Hydrogen-bonded assembly of methanol on Cu(111)

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Investigation of methanol’s surface chemistry on metals is a crucial step towards understanding the reactivity of this important chemical feedstock. Cu is a relevant metal for methanol synthesis and reforming, but due to the weak interaction of methanol with Cu, an atomic scale view of methanol’s coverage-dependent ordering and self-assembly on Cu(111), the most abundant facet of most nanoparticles, has not yet been possible. Low and variable temperature scanning tunneling microscopy coupled with density functional theory reveal a coverage-dependent range of highly ordered structures stabilized by two hydrogen bonds per molecule. While extended chains that resemble the hydrogen-bonded zigzag structures reported for solid methanol are an efficient way to pack methanol at higher coverages, lower surface coverages yield isolated hexamer units. These hexamers form the same number of hydrogen bonds as the chains but appear to repel one another on the surface. Annealing treatments lead to the desorption of methanol with almost no decomposition. This data serves as a useful guide to both the preferred adsorption geometries and energies of a variety of methanol structures on Cu(111) surfaces as a function of surface coverage.

Introduction

Methanol (MeOH) is a versatile small molecule that can act as an intermediate in certain chemical processes or as a hydrogen storage molecule that provides a safer way to transport hydrogen fuel. Both of these applications require a fundamental understanding of MeOH decomposition to efficiently convert MeOH into the desired product. The current industry standard catalyst for MeOH decomposition (as well as MeOH synthesis and steam-reforming) is Cu/ZnO/Al2O3 catalyst for MeOH decomposition (as well as MeOH synthesis and steam-reforming) is Cu/ZnO/Al2O3, Cu/ZnO/Al2O3, and Cu/ZnO/Al2O3, Cu/ZnO/Al2O3, respectively. This material however, is highly active and poisoned by contaminants such as steam, CO, and CO2, making it impractical for many industrial applications.

In particular, understanding the interaction of MeOH with copper surfaces by means of vibrational spectroscopy4-13, photoelectron spectroscopy,4-9,14-16, and theory have shown that MeOH does not appreciably react on the bare copper surface but pre-adsorbing oxygen on copper greatly improved reactivity. There have been STM studies focusing on the MeOH–Cu system,10,28-33 but up to this point only partially decomposed MeOH has been observed, usually in the form of methoxy after pre-dosing oxygen onto Cu(110). It would be advantageous to understand how intact MeOH interacts and assembles on the bare Cu(111) surface because the energetics of subsequent reactions will be dominated by the initial state of the reactant. Specifically, hydrogen bond directed self-assembly will lead to well-defined molecular densities and geometries and a lowering of the reactant’s energy via stabilizing hydrogen bonds. In particular, understanding the interaction of MeOH on a Cu(111) surface is significant because {111} facets constitute a large percentage of the surface area of real catalyst nanoparticles under reaction conditions.34

In this study we report the direct observation of intact MeOH on a Cu(111) surface by STM. Previous temperature
programmed desorption (TPD) studies of MeOH on Cu(111) provide a temperature range over which we can obtain atomic scale snapshots of the progression of MeOH structures as a function of surface coverage up to desorption.\textsuperscript{4,11} Similar to adsorption on Au(111),\textsuperscript{35,36} the MeOH structures are dictated by hydrogen bonding interactions between adjacent molecules. These interactions are facilitated by MeOH binding atop on Cu(111) via one of the lone pairs on the oxygen atom with the O–H bond roughly parallel to the surface.\textsuperscript{8} This orientation leaves the MeOH molecule with the ability to form two hydrogen bonds to other MeOH molecules parallel to the surface. Density functional theory (DFT) calculations are used to determine the exact structure and energetic stabilities of the MeOH assemblies and also reveal that for chains of MeOH at 1 monolayer (ML) coverage there is a slight energetic preference in having two different, alternating chain spacings rather than one constant spacing leading to a Peierls like distortion.

**Experimental**

All experiments were performed with Omicron NanoTechnology\textsuperscript{38} variable-temperature (VT) and low-temperature (LT) ultra-high vacuum STMs. Data was recorded with Vecco and Omicron etched W and 85 : 15 Pt–Ir tips. The Pt–Ir tips were mechanically cut with pliers and washed in MeOH before being introduced to the UHV system. Once in vacuum the tips were conditioned by applying voltage pulses while scanning a clean Cu(111) surface. The electrochemically etched W tips were purchased from OmicronNanotechnology\textsuperscript{38} and Vecco and treated identically to the Pt–Ir tips. 99.8 % ultrapure HPLC grade MeOH from Alfa Aesar was further purified by freeze–pump–thaw cycles.

In the VT STM setup, the Cu(111) was prepared with many consecutive Ar\textsuperscript{+} sputter (1.5 keV/12 μA) and anneal (1000 K) cycles. The final cleaning cycle procedure was a 20 min sputter followed by a 10 min anneal. Before cooling the STM stage with liquid helium \textit{via} a flow cryostat, the base pressure in the STM chamber was <1 × 10\textsuperscript{-10} mbar. Pre-cooling the STM stage before the sample was loaded decreased the pressure in the STM chamber (<5 × 10\textsuperscript{-11} mbar). Very low pressures were required to ensure sample cleanliness for extended periods of time at low temperatures. MeOH was dosed directly onto the 30 K (VT) or 5 K (LT) surface \textit{via} a collimated molecular doser in the STM chamber. Annealing experiments were performed \textit{in situ} in the STM chamber with the STM tip held several μm away from the surface. For LT experiments, after cleaning, the crystal was transferred in less than 5 minutes in vacuum (<5 × 10\textsuperscript{-10} mbar) to the pre-cooled STM. In approximately 40 minutes the sample cooled from room temperature to 5 K. In all of the scanning conditions the voltage refers to the sample bias. Sample temperatures measured in the STM stage are accurate and reproducible to within 3 K. A monolayer of MeOH is defined by the repeat unit of the extended chain structure observed at high coverage (Fig. 1) in which there is 1 MeOH molecule per 3 Cu atoms. Typical STM gap conditions for imaging MeOH on Cu(111) were between −1.0 V to 1.0 V and 2–10 pA.

All calculations were performed using periodic DFT as implemented in the VASP code\textsuperscript{37,38} and using an accurate version of the non-local van der Waals density functional of Dion et al.,\textsuperscript{39} referred to as “optB88-vdW”.\textsuperscript{40,41} The computational setup is similar to our previous works, where the improved performance of optB88-vdW over standard functionals such as PBE is also discussed.\textsuperscript{36,42–44} Valence electrons were expanded in a plane wave basis with 500 eV cut-off energy, whilst inner core electrons were treated with the projector augmented-wave method.\textsuperscript{45} A Monkhorst–Pack grid\textsuperscript{46} with \(k\)-point samplings of at least 12 × 12 × 1 per (1 × 1) surface unit cell was considered. The metal slabs were 3 layers thick, separated by 1.5 nm, with the Cu atoms in the bottom layer fixed in their bulk optimal position, \(\sigma_{Cu} = 0.363\) nm. The adsorption of MeOH chains was modeled with \(6 \times \sqrt{3}\) and \(7\sqrt{3} \times \sqrt{3}\) surface cells, whilst MeOH single molecules and hexamers were modeled with \(4 \times 4\) and \(6 \times 6\) surface cells, respectively. In all cases, a dipole correction along the direction perpendicular to the Cu(111) surface was applied and geometry optimizations were carried out with the optB88-vdW functional, low tunneling currents (<10 pA) were used to minimize disruption of the MeOH assemblies during STM imaging. Fig. S1 (ESI\textsuperscript{w}) demonstrates that, even with low tunneling currents, it was still possible to perturb the overlay by scanning.

**Results and discussion**

Experiments were performed by dosing multilayers of MeOH and then annealing to progressively higher temperatures in order to induce partial desorption, rearrangement, and hence structural changes in the MeOH overlay. The temperature ranges were based on temperature programmed desorption data for MeOH on a bare Cu(111) surface.\textsuperscript{9} After each anneal the system was subsequently cooled to 30 K in order to acquire high quality images of the equilibrated structures. Due to the relatively small adsorption energy of individual MeOH molecules on Cu(111) (−451 meV per MeOH with the optB88-vdW functional), low tunneling currents (<10 pA) were used to minimize disruption of the MeOH assemblies during STM imaging. Fig. 1A reports results for MeOH on Cu(111) at the highest coverage obtained in the STM experiments. MeOH forms long chains that run across the Cu terrace. The chains are spaced 1.56 ± 0.04 nm apart, resulting in a unit cell for this structure of 1.56 ± 0.04 nm × 0.41 ± 0.04 nm corresponding to a 6 × \(\sqrt{3}\) surface unit cell. High resolution STM images (in which molecular resolution within the chains is just about discernable) and DFT calculations reveal that at this coverage (defined as 1 ML) there is one MeOH per 3 surface Cu atoms. At this coverage DFT identifies a stable chain structure in which MeOH groups are adsorbed at atop sites with adjacent MeOH.
molecules hydrogen bonding to each other in a zig-zag fashion. The DFT structure for a single chain is shown in Fig. 1B. It has the same basic structure as the chains characterized by us recently for MeOH on Au(111)\(^{36}\) and the adsorption structure is very similar to that of water on metals.\(^{48,49}\) The adsorption energy per MeOH of this structure is \(-674\) meV. However, the problem with this simple monolayer of uniformly spaced MeOH chains is that it has a \(3 \times \sqrt{3}\) surface unit cell and is inconsistent with the observed \(6 \times \sqrt{3}\) unit cell. This suggests that the chains observed here are something more interesting than a simple uniformly spaced arrangement of MeOH chains. Indeed higher resolution images (shown below) reveal that the chains seen in Fig. 1A are in fact pairs of MeOH chains that we term “double chains”. When we use DFT to consider possible structures for pairs of chains in the appropriate \(6 \times \sqrt{3}\) surface cell we do indeed identify double chain structures that are slightly more stable than the simple \(3 \times \sqrt{3}\) chain structure. Details of the various double chain structures considered and their adsorption energies are given in the ESI.\(^\dagger\) The most stable double chain structure identified is shown in Fig. 1C. It has an adsorption energy of \(-688\) meV per MeOH, which is \(14\) meV per MeOH more stable than the simple \(3 \times \sqrt{3}\) chains. The double chains have the same basic structure as the single chains in that they are comprised of zig-zag H bonded arrangements of MeOH molecules adsorbed at atop sites of the underlying substrate. The key difference is that there is a Peierls like distortion of the chain–chain separations, with an alteration between a short chain–chain distance of \(0.755\) nm and a long chain–chain distance of \(0.793\) nm. Associated with the Peierls like distortion is a slight out of plane buckling (tilting) of the MeOH groups in the dimerized chains as seen in Fig. 1E. Simulated STM images shown in Fig. 1D highlight the pairing of the rows and are in good agreement with the STM images obtained experimentally. In the STM measurements reported in Fig. 1A it is the pairs of closely spaced chains that are imaged as individual bright lines. DFT reveals that there is a small (26 meV per MeOH) preference for the methyl groups in adjacent chains to be staggered rather than directly facing each other. In the structure shown in Fig. 1C the O–H···O hydrogen bond network within each chain runs within each chain runs in the same direction. However, the DFT calculations indicate a negligible difference between this structure and one where the O–H···O hydrogen bond networks of the two chains in the unit cell run in opposite directions. The O–O distances along the chains range from \(0.262\) nm to \(0.269\) nm and the shortest O–Cu distances are ca. \(0.244\) nm.

Performing anneals above \(135\) K resulted in partial desorption of the monolayer. Desorption is evidenced by a lowering of the surface coverage and an increased spacing of the MeOH double chains: \(1.9 \pm 0.15\) nm after a \(140\) K anneal.
As seen in Fig. 2A, the chains are slightly more disordered and run in 3 equivalent directions coincident with the $\sqrt{3}$ directions of the underlying Cu lattice. Further support for the MeOH still existing in double chains at this coverage is highlighted by the white squares in Fig. 2B. The upper square illustrates the unzipping of a double chain at one end, while the lower square highlights unzipping in the middle of the chain. If the observed chains were composed of single rows of hydrogen bonded MeOH molecules then this type of defect would not be feasible within a linear chain. Also, some very high resolution STM tip states were capable of imaging the internal structure of the double chain revealing that they are comprised of two separate chains as seen in the inset in Fig. 2A.

Further annealing to 145 K lowered the surface coverage and increased the conversion of the double chains into single chains and MeOH hexamers. In order to understand why more single chains are observed at lower coverages we performed DFT calculations of various structures in a large $7\sqrt{3} \times \sqrt{3}$ unit cell. These calculations reveal that single well-separated chains – with a separation between chains in adjacent unit cells of 2.712 nm – have an adsorption energy of $-699$ meV per MeOH. This is a slightly larger (more stable) adsorption energy than that obtained for the most stable isolated MeOH double chain, which has an adsorption energy of $-685$ meV per MeOH in the same $7\sqrt{3} \times \sqrt{3}$ unit cell. Therefore at low coverage individual chains repel each other. Recalling that the adsorption energy for the most stable double chains at 1 ML is $-688$ meV, we see that overall the interaction between chains, even at higher coverages, is also repulsive. Through dimerization, however, some of this repulsion can be minimized at high coverage by the Peierls like distortion which lowers the energy in the repulsive system by actually moving half of the rows closer to one another.

From the STM images at these higher annealing temperatures (Fig. 2C) it is apparent that the molecules do not cluster into islands. Instead, it appears there is uniform spacing between all individual MeOH structures that is indicative of a repulsive interaction between the units. Hexamers can be thought of as "inert" because once a hexamer is formed all the H bonds are saturated and there is no incentive for two hexamers to

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**Fig. 2** (A) and (B) STM images taken after a 140 K anneal was performed to induce partial desorption of the MeOH monolayer. (A) The double chains are slightly more disordered compared to the 1 ML case and are spaced further apart: $1.9 \pm 0.15$ nm. Inset: Higher resolution imaging reveals that double chains are comprised of two single chains. (B) The white boxes highlight areas where the double chains of MeOH are partially unzipped into single MeOH chains. (C) After a 145 K anneal the double chains are almost completely unzipped to form single chains and hexamers of MeOH. All images taken at 28 K.

**Fig. 3** STM images after a 140 K anneal. (A) Higher resolution image in which the periodicities of the MeOH double chains and the single MeOH features are visible. (B) The double chains of MeOH are spaced far enough apart ($1.9 \pm 0.15$ nm) to accommodate additional MeOH molecules between them which appear as single chains of equivalent height but narrower in width.
MeOH hexamers. Cu(110). chains was also observed recently for ice-like water chains on Note that a similar repulsion between hydrogen bonded water space to move apart at lower coverages supports this argument. (Fig. 3B) and the hexamers (Fig. 4A) when they have the uniformity in the separation between both the chains increasing their separation from 1.56 nm to 1.9 nm. The chains move apart from each other in a regular manner (Fig. 2 and 3 reveal that after a 140 K anneal chain structures when the coverage is reduced from 1 ML. The different net charges in a plane parallel to the surface and therefore the chains repel one another. This same effect is also at play in separating the chain structures when the coverage is reduced from 1 ML. The STM images in Fig. 2 and 3 reveal that after a 140 K anneal the chains move apart from each other in a regular manner increasing their separation from 1.56 nm to 1.9 nm. The uniformity in the separation between both the chains (Fig. 3B) and the hexamers (Fig. 4A) when they have the space to move apart at lower coverages supports this argument. Note that a similar repulsion between hydrogen bonded water chains was also observed recently for ice-like water chains on Cu(111).30

Fig. 3A contains an example of a typical high resolution image obtained for MeOH molecules in chains on Cu(111). From images like this it was determined that the MeOH molecules along the side of a chain are spaced 0.41 ± 0.04 nm apart, comparable to the \(\sqrt{3}\) spacing on Cu(111). In Fig. 3A one can also see that after a 140 K anneal the MeOH double chains are spaced far enough apart to accommodate additional MeOH molecules between adjacent rows. This is also evident in Fig. 3B which is of a larger area. The thinner protrusions in between MeOH double chains could either be MeOH single chains or isolated MeOH molecules that are being moved up and down the rows by the STM tip, being imaged multiple times and appearing as single chains.

The STM images in Fig. 4 show that after a 150 K anneal, the MeOH that remains on the surface is present in the form of hexamers. The hexamers do not cluster together, again indicating a repulsive interaction between them. Fig. 4A shows a group of MeOH hexamers recorded at 30 K. However, in order to get conclusive evidence for their structure, low coverage experiments had to be performed on a LT-STM at 5 K. These images revealed each of the clusters had six distinct lobes, as shown in Fig. 4B, which is in good agreement with simulated STM images of MeOH hexamers (Fig. 4D). Our DFT calculations reveal that isolated MeOH hexamers are equally as stable as the 1 ML MeOH chains at 0 K \(E_{\text{ads}} = -688\) meV per MeOH. The fact that hexamers are the only species present at low coverage infers that they should be more stable than chains. However, the DFT calculations consider only infinitely long, perfect chains with two hydrogen bonds per molecule whereas at low coverage the options are shorter chains or cyclic structures. Therefore, hexamers in which each of the six MeOH molecules has a full complement of two hydrogen bonds will be energetically preferred at low coverage over short chains in which the MeOH molecule at each of the chains has only one hydrogen bond.

Interestingly, in the hexamer conformation each MeOH molecule adsorbs near atop with the O–H bonds roughly parallel to the surface. Each MeOH donates and accepts just one H bond yielding a cyclic MeOH hexamer. This results in the hexamer being roughly planar with either a clockwise or anticlockwise direction of the hydrogen bonded network and hence an associated chirality. We find in the optimized DFT structures that this asymmetry results in a slight rotation of the hexamer with respect to the Cu lattice as seen Fig. 4C and D in that an anticlockwise hydrogen bonded network leads to a \(\sim 5^\circ\) anticlockwise rotation of the simulated DFT image and vice versa. The fact that experimentally we find equal numbers of clockwise and anticlockwise hexamers supports this conclusion that the hexamers are themselves chiral.

It is instructive to briefly compare the MeOH assemblies on Cu(111) to those on Au(111).35,36 For example, while the lattice constants of Cu and Au are different (in our DFT calculations Cu–Cu distance: 0.259 nm vs. Au–Au distance: 0.295 nm), the spacings within the MeOH hexamers are very similar (O–O distance on Cu: 0.265 nm vs. O–O distance on Au: 0.268 nm). This indicates that the MeOH molecules in the
hexamers adjust their orientation so as to maximize the hydrogen bond distances while still binding at near atom positions. Interestingly, the effect of the lattice constant on the hydrogen bonding backbone is more evident for the case of chains. For example, isolated single chains on Cu show an O–O distance (0.261 nm) slightly shorter than on Au (0.277 nm). Moreover, the O–O–O angle on Cu is 113.9° compared to the 132.5° computed on Au, making the chains on Au “straighter” to compensate for its larger lattice constant.

Conclusions

By acquiring snapshots of the equilibrium MeOH structures formed during thermally activated desorption of MeOH from Cu(111) we have uncovered the preferred hydrogen bonded MeOH assemblies over a range of surface coverage. Double chains of MeOH are the favored structure at monolayer coverage which then evolve to single chains and finally hexamers as the coverage drops. In all structures the MeOH molecules adsorb above atop sites of the Cu substrate with each MeOH hydrogen bonded to its two nearest MeOH neighbors. The high coverage data shows an interesting effect in terms of lateral interaction between adjacent MeOH chains. Measurements from STM images indicate the chains are spaced ~1.56 nm apart with a noticeable contrast between adjacent double chains. DFT calculations reveal that a Peierls distortion in which adjacent chains move together while the overall spacing remains the same leads to a stabilization of the system. Since the hexamers are the last structure observed before desorption, and are the only species present at low coverage, we can infer that they are the most thermodynamically favored structure for MeOH at low coverage. DFT calculations yield a very similar adsorption structure and hydrogen bonding pattern for the infinite single and double chains and hexamers, and predict that they all have similar energies. However, at low coverage, given the option of forming chains of finite length with dangling hydrogen bonds versus discrete hexamers with a full complement of hydrogen bonds, hexamers should be energetically preferred. Given that Cu is the active metal in catalysts for MeOH synthesis, decomposition and steam-reforming, knowledge of the structure and stability of MeOH in a variety of ordered assemblies on Cu is the first step in understanding its subsequent reactivity. In order to investigate reaction pathways and identify important intermediates like methoxy, which unlike MeOH does not have the ability to hydrogen bond, one must be able to recognize different species. The fact that MeOH forms very well defined hydrogen bonded structures at all surface coverages will hopefully allow it to be differentiated from reaction intermediates using STM. Future work is aimed at interrogating the active sites and reaction intermediates for MeOH decomposition and reforming on both oxidized Cu(111) and Pd/Cu alloys.

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References