

# Water-involved methane selective catalytic oxidation by dioxygen over copper-zeolites

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**Abstract:** The selective oxidation of methane to methanol is a dream reaction of direct methane functionalization, which remains a key challenge in catalysis and a hot issue of controversy. Herein, we report the water-involved methane selective catalytic oxidation by dioxygen over copper-zeolites. At 573 K, a state-of-the-art methanol space-time yield of 543 mmol/mol<sub>Cu</sub>/h with methanol selectivity of 91 % is achieved with Cu-CHA catalyst. Temperature-programmed surface reactions with isotope labelling determine water as the dominating oxygen and hydrogen source of hydroxyl in methanol while dioxygen participates in the reaction through reducing to water. Spectroscopic analyses reveal the fast redox cycle of Cu<sup>2+</sup>-Cu<sup>+</sup>-Cu<sup>2+</sup> during methane selective oxidation, which is closely related to the high catalytic activity of Cu-CHA. Density functional theory calculations suggest that both CuOH monomer and dimer in Cu-CHA can catalyze the selective oxidation of methane to methanol with Cu-OOH as the key reaction intermediate, and meanwhile, various copper sites undergo interconversion under reaction conditions.

Methane, the main component of natural gas, is an abundant fossil resource widely distributed throughout the earth (1). In the energy-intensive industrial processes, methane is first converted to the syngas via reforming or partial oxidation (2), and then transformed to fuel and chemicals. By contrast, the direct functionalization of methane appears to be more intriguing; however, it is greatly challenged by the large C-H bond dissociation energy of 435 kJ/mol. Several strategies, for example the oxidative or nonoxidative coupling (3-5) and the dehydroaromatization (6, 7), have been developed for the direct transformation of methane to chemicals (8). The selective oxidation of methane to methanol triggers persistent interests because this type of oxidative C-H bond activation is thermodynamically favorable under relatively mild conditions. The dream reaction of methane-to-methanol (MTM) has been accomplished with molecular Periana catalyst (9) and its solid analogue (10) in strong acidic media via multistep oxyfunctionalization, which unfortunately suffers from both economic and environment concerns.

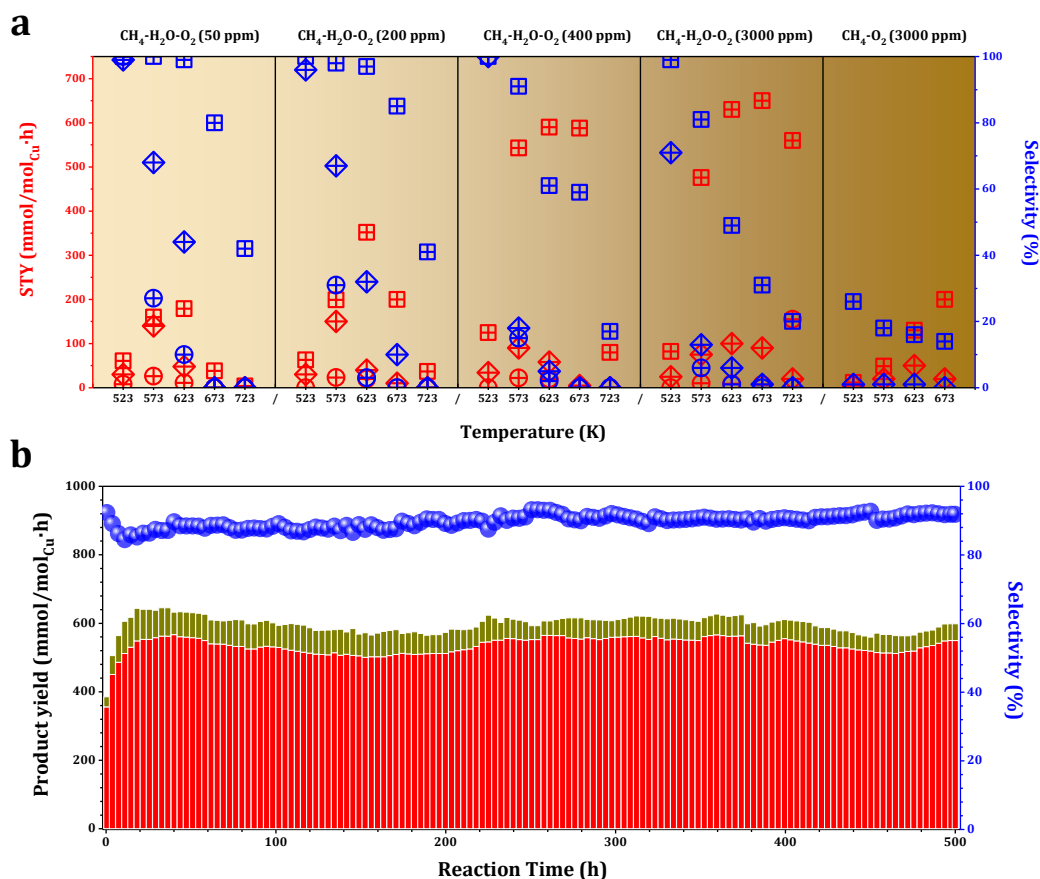
Inspired by nature methane monooxygenase (MMO) that can catalyze the oxidation of methane by dioxygen under ambient conditions (11), the first-row transition metal cations stabilized by zeolite matrix, for example iron-zeolites (12, 13) and copper-zeolites (14-24), and copper in metal-organic frameworks (25, 26) have been developed as candidate materials for MTM transformation. A stepwise strategy consisting of i) sample activation in dioxygen at high temperature, ii) methane introduction at low temperature and iii) product extraction with water steam, is commonly employed, which tactfully blocks the co-existence of methane and dioxygen and accordingly hinders the over-oxidation of methanol (16-21). However, this is a chemical looping process and the maximum productivity of methanol is self-limited in one complete cycle (typically a dozen hours). To establish a promising MTM transformation, a continuous catalytic process is desired (27) and several key requirements should be satisfied, namely i) the use of abundant and inexpensive oxidants like dioxygen, ii) a high selectivity to methanol, iii) a sustainable methane conversion rate, and iv) good catalyst stability during operation.

