojas, S.; Navarro, R. M.; Fierro, J. L. G.
 Direct Methane Conversion Routes to Chemicals and Fuels. *Catal. Today* 2011, *171*, 15–23.
- (17) Stöcker, M. Methanol-to-Hydrocarbons: Catalytic Materials and Their Behavior.
 Microporous Mesoporous Mater. 1999, 29, 3–48.
- (18) Gesser, H. D.; Hunter, N. R.; Prakash, C. B. The Direct Conversion of Methane to Methanol by Controlled Oxidation. *Chem. Rev.* **1985**, 85, 235–244.
- (19) Schwarz, H. Chemistry with Methane: Concepts Rather than Recipes. *Angew. Chemie -Int. Ed.* 2011, *50*, 10096–10115.
- (20) Starokon, E. V.; Parfenov, M. V.; Arzumanov, S. S.; Pirutko, L. V.; Stepanov, A. G.;
 Panov, G. I. Oxidation of Methane to Methanol on the Surface of FeZSM-5 Zeolite. *J. Catal.* 2013, *300*, 47–54.
- (21) Olivos Suarez, A. I.; Szécsényi, Á.; Hensen, E. J. M.; Ruiz-Martínez, J.; Pidko, E. A.;
 Gascon, J. Strategies for the Direct Catalytic Valorization of Methane Using
 Heterogeneous Catalysis: Challenges and Opportunities. *ACS Catal.* 2016, *6*, 2965–2981.
- (22) Conley, B. L.; Tenn, W. J.; Young, K. J. H.; Ganesh, S. K.; Meier, S. K.; Ziatdinov, V. R.;

Mironov, O.; Oxgaard, J.; Gonzales, J.; Goddard, W. A.; et al. Design and Study of Homogeneous Catalysts for the Selective, Low Temperature Oxidation of Hydrocarbons. *J. Mol. Catal. A Chem.* **2006**, *251*, 8–23.

- (23) Copéret, C. C-H Bond Activation and Organometallic Intermediates on Isolated Metal Centers on Oxide Surfaces. *Chem. Rev.* 2010, *110*, 656–680.
- (24) Kwapien, K.; Paier, J.; Sauer, J.; Geske, M.; Zavyalova, U.; Horn, R.; Schwach, P.;
 Trunschke, A.; Schlogl, R. Sites for Methane Activation on Lithium-Doped Magnesium
 Oxide Surfaces. *Angew. Chemie Int. Ed.* 2014, *53*, 8774–8778.
- (25) Ess, D. H.; Goddard, W. A.; Periana, R. A. Electrophilic, Ambiphilic, and Nucleophilic C-H Bond Activation: Understanding the Electronic Continuum of C-H Bond Activation through Transition-State and Reaction Pathway Interaction Energy Decompositions. *Organometallics* 2010, *29*, 6459–6472.
- (26) Labinger, J. A. Labinger, J. A. In Alkane C-H Activation by Single-Site Metal Catalysis;
 Pérez, P. J., Ed.; Springer: Netherlands: Dordrecht, 2012; Vol. 38, Pp 17 71. In Alkane
 C-H Activation by Single-Site Metal Catalysis; 2012; Vol. 38, pp 17–71.
- (27) Labinger, J. A. Platinum-Catalyzed C–H Functionalization. *Chem. Rev.* 2017, *117*, 8483–8496.
- (28) Grasselli, R. K. Fundamental Principles of Selective Heterogeneous Oxidation Catalysis.
 Top. Catal. 2002, *21*, 79–88.
- (29) Grasselli, R. K. Advances and Future Trends in Selective Oxidation and Ammoxidation Catalysis. *Catal. Today* **1999**, *49*, 141–153.
- (30) Guo, Z.; Liu, B.; Zhang, Q.; Deng, W.; Wang, Y.; Yang, Y. Recent Advances in Heterogeneous Selective Oxidation Catalysis for Sustainable Chemistry. *Chem. Soc. Rev.*

2014, *43*, 3480–3524.

- (31) Gartner, C. A.; van Veen, A. C.; Lercher, J. A. Oxidative Dehydrogenation of Ethane:
 Common Principles and Mechanistic Aspects. *ChemCatChem* 2013, *5*, 3196–3217.
- (32) Schlögl, R. Selective Oxidation: From a Still Immature Technology to the Roots of Catalysis Science. *Top. Catal.* 2016.
- (33) de Vekki, A. V.; Marakaev, S. T. Catalytic Partial Oxidation of Methane to Formaldehyde. *Russ. J. Appl. Chem.* 2009, *82*, 521–536.
- Woertink, J. S.; Smeets, P. J.; Groothaert, M. H.; Vance, M. A.; Sels, B. F.; Schoonheydt,
 R. A.; Solomon, E. I. A [Cu2O]2+ Core in Cu-ZSM-5, the Active Site in the Oxidation of Methane to Methanol. *Proc. Natl. Acad. Sci. U. S. A.* 2009, *106*, 18908–18913.
- (35) Dubkov, K. A.; Sobolev, V. I.; Panov, G. I. Low-Temperature Oxidation of Methane to Methanol on FeZSM-5 Zeolite. *Kinet. Catal.* **1998**, *39*, 72–79.
- (36) Sobolev, V. I.; Dubkov, K. A.; Panna, O. V.; Panov, G. I. Selective Oxidation of Methane to Methanol on a FeZSM-5 Surface. *Catal. Today* **1995**, *24*, 251–252.
- (37) Starokon, E. V.; Parfenov, M. V.; Pirutko, L. V.; Abornev, S. I.; Panov, G. I. Room-Temperature Oxidation of Methane by Alpha-Oxygen and Extraction of Products from the FeZSM-5 Surface. *J. Phys. Chem. C* 2011, *115*, 2155–2161.
- (38) Parfenov, M. V.; Starokon, E. V.; Pirutko, L. V.; Panov, G. I. Quasicatalytic and Catalytic Oxidation of Methane to Methanol by Nitrous Oxide over FeZSM-5 Zeolite. *J. Catal.*2014, *318*, 14–21.
- Roduner, E.; Kaim, W.; Sarkar, B.; Urlacher, V. B.; Pleiss, J.; Gläser, R.; Einicke, W. D.;
 Sprenger, G. A.; Beifuß, U.; Klemm, E.; et al. Selective Catalytic Oxidation of C-H Bonds with Molecular Oxygen. *ChemCatChem* 2013, *5*, 82–112.

- (40) Liu, X.; Ryabenkova, Y.; Conte, M. Catalytic Oxygen Activation versus Autoxidation for Industrial Applications: A Physicochemical Approach. *Phys. Chem. Chem. Phys.* 2015, 17, 715–731.
- (41) Rybak-Akimova, E. V. Mechanisms of Oxygen Binding and Activation at Transition Metal Centers. In *Physical Inorganic Chemistry: Reactions, Processes, and Applications*; John Wiley & Sons: Hoboken, NJ, 2010; pp 109–188.
- (42) Groothaert, M. H.; Smeets, P. J.; Sels, B. F.; Jacobs, P. A.; Schoonheydt, R. A. Selective Oxidation of Methane by the Bis (μ-Oxo) Dicopper Core Stabilized on ZSM-5 and Mordenite Zeolites. *J. Am. Chem. Soc.* 2005, *127*, 1394–1395.
- (43) Alayon, E. M. C.; Nachtegaal, M.; Kleymenov, E.; Van Bokhoven, J. A. Determination of the Electronic and Geometric Structure of Cu Sites during Methane Conversion over Cu-MOR with X-Ray Absorption Spectroscopy. *Microporous Mesoporous Mater.* 2013, *166*, 131–136.
- (44) Alayon, E. M. C.; Nachtegaal, M.; Ranocchiari, M.; van Bokhoven, J. A. Catalytic
 Conversion of Methane to Methanol over Cu–Mordenite. *Chem. Commun.* 2012, *48*, 404–406.
- (45) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fuji, H. Platinum Catalysts for the High-Yield Oxidation of Methane to a Methanol Derivative. *Science (80-.).* 1998, 280, 560–564.
- (46) Ahlquist, M.; Nielsen, R. J.; Periana, R. A.; Goddard, W. A. Product Protection, the Key to Developing High Performance Methane Selective Oxidation Catalysts. *J. Am. Chem. Soc.* 2009, *131*, 17110–17115.
- (47) Ravi, M.; Ranocchiari, M.; van Bokhoven, J. A. The Direct Catalytic Oxidation of

Methane to Methanol—A Critical Assessment. *Angew. Chemie - Int. Ed.* **2017**, *56*, 16464–16483.

