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## Monomeric Copper (II) Sites Supported on Alumina Selectively Convert Methane to Methanol

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**Abstract:** Monomeric  $Cu^{II}$  sites supported on alumina, prepared via surface organometallic chemistry, selectively convert  $CH_4$  to  $CH_3OH$ . This reaction takes place via formation of  $CH_3O$  surface species with the concomitant reduction of two monomeric  $Cu^{II}$  sites to  $Cu^{I}$ , according to mass balance analysis, IR, solid-state NMR, XAS and EPR studies. This material contains a significant fraction of Cu active sites (22 %) and displays a selectivity for  $CH_3OH$  exceeding 83 %, based on the number of electrons involved for this transformation. These alumina-supported  $Cu^{II}$  sites show short reaction time and demonstrate that C-H bond activation along with methoxy surface species formation can occur on pairs of monomeric  $Cu^{II}$  sites.

CH<sub>4</sub>, the main constituent of natural gas, is increasingly produced by fracking and widely available at extraction sites for fossil fuel. Its transport as liquefied natural gas is, however, expensive and energy intensive, hence it is often flared despite the highly negative environmental impacts and loss of resource. Finding efficient routes to convert on-site CH<sub>4</sub> to liquid fuels or chemicals is, therefore, of significant economic and environmental importance. As such, its direct conversion to CH<sub>3</sub>OH is noteworthy since it provides a liquid that can be directly used as chemical feedstock, fuel or fuel additive. However, this process remains a grand challenge because overoxidation is favored due to the higher reactivity of CH<sub>3</sub>OH than CH<sub>4</sub>.<sup>[1-5]</sup> In nature, bacterial enzymes, such as methane monooxygenases, are able to oxidize CH<sub>4</sub> to CH<sub>3</sub>OH in high selectivity using O<sub>2</sub> as primary oxidant.<sup>[6]</sup> These enzymes, containing Cu or Fe metal centers, have been a source of inspiration to design materials for the conversion of CH<sub>4</sub> to CH<sub>3</sub>OH under mild reaction conditions.<sup>[7]</sup> Attempts to perform this reaction catalytically with tailored materials have been mostly unsuccessful since at high conversion the selectivity towards CH<sub>3</sub>OH is low. This hurdle can be in principle overcome by using the concept of chemical looping, that consists in decoupling the steps of oxidation of Cu sites and their reaction with CH<sub>4</sub>.<sup>[8]</sup> The last step of the cycle consists of the desorption of the methoxy species strongly bound to the copper sites using a protic solvent. Of the various systems that have been investigated, Cuexchanged zeolites have shown potential for the selective oxidation of CH4 to CH3OH using molecular oxygen as oxidant source.<sup>[9-13]</sup> The structure of the active sites is highly debated, with evidence for both ( $\mu$ -oxo) dicopper <sup>[9,14]</sup> and tris( $\mu$ -oxo) trinuclear copper centers (Figure 1a);[15] recent theoretical studies also suggest that monomeric Cu sites should not be excluded.<sup>[16,17]</sup>

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Dr. A. P. van Bavel, Dr. A. D. Horton Shell Global Solutions International B.V. Grasweg 31, 1031 HW Amsterdam, The Netherlands A major challenge in these systems is associated with the presence of a small fraction of active sites (often below 30% even if the presence of 90% of active sites – 0.47 mol CH<sub>3</sub>OH/mol Cu – have been recently reported),<sup>[18,19]</sup> rendering unequivocal conclusions regarding active site structure difficult.<sup>[13]</sup> Cu supported on non-zeolitic materials namely amorphous silica, has also shown to be reactive for this transformation, indicating that confinement is not required, but the methanol yield does not exceed 3.6% CH<sub>3</sub>OH per Cu.<sup>[20,21]</sup>

Surface organometallic chemistry (SOMC)<sup>[22,23]</sup> combined with thermolytic molecular precursors (TMP)<sup>[24]</sup> has emerged as a powerful approach to generate supported isolated metal sites with tailored nuclearity and oxidation state for a broad range of metals.<sup>[25,26]</sup> This approach consists of grafting tailored molecular precursors on supports with a controlled OH density, followed by a post-treatment that removes organic ligands and generates the desired isolated metal sites. Since nuclearity and local environment are both key features for the selective CH<sub>4</sub> to CH<sub>3</sub>OH conversion on Cu sites, we reasoned that the SOMC/TMP approach could be ideal to generate monomeric Cu<sup>II</sup> sites and to evaluate their reactivity for this reaction.