We report here the continuous production of methanol from methane selective

catalytic oxidation in the presence of water and dioxygen. With the elaborate optimizing of catalytic materials and reaction conditions, high methanol selectivity and space-time yield can be simultaneously achieved, which makes an important step forward for the oxidative functionalization of methane. A clear picture of MTM mechanism is depicted via the combination of spectroscopic analyses and theoretical calculations, which clarifies the current misunderstandings and will stimulate the further development of this dream reaction.

### **Catalytic performance of copper-zeolites in methane oxidation**

Copper-zeolites were prepared via wet ion-exchange (see supplementary materials for details, and Fig. S1-6 and Table S1 for preliminary characterization results) and applied in methane catalytic oxidation in the presence of water and dioxygen under different conditions. The reaction temperature was raised from 473 to 523~723 K to promote methane conversion, and meanwhile, the concentration of dioxygen was regulated (from impurities in methane and water, and extra dioxygen) to minimize byproduct carbon dioxide production. Cu-CHA, in significant contrast to other copper-zeolites such as Cu-MOR and Cu-MFI, exhibited remarkable catalytic activity in MTM (see catalyst and reaction condition optimization in Fig. S7-21). The catalytic performance of Cu-CHA was controlled by multiple factors, including but not limited to the reaction temperature, the dioxygen concentration and the space velocity.



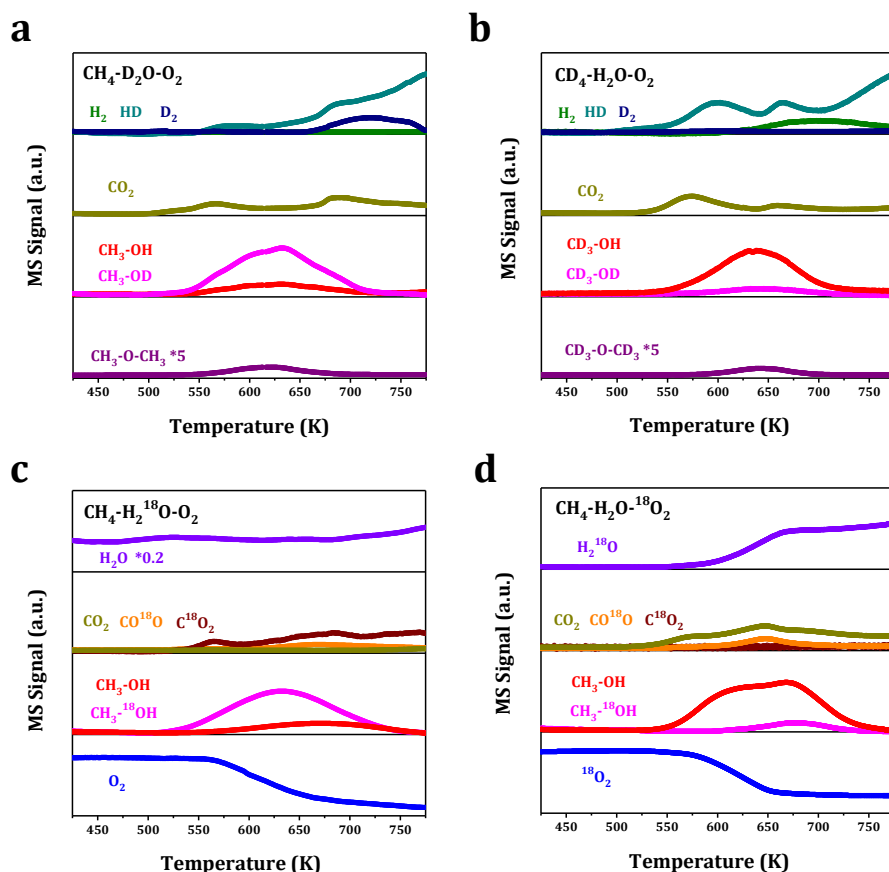
**Figure 1. Steady-state methane selective catalytic oxidation to methanol. (a):** Methane conversion on Cu-CHA (square), Cu-MOR (circle) and Cu-MFI (diamond) catalysts under different conditions. Typical reaction conditions: 0.1 g catalyst, total flowrate= 60 mL/min; 98% CH<sub>4</sub>, 0 or 2% H<sub>2</sub>O, 50~3000 ppm O<sub>2</sub>; **(b):** Time-on-stream behaviors of Cu-CHA in methane catalytic oxidation to methanol (red column) and carbon dioxide (yellow column). Reaction conditions: 0.1 g catalyst, total flowrate= 60 mL/min; 98% CH<sub>4</sub>, 2% H<sub>2</sub>O, 400 ppm O<sub>2</sub>, temperature= 573 K.