- (48) Sen, A.; Benvenuto, M. a.; Lin, M.; Hutson, A. C.; Basickes, N. Activation of Methane and Ethane and Their Selective Oxidation to the Alcohols in Protic Media. *J. Am. Chem. Soc.* **1994**, *116*, 998–1003.
- (49) Liu, C.-C.; Mou, C.-Y.; Yu, S. S. F.; Chan, S. I. Heterogeneous Formulation of the Tricopper Complex for Efficient Catalytic Conversion of Methane into Methanol at Ambient Temperature and Pressure. *Energy Environ. Sci.* **2016**, *9*, 1361–1374.
- (50) Ross, M. O.; Rosenzweig, A. C. A Tale of Two Methane Monooxygenases. J. Biol. Inorg. Chem. 2016, 1–13.
- (51) Ab Rahim, M. H.; Forde, M. M.; Jenkins, R. L.; Hammond, C.; He, Q.; Dimitratos, N.; Lopez-Sanchez, J. A.; Carley, A. F.; Taylor, S. H.; Willock, D. J.; et al. Oxidation of Methane to Methanol with Hydrogen Peroxide Using Supported Gold-Palladium Alloy Nanoparticles. *Angew. Chemie - Int. Ed.* **2013**, *52*, 1280–1284.
- (52) Culpepper, M. A.; Rosenzweig, A. C. Architecture and Active Site of Particulate Methane Monooxygenase. *Crit. Rev. Biochem. Mol. Biol.* 2012, 47, 483–492.
- (53) Shan, J.; Li, M.; Allard, L. F.; Lee, S.; Flytzani-Stephanopoulos, M. Mild Oxidation of Methane to Methanol or Acetic Acid on Supported Isolated Rhodium Catalysts. *Nature* 2017, *551*, 605–608.
- (54) Tsai, M.-L.; Hadt, R. G.; Vanelderen, P.; Sels, B. F.; Schoonheydt, R. A.; Solomon, E. I.
 [Cu2O]2+ Active Site Formation in Cu–ZSM-5: Geometric and Electronic Structure
 Requirements for N2O Activation. *J. Am. Chem. Soc.* 2014, *136*, 3522–3529.
- (55) Sheppard, T.; Hamill, C. D.; Goguet, A.; Rooney, D. W.; Thompson, J. M. A Low

Temperature, Isothermal Gas-Phase System for Conversion of Methane to Methanol over Cu–ZSM-5. *Chem. Commun.* **2014**, *50*, 11053.

- (56) Wood, B. R.; Reimer, J. A.; Bell, A. T.; Janicke, M. T.; Ott, K. C. Methanol Formation on Fe/Al-MFI via the Oxidation of Methane by Nitrous Oxide. J. Catal. 2004, 225, 300–306.
- (57) Chow, Y. K.; Dummer, N. F.; Carter, J. H.; Meyer, R. J.; Armstrong, R. D.; Williams, C.; Shaw, G.; Yacob, S.; Bhasin, M. M.; Willock, D. J.; et al. A Kinetic Study of Methane Partial Oxidation over Fe-ZSM-5 Using N2O as an Oxidant. *ChemPhysChem* 2018, 402–411.
- (58) Kim, Y.; Kim, T. Y.; Lee, H.; Yi, J. Distinct Activation of Cu-MOR for Direct Oxidation of Methane to Methanol. *Chem. Commun.* **2017**.
- (59) Hammond, C.; Jenkins, R. L.; Dimitratos, N.; Lopez-Sanchez, J. A.; Ab Rahim, M. H.; Forde, M. M.; Thetford, A.; Murphy, D. M.; Hagen, H.; Stangland, E. E.; et al. Catalytic and Mechanistic Insights of the Low-Temperature Selective Oxidation of Methane over Cu-Promoted Fe-ZSM-5. *Chem. - A Eur. J.* **2012**, *18*, 15735–15745.
- (60) Hammond, C.; Forde, M. M.; Ab Rahim, M. H.; Thetford, A.; He, Q.; Jenkins, R. L.;
 Dimitratos, N.; Lopez-Sanchez, J. A.; Dummer, N. F.; Murphy, D. M.; et al. Direct
 Catalytic Conversion of Methane to Methanol in an Aqueous Medium by Using CopperPromoted Fe-ZSM-5. *Angew. Chemie Int. Ed.* 2012, *51*, 5129–5133.
- (61) Hammond, C.; Dimitratos, N.; Jenkins, R. L.; Lopez-Sanchez, J. A.; Kondrat, S. A.; Hasbi Ab Rahim, M.; Forde, M. M.; Thetford, A.; Taylor, S. H.; Hagen, H.; et al. Elucidation and Evolution of the Active Component within Cu/Fe/ZSM-5 for Catalytic Methane Oxidation: From Synthesis to Catalysis. ACS Catal. 2013, 3, 689–699.
- (62) Hammond, C.; Dimitratos, N.; Lopez-Sanchez, J. A.; Jenkins, R. L.; Whiting, G.;

Kondrat, S. A.; Ab Rahim, M. H.; Forde, M. M.; Thetford, A.; Hagen, H.; et al. Aqueous-Phase Methane Oxidation over Fe-MFI Zeolites; Promotion through Isomorphous Framework Substitution. *ACS Catal.* **2013**, *3*, 1835–1844.

- (63) Xu, J.; Armstrong, R.; Shaw, G.; Dummer, N. F.; Freakley, S. J.; Taylor, S. H.; Hutchings,
 G. J. Continuous Selective Oxidation of Methane to Methanol over Cu- and Fe-Modified
 ZSM-5 Catalysts in a Flow Reactor. *Catal. Today* 2016, 270, 93–100.
- (64) Natinsky, B. S.; Lu, S.; Copeland, E. D.; Quintana, J. C.; Liu, C. Solution Catalytic Cycle of Incompatible Steps for Ambient Air Oxidation of Methane to Methanol. *ACS Cent. Sci.* 2019, *5*, 1584–1590.
- (65) Iwamoto, M.; Yokoo, S.; Sakai, K.; Kagawa, S. Catalytic Decomposition of Nitric Oxide over Copper(II)-Exchanged, Y-Type Zeolites. *J. Chem. Soc. Faraday Trans. 1* 1981, 77, 1629.
- (66) Iwamoto, M.; Furukawa, H.; Mine, Y.; Uemura, F.; Mikuriya, S.; Kagawa, S. Copper(II) Ion-Exchanged ZSM-5 Zeolites as Highly Active Catalysts for Direct and Continuous Decomposition of Nitrogen Monoxide. *J. Chem. Soc. Chem. Commun.* 1986, No. 16, 1272.
- (67) Groothaert, M. H.; Bokhoven, J. a Van; Andrea, A.; Weckhuysen, B. M.; Schoonheydt, R. a. Bis (u-Oxo) Dicopper in Cu-ZSM-5 and Its Role in the Decomposition of NO: A Combined in Situ XAFS, UV–Vis–Near-IR , and Kinetic Study. *J. Am. Chem. Soc.* 2003, *125*, 7629–7640.
- (68) Smeets, P. J.; Groothaert, M. H.; Schoonheydt, R. A. Cu Based Zeolites: A UV-Vis Study of the Active Site in the Selective Methane Oxidation at Low Temperatures. *Catal. Today* 2005, *110*, 303–309.

