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Sushkevich, V. L., Palagin, D., & van Bokhoven, J. A. (2019). Water molecules facilitate hydrogen release in anaerobic oxidation of methane to methanol over Cu/Mordenite. ACS Catalysis. <https://doi.org/10.1021/acscatal.9b02702>

Water Molecules Facilitate Hydrogen Release in Anaerobic Oxidation of Methane to Methanol over Cu/Mordenite

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Abstract

Development of a suitable mild-conditions process for direct conversion of methane to methanol faces multiple challenges, the principal ones being the higher reactivity of the primary oxidation products and the need for temperature swings in the typically employed chemical looping procedures. To circumvent these problems, the use of water as a mild oxidant has been recently suggested, leading to the concurrent formation of molecular hydrogen. By means of *ab initio* calculations we address the experimentally observed features of the reaction to identify possible reaction pathways of such hydrogen release. We propose that, alongside with a strong stabilising effect of water, short-lived [Cu–H] intermediate species play a crucial role in the mechanism of the reaction. Proton transfer from the Brønsted acid site of the zeolite framework via an adsorbed water molecule to the Cu^I species generates a [Cu–H] intermediate, which then facilitates the release of molecular hydrogen. This allows the reaction to proceed over a relatively

low-energy transition state configuration. At the same time, excess of water leads to the increased complexity of the concerted transition state, which results in hindering of the hydrogen transfer and the increase of the corresponding energy barrier.

Keywords

copper zeolites; methane to methanol; mechanism; density functional theory; reactive intermediates; anaerobic oxidation

Introduction

Direct partial oxidation of methane to methanol is a process of high industrial potential, offering a sustainable route from natural gas to fuels and chemicals.^{1–4} However, due to higher chemical reactivity of methanol with respect to methane, the development of selective catalytic process is challenging, as higher methane conversion comes at the price of lower selectivity towards methanol, associated with overoxidation.⁵ To overcome this problem, a stepwise process using a copper-exchanged ZSM-5 zeolite as active material has been suggested,⁶ inspired by the methane mono-oxygenase (MMO) bacteria capable of oxidising methane to methanol directly.⁷ A typical stepwise chemical looping process consists of three steps. The material is first activated at high temperature (normally, above 400°C).⁸ Oxygen is then removed from the reactor and methane reacts with the material at about 200°C. Finally, methanol is extracted with liquid water⁶ or desorbed by steam,⁹ after which the next cycle starts. Other materials were also tested, with many copper zeolites found to be active in this process, notably copper exchanged mordenite (CuMOR).^{10–13} A number of reviews have recently been published on the topic, and we refer interested readers to these.^{3,8,14–22} Together with that, an isothermal looping protocol aiming to avoid the temperature swing has been suggested, enabling the operation at a constant temperature of 200°C.^{23,24} This allows for shorter cycle time and increases the yield of methanol per unit of time.²¹

Furthermore, we have recently shown that, under specific conditions, the oxygen activation step can be excluded.²⁵ Instead, a process of selective anaerobic oxidation of methane is possible, where water molecules play a crucial role, acting both as a necessary source of oxygen atoms to recover the activity of the material by reoxidising the copper active center, and as a stabilising agent for the active site, facilitating desorption of methanol.^{25,26} This occurs uniquely in copper exchanged zeolites and allows driving the otherwise endothermic Cu^I oxidation reaction.^{26,27} Instead of using oxygen, only the presence of water is required, while the reactivation of the zeolite material is done in an inert atmosphere during high temperature treatment.

Our previous study shows that anaerobic oxidation of methane to methanol over copper exchanged mordenite involves methane oxidation over Cu^{II} oxo active centers, followed by Cu^I reoxidation by water with a consequent formation of molecular hydrogen.²⁵ An active center first reacts with methane via the formation of a CH₃ fragment bound to a copper atom of the CuMOR active site and a proton abstraction by the zeolite framework. After the activation of methane on the copper atom, a methoxy species is formed and both copper atoms are reduced to Cu^I. Subsequent addition of water facilitates two concurrent processes: a) the hydrolysis of the methoxy species to produce methanol, and b) the substitution of the methoxy species at the active center to the water molecule. Subsequent desorption of methanol is followed by the two-electron reduction process, which leads to the formation of molecular hydrogen, and thus regeneration of the original Cu^{II}–O–Cu^{II} active site (Scheme 1). This reaction is highly endothermic, with overall free energy change calculated as +121 kJ/mol. However, excess of water leads to the formation of highly stable Cu–(OH)₂–Cu dihydroxo species (117 kJ/mol more stable than the original mono(μ -oxo)dicopper center). In combination with the possibility of further stabilisation due to chemisorption of additional water molecules, the anaerobic oxidation of methane to methanol is rendered thermodynamically feasible.²⁶