Experimentally, a methanol space time yield (STY) of 542 mmol/mol<sub>Cu</sub>/h (195 μmol/g<sub>cat</sub>/h) with methanol selectivity of 91 % was achieved at 573 K in the presence 2% water and 400 ppm dioxygen (Fig. 1a). This STY value is over an order of magnitude higher than previous reports on copper-zeolites in similar catalytic processes (Table S2). High reaction temperature of 573 K is crucial to trigger the fast Cu<sup>2+</sup>-Cu<sup>+</sup>-Cu<sup>2+</sup> redox cycle (vide infra) to promote methane conversion, and meanwhile

the extremely low dioxygen/methane ratio ( $<1/2000$ ) is the key to maintain the high selectivity toward desired product methanol. The time-on-stream behaviors of Cu-CHA in MTM were further investigated, and both the methanol selectivity and STY were amazingly stable in 500 hours' operation (Fig. 1b). These data clearly demonstrate the potential of a one-step catalytic process for the continuous production of methanol from methane selective oxidation. Since 2 % water was employed as the reagent, methanol aqueous solution with mass fraction of 1.2 % could be obtained from MTM (Fig. S22) and it is valuable for further utilization.

### **Isotope labelling of reaction pathway**

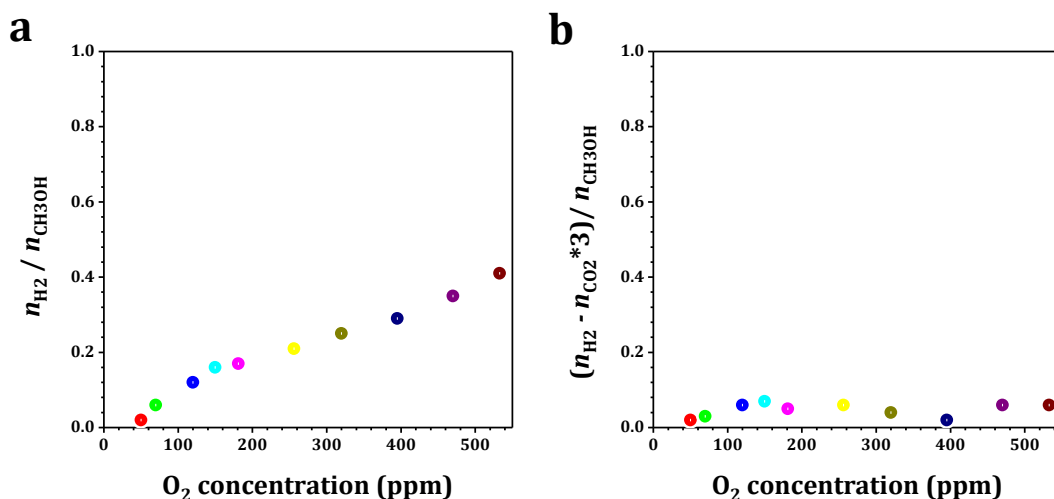
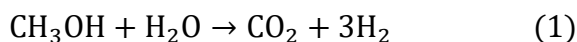
For insight into the reaction pathway of MTM, temperature-programmed surface reactions (TPSR) with isotope labelling were performed. In the TPSR mode, methane oxidation started at  $\sim 523$  K, generating methanol as the desired product and carbon dioxide as the byproduct on Cu-CHA in the presence of water and dioxygen (Fig. S23; carbon dioxide was detected as the dominating product on Cu-MOR and Cu-MFI, Fig. S24 & S25). Dihydrogen was also detected in the outlet, but its amount was lower than methanol and slightly lagged behind methanol. In the absence of water, carbon dioxide was detected as the dominating product and trace methanol could be detected at above 673 K when water was produced from methane total oxidation (Fig. S26), indicating the key role of water in MTM. With  $^{13}\text{CH}_4$  as the isotopically labelled reagent, the carbon source of methanol and carbon dioxide was definitely confirmed to be methane (Fig. S27).