- (69) Sheppard, T.; Daly, H.; Goguet, A.; Thompson, J. M. Improved Efficiency for Partial Oxidation of Methane by Controlled Copper Deposition on Surface-Modified ZSM-5.
 ChemCatChem 2016, 8, 560–570.
- (70) Vanelderen, P.; Hadt, R. G.; Smeets, P. J.; Solomon, E. I.; Schoonheydt, R. A.; Sels, B. F. Cu-ZSM-5: A Biomimetic Inorganic Model for Methane Oxidation. *J. Catal.* 2011, 284, 157–164.
- (71) Vanelderen, P.; Snyder, B. E. R.; Tsai, M.-L.; Hadt, R. G.; Vancauwenbergh, J.;
 Coussens, O.; Schoonheydt, R. A.; Sels, B. F.; Solomon, E. I. Spectroscopic Definition of the Copper Active Sites in Mordenite: Selective Methane Oxidation. *J. Am. Chem. Soc.*2015, *137*, 6383–6392.
- (72) Grundner, S.; Markovits, M. A. C.; Li, G.; Tromp, M.; Pidko, E. A.; Hensen, E. J. M.; Jentys, A.; Sanchez-Sanchez, M.; Lercher, J. A. Single-Site Trinuclear Copper Oxygen Clusters in Mordenite for Selective Conversion of Methane to Methanol. *Nat. Commun.* 2015, *6*, 7546.
- (73) Grundner, S.; Luo, W.; Sanchez-Sanchez, M.; Lercher, J. A. Synthesis of Single-Site Copper Catalysts for Methane Partial Oxidation. *Chem. Commun.* 2016, *52*, 2553–2556.
- Baerlocher, C.; McCusker, L. B.; Olson, D. H. Atlas of Zeolite Framework Types;
 Elsevier: Amsterdam, The Netherlands, 2007.; Elsevier: Amsterdam, The Netherlands, 2007.
- (75) Markovits, M. A. C.; Jentys, A.; Tromp, M.; Sanchez-Sanchez, M.; Lercher, J. A. Effect of Location and Distribution of Al Sites in ZSM-5 on the Formation of Cu-Oxo Clusters Active for Direct Conversion of Methane to Methanol. *Top. Catal.* **2016**, *59*, 1554–1563.
- (76) Li, G.; Vassilev, P.; Sanchez-Sanchez, M.; Lercher, J. A.; Hensen, E. J. M.; Pidko, E. A.

Stability and Reactivity of Copper Oxo-Clusters in ZSM-5 Zeolite for Selective Methane Oxidation to Methanol. *J. Catal.* **2016**, *338*, 305–312.

- (77) Park, M. B.; Ahn, S. H.; Mansouri, A.; Ranocchiari, M.; van Bokhoven, J. A.
 Comparative Study of Diverse Copper Zeolites for the Conversion of Methane into Methanol. *ChemCatChem* 2017, *9*, 3705–3713.
- (78) Ikuno, T.; Grundner, S.; Jentys, A.; Li, G.; Pidko, E. A.; Fulton, J. L.; Sanchez-Sanchez, M.; Johannes A. Lercher. Formation of Cu-Oxo Clusters Active for Methane Oxidation in Cu-Exchanged Mordenite. *J. Phys. Chem. C* 2019, *123*, 8759–8769.
- (79) Zheng, J.; Lee, I.; Khramenkova, E.; Wang, M.; Peng, B.; Gutierrez, O.; Fulton, J. L.;
 Camaioni, D.; Khare, R.; Jentys, A.; et al. Importance of Methane Chemical Potential for Its Conversion to Methanol on Cu-Exchanged Mordenite. *Chem. - A Eur. J.* 2020, 10.1002/chem.202000772.
- (80) Vogiatzis, K. D.; Li, G.; Hensen, E. J. M.; Gagliardi, L.; Pidko, E. A. The Electronic Structure of the [Cu3(μ-O)3]2+ Cluster in Mordenite Zeolite and Its Effects on the Methane to Methanol Oxidation. *J. Phys. Chem. C* 2017, *121*, 22295–22302.
- (81) Mahyuddin, M. H.; Tanaka, T.; Staykov, A.; Shiota, Y.; Yoshizawa, K. Dioxygen Activation on Cu-MOR Zeolite: Theoretical Insights into the Formation of Cu2O and Cu3O3 Active Species. *Inorg. Chem.* 2018, *57*, 10146–10152.
- (82) Mahyuddin, M. H.; Tanaka, T.; Shiota, Y.; Staykov, A.; Yoshizawa, K. Methane Partial Oxidation over [Cu2(μ-O)]2+ and [Cu3(μ-O)3]2+ Active Species in Large-Pore Zeolites. *ACS Catal.* 2018, *8*, 1500–1509.
- (83) Pappas, D. K.; Martini, A.; Dyballa, M.; Kvande, K.; Teketel, S.; Lomachenko, K. A.;Baran, R.; Glatzel, P.; Arstad, B.; Berlier, G.; et al. The Nuclearity of the Active Site for

Methane to Methanol Conversion in Cu-Mordenite: A Quantitative Assessment. J. Am. Chem. Soc. 2018, 140, 15270–15278.

- (84) Borfecchia, E.; Pappas, D. K.; Dyballa, M.; Lomachenko, K. A.; Negri, C.; Signorile, M.; Berlier, G. Evolution of Active Sites during Selective Oxidation of Methane to Methanol over Cu-CHA and Cu-MOR Zeolites as Monitored by Operando XAS. *Catal. Today* 2018, *333*, 17–27.
- (85) Ipek, B.; Wulfers, M. J.; Kim, H.; Göltl, F.; Hermans, I.; Smith, J. P.; Booksh, K. S.;
 Brown, C. M.; Lobo, R. F. Formation of [Cu2O2]2+ and [Cu2O]2+ toward C–H Bond
 Activation in Cu-SSZ-13 and Cu-SSZ-39. ACS Catal. 2017, 7, 4291–4303.
- (86) Pappas, D. K.; Borfecchia, E.; Dyballa, M.; Pankin, I. A.; Lomachenko, K. A.; Martini, A.; Signorile, M.; Teketel, S.; Arstad, B.; Berlier, G.; et al. Methane to Methanol:
 Structure-Activity Relationships for Cu-CHA. *J. Am. Chem. Soc.* 2017, *139*, 14961–14975.
- (87) Negri, C.; Signorile, M.; Porcaro, N. G.; Borfecchia, E.; Berlier, G.; Janssens, T. V. W.;
 Bordiga, S. Dynamic CuII/CuI Speciation in Cu-CHA Catalysts by in Situ Diffuse
 Reflectance UV–Vis-NIR Spectroscopy. *Appl. Catal. A Gen.* 2019, 578, 1–9.
- (88) Zhao, Z.-J.; Kulkarni, A.; Vilella, L.; Norskov, J. K.; Studt, F. Theoretical Insights into the Selective Oxidation of Methane to Methanol in Copper-Exchanged Mordenite. *ACS Catal.* 2016, *6*, 3760–3766.
- (89) Kulkarni, A. R.; Zhao, Z.-J.; Siahrostami, S.; Norskov, J. K.; Studt, F. Mono-Copper Active Site for Partial Methane Oxidation in Cu-Exchanged 8MR Zeolites. *ACS Catal.*2016, *6*, 6531–6536.
- (90) Oord, R.; Schmidt, J. E.; Weckhuysen, B. M. Methane-to-Methanol Conversion over

Zeolite Cu-SSZ-13, and Its Comparison with the Selective Catalytic Reduction of NOx with NH3. *Catal. Sci. Technol.* **2018**, *8*, 1028–1038.