The originally proposed anaerobic mechanism has been previously carefully scrutinised by Mahyuddin *et al.*,³⁵ who have suggested that a direct formation of hydrogen from the

Scheme 1: Schematic summary of the mechanism of anaerobic oxidation of methane to methanol originally proposed in Ref. 25. Mono(μ -oxo)dicopper species is assumed as an active site, as such a dicopper species seems to be a logical choice for modelling a two-electron hydrogen reduction process,^{28–30} although further sizes of active centers have also been suggested.^{31–34} The final product is a fully hydrated dihydroxo species, as suggested in Ref. 26. The $\ominus$ sign on lattice oxygen atoms adjacent to aluminium is to illustrate the negative charge created by substituting silicon with aluminium, and does not imply the existence of deprotonated O^- ions in the presence of water.

adsorbed water molecule is unlikely to occur. At the same time, they have demonstrated that a water molecule helps reducing high methanol desorption energies by about 50% for both mordenite (CuMOR) and mazzite (CuMAZ) zeolites. Similar findings were also reported earlier for Cu-ZSM-5.³⁶

While the methane activation step is extensively studied,³⁷ the hydrogen formation mechanism is still poorly understood. A recent work by Brezicki et al.³³ emphasizes the importance of the influence the oxygen and water impurities have on the copper speciation and reactivity. This makes the question of how exactly the anaerobic system is able to facilitate the conversion of methane to methanol especially relevant. Theoretical calculations can predict the activation barriers for the process, therefore providing a crucial insight into the mechanistic nature of such process. The present study is thus aimed at an *ab initio* identification of a feasible reaction pathway of molecular hydrogen release in the process of anaerobic methane oxidation over copper-exchanged mordenite.

We found that the proton transfer from the Brønsted acid site of the zeolite framework via an adsorbed water molecule to the Cu^{I} species generates a $[\text{Cu-H}]$ intermediate, which then facilitates the release of molecular hydrogen. This allows the reaction to proceed over

a relatively low-energy transition state configuration. The minimum of two water molecules per active copper site are required to render the anaerobic oxidation of methane to methanol possible. At the same time, excess of water leads to the increased complexity of the concerted transition state, thus hindering the hydrogen transfer and increasing corresponding energy barriers.

Methodology

In order to investigate how exactly such a hydrogen release is achieved, and what role water and various possible intermediates may play in the process of anaerobic conversion of methane to methanol, we rely on density functional theory (DFT) to construct a possible reaction mechanism by identification of reaction intermediates and transition states connecting them. As identifying all relevant configurations of the active sites is a very multidimensional optimisation problem, chemical intuition is often not sufficient to identify the best structures to take into account. Pidko has recently discussed the importance of choosing correct structural models and their influence on the resulting predictions.¹⁹ We have previously studied the influence of geometrical configurations of the chosen intermediates on the calculated reaction profiles using the example of a smaller cluster based system.³⁸ We have shown that dramatic geometry change between the reaction intermediates can lead to very high energy barriers and thus be prohibitive for the whole process. Therefore, an unbiased exploration of the configurational space must ideally be carried out.

We have tried to achieve this by constructing a pool of initial candidate structures for every reaction intermediate by running a series of molecular dynamics (MD) simulations corresponding to possible reaction steps starting from the formation of the methoxy species on the mono(μ -oxo)dicopper active center of mordenite, proceeding to the formation of molecular hydrogen and subsequent generation of dihydroxo species. Each MD run starts with the initial perturbation of the newly found intermediate, followed by the 100 ps simulation.

We let the system evolve freely, and add water molecules to the simulation box as needed for proceeding towards the expected final products. The initial configurations for every intermediate discussed below were obtained as snapshots of such MD trajectories.