**Figure 2. Temperature-programmed surface reactions of methane oxidation on Cu-CHA with isotope labelling. (a):  $\text{CH}_4\text{-D}_2\text{O-O}_2$  system; (b):  $\text{CD}_4\text{-H}_2\text{O-O}_2$  system; (c):  $\text{CH}_4\text{-H}_2^{18}\text{O-O}_2$  system; (d):  $\text{CH}_4\text{-H}_2\text{O-}^{18}\text{O}_2$  system. Reaction conditions: 0.1 g catalyst, total flowrate= 60 mL/min; 98% methane, 2% water,  $400\pm 50$  ppm dioxygen.**

Deuterium labelling experiments ( $\text{D}_2\text{O}$  as reagent in Fig. 2a and  $\text{CD}_4$  as reagent in Fig. 2b) indicated that the hydrogen in the hydroxyl of methanol dominantly came from water while the dihydrogen was apparently produced via the combination of hydrogen abstracted from methane and dissociated from water. Subsequently,  $^{18}\text{O}$  labelling experiments were performed to reveal the active oxidant in MTM. With  $\text{H}_2^{18}\text{O}$  as the isotopically labelled reagent (Fig. 2c),  $\text{CH}_3^{18}\text{OH}$  was observed as the dominating product together with significant amount of  $\text{CH}_3\text{OH}$  due to the presence of non-labelled water in the reaction system. It seems that water acted as the dominating oxidant in methane conversion. The absence of non-labelled  $\text{CO}_2$  ruled out the direct oxidation of methane by dioxygen, and the  $\text{C}^{18}\text{O}_2$  and  $\text{CO}^{18}\text{O}$  should come from the  $\text{CH}_3^{18}\text{OH}$

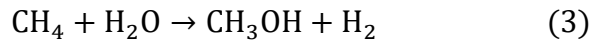
reforming (major route, Equation 1) and oxidation (minor route, Fig. S28, Equation 2), respectively. Meanwhile, the consumption of non-labelled dioxygen was observed at >573 K, confirming the participation of dioxygen in MTM. With  $^{18}\text{O}_2$  as the isotopically labelled reagent (Fig. 2d), the oxygen in methanol product was further confirmed to be from water and the carbon dioxide byproduct mainly from methanol reforming. The consumption of  $^{18}\text{O}_2$  and the formation of  $\text{H}_2^{18}\text{O}$  were observed at >573 K, demonstrating the pathway of dioxygen participation in the reaction.



**Figure 3. Dihydrogen production during methane selective oxidation catalyzed by Cu-CHA zeolite. (a):** Effect of dioxygen concentration in the reaction system on the ratio of dihydrogen to methanol in the product; **(b):** Effect of dioxygen concentration in the reaction system on the ratio of dihydrogen to methanol in the product with the secondary reforming of methanol excluded. Reaction conditions: 0.1 g catalyst, total flowrate= 60 mL/min; 98%  $\text{CH}_4$ , 2%  $\text{H}_2\text{O}$  50~550 ppm  $\text{O}_2$ , He balance.

According to the TPSR results, both water and dioxygen participate in the MTM reaction. Providing methane is oxidized by water, dihydrogen should be produced together with methanol with stoichiometric ratio of 1 (Equation 3). However, the ratio