- (91) Sushkevich, V. L.; Palagin, D.; van Bokhoven, J. A. The Effect of the Active-Site Structure on the Activity of Copper Mordenite in the Aerobic and Anaerobic Conversion of Methane into Methanol. *Angew. Chemie - Int. Ed.* **2018**, *57*, 8906–8910.
- (92) Sushkevich, V. L.; Verel, R.; Van Bokhoven, J. A. Pathways of Methane Transformation over Copper-Exchanged Mordenite as Revealed by in Situ NMR and IR Spectroscopy. *Angew. Chemie* 2019, *131*, 2–11.
- Mahyuddin, M. H.; Shiota, Y.; Staykov, A.; Yoshizawa, K. Theoretical Overview of Methane Hydroxylation by Copper–Oxygen Species in Enzymatic and Zeolitic Catalysts. *Acc. Chem. Res.* 2018, *51*, 2382–2390.
- (94) Palagin, D.; Knorpp, A.; B. P. Prieto, A.; Ranocchiari, M.; van Bokhoven, J. Assessing Relative Stability of Copper Oxide Clusters as Active Sites of CuMOR Zeolite for Methane to Methanol Conversion: Size Matters? *Nanoscale* 2017, *9*, 1144–1153.
- (95) Tomkins, P.; Mansouri, A.; Bozbag, S. E.; Krumeich, F.; Park, M. B.; Alayon, E. M. C.; Ranocchiari, M.; Van Bokhoven, J. A. Isothermal Cyclic Conversion of Methane into Methanol over Copper-Exchanged Zeolite at Low Temperature. *Angew. Chemie - Int. Ed.* 2016, *55*, 5467–5471.
- (96) Smeets, P. J.; Hadt, R. G.; Woertink, J. S.; Vanelderen, P.; Schoonheydt, R. A.; Sels, B.
 F.; Solomon, E. I. Oxygen Precursor to the Reactive Intermediate in Methanol Synthesis by Cu-ZSM-5. *J. Am. Chem. Soc.* 2010, *132*, 14736–14738.
- (97) Smeets, P. J.; Woertink, J. S.; Sels, B. F.; Solomon, E. I.; Schoonheydt, R. A. Transition-Metal Ions in Zeolites: Coordination and Activation of Oxygen. *Inorg. Chem.* 2010, 49,

3573-3583.

- (98) Vanelderen, P.; Vancauwenbergh, J.; Sels, B. F.; Schoonheydt, R. A. CoordinationChemistry and Reactivity of Copper in Zeolites. *Coord. Chem. Rev.* 2013, 257, 483–494.
- (99) Alayon, E. M. C.; Nachtegaal, M.; Bodi, A.; Ranocchiari, M.; van Bokhoven, J. A. Bis(μ-Oxo) versus Mono(μ-Oxo)Dicopper Cores in a Zeolite for Converting Methane to Methanol: An in Situ XAS and DFT Investigation. *Phys. Chem. Chem. Phys.* 2015, *4*, 1166–1169.
- (100) Larsen, S. C.; Aylor, A.; Bell, A. T.; Reimer, J. A. Electron Paramagnetic Resonance Studies of Copper Ion-Exchanged ZSM-5. *J. Phys. Chem.* **1994**, *98*, 11533–11540.
- (101) Trout, B. L.; Chakraborty, A. K.; Bell, A. T. Local Spin Density Functional Theory Study of Copper Ion-Exchanged ZSM-5. *J. Phys. Chem* **1996**, *100*, 4173–4179.
- (102) Borfecchia, E.; Lomachenko, K. A.; Giordanino, F.; Falsig, H.; Beato, P.; Soldatov, A. V.;
 Bordiga, S.; Lamberti, C. Revisiting the Nature of Cu Sites in the Activated Cu-SSZ-13
 Catalyst for SCR Reaction. *Chem. Sci.* 2015, *6*, 548–563.
- (103) Sushkevich, V. L.; Palagin, D.; Ranocchiari, M.; van Bokhoven, J. A. Selective Anaerobic Oxidation of Methane Enables Direct Synthesis of Methanol. *Science (80-.).* 2017, *356*, 523–527.
- (104) Alayon, E. M. C.; Nachtegaal, M.; Bodi, A.; Van Bokhoven, J. A. Reaction Conditions of Methane-to-Methanol Conversion Affect the Structure of Active Copper Sites. *ACS Catal.* 2013, *4*, 16–22.
- (105) Sushkevich, V. L.; van Bokhoven, J. Effect of Brønsted Acid Sites on the Direct Conversion of Methane into Methanol over Copper-Exchanged Mordenite. *Catal. Sci. Technol.* 2018, 8, 4141–4150.

- (106) Wu, J.-F.; Gao, X.-D.; Wu, L.-M.; Wang, W. D.; Yu, S.-M.; Bai, S. Mechanistic Insights on the Direct Conversion of Methane into Methanol over Cu/Na–ZSM-5 Zeolite:
 Evidence from EPR and Solid-State NMR. ACS Catal. 2019, 8677–8681.
- (107) Dyballa, M.; Thorshaug, K.; Pappas, D. K.; Borfecchia, E.; Kvande, K.; Bordiga, S.;
 Berlier, G.; Lazzarini, A.; Olsbye, U.; Beato, P.; et al. Zeolite Surface Methoxy Groups as
 Key Intermediates in the Stepwise Conversion of Methane to Methanol. *ChemCatChem*2019, *11*, 5022–5026.
- (108) Sushkevich, V. L.; van Bokhoven, J. A. Methane-to-Methanol: Activity Descriptors in Copper-Exchanged Zeolites for the Rational Design of Materials. *ACS Catal.* 2019, *9*, 6293–6304.
- (109) Sushkevich, V. L.; van Bokhoven, J. A. Kinetic Study and Effect of Water on Methane
 Oxidation to Methanol over Copper-Exchanged Mordenite. *Catal. Sci. Technol.* 2020, *10*, 382–390.
- (110) Gabrienko, A. A.; Yashnik, S. A.; Kolganov, A. A.; Sheveleva, A. M.; Arzumanov, S. S.; Fedin, M. V; Tuna, F.; Stepanov, A. G. Methane Activation on H-ZSM-5 Zeolite with Low Copper Loading. The Nature of Active Sites and Intermediates Identified with the Combination of Spectroscopic Methods. *Inorg. Chem.* **2020**, *59*, 2037–2050.
- (111) Zhu, J.; Sushkevich, V. L.; Knorpp, A. J.; Newton, M. A.; Mizuno, S. C. M.; Wakihara, T.; Okubo, T.; Liu, Z.; Bokhoven, J. A. Van. Cu-Erionite Zeolite Achieves High Yield in Direct Oxidation of Methane to Methanol by Isothermal Chemical Looping. *Chem. Mater.* 2020, *32*, 1448–1453.
- (112) Narsimhan, K.; Michaelis, V. K.; Mathies, G.; Gunther, W. R.; Griffin, R. G.; Román-Leshkov, Y. Methane to Acetic Acid over Cu-Exchanged Zeolites: Mechanistic Insights

from a Site-Specific Carbonylation Reaction. J. Am. Chem. Soc. 2015, 137, 1825–1832.

- (113) Dyballa, M.; Pappas, D. K.; Kvande, K.; Borfecchia, E.; Arstad, B.; Beato, P.; Olsbye, U.; Svelle, S. On How Copper Mordenite Properties Govern the Framework Stability and Activity in the Methane-to-Methanol Conversion. ACS Catal. 2019, 9, 365–375.
- (114) Beznis, N. V.; Weckhuysen, B. M.; Bitter, J. H. Cu-ZSM-5 Zeolites for the Formation of Methanol from Methane and Oxygen: Probing the Active Sites and Spectator Species. *Catal. Letters* 2010, *138*, 14–22.
- (115) Kulkarni, A. R.; Zhao, Z.; Siahrostami, S.; Nørskov, J. K.; Studt, F. Cation-Exchanged Zeolites for the Selective Oxidation of Methane to Methanol. *Catal. Sci. Technol.* 2017, 8, 114–123.
- (116) Haack, P.; Kärgel, A.; Greco, C.; Dokic, J.; Braun, B.; Pfaff, F. F.; Mebs, S.; Ray, K.; Limberg, C. Access to a CuII-O-CuII Motif: Spectroscopic Properties, Solution Structure, and Reactivity. *J. Am. Chem. Soc.* **2013**, *135*, 16148–16160.
- (117) Knorpp, A. J.; Newton, M. A.; Pinar, A. B.; van Bokhoven, J. A. Conversion of Methane to Methanol on Copper Mordenite: Redox Mechanism of Isothermal and High Temperature Activation Procedures. *Ind. Eng. Chem. Res.* 2018, *57*, acs.iecr.8b01183.
- (118) Artiglia, L.; Sushkevich, V. L.; Palagin, D.; Knorpp, A. J.; Roy, K.; van Bokhoven, J. A. In Situ X-Ray Photoelectron Spectroscopy Detects Multiple Active Sites Involved in the Selective Anaerobic Oxidation of Methane in Copper-Exchanged Zeolites. *ACS Catal.* 2019, 6728–6737.
- (119) Palagin, D.; Sushkevich, V. L.; Van Bokhoven, J. A. Water Molecules Facilitate
 Hydrogen Release in Anaerobic Oxidation of Methane to Methanol over Cu/Mordenite.
 ACS Catal. 2019, 9, 10365–10374.