Here, we report the synthesis of a monomeric Cu<sup>II</sup> siloxide [Cu(OSi(OtBu)<sub>3</sub>)<sub>2</sub>(TMEDA)] precursor molecular (1; tetramethylethylenediamine, TMEDA) and its use to generate isolated Cu<sup>II</sup> sites on alumina with the goal to preserve a silicon and aluminum environment, as found in zeolites, without the microporous environment (Figure 1b-c). We also prepared a dimeric complex,  $[Cu(\kappa^2,\mu^2-OSi(OtBu)_3)(OSi(OtBu)_3)]_2$  (2, Figure 1b), as a spectroscopic molecular probe for oxygen-bridged dimeric Cu species and to evaluate its surface chemistry towards the generation of Cull sites. Using a combination of spectroscopic methods (UV-Vis, EPR, XAS), we show that independently of the molecular precursors 1 or 2, mononuclear Cull sites in an alumino-silicate environment are mostly formed after thermal treatment at 700 °C. These mononuclear sites show unprecedented reactivity, activating CH<sub>4</sub> within minutes at 200 °C and yielding CH<sub>3</sub>OH after hydrolysis in high selectivity (>80%). CH<sub>4</sub> activation takes place on a high fraction of proximal monomeric Cull sites (22% of Cu) dispersed at the alumina surface via a 2-electron oxidation process, indicating that di- or tri-nuclear Cu-µ-oxo sites and/or micropores are not required for the selective conversion of CH<sub>4</sub> to CH<sub>3</sub>OH, thus contrasting the expected situation in the corresponding zeolitic materials.

First, the dimeric complex (2) was prepared by reaction of  $[Cu(OTf)_2]_x$  with 2 equiv. of NaOSi(OtBu)<sub>3</sub> in THF and is further converted to  $[Cu(OSi(OtBu)_3)_2(TMEDA)]$  (1) upon addition of TMEDA. The complex (1) is isolated as light green single crystals in 54% overall yield; it crystalizes in the *P*-1 space group, where Cu occupies a distorted tetrahedral environment  $(\tau_4' = 0.65)$  as found in  $[Cu(OSi(OtBu)_3)_2(py)_2]$ .<sup>[27]</sup> This complex is associated with (i) a typical EPR spectrum with  $g_\perp > g_{\parallel} \approx g_e$  and a  $d_{z2}$  ground state ( $g_\perp = 2.27$ ;  $g_{\parallel} = 2.00 A_{\parallel} \approx 450$  MHz, Fig. S1) and (ii) an optical spectrum with characteristic  $\lambda_{max}$  at 267 and 317 nm associated with the ligand to metal charge transfer (LMCT) of the two terminal siloxides ligands and the two nitrogen ligands bound to Cu, respectively (Fig. S2). For (2),  $[Cu(\kappa^2,\mu^2-OSi(OtBu)_3)$  (OSi(OtBu)\_3)]\_2, isolated in 56% yield as light green single crystals, the two Cu centers adopt a distorted square planar geometry ( $\tau_4' = 0.38$  Cu<sub>1</sub> and 0.27 Cu<sub>2</sub>),

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Figure 1. a) Proposed active sites in Cu-exchanged zeolites b) synthesis and structure of Cu<sup>II</sup> molecular precursors (1 and 2) c) strategy and results towards generating monomeric Cu<sup>II</sup> sites on alumina.

Its EPR spectrum shows  $g_{\parallel} > g_{\perp} > g_e$  associated with a  $d_{x^2-y^2}$  ground state, while the UV-Vis spectrum shows bands at 248 and 347 nm, associated with the LMCT bands arising from the terminal and bridging oxygen atoms respectively (see ESI, Section 1 for a complete characterization).