The approach outlined above was, for instance, crucial to identify the involvement of the [Cu–H] species in the reaction mechanism, corresponding to the reaction intermediates III and IV, as well as adjacent transition states (see Fig. 1). Having known experimentally²⁵ and theoretically²⁶ that the reaction proceeds from the methoxy species (intermediate I) via the adsorbed methanol (intermediate II) to the release of hydrogen (intermediate V) and, finally, to the formation of the stable dihydroxo species (intermediate VI), we thus were able to identify important new reaction steps, directly responsible for facilitating the release of molecular hydrogen.

All identified configurations of reaction intermediates and the corresponding transition states were subsequently re-optimised at a DFT level, leading to the reaction pathway presented in Fig. 1. All energies are based on DFT calculations, and are given relative to the initial mono(μ -oxo)dicopper center, allowing direct comparison of the obtained thermodynamics with the originally proposed mechanism.^{25,26} Detailed technical details are given in the Computational Details section and Supporting Information.

Discussion of the reaction mechanism

We start our simulation with the methoxy species formed on the mono(μ -oxo)dicopper center (-54 kJ/mol, structure I in Fig. 1). The choice of the mono(μ -oxo)dicopper site was governed by the right stoichiometry, under the assumption that two aluminium atoms are present in the 8-member ring (8MR) channel of mordenite.^{6,10,11,13,18,32} The reaction starts with the adsorption of the first water molecule, stabilising the system by 38 kJ/mol (structure I' in Fig. 1), which is within the previously reported range of the heat of adsorption of water in zeolites.^{39,40} As Cu^I is known to react with water to a lesser extent than Cu^{II}, such

stabilisation is moderate, and is achieved through water molecules forming three hydrogen bonds with the framework oxygen atoms.

The first transition state subsequently corresponds to the activation of the first adsorbed water molecule on the copper atom, followed by the transfer of hydrogen to the methoxy species to form methanol (Scheme 2). The Gibbs free energy of this step (-70 kJ/mol) agrees with the previously identified energy change from the methoxy species to the adsorbed methanol (-75 kJ/mol²⁵). The corresponding transition state energy amounts to 72 kJ/mol. In order to follow the changes in the nature of chemical bonding of copper atoms, we calculate the electron binding energy of Cu $2p_{3/2}$ electrons using standard definitions of ionisation energies from respective core levels⁴¹ and summarise these data in Table 1. We have shown recently, that these values can be correlated to the formal oxidation state of copper atoms, as probed by the X-ray photoelectron spectroscopy (XPS).⁴² Thus, all intermediates between I (methoxy species) and II (hydroxy species) exhibit the formal oxidation state of copper $+1$.

Scheme 2: Reaction steps proceeding via TS1. Formation of methanol from methoxy species.

The reaction proceeds with the adsorption of the second water molecule, providing additional 36 kJ/mol of stabilisation (structure II' in Fig. 1). The second transition state corresponds to a hydrogen atom transfer from the Brønsted acid site of the zeolite framework via the second adsorbed water molecule to the Cu^I form of the active site (Scheme 3). Such a concerted transition state can be viewed as a (nearly) ring-like transfer of a proton

involving the adsorbed water molecule. Hydrogen atoms in such a system are extremely mobile and the proton exchange between the adsorbed water molecules and the surrounding zeolite framework is to be expected.⁴³ It should, however, be emphasized that this transition state has been identified under the assumption of the single barrier path connecting two adjacent local minima. Other alternative pathways between the intermediates II' and III could potentially exist, although none were identified in this study.

The calculation of the Cu $2p_{3/2}$ electron binding energies reveals an increase from 932.4 eV to 934.5 eV, the values typically found to correspond to Cu^I and Cu^{II} species, respectively.⁴⁴ The change of the oxidation state of copper atoms points to the electron transfer reaction, suggesting the transformation of the proton from the Brønsted acid site (H⁺) into the hydride ion (H⁻) stabilised over the copper species, i.e. [Cu-H]. This reaction step is completed with the desorption of methanol (endothermic by 47 kJ/mol, structure IV in Fig. 1) and the adsorption of the third water molecule (exothermic by 44 kJ/mol, structure IV' in Fig. 1).