- (120) Sushkevich, V. L.; Palagin, D.; Ranocchiari, M.; van Bokhoven, J. A. Response to Comment on "Selective Anaerobic Oxidation of Methane Enables Direct Synthesis of Methanol." *Science (80-.).* **2017**, *358.*
- (121) Periana, R. A. Comment on "Selective Anaerobic Oxidation of Methane Enables Direct Synthesis of Methanol." *Science (80-.).* 2017, 358.
- (122) Labinger, J. A. Comment on "Selective Anaerobic Oxidation of Methane Enables Direct Synthesis of Methanol." *Science* (80-.). 2018, 359.
- (123) Knorpp, A. J.; Pinar, A. B.; Newton, M.; Sushkevich, V.; van Bokhoven, J. A. Copper-Exchanged Omega (MAZ) Zeolite: Copper-Concentration Dependent Active Sites and Its Unprecedented Methane to Methanol Conversion. *ChemCatChem* 2018, *5232*, 5593– 5596.
- (124) Knorpp, A. J.; Newton, M. A.; van Bokhoven, J. A. Comparative Performance of Cu-Zeolites in the Isothermal Conversion of Methane to Methanol. *Chem. Commun.* 2019, *55*, 11794–11797.
- (125) Pappas, D. K.; Borfecchia, E.; Dyballa, M.; Lomachenko, K. A. Understanding and Optimizing the Performance of Cu-FER for The Direct CH4 to CH3OH Conversion. *ChemCatChem* **2019**, *11*, 621–627.
- (126) Knorpp, A. J.; Newton, M. A.; Sushkevich, V. L.; Zimmermann, P. P.; Pinar, A. B.; van Bokhoven, J. A. The Influence of Zeolite Morphology on the Conversion of Methane to Methanol on Copper-Exchanged Omega Zeolite (MAZ). *Catal. Sci. Technol.* 2019, *9*, 2806–2811.
- (127) Pappas, D. K.; Borfecchia, E.; Lomachenko, K. A.; Lazzarini, A.; Gutterød, E. S.;Dyballa, M.; Martini, A.; Berlier, G.; Bordiga, S.; Lamberti, C.; et al. Cu-Exchanged

Ferrierite Zeolite for the Direct CH4 to CH3OH Conversion: Insights on Cu Speciation from X-Ray Absorption Spectroscopy. *Top. Catal.* **2019**, *62*, 712–723.

- (128) Snyder, B. E. R.; Vanelderen, P.; Schoonheydt, R. A.; Sels, B. F.; Solomon, E. I. Second-Sphere Effects on Methane Hydroxylation in Cu-Zeolites. *J. Am. Chem. Soc.* 2018, *140*, 9236–9243.
- (129) Ravi, M.; Sushkevich, V. L.; Knorpp, A. J.; Newton, M. A.; Palagin, D.; Pinar, A. B.;
 Ranocchiari, M.; Bokhoven, J. A. Van. Misconceptions and Challenges in Methane-to Methanol over Transition-Metal-Exchanged Zeolites. *Nat. Catal.* 2019, *2*, 485–494.
- (130) Ipek, B.; Lobo, R. F. Catalytic Conversion of Methane to Methanol on Cu-SSZ-13 Using N2O as Oxidant. *Chem. Commun.* 2016, *52*, 13401–13404.
- (131) Narsimhan, K.; Iyoki, K.; Dinh, K.; Román-Leshkov, Y. Catalytic Oxidation of Methane into Methanol over Copper-Exchanged Zeolites with Oxygen at Low Temperature. ACS Cent. Sci. 2016, 2, 424–429.
- (132) Dinh, K. T.; Sullivan, M. M.; Narsimhan, K.; Serna, P.; Meyer, R. J.; Dinca, M.; Roman-Leshkov, Y. Continuous Partial Oxidation of Methane to Methanol Catalyzed by Diffusion-Paired Cu Dimers in Copper-Exchanged Zeolites. *J. Am. Chem. Soc.* 2019, *141*, 11641–11650.
- (133) Latimer, A. A.; Kulkarni, A. R.; Aljama, H.; Montoya, J. H.; Yoo, J. S.; Tsai, C.; Abild-Pedersen, F.; Studt, F.; Nørskov, J. K. Understanding Trends in C–H Bond Activation in Heterogeneous Catalysis. *Nat. Mater.* **2016**, *1*, 1–6.
- (134) Dinh, K. T.; Sullivan, M. M.; Serna, P.; Meyer, R. J.; Dincă, M.; Román-Leshkov, Y. Viewpoint on the Partial Oxidation of Methane to Methanol Using Cu- and Fe-Exchanged Zeolites. ACS Catal. 2018, 8, 8306–8313.

- (135) Lange, J.-P.; Sushkevich, V. L.; Knorpp, A. J.; van Bokhoven, J. A. Methane-to-Methanol via Chemical Looping: Economic Potential and Guidance for Future Research. *Ind. Eng. Chem. Res.* 2019, 58, 8674–8680.
- (136) Vanelderen, P.; Vancauwenbergh, J.; Tsai, M.-L.; Hadt, R. G.; Solomon, E. I.; Schoonheydt, R. A.; Sels, B. F. Spectroscopy and Redox Chemistry of Copper in Mordenite. *ChemPhysChem* **2014**, *15*, 91–99.
- (137) Kammert, J. D. The Reduction of Carboxylic Acids to Alcohols over Palladium-Promoted Rhenium and Tungsten Oxides, University of Virginia, 2019.
- (138) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-Ray Absorption Spectroscopy Using IFEFFIT. *J. Synchrotron Radiat.* **2005**, *12*, 537–541.
- (139) Paolucci, C.; Parekh, A. A.; Khurana, I.; Di Iorio, J. R.; Li, H.; Albarracin Caballero, J. D.; Shih, A. J.; Anggara, T.; Delgass, W. N.; Miller, J. T.; et al. Catalysis in a Cage: Condition-Dependent Speciation and Dynamics of Exchanged Cu Cations in SSZ-13 Zeolites. *J. Am. Chem. Soc.* 2016, *138*, 6028–6048.
- (140) Lomachenko, K. A.; Martini, A.; Pappas, D. K.; Negri, C.; Dyballa, M.; Berlier, G.;
 Bordiga, S. The Impact of Reaction Conditions and Material Composition on the Stepwise
 Methane to Methanol Conversion over Cu-MOR: An Operando XAS Study. *Catal. Today*2019, *336*, 99–108.
- (141) Fulton, J. L.; Hoffmann, M. M.; Darab, J. G.; Palmer, B. J.; Stern, E. A. Copper(I) and Copper(II) Coordination Structure under Hydrothermal Conditions at 325 °C: An X-Ray Absorption Fine Structure and Molecular Dynamics Study. *J. Phys. Chem. A* 2000, *104*, 11651–11663.
- (142) Kau, L. shan; Spira-solomon, D. J.; Penner-Hahn, J. E.; Hodgson, K. O.; Solomon, E. I.