Grafting of 1 on alumina partially dehydroxylated at 700 °C  $(Al_2O_{3-700}, \Theta = 0.7 \text{ OH.nm}^{-2})$  in C<sub>6</sub>H<sub>6</sub> yields trace amounts of HOSi(OtBu)<sub>3</sub> and 0.9 equiv. of isobutene per surface OH. The blue solid recovered after washing and drying under high vacuum (10<sup>-5</sup> mbar) contains 0.46 wt% Cu, corresponding to 0.46 Cu.nm<sup>-2</sup>. IR spectroscopy of the grafted material shows the disappearance of bands associated with surface OH groups and concomitant appearance of v(C-H) and  $\delta$ (C-H) bands at 2975–2801 cm<sup>-1</sup> and 1470–1365 cm<sup>-1</sup>, respectively (Fig. S8-9). Cu K-edge X-ray absorption spectroscopy (XAS) reveals a complex grafting process as evidenced by the appearance of a pre-edge feature at 8982.0 eV in the spectrum (Fig. S14), indicating partial reduction of a fraction of Cull to Cul; the presence of Cu<sup>II</sup> sites being confirmed by EPR (Fig. S.12). However, treatment under a flow of dry synthetic air at 700 °C yields a green solid 1-a700 free of organic ligands according to IR spectroscopy (Fig. S8-9). This material contains exclusively Cu<sup>II</sup> sites as evidenced by XAS with an edge energy at 8986.0 eV (Fig. S14). The UV-vis spectrum of 1-a700 shows a broad band centered at 900 nm, corresponding to the d-d transition of Cull species, and a sharp signal centered at 250 nm (Fig. S10), corresponding to the LMCT of oxygen to a single Cu center (Cu2+-O2-), consistent with the presence of monomeric Cull ions.<sup>[28]</sup> The absence of absorption bands from 300-600 nm shows that CuO clusters or peroxo- or µ-oxo species ,if present at all, are only minor species, in contrast to the significant amount of Cu associated to the reactivity with CH4  $^{[29,\widetilde{3}0]}$ . EPR spectroscopy shows the presence of an anisotropic signal with an axial configuration, implying the localization of the unpaired electron in the  $d_{x^2-y^2}$  orbital (g<sub>I</sub> = 2.31 A<sub>I</sub> ≈ 540 MHz; g<sub>⊥</sub> = 2.11, Fig. S12). However, the signal cannot be completely described by a single axial parameter due to the broadening induced from magnetic dipole-dipole interactions between isolated paramagnetic surface species.<sup>[31,32]</sup> Fitting the EXAFS (Fig. 2) spectra is consistent with an average 3 O in the first coordination sphere. The fitted bond distances are long for terminal Cu-O-Si/Al but are expected for the constrained geometry  $\kappa^2$ , determined from the crystal structure of the molecular complexes (Fig S3). Interestingly, only a single Al/Si atom can

be fitted in the second coordination shell, which is fewer than expected, but the Al/Si contribution to the scattering of the second shell was found to be minor for **2** (Fig. S23).



Figure 2. (left to right) Fourier transform of Cu K-edge EXAFS spectra for the activated material (1-a<sub>700</sub>), the mononuclear (1) and dinuclear (2) complexes

Material	Element	CN <sup>[a]</sup>	R (Å) <sup>[b]</sup>	DW (2 σ <sup>2</sup> ) <sup>[c]</sup>	R (%) <sup>[d]</sup>
1-a <sub>700</sub>	0	3	1.93	0.016	22.8
	Si/Al	1.1	2.8	0.022	
1	0	2	1.83	0.004	37
	Ν	2	2.19	0.027	
2	0	1	1.81	0.007	20.2
	0	1	1.92	0.012	
	0	0.5	2.26	0.013	
	0	0.5	2.49	0.007	
	Cu	1	2.88	0.01	

**Table 1.** Curve fitting analysis of the activated material (1-a<sub>700</sub>) and the mononuclear (1) and dinuclear (2) molecular precursors. [a] Coordination number (± 10%) [b] Scatterer distance from central atom (± 1.5-2%) [c] Debye-Waller factor where  $\sigma$  is the root mean square inter-nuclear separation (Å) [d]  $\Sigma_i^{\rm N}$  1/ $\sigma_i$  ( $\chi^{\rm e}$  (k) -  $\chi^{\rm i}$  (k)<sup>2</sup> x 100% (see ESI for complete definition).

The absence of an extra Cu coordination in the fit of **1-a<sub>700</sub>** is similar to monomeric **1** and in sharp contrast to what is observed for dimeric **2** (Fig. 2), confirming the presence of monomeric Cu<sup>II</sup>

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species (See ESI Section 4 for detailed discussion on EXAFS). Grafting of the dimeric complex 2 on  $Al_2O_{3-700}$  followed by the same thermal treatment provides a material containing mostly monomeric sites according to all spectroscopic data. The complete characterization of the grafted (1-a, 2-a) and activated (1-a<sub>700</sub> and 2-a<sub>700</sub>) materials are included in the ESI (Section 2).

The optimal conditions found for the partial oxidation of CH<sub>4</sub> to CH<sub>3</sub>OH using 1-a<sub>700</sub> (Table S2) are as follows: activation at 700 °C under synthetic air, followed by reaction under 6 bars of CH<sub>4</sub> for 30 min at 200 °C. While reaction of Al<sub>2</sub>O<sub>3-700</sub> with CH<sub>4</sub> did not provide any CH<sub>3</sub>OH after water extraction<sup>[33]</sup> (Table S2), material 1-a700 yields 11% CH<sub>3</sub>OH per total Cu, indicating that the reaction takes place on Cu sites and that 22% of them are involved in this two-electron process (vide infra).<sup>[34]</sup> These mononuclear sites react within minutes at 200 °C with CH4 to give high CH<sub>3</sub>OH selectivity (>80%) on a significant fraction of Cu surface sites (22% of Cu), clearly indicating that having di- or tri-nuclear sites on crystalline oxide materials is not a requirement for the selective conversion of CH<sub>4</sub> to CH<sub>3</sub>OH.<sup>[35]</sup> Moreover, in situ XAS (Fig. 3a) shows that about. 27% of the total Cu<sup>II</sup> is reduced to Cu<sup>I</sup>, which is close to the expected 22%, considering the CH<sub>3</sub>OH yield and the need of 2 electrons per CH<sub>3</sub>OH formed. This performance corresponds to an electron efficiency of the  $\mbox{Cu}^{ll}$  sites for  $\mbox{CH}_3\mbox{OH}$  above 83%, implying a greater selectivity for CH<sub>3</sub>OH (> 83%), based on the electron implied for overoxidized products formation. The low amount of side products precludes their quantification in the gas phase but the analysis of the reacted material and the product by IR and NMR spectroscopy shows that CH<sub>3</sub>O-species along with trace amounts of HCOO- and CO are formed upon reaction with CH<sub>4</sub> as confirmed by using <sup>13</sup>CH<sub>4</sub> (Fig. S19-S21). The material 2-a<sub>700</sub> has a similar performance yielding 9% CH<sub>3</sub>OH, 23% Cu reduction and an electron efficiency of 75% (see Table S2 and Fig. S22).



Figure 3. In situ X-Band EPR spectroscopy at room temperature under batch conditions (a) and Cu K-edge XANES spectroscopy under flow conditions. The \* indicates the presence of a very weak signal that remains unaffected upon reaction with methane. (b) for 1-a700 before (blue) and after (red) reaction with 6 bars of CH<sub>4</sub> for 30 min and after reduction under 1 bar of CH<sub>4</sub> at 500 °C (black).

In situ EPR spectroscopy confirms the aforementioned quantification (Fig. 3a): after 30 min of reaction (6 bar  $CH_4$ , 200 °C), the EPR signal of  $Cu^{II}$  decreased by 23%. The decrease of

signal the FPR precludes the involvement of antiferromagnetically coupled centers (i.e., bridged µ-oxo Cu dimer and Ču oxide clusters<sup>[36]</sup>) hence confirming the combined Cull/Cul redox reaction of two proximal monomeric Cu sites, which are not magnetically coupled with each other. The EPR parameters and the UV-vis spectra (Fig. 3a and S17) before and after reaction are similar, implying similitude in the local environment of the monomeric Cu centers. We surmise that the intrinsic limitation of this system must be related to a requirement for two sufficiently proximal reactive Cu<sup>II</sup> monomers on the oxide surface in order to perform this overall 2-electron oxidation process rather than a structural configuration requirement of the monomeric sites. The fraction of Cu becoming EPR-silent (23%), from the reduction of Cu<sup>II</sup> to Cu<sup>I</sup>, is consistent with the 22% expected from the CH<sub>3</sub>OH extraction.

In this work, we have demonstrated that oxygen-activated monomeric Cu<sup>II</sup> sites supported on alumina, generated via SOMC/TMP, show fast reactivity and are selective for the conversion of CH<sub>4</sub> to CH<sub>3</sub>OH. It has been demonstrated that these monomeric copper(II) sites on non-crystalline support with specific spectroscopic signatures are selective for the formation of methoxy intermediates and that di- or tri-nuclear centers are not required for this transformation on oxide materials. This discovery opens up opportunities to develop novel materials for the selective partial oxidation of CH<sub>4</sub> to CH<sub>3</sub>OH.

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**Keywords:** alumina • C-H activation • copper • methane • methanol

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One plus one equals two: Methane was selectively converted to methanol by copper(II) sites generated on  $\gamma$ -alumina support using surface organometallic chemistry and thermal molecular precursor approach. The activation of the material at high temperature under oxygen generates monomeric Cu sites. An important fraction of these sites formed are capable of partially oxidize methane to methanol under mild conditions.



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