Scheme 3: Reaction steps proceeding via TS2. Formation of copper hydride intermediate.

Recently, Kulkarni *et al.* have suggested that such [Cu-H] intermediates might exist in the case of copper-exchanged chabazite (Cu-SSZ-13).⁴⁵ Copper hydrides are known to encompass a broad array of applications in catalysis, among which a sunlight-induced hydrogen elimination from a copper hydride nanocluster is perhaps the most relevant to the present

study.⁴⁶ These reports are in line with the spectroscopic evidence of the presence of such intermediates in the process of reduction of Cu^{II} to Cu^I in zeolites by hydrogen,⁴⁷ as well as the works on the ability of silver hydrides in ZSM-5 zeolite to mediate transformations in the process of activation of methane.⁴⁸ According to Kulkarni *et al.*,⁴⁵ similar [Cu-H] species formed at the copper monomer species is about 100 kJ/mol higher in energy compared to the original copper monomers. Our calculations reveal the increase of relative energies up to 86 kJ/mol (from -124 kJ/mol to -38 kJ/mol, Fig. 1, structures II and IV). Crucially, the adsorption of water and/or methanol further decreases the energy of the system. As such, the observed transition state barrier of 105 kJ/mol, corresponding to the concerted transition of the hydrogen atom between the Brønsted acid site, water molecule, and the copper atom, is an upper limit estimate (see the discussion of the influence of the variable number of water molecules on the resulting energetics of the reaction in Section IV).

As discussed above, TS2 is facilitated by the Brønsted acid formed with the lattice oxygen atom. Brønsted acid sites have been shown in the literature to play an important role in the process of direct conversion of methane to methanol.⁴⁹⁻⁵³ In the original publication on the anaerobic methane oxidation we have reported that the number of observed Brønsted acid sites estimated from the infrared spectroscopy of adsorbed pyridine scaled linearly with the total number of methoxy surface species.²⁵ This indicates that the C-H bond cleavage coincides with methoxy and Brønsted acid site formation and a concerted reaction of copper core and zeolite framework. This was confirmed by DFT, showing that such a transfer is energetically favourable. Given the above evidence of the involvement of the Brønsted acid sites in the mechanism of the reaction, we are confident that the reaction pathway suggested in the current manuscript does not contradict the experimental findings.

Subsequent evolution of the system involves the approach of the third water molecule, which facilitates migration of the hydrogen atom of the hydroxy species towards the hydride of the [Cu-H] species (Scheme 4). Water helps bringing two hydrogen atoms together, but is not itself consumed during the reaction. This enables the formation of molecular hydrogen,

Scheme 4: Reaction steps proceeding via TS3. Formation of molecular hydrogen.

and concurrent reformation of the mono(μ -oxo)dicopper center. The intermediate V in Fig. 1 has an energy of -7 kJ/mol, which agrees reasonably well with the total energy of the reaction, taking into account the hydration effect of water. The corresponding transition state barrier amounts to 87 kJ/mol. The copper atoms of the active site of zeolite retain their formal oxidation state of +2 at this step, as evidenced by nearly constant values of the corresponding Cu $2p_{3/2}$ electron binding energies (934.5 eV vs. 934.6 eV for intermediates III and V, see Table 1).

Table 1: Calculated Cu $2p_{3/2}$ electron binding energies and formal oxidation states of copper atoms in the active site intermediates I to VI in Fig. 1.

Intermediate in Fig. 1	Name	Structure	Cu $2p_{3/2}$ BE, eV	Formal oxidation state of Cu
I & I'	methoxy		932.2	+1
II & II'	hydroxy		932.4	+1
III, IV, & IV'	hydride		934.5	+2
V	mono(μ -oxo)		934.6	+2
VI	dihydroxo		934.4	+2

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Figure 1: Mechanism of the anaerobic oxidation of methane to methanol involving [Cu–H] intermediates. Insets denoted with Roman numerals from I to VI and marked with black circles correspond to the main local minima. Insets denoted with the prime symbol and marked with green circles correspond to the intermediates stabilised with the adsorption of water. Insets marked by blue brackets correspond to transition states, with black arrows indicating the direction of the shift of the atoms involved in the transition. For clarity, only copper centers are shown, except for the TS2 and the intermediate II', where the Al atom next to the Brønsted acid site, involved in the hydrogen transfer, is also shown. All energies are given in kJ/mol and are relative to the mono(μ -oxo)dicopper center in the 8MR of CuMOR.