X-Ray Absorption Edge Determination of the Oxidation State and Coordination Number of Copper: Application to the Type 3 Site in Rhus Vernicifera Laccase and Its Reaction with Oxygen. J. Am. Chem. Soc. **1987**, *109*, 6433–6442.

- (143) Lamble, G.; Moen, A.; Nicholson, D. G. Structure of the Diamminecopper(I) Ion in Solution. J. Chem. Soc. Faraday Trans. 1994, 90, 2211–2213.
- (144) Chaboy, J.; Muñoz-Páez, A.; Carrera, F.; Merkling, P.; Marcos, E. S. Ab Initio X-Ray Absorption Study of Copper K -Edge XANES Spectra in Cu(II) Compounds. *Phys. Rev. B* - *Condens. Matter Mater. Phys.* 2005, *71*, 1–7.
- (145) Cheng, N.; Wei, Y.-L.; Yang, Y.-W.; Lee, J.-F. Effect of Water on XAS Spectrum of Cu (NO3) 2 Reference. *Phys. Scr.* 2005, 2005, 907–908.
- (146) Millar, G. J.; Canning, A.; Rose, G.; Wood, B.; Trewartha, L.; Mackinnon, I. D. R.
 Identification of Copper Species Present in Cu-ZSM-5 Catalysts for NOx Reduction. *J. Catal.* 1999, 183, 169–181.
- (147) Castagnola, N. B.; Kropf, A. J.; Marshall, C. L. Studies of Cu-ZSM-5 by X-Ray Absorption Spectroscopy and Its Application for the Oxidation of Benzene to Phenol by Air. *Appl. Catal. A Gen.* **2005**, *290*, 110–122.
- (148) Da Costa, P.; Modén, B.; Meitzner, G. D.; Lee, D. K.; Iglesia, E. Spectroscopic and Chemical Characterization of Active and Inactive Cu Species in NO Decomposition Catalysts Based on Cu-ZSM5. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4590–4601.
- (149) Buono, C.; Martini, A.; Pankin, I. A.; Pappas, D. K.; Negri, C.; Kvande, K.; Lomachenko, K. A. Local Structure of Cu(I) Ions in the MOR Zeolite: A DFT-Assisted XAS Study. *Radiat. Phys. Chem.* 2018, *in press.*
- (150) Solomon, E. I.; Heppner, D. E.; Johnston, E. M.; Ginsbach, J. W.; Cirera, J.; Qayyum, M.;

Kieber-Emmons, M. T.; Kjaergaard, C. H.; Hadt, R. G.; Tian, L. Copper Active Sites in Biology. *Chem. Rev.* **2014**, *114*, 3659–3853.

- (151) Martini, A.; Borfecchia, E.; Lomachenko, K. A.; Pankin, I.; Negri, C.; Berlier, G.; Beato,
 P.; Falsig, H.; Bordiga, S.; Lamberti, C. Composition-Driven Cu-Speciation and
 Reducibility in Cu-CHA Zeolite Catalysts: A Multivariate XAS/FTIR Approach to
 Complexity. *Chem. Sci.* 2017, *8*, 6836–6851.
- (152) Gao, F.; Washton, N. M.; Wang, Y.; Kollár, M.; Szanyi, J.; Peden, C. H. F. Effects of Si/Al Ratio on Cu/SSZ-13 NH3-SCR Catalysts: Implications for the Active Cu Species and the Roles of Brønsted Acidity. J. Catal. 2015, 331, 25–38.
- (153) Sushkevich, V. L.; Smirnov, A. V.; van Bokhoven, J. A. Autoreduction of Copper in Zeolites: Role of Topology, Si/Al Ratio, and Copper Loading. J. Phys. Chem. C 2019, 123, 9926–9934.
- (154) Sushkevich, V. L.; Van Bokhoven, J. A. Revisiting Copper Reduction in Zeolites: The Impact of Autoreduction and Sample Synthesis Procedure. *Chem. Commun.* 2018, *54*, 7447.
- (155) Sárkány, J.; D'Itri, J. L.; Sachtler, W. M. H. Redox Chemistry in Excessively Ion-Exchanged Cu/Na-ZSM-5. *Catal. Letters* **1992**, *16*, 241–249.
- (156) Li, H.; Paolucci, C.; Khurana, I.; Wilcox, L. N.; Göltl, F.; Albarracin-Caballero, J. D.;
 Shih, A. J.; Ribeiro, F. H.; Gounder, R.; Schneider, W. F. Consequences of Exchange-Site Heterogeneity and Dynamics on the UV-Visible Spectrum of Cu-Exchanged SSZ-13. *Chem. Sci.* 2019, *10*, 2373–2384.
- (157) Saha, D.; Grappe, H. A.; Chakraborty, A.; Orkoulas, G. Postextraction Separation, On-Board Storage, and Catalytic Conversion of Methane in Natural Gas: A Review. *Chem.*

Rev. **2016**, *116*, 11436–11499.

- (158) Schwach, P.; Pan, X.; Bao, X. Direct Conversion of Methane to Value-Added Chemicals over Heterogeneous Catalysts: Challenges and Prospects. *Chem. Rev.* 2017, *117*, 8497–8520.
- (159) Brezicki, G.; Kammert, J. D.; Gunnoe, T. B.; Paolucci, C.; Davis, R. J. Insights into the Speciation of Cu in the Cu-H-Mordenite Catalyst for the Oxidation of Methane to Methanol. ACS Catal. 2019, 9, 5308–5319.
- (160) Ross, M. O.; MacMillan, F.; Wang, J.; Nisthal, A.; Lawton, T. J.; Olafson, B. D.; Mayo,
 S. L.; Rosenzweig, A. C.; Hoffman, B. M. Particulate Methane Monooxygenase Contains
 Only Mononuclear Copper Centers. *Science (80-.).* 2019, *364*, 566–570.
- (161) Wang, V. C.-C.; Maji, S.; Chen, P. P.-Y.; Lee, H. K.; Yu, S. S.-F.; Chan, S. I. Alkane
 Oxidation: Methane Monooxygenases, Related Enzymes, and Their Biomimetics. *Chem. Rev.* 2017, *117*, 8574–8621.
- (162) Balasubramanian, R.; Smith, S. M.; Rawat, S.; Yatsunyk, L. A.; Stemmler, T. L.;
 Rosenzweig, A. C. Oxidation of Methane by a Biological Dicopper Centre. *Nature* 2010, 465, 115–119.
- (163) Chan, S. I.; Yu, S. S. F. Controlled Oxidation of Hydrocarbons by the Membrane-Bound Methane Monooxygenase: The Case for a Tricopper Cluster. *Acc. Chem. Res.* 2008, *41*, 969–979.
- (164) Wang, Y.; Rosowski, F.; Schlögl, R.; Trunschke, A. Molecular Oxygen Activation on the Surface of Vanadium Pentoxide. *Prep.*
- (165) Kammert, J. D.; Brezicki, G.; Acevedo-Esteves, R.; Stavitski, E.; Davis, R. J. High-Throughput Operando-Ready X-Ray Absorption Spectroscopy Flow Reactor Cell for

Powder Samples. Rev. Sci. Instrumen. 2020, 91, 10.1063/1.5124301.