of dihydrogen to methanol was far below 1 and also depended on the concentration of dioxygen in the reaction system (Fig. 3a), i.e.  $n_{\text{H}_2}/n_{\text{CH}_3\text{OH}}$  ratio increased with increasing dioxygen concentration from 50 to 550 ppm (high methanol selectivity of >85% was achieved in all cases). Considering that methanol could be further transformed to carbon dioxide via secondary reforming (Equation 1), the dihydrogen contribution from reforming was further deducted to give the intrinsic  $n_{\text{H}_2}/n_{\text{CH}_3\text{OH}}$  ratio in methane selective oxidation. It is amazing to reveal that only very low amount of dihydrogen was produced along with methanol formation, i.e.  $(n_{\text{H}_2} - n_{\text{CO}_2} * 3) / n_{\text{CH}_3\text{OH}} < 0.1$ , at all dioxygen concentrations of 50~550 ppm. That is, dihydrogen was mainly produced from secondary methanol reforming instead of methane direct oxidation, in good agreement with the lagged formation of dihydrogen (Fig. S23). Now, we can present a picture of MTM pathway in the presence of water and dioxygen (shown as [O] for simplicity), as shown in Equation 4. From the view of element balance, methane can be oxidized by [O], but the presence of water is essential to initiate the reaction and becomes the main source of oxygen in methanol.

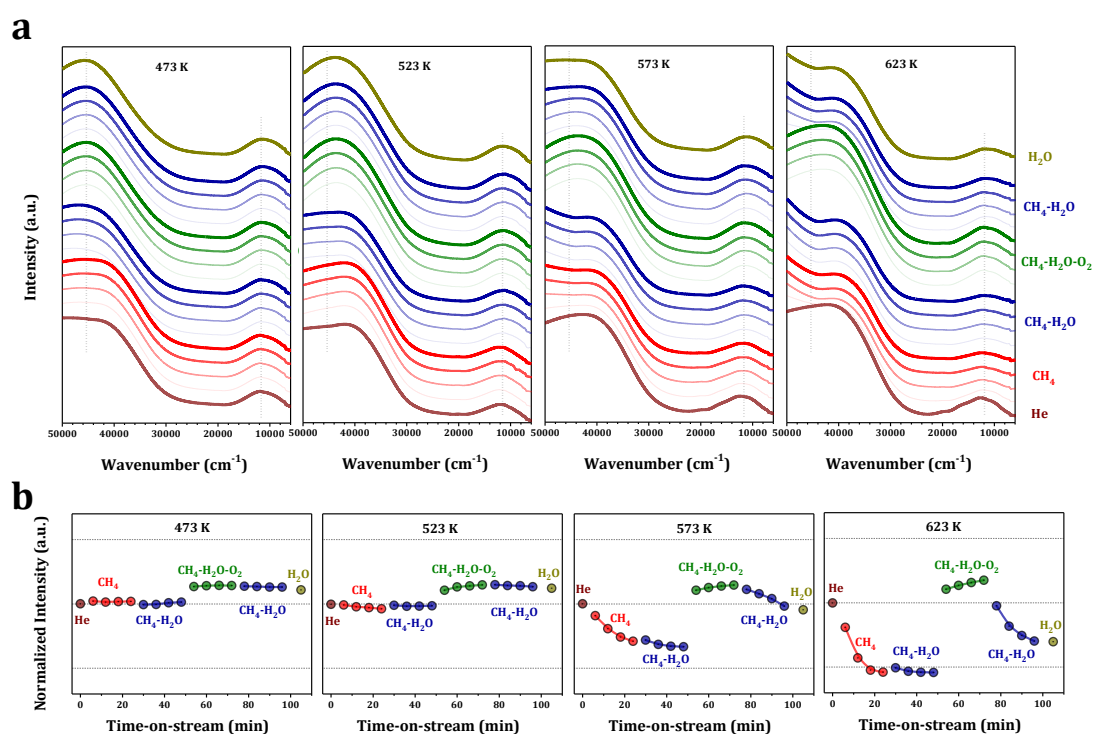


### Dynamic changes in copper sites during reaction

The active copper sites in Cu-zeolites for MTM have been hotly debated (14, 16-20, 28-32). The topology and composition of zeolite host show significant impacts on the structure of copper sites, which also undergo dynamic changes under various conditions (33-35). Here, the dynamic changes of copper sites in CHA under reaction relevant conditions were investigated by ultraviolet-visible-near infrared (UV-Vis-NIR) spectroscopy. The spectrum of Cu-CHA (473 K in He, Fig. S29) showed clear d-d transitions of  $\text{Cu}^{2+}$  ( $3d^9$ ) at  $\sim 12000 \text{ cm}^{-1}$  and ligand-to-metal charge transfer (LMCT) transitions of isolated  $\text{Cu}^{2+}$  ( $\text{O}^{2-}\text{Cu}^{2+} \rightarrow \text{O}^-\text{Cu}^+$ ) at  $50000 \sim 45000 \text{ cm}^{-1}$  (36-38). The Cu-CHA sample was then treated in different atmospheres at increasing temperature from 473 to 773 K to demonstrate the dynamic changes of copper sites (Fig. S30).