Finally, the adsorbed water on the mono(μ -oxo)dicopper species loses the hydrogen atom, leading to the formation of a stable hydrated Cu-(OH)₂-Cu dihydroxo species (Scheme 5). The corresponding transition state energy amounts to a mere 60 kJ/mol, which agrees well with the similar energy of the first transition barrier, as their nature is quite similar (water activation, followed by the proton transfer to another oxygen atom). The formal oxidation state of copper atoms remains +2.

Scheme 5: Reaction steps proceeding via TS4. Formation of dihydroxo species.

The energy of the final product corresponds to the energy of the reaction (+121 kJ/mol) plus the energy of formation of the dihydroxo species (−117 kJ/mol) plus the hydrogen bonds formed with the third water molecule (−44 kJ/mol).

Notably, all transition states involve the transfer of a hydrogen atom. The processes involving the transfer of a proton (H^+) to the nearest oxygen atom (as is the case for TS1 and TS4) have lower transition state barriers (~ 60 – 70 kJ/mol), while the processes involving the transfer of a hydride (H^-) leading to the formation of either a [Cu–H] species (TS2) or molecular hydrogen (TS3) have higher transition state barriers (~ 90 – 100 kJ/mol). As such, the formation of the hydride species and its transfer might correspond to the rate-limiting step of the overall reaction of the molecular hydrogen release. It seems plausible that the higher barriers might further be lowered by assuming a more complex transition state configuration, involving adjacent oxygen atoms, such as other water molecules in the same pore of zeolite.

Although the suggested reaction pathway involves a significant energy range, a careful thermodynamic analysis of the experimental feasibility of such process indicates that the surface concentrations of the reactants and products as well as the stabilising effect of addi-

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3 tional water molecules, as discussed in the original publications on the anaerobic oxidation of
4 methane to methanol,^{25,26} fully support the feasibility of the proposed reaction. The problem
5 of the favourable back rates of the reaction is resolved by the conditions of the reaction and
6 removal of the products, since the overall process proceeds step wise.²¹
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11 As mentioned in our original paper,²⁵ water does not only participate in the reaction
12 mechanism, but it also plays a dominant role in the stabilisation of the formed mono(μ -
13 oxo) copper core by introducing an enthalpic effect in addition to the entropic effect. The
14 formation of dihydroxo species provides an additional 117 kJ/mol of stabilisation energy.
15 The strong interaction of the Cu(II) species with water in zeolites is a unique feature, which
16 helps to thermodynamically drive the reaction. To remove excess water after the reaction,
17 the CuMOR material is typically purged in dry helium at a temperatures above 673 K. This
18 step is similar to the first activation of an as-made Cu/zeolite, where dehydration of Cu^{II}
19 species generates the active sites.
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29 The exact amount of consumed water under experimental conditions is of utmost interest
30 and can be theoretically analysed by constructing the isotherms of water adsorption on active
31 sites of zeolites according, for example, to the classical Langmuir model.^{54,55} A simplified
32 analysis has been carried out, as presented in Section S7. We found that the adsorption of
33 at least two water molecules at the same active site is compatible with typical experimental
34 conditions. It should be emphasized, that adsorption of water is not only possible on copper
35 active sites, but also on the zeolite framework itself. This dramatically increases the number
36 of easily accessible water molecules, already confined within the vicinity of the active sites,
37 and readily available for the reaction. Zeolites in general, including metal exchanged zeolites,
38 are known to have a very high water adsorption capacity.⁵⁶ For instance, in the work by Nan
39 et al.,⁵⁵ the maximum observed water adsorption capacity of silver-exchanged mordenite was
40 reported to be as high as 20 wt. %. For comparison, adsorption of two water molecules per
41 unit cell of our sample would be equivalent to only around 1.2 wt. %.
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Mechanism with multiple water molecules

In Section II we have analysed the reaction steps that implied gradual addition of water, with the maximum of three water molecules added to the system. Under real experimental conditions, however, water steam is purged through the system, making the presence of multiple water molecules possible at every stage of the reaction.⁵⁷ Such excess of water may influence the reaction barriers or even the reaction mechanism altogether. To test this, we add up to three additional water molecules at every step of the reaction, thus bringing the maximal total number of water molecules in the reaction mechanism from three (Fig. 1) to six (Fig. 2). In Fig. 2, each of the original intermediates I to VI are, therefore, now stabilised with additional one, two, or three water molecules, added at every step of the reaction beyond the three water molecules gradually added throughout the reaction pathway proposed above (structures I', II', and IV' in Fig. 1).

As discussed above, each water molecule is expected to lower the total energy of the system by 30–40 kJ/mol due to the formation of additional hydrogen bonds.^{39,40} Indeed, adding one extra water molecule at each step of the reaction (green line in Fig. 2) lowers the total energies of the five intermediates by 22 to 44 kJ/mol. Most importantly, adding one water molecule also reduces the transition energy barriers by 5 to 12 kJ/mol. Notably, the largest gain in energy of the transition states is observed in the case of transition states TS2 and TS3, corresponding to the migration of a H^- hydride to form a $[\text{Cu-H}]$ intermediate respectively molecular hydrogen, i.e. the steps that required overcoming the highest energy barriers in the originally proposed mechanism.

This trend is mostly maintained upon adding the second additional water molecule at every step of the reaction (cyan line in Fig. 2). The energies of the intermediates are further lowered by 17–41 kJ/mol, while the transition energy barriers are lowered by additional 6 and 13 kJ/mol in the case of TS1 and TS2, respectively. TS4 is lowered in energy by only 1 kJ/mol, while TS3 barrier is actually increased by 1 kJ/mol. Again, the largest gain is observed in the case of TS2, originally the highest transition state barrier.

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Figure 2: Mechanism of the anaerobic oxidation of methane to methanol involving [Cu–H] intermediates with multiple additional water molecules. The red pathway corresponds to the pathway with gradual addition of water (see Fig. 1). The green, cyan, and magenta pathways correspond to the reaction pathways with one, two, and three extra water molecules added at each step of the reaction compared to Fig. 1, respectively.

However, at this level of hydration the system clearly reaches a saturation point, corresponding to the total of five water molecules in the single pore of zeolite after the desorption of molecular hydrogen. While further addition of water (magenta line in Fig. 2) still lowers the total energy of the system by 22–58 kJ/mol (the highest energy gain is observed in the case of the formation of the last dihydroxo species), the transition state barriers actually increase. This increase is systematic, as it is observed for all four considered transition states, and amounts to noticeable 9–16 kJ/mol. Indeed, in the case of TS1 and TS4 the energy barriers are actually higher than those without extra water (red line in Fig. 2).

Figure 3: Comparison of the TS2 in the case of A) a single water molecule, and B) three additional water molecules in the same pore of zeolite. Arrows indicate the direction of the transfer of hydrogen atoms.

Such a saturation effect can be explained from the point of view of the increased complexity of the highly concerted transition states. While in the case of TS2 the original transition state already involves a concerted transition of a proton from the Brønsted acid site via the adsorbed water molecule to the copper atom (Fig. 3, A), the transition state corresponding to the presence of three extra water molecules involves exchange of protons between two additional water molecules at the same step of the reaction (Fig. 3, B). This leads to an overly complex process of hydrogen transfer and, ultimately, to the increased energy barriers and energetic hindering of the entire reaction.

Conclusions

A plausible mechanism for the formation of molecular hydrogen in the process of anaerobic oxidation of methane to methanol has been suggested based on *ab initio* simulations. In the process of conversion of a methoxy species to a dihydroxy dicopper site, up to four transition states are identified, all of which include a hydrogen atom transfer. The electronic nature of the transferred hydrogen atom influences the height of energy barriers. The processes involving the transfer of a proton (H^+) to the nearest oxygen atom have lower transition state barriers ($\sim 60\text{--}70$ kJ/mol), while the processes involving the transfer of a hydride (H^-) leading to the formation of either a $[\text{Cu}\text{--}\text{H}]$ species or a molecular hydrogen have higher transition state barriers ($\sim 90\text{--}100$ kJ/mol). Hydrogen bonds formed by the water molecules and the reaction products within the zeolite pore provide additional stabilisation of all intermediate structures, which allows constructing the reaction pathway with relatively low energy barriers.

The Brønsted acid site plays an important role in the process of anaerobic oxidation of methane to methanol, as it is involved in the concerted transition state facilitating the formation of a $[\text{Cu}\text{--}\text{H}]$ intermediate, crucial for the release of molecular hydrogen. The combination of the mobility of the Brønsted acid site's proton and the stability of the complexes with adsorbed water plays the key role in the proposed mechanism.

The currently proposed mechanism assumes the minimum of two water molecules required for the formation of one methanol and one hydrogen molecule (one water molecule for reoxidation of the active site and another for the formation of the dihydroxo species), with five water molecules yielding the lowest transition energy barriers overall, with the highest barrier of only 80 kJ/mol in this case, corresponding to the concerted transition state leading to the formation of a $[\text{Cu}\text{--}\text{H}]$ intermediate. Further increase of the amount of water influences the configurations of the transition states unfavourably, leading to the overly complex concerted transition states, resulting in energetic hindering of the reaction by making the abstraction of molecular hydrogen less likely.

Computational details

All ground-state total energy calculations in this work have been performed with the all-electron full-potential DFT code FHI-aims^{58,59} within the periodic boundary conditions model. Electronic exchange and correlation was treated on the hybrid functional level with the PBE0 functional.⁶⁰ All geometry optimisations were done with the “tier2” atom-centered basis set using “tight” settings for numerical integrations. Tkatchenko-Scheffler dispersion correction⁶¹ has been used to account for the van der Waals energies arising from the attraction between induced dipoles formed due to charge fluctuations in the interacting species. All geometries reported herein correspond to locally optimised intermediate configurations. If several local minima were identified for the intermediates, the one with lowest relative energy has been chosen.

All energy values are computed as free Gibbs energies corresponding to the experimental temperature of 473 K and a pressure of 7 bar. In the spirit of *ab initio* thermodynamics,⁶² we calculated the translational, rotational, and vibrational contributions to the Gibbs free energy according to the following formula:

$$G(T, p) = G_{\text{electr.}} + \sum_i \left\{ N_A \frac{\hbar v_i}{2} + RT \ln \left[1 - \exp \left(\frac{-\hbar v_i}{k_B T} \right) \right] \right\} - RT \ln \left(\frac{(2\pi k_B T m)^{3/2}}{h^3} \cdot \frac{k_B T}{p} \right) - RT \ln \left[\frac{8\pi^2}{\sigma} \left(\frac{2\pi k_B T}{h^2} \right)^{3/2} \cdot (I_A I_B I_C)^{1/2} \right], \quad (1)$$

where T is temperature, p – pressure, G – total Gibbs free energy, G_{electr} – electronic Gibbs free energy, N_A – Avogadro number, R – ideal gas constant, v_i – vibrational frequency with an index i , k_B – Boltzmann constant, h – Planck constant, $\hbar$ – reduced Planck constant, m – mass, σ – classical symmetry number, I_X – moments of inertia. The four terms of the right hand side of the equation correspond to the electronic, vibrational, translational, and rotational contributions to free energy, respectively. The first term of the vibrational free energy accounts for zero-point vibrations. The translational, rotational, and vibrational

contributions are easily calculated from the structural data and the calculated vibrational spectrum. The $G_{(\text{electr.})}$ term is then equal to the calculated total energy of the system.

DFT calculations presented in the current manuscript relied on the automatic optimisation of the spin states as implemented in the FHI-aims package. All intermediates presented correspond to the singlet spin states, consistent with the previously suggested spin state inversion after the formation of the methoxy species.^{35,63–65} For a detailed discussion of the spin states see Supporting Information, Section S1).

Due to a very big size of the unit cell (a periodic model of CuMOR features a unit cell consisting of 147 atoms and measuring $18.0 \times 20.0 \times 7.0 \text{ \AA}^3$) and the fact that all electrons are accounted for explicitly (1504 electrons in total), Brillouin zone integration is performed with a reciprocal space mesh consisting of only the gamma point.

All systems correspond to the periodic model of the mordenite structure, having 8- and 12-ring channels running parallel to the c axis, which are intersected by sinusoidal 8-ring channels that run parallel to the b axis. These form side pockets that connect the 12-ring channel with the 8-ring channel. There are two 12-ring and two 8-ring channels per unit cell of mordenite. Two symmetrically located aluminium atoms per 8-ring channel have been assumed (both occupying T2 sites), which corresponds to the Si/Al ratio of 11.

The reaction is considered to take place in the space of the 12 MR channels of MOR, with the relatively high concentration of framework Al found to stabilise copper oxo species in the 8 MR of the side pockets of mordenite.^{13,64} Alternative siting of copper in the 12 MR has been suggested by Zhao et al.,⁶⁶ but is not expected to yield qualitative difference to the presented mechanism (see Supporting Information, Section S2).

The nudged elastic band (NEB) method⁶⁷ as implemented in the ASE package⁶⁸ was used to find the transition paths and corresponding energy barriers between given initial and final states, which were defined as the locally optimised structures of adjacent reaction intermediates. A chain of 12 replicas of the system has been constructed for every transition-state calculation, and the forces were allowed to relax with a threshold of $0.05 \text{ eV/\AA}$. The two

states are assumed to be connected by a single barrier path. The stability of the identified local minima has been confirmed by vibrational frequency analysis, ensuring that no reported structures feature imaginary frequencies in vibrational spectra. All identified transition states involve the shift of the hydrogen atom, and have one imaginary vibrational frequency each, corresponding to the direction of such a shift.

All molecular dynamics (MD) simulations have been carried out using the FHI-aims package.⁵⁸ To model the interactions between atoms, all energies and forces were calculated at the level of PBE functional.⁶⁹ The Velocity Verlet algorithm⁷⁰ was used to integrate the equations of motion in the NVT ensemble. The length of time step was chosen as 1 fs. The Nosé-Hoover thermostat^{71,72} was used to conserve the temperature. The molecular dynamics simulation was used to generate the initial geometry guesses for the intermediates. For every step of the reaction, we started from the randomly disturbed structure, added another water molecule, equilibrated for 10 ps and then ran a simulation at 473 K using NVT ab initio molecular dynamics at the GGA level, then subsequently optimized the geometry and evaluated the energy with the PBE0 functional including Tkatchenko-Scheffler van der Waals (TS) corrections. All the geometries reported in the manuscript, and, most crucially, all the reported energetics (including the transition state barriers) were recomputed with the hybrid functional DFT. Initial perturbation was added to the system at the beginning of every MD simulation to accommodate possible transition state crossings. See Supporting Information, Section S3 for more details on the MD simulations.

For comparison, the electronic levels of Cu $2p_{3/2}$ electrons in various copper species were also systematically recomputed on the quantum mechanical level within the coupled cluster approach using single and double substitutions from the Hartree-Fock determinant (CCSD)⁷³ with a cc-pVDZ functional,⁷⁴ without ever obtaining any qualitative changes that would conflict with the conclusions deduced from the standard PBE0 calculations (see Supporting Information, Section S4). All CCSD calculations were done with the cluster models of the active sites in the corresponding pore of the zeolite, using the Gaussian16 suite.⁷⁵

Supporting Information

Discussion of the choice of the spin states of the reaction intermediates (Section S1). Discussion of the location of the copper dimer species within the zeolite pore (Section S2). Details of the MD simulations (Section S3). Comparison of PBE0 and CCSD calculated electron binding energies (Section S4). Important geometrical parameters of all reaction intermediates (Section S5). Analysis of the geometrical and electronic configuration of the [Cu–H] intermediate (Section S6). Analysis of the water content in the zeolite under reaction conditions (Section S7). Cartesian coordinates and lattice parameters of all identified intermediates and transition states in Fig. 1 (Section S8).

Acknowledgments

The authors acknowledge the use of the computing facilities of the Swiss National Supercomputing Centre (CSCS) within the s878 project, as well as the use of the Merlin5 cluster computer at Paul Scherrer Institut. We thank the Energy System Integration (ESI) platform of the Paul Scherrer Institute for financial support.

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Table of Contents Graphics