- (166) Wulfers, M. J.; Tekete, S.; Ipek, B.; Lobo, R. F. Conversion of Methane to Methanol on Copper-Containing Small-Pore Zeolites and Zeotypes. *Chem. Commun.* 2015, *51*, 4447– 4450.
- (167) Al, C.; Giordanino, F.; Vennestrøm, P. N. R.; Lundegaard, L. F.; Stappen, F. N.; Mossin, S.; Beato, P.; Lamberti, C. Characterization of Cu-Exchanged SSZ-13: A Comparative FTIR, UV-Vis, and EPR Study with Cu-ZSM-5 and Cu-β with Similar Si/Al and Cu/Al Ratios. *Dalt. Trans.* 2013, *42*, 12741–12761.
- (168) Kurnaz, E.; Fellah, M. F.; Onal, I. A Density Functional Theory Study of C-H Bond Activation of Methane on a Bridge Site of M-O-M-ZSM-5 Clusters (M = Au, Ag, Fe and Cu). *Microporous Mesoporous Mater.* 2011, *138*, 68–74.
- (169) Elwell, C. E.; Gagnon, N. L.; Neisen, B. D.; Dhar, D.; Spaeth, A. D.; Yee, G. M.; Tolman,
 W. B. Copper-Oxygen Complexes Revisited: Structures, Spectroscopy, and Reactivity. *Chem. Rev.* 2017, *117*, 2059–2107.
- (170) Vilella, L.; Studt, F. The Stability of Copper Oxo Species in Zeolite Frameworks. *Eur. J. Inorg. Chem.* 2016, 1514–1520.
- (171) Engedahl, U.; Grönbeck, H.; Hellman, A. First-Principles Study of Oxidation State and Coordination of Cu-Dimers in Cu-SSZ-13 during Methane-to-Methanol Reaction Conditions. J. Phys. Chem. C 2019, 123, 26145–26150.
- (172) Kim, H.; Kosuda, K. M.; Van Duyne, R. P.; Stair, P. C. Resonance Raman and Surfaceand Tip-Enhanced Raman Spectroscopy Methods to Study Solid Catalysts and Heterogeneous Catalytic Reactions. *Chem. Soc. Rev.* **2010**, *39*, 4820–4844.
- (173) Król, M.; Mozgawa, W.; Barczyk, K.; Bajda, T.; Kozanecki, M. Changes in the

Vibrational Spectra of Zeolites Due to Sorption of Heavy Metal Cations. *J. Appl. Spectrosc.* **2013**, *80*, 644–650.

- (174) Cui, M.; Wang, L.; Zhang, Y.; Wang, Y.; Meng, C. Changes of Medium-Range Structure in the Course of Crystallization of Mordenite from Diatomite. *Microporous Mesoporous Mater.* 2015, 206, 52–57.
- (175) Twu, J.; Dutta, P. K.; Kresge, C. T. Vibrational Spectroscopic Examination of the Formation of Mordenite Crystals. J. Phys. Chem. 1991, 95, 5267–5271.
- (176) Haack, P.; Limberg, C.; Ray, K.; Braun, B.; Kuhlmann, U.; Hildebrandt, P.; Herwig, C.
 Dinuclear Copper Complexes Based on Parallel β-Diiminato Binding Sites and Their
 Reactions with O2: Evidence for a Cu-O-Cu Entity. *Inorg. Chem.* 2011, *50*, 2133–2142.
- (177) Kvande, K.; Pappas, D. K.; Dyballa, M.; Buono, C.; Signorile, M.; Borfecchia, E.; Lomachenko, K. A.; Arstad, B.; Bordiga, S.; Berlier, G. Comparing the Nature of Active Sites in Cu-Loaded SAPO-34 and SSZ-13 for the Direct Conversion of Methane to Methanol. *Catalysts* **2020**, *10*, 191.
- (178) Broclawik, E.; Datka, J.; Gil, B.; Kozyra, P. T-O-T Skeletal Vibration in CuZSM-5
 Zeolite: IR Study and Quantum Chemical Modeling. *Phys. Chem. Chem. Phys.* 2000, 2, 401–405.
- (179) Majdan, M.; Kowalska-Ternes, M.; Pikus, S.; Staszczuk, P.; Skrzypek, H.; Zięba, E.
 Vibrational and Scanning Electron Microscopy Study of the Mordenite Modified by Mn,
 Co, Ni, Cu, Zn and Cd. J. Mol. Struct. 2003, 649, 279–285.
- (180) Nauert, S. L.; Rosen, A. S.; Kim, H.; Snurr, R. Q.; Stair, P. C.; Notestein, J. M. Evidence for Copper Dimers in Low-Loaded CuOx/SiO2 Catalysts for Cyclohexane Oxidative Dehydrogenation. ACS Catal. 2018, 8, 9775–9789.

- (181) Haack, P.; Limberg, C. Molecular CuII-O-CuII Complexes: Still Waters Run Deep. Angew. Chemie - Int. Ed. 2014, 53, 4282–4293.
- (182) Martini, A.; Pankin, I. A.; Marsicano, A.; Lomachenko, K. A.; Borfecchia, E. Wavelet Analysis of a Cu-Oxo Zeolite EXAFS Simulated Spectrum. *Radiat. Phys. Chem.* 2019, in press.
- (183) Larsen, S. C.; Aylor, A.; Bell, A. T.; Reimer, J. A. Electron Paramagnetic Resonance Studies of Copper Ion-Exchanged ZSM-5. J. Phys. Chem 1994, 98, 11533–11540.
- (184) Hun, J.; Varga, T.; Peden, C. H. F.; Gao, F.; Hanson, J. C.; Szanyi, J. Following the Movement of Cu Ions in a SSZ-13 Zeolite during Dehydration, Reduction and Adsorption : A Combined in Situ TP-XRD, XANES / DRIFTS Study. J. Catal. 2014, 314, 83–93.
- (185) Gao, F.; Walter, E. D.; Kollar, M.; Wang, Y.; Szanyi, J.; Peden, C. H. F. Understanding Ammonia Selective Catalytic Reduction Kinetics over Cu/SSZ-13 from Motion of the Cu Ions. J. Catal. 2014, 319, 1–14.
- (186) Kucherov, A. V. Water as a Key Factor Providing an Easy Migration/Redistribution of Cu2+ Species in CuO/HZSM-5. *Mendeleev Commun.* 2016, 26, 254–255.
- (187) Gao, F.; Washton, N. M.; Wang, Y.; Kollár, M.; Szanyi, J.; Peden, C. H. F. Effects of Si/Al Ratio on Cu/SSZ-13 NH3-SCR Catalysts: Implications for the Active Cu Species and the Roles of Brønsted Acidity. J. Catal. 2015, 331, 25–38.
- (188) Mahyuddin, M. H.; Staykov, A.; Shiota, Y.; Miyanishi, M.; Yoshizawa, K. Roles of Zeolite Confinement and Cu–O–Cu Angle on the Direct Conversion of Methane to Methanol by [Cu2(μ-O)]2+-Exchanged AEI, CHA, AFX, and MFI Zeolites. *ACS Catal.* 2017, *7*, 3741–3751.

- (189) Xu, J.; Liu, B. Modeling C–H Bond Activation and Oxidations of Alkanes over Cu–MOR Using First-Principles Methods. J. Phys. Chem. C 2019, 10.1021/acs.jpcc.9b00194.
- (190) Kolganov, A. A.; Gabrienko, A. A.; Yashnik, S. A.; Pidko, E. A.; Stepanov, A. G. Nature of the Surface Intermediates Formed from Methane on Cu-ZSM-5 Zeolite: A Combined Solid-State Nuclear Magnetic Resonance and Density Functional Theory Study. ACS Appl. Mater. Interfaces 2020.
- (191) Newton, M. A.; Knorpp, A. J.; Pinar, A. B.; Sushkevich, V. L.; Palagin, D.; van Bokhoven, J. A. On the Mechanism Underlying the Direct Conversion of Methane to Methanol by Copper Hosted in Zeolites; Braiding Cu K-Edge XANES and Reactivity Studies. J. Am. Chem. Soc. 2018, 140, 10090–10093.
- (192) Gol'dshleger, N. F.; Es'kova, V. V.; Shilov, A. E.; Shteinman, A. A. Reactions of Alkanes in Solutions of Chloride Complexes of Platinum. *Russ. J. Phys. Chem.* **1972**, *46*, 785–786.
- (193) Shilov, A. E.; Shul, G. B. Activation of C H Bonds by Metal Complexes. *Chem. Rev.* 1997, 97, 2879–2932.
- (194) Webb, J. R.; Bolano, T.; Gunnoe, T. B. Catalytic Oxy-Functionalization of Methane and Other Hydrocarbons: Fundamental Advancements and New Strategies. *ChemSusChem* 2011, 4, 37–49.
- (195) Palkovits, R.; Antonietti, M.; Kuhn, P.; Thomas, A.; Schüth, F. Solid Catalysts for the Selective Low-Temperature Oxidation of Methane to Methanol. *Angew. Chemie Int. Ed.* **2009**, *48*, 6909–6912.
- (196) Palkovits, R.; von Malotki, C.; Baumgarten, M.; Müllen, K.; Baltes, C.; Antonietti, M.; Kuhn, P.; Weber, J.; Thomas, A.; Schüth, F. Development of Molecular and Solid Catalysts for the Direct Low-Temperature Oxidation of Methane to Methanol.

ChemSusChem **2010**, *3*, 277–282.

- (197) Soorholtz, M.; White, R. J.; Zimmermann, T.; Titirici, M.-M.; Antonietti, M.; Palkovits, R.; Schüth, F. Direct Methane Oxidation over Pt-Modified Nitrogen-Doped Carbons. *Chem. Commun.* 2013, 49, 240–242.
- (198) McKee, D. W.; Norton, F. J. Catalytic Exchange of Methane and Deuterium on Platinum, Ruthenium, and Platinum-Ruthenium Alloys. *J. Phys. Chem.* **1964**, *68*, 481–489.
- (199) Luntz, A. C.; Bethune, D. S. Activation of Methane Dissociation on a Pt(111) Surface. J. Chem. Phys. 1989, 90, 1274.
- (200) Viñes, F.; Lykhach, Y.; Staudt, T.; Lorenz, M. P. A.; Papp, C.; Steinrück, H. P.; Libuda, J.; Neyman, K. M.; Görling, A. Methane Activation by Platinum: Critical Role of Edge and Corner Sites of Metal Nanoparticles. *Chem. A Eur. J.* 2010, *16*, 6530–6539.
- (201) Wei, J.; Iglesia, E. Mechanism and Site Requirements for Activation and Chemical Conversion of Methane on Supported Pt Clusters and Turnover Rate Comparisons among Noble Metals. J. Phys. Chem. B 2004, 108, 4094–4103.
- (202) Chin, Y. H.; Buda, C.; Neurock, M.; Iglesia, E. Reactivity of Chemisorbed Oxygen Atoms and Their Catalytic Consequences during CH4-O2 Catalysis on Supported Pt Clusters. J. Am. Chem. Soc. 2011, 133, 15958–15978.
- (203) Pouy, M. J.; Milczek, E. M.; Figg, T. M.; Otten, B. M.; Prince, B. M.; Gunnoe, T. B.;
 Cundari, T. R.; Groves, J. T. Flavin-Catalyzed Insertion of Oxygen into Rhenium-Methyl
 Bonds. J. Am. Chem. Soc. 2012, 134, 12920–12923.
- (204) Conley, B. L.; Ganesh, S. K.; Gonzales, J. M.; Tenn, W. J.; Young, K. J. H.; Oxgaard, J.;
 Goddard, W. A.; Periana, R. A. Facile Functionalization of a Metal Carbon Bond by OAtom Transfer. *J. Am. Chem. Soc.* 2006, *128*, 9018–9019.
- (205) Parmon, V. N.; Panov, G. I.; Uriarte, A.; Noskov, A. S. Nitrous Oxide in OxidationChemistry and Catalysis: Application and Production. *Catal. Today* 2005, *100*, 115–131.
- (206) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. Nonionic Triblock and Star Diblock Copolymer and Oligomeric Surfactant Syntheses of Highly Ordered, Hydrothermally Stable, Mesoporous Silica Structures. *J. Am. Chem. Soc.* 1998, *120*, 6024–6036.
- (207) Fu, Q.; Saltsburg, H.; Flytzani-stephanopoulos, M. Active Nonmetallic Au and Pt Species on Ceria-Based Water-Gas Shift Catalysts. *Science* (80-.). **2003**, *301*, 935–938.
- (208) Zhu, J.; Wang, T.; Xu, X.; Xiao, P.; Li, J. Pt Nanoparticles Supported on SBA-15:
 Synthesis, Characterization and Applications in Heterogeneous Catalysis. *Appl. Catal. B Environ.* 2013, *130–131*, 197–217.
- (209) PDF-4+. International Centre for Diffraction Data 2014.
- (210) Anderson, A. D.; Deluga, G. A.; Moore, J. T.; Vergne, M. J.; Hercules, D. M.; Kenik, E. A.; Lukehart, C. M. Preparation of Pt-Re/Vulcan Carbon Nanocomposites Using a Single-Source Molecular Precursor and Relative Performance as a Direct Methanol Fuel Cell Electrooxidation Catalyst. *J. Nanosci. Nanotechnol.* 2004, *4*, 809–816.
- (211) Falcone, D. D.; Hack, J. H.; Klyushin, A. Y.; Knop-Gericke, A.; Schlögl, R.; Davis, R. J. Evidence for the Bifunctional Nature of Pt-Re Catalysts for Selective Glycerol Hydrogenolysis. *ACS Catal.* 2015, *5*, 5679–5695.
- (212) Burch, R.; Attard, G. A.; Daniells, S. T.; Jenkins, D. J.; Breen, J. P.; Hu, P. Low-Temperature Catalytic Decomposition of N2O on Platinum and Bismuth-Modified Platinum: Identification of Active Sites. *Chem. Commun.* 2002, 44, 2738–2739.
- (213) Duke, A. S.; Galhenage, R. P.; Tenney, S. A.; Sutter, P.; Chen, D. A. In Situ Studies of

Carbon Monoxide Oxidation on Platinum and Platinum–Rhenium Alloy Surfaces. *J. Phys. Chem. C* **2015**, *119*, 381–391.

- (214) Dietz, W. A. Response Factors for Gas Chromatographic Analyses. J. Gas Chromatogr.
 1967, 5, 68–71.
- (215) Bozbag, S. E.; Alayon, E. M. C.; Pecháček, J.; Nachtegaal, M.; Ranocchiari, M.; van Bokhoven, J. A. Methane to Methanol over Copper Mordenite: Yield Improvement Through Multiple Cycles and Different Synthesis Techniques. *Catal. Sci. Technol.* 2016, 6, 5011–5022.
- (216) Dutta, P. K.; Puri, M. Synthesis and Structure of Zeolite ZSM-5: A Raman Spectroscopic Study. J. Phys. Chem. 1987, 91, 4329–4333.
- (217) Chen, P.; Root, D. E.; Campochiaro, C.; Fujisawa, K.; Solomon, E. I. Spectroscopic and Electronic Structure Studies of the Diamagnetic Side-On CuII-Superoxo Complex Cu(O2)[HB(3-R-5-IPrpz)3]: Anti- Ferromagnetic Coupling versus Covalent Delocalization. *J. Am. Chem. Soc.* 2003, *125*, 466–474.
- (218) Aboelella, N. W.; Gherman, B. F.; Hill, L. M. R.; York, J. T.; Holm, N.; Young, V. G.;
 Cramer, C. J.; Tolman, W. B. Effects of Thioether Substituents on the O2 Reactivity of β Diketiminate- Cu(I) Complexes: Probing the Role of the Methionine Ligand in Copper Monooxygenases. *J. Am. Chem. Soc.* 2006, *128*, 3445–3458.
- (219) Sarangi, R.; Aboelella, N.; Fujisawa, K.; Tolman, W. B.; Hedman, B.; Hodgson, K. O.;
 Solomon, E. I. X-Ray Absorption Edge Spectroscopy and Computational Studies on
 LCuO2 Species: Super- Oxide–CuII versus Peroxide–CuIII Bonding. *J. Am. Chem. Soc.*2006, *128*, 8286–8296.
- (220) Carrott, P. J. M.; Sheppard, N. Infrared Study of the Adsorption of 16O2, 16O18O and

18O2 on Cr2O3. J. Chem. Soc. Faraday Trans. 1 1983, 79, 2425–2437.