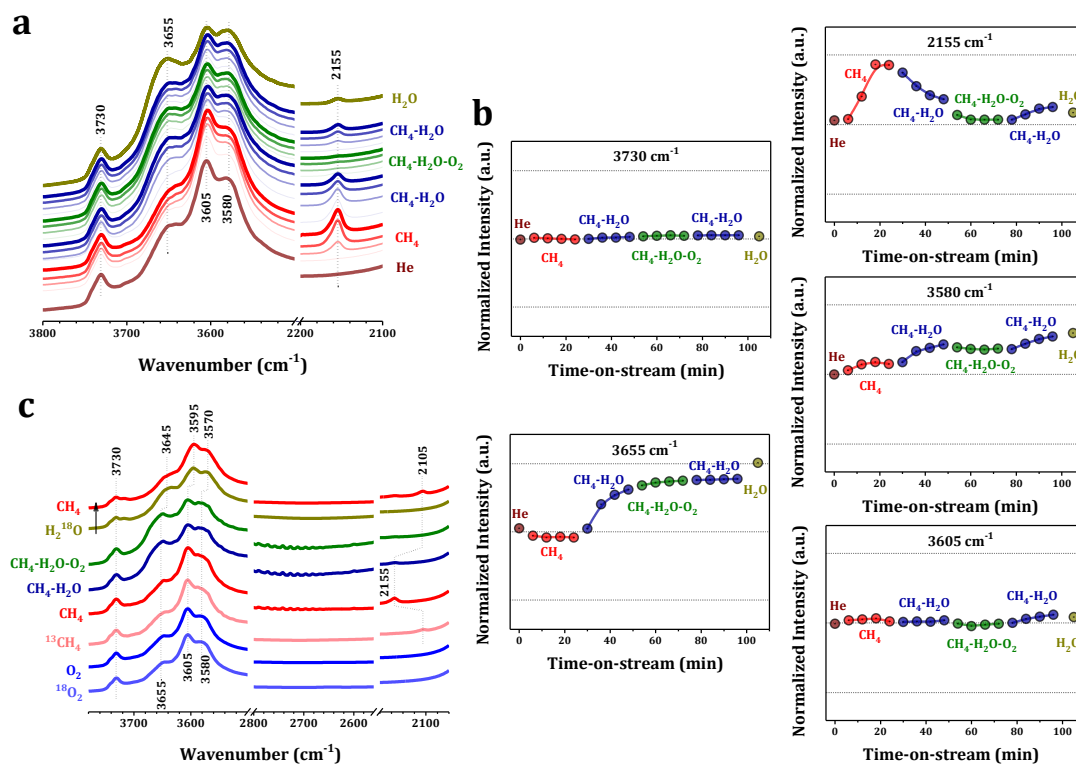
Treating in oxygen or water resulted in a slight increase in the intensity of band at  $12000\text{ cm}^{-1}$  and noticeable shifts in the band at  $40000\sim 30000\text{ cm}^{-1}$ , probably due to the reconstruction and creation of a small quantify of isolated  $\text{Cu}^{2+}$  species. Treating in methane resulted in significant declines in the intensities of bands at  $12000\text{ cm}^{-1}$  and  $50000\sim 45000\text{ cm}^{-1}$ , due to the reduction of  $\text{Cu}^{2+}$  in methane. The charge transfer transitions of  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  were highly overlapped and their interpretation might be misleading, while the decline in the intensity of band at  $12000\text{ cm}^{-1}$  clearly revealed the reduction of isolated  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  since no d-d transitions occur for  $\text{Cu}^+$  with fully occupied d shell (37). Interestingly, the  $\text{Cu}^+$  could be readily oxidized back to  $\text{Cu}^{2+}$  in  $\text{H}_2\text{O}-\text{O}_2$  at  $573\text{ K}$  (Fig. S31). That is, a redox cycle of  $\text{Cu}^{2+}-\text{Cu}^+-\text{Cu}^{2+}$  in Cu-CHA might involve in the reaction system of  $\text{CH}_4-\text{H}_2\text{O}-\text{O}_2$ .



**Figure 4. UV-Vis-NIR spectroscopic analyses of copper sites in Cu-CHA zeolite.**

(a): In situ UV-Vis-NIR spectra of Cu-CHA sample under different atmospheres at  $473\sim 623\text{ K}$ . Conditions:  $25\text{ mg}$  catalyst, total flowrate =  $15\text{ mL/min}$ ; 0 or 98%  $\text{CH}_4$ , 0 or 2%  $\text{H}_2\text{O}$ , 0 or 400 ppm  $\text{O}_2$ , He balance; (b): Dynamic changes in the intensities of absorption band at  $\sim 12000\text{ cm}^{-1}$ .

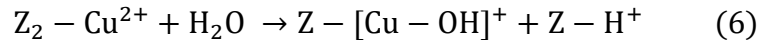
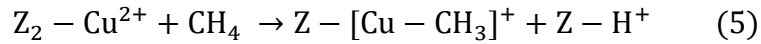
The dynamic changes of copper species in Cu-CHA under different atmospheres at a constant temperature were then focused. At low temperatures of 473 and 523 K, the introduction of dioxygen ( $\text{CH}_4\text{-H}_2\text{O-O}_2$ ) resulted in the oxidation of  $\text{Cu}^+$  species (those existed in parent Cu-CHA due to the auto-reduction of  $\text{Cu}^{2+}$  in helium) to  $\text{Cu}^{2+}$ , while the  $\text{Cu}^{2+}$  species were quite stable in  $\text{H}_2\text{O}$  or  $\text{CH}_4\text{-H}_2\text{O}$  (Fig. 4a). At high temperatures of 573 and 623 K, the dynamic changes of copper species between the isolated  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  under different atmospheres were clearly demonstrated (Fig. 4b). Typically, isolated  $\text{Cu}^{2+}$  species in Cu-CHA were quickly (partially) reduced by methane to  $\text{Cu}^+$ , which could not be oxidized back to  $\text{Cu}^{2+}$  simply by water. On the other hand, the introduction of trace dioxygen resulted in the fast re-oxidation of  $\text{Cu}^+$  to  $\text{Cu}^{2+}$ . According to these results, isolated copper species should exist in the form of stable  $\text{Cu}^{2+}$  in Cu-CHA in  $\text{CH}_4\text{-H}_2\text{O-O}_2$  at 473~623 K and the fast redox cycle of  $\text{Cu}^{2+}\text{-Cu}^+\text{-Cu}^{2+}$  should involve in MTM reaction at 573~623 K. This should be the key reason for the much higher MTM activity achieved in this study in comparison with literature reports under slightly different reaction conditions (23, 24). Besides, no fingerprint absorption features for dicopper species in the region of 20000~25000  $\text{cm}^{-1}$  (28, 29) were observed under all employed conditions.



**Figure 5. FTIR spectroscopic analyses of Cu-CHA zeolite.** (a): In situ FTIR spectra of Cu-CHA sample under different atmospheres at 573 K. Conditions: 25 mg catalyst, total flowrate= 15 mL/min; 0 or 98% CH<sub>4</sub>, 0 or 2% H<sub>2</sub>O, 0 or 400 ppm O<sub>2</sub>, He balance; (b): Dynamic changes in the intensities of selected FTIR bands; (c): Steady-state FTIR spectra of Cu-CHA sample under different atmospheres with isotope labelling at 573 K. Conditions: 25 mg catalyst, total flowrate= 15 mL/min; 0 or 98% methane, 0 or 2% water, 0 or 400±50 ppm dioxygen.

For more information on Cu-CHA for MTM, in situ FTIR spectroscopic analyses were performed at 573 K. As shown in Fig. 5a, several IR bands at 3730, 3655, 3605 and 3580 cm<sup>-1</sup> were observed for Cu-CHA in flowing helium, due to Si-OH, Cu(II)-OH, two types of Si-OH-Al species, respectively (34, 39). The Si-OH was very stable under different atmospheres and regarded as a reference for quantitative analyses (Fig. 5b). Feeding methane to Cu-CHA resulted in the quick appearance of IR band at 2155 cm<sup>-1</sup> due to the formation of carbonyl group on Cu<sup>+</sup> (40), and the carbonyl group could be employed as in situ probe to titrate Cu<sup>+</sup> centers. The intensity of IR band at 2155 cm<sup>-1</sup> decreased gradually with the introduction of water (CH<sub>4</sub>-H<sub>2</sub>O) and disappeared with the

further introduction of dioxygen (CH<sub>4</sub>-H<sub>2</sub>O-O<sub>2</sub>). Removal of the O<sub>2</sub> from CH<sub>4</sub>-H<sub>2</sub>O-O<sub>2</sub> stream resulted in the reappearance of Cu<sup>+</sup> centers. These results agree well with the dynamic changes of copper sites as revealed by in situ UV-Vis-NIR spectroscopy (Fig. 4). Meanwhile, a noticeable increase in the intensity of Brønsted acid sites in the six-membered rings (3580 cm<sup>-1</sup>) was observed upon methane activation, following the possible pathway of Equation 5 (Z: Zeolite Si-O-Al site). To confirm the hypothesis, CD<sub>4</sub> was fed to Cu-CHA and the formation of deuterated Brønsted acid sites at 2640 cm<sup>-1</sup> could be identified (Fig. S32). With the introduction of water (CH<sub>4</sub>-H<sub>2</sub>O), the intensities of IR bands due to the Brønsted acid sites in the six-membered rings (3580 cm<sup>-1</sup>) and Cu(II)-OH (3655 cm<sup>-1</sup>) increased synchronously due to the hydrolysis of bare copper sites (Equation 6).

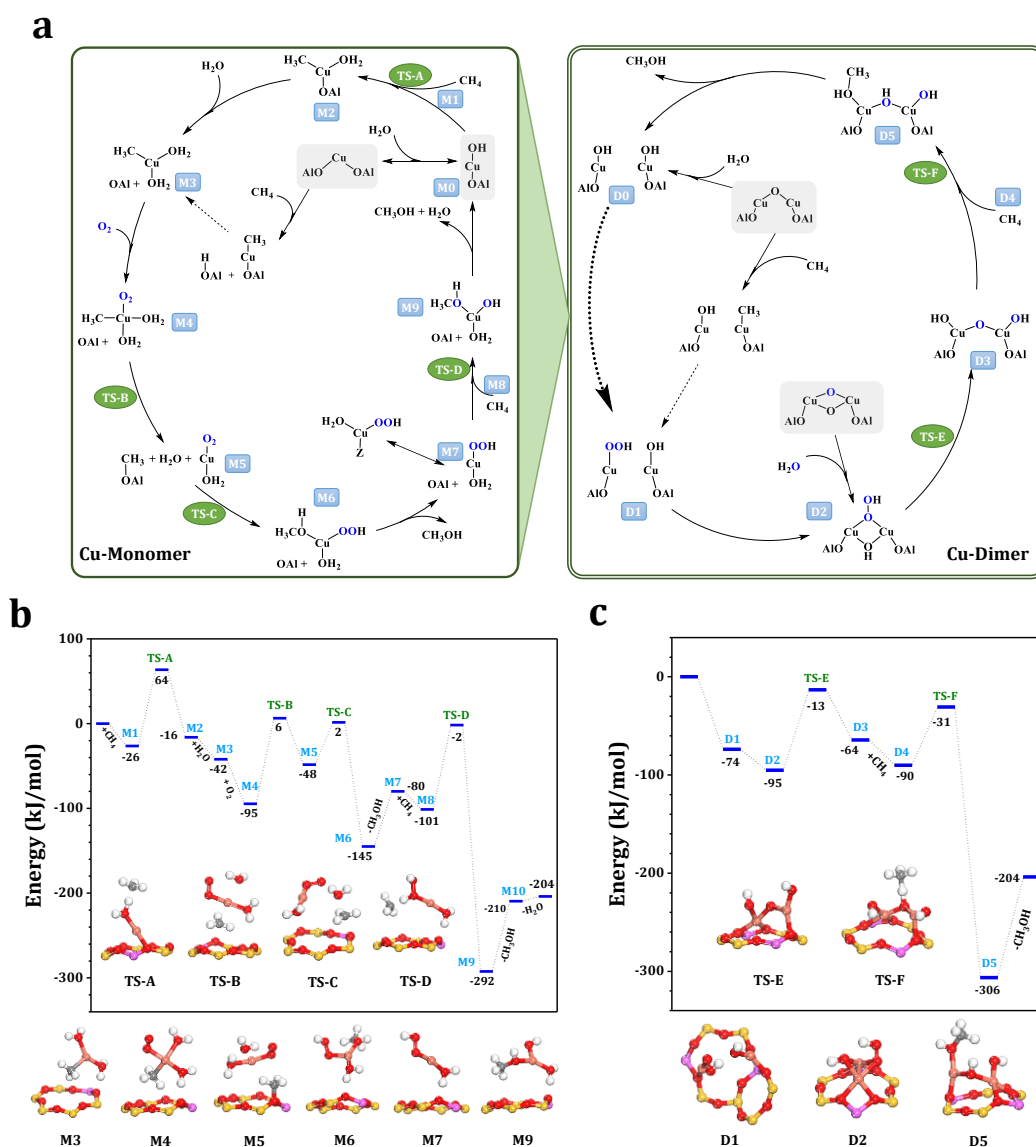


The steady-state FTIR spectra of Cu-CHA sample under different atmospheres were then recorded. As shown in Fig. 5c, treating in isotope-labelled <sup>18</sup>O<sub>2</sub> did not bring about significant changes in the structure of Cu-CHA, excluding the gas-phase oxygen isotope exchange by dioxygen. In contrast, treating in H<sub>2</sub><sup>18</sup>O resulted in the oxygen isotope exchange in Si-OH-Al (from 3605 and 3580 cm<sup>-1</sup> to 3595 and 3570 cm<sup>-1</sup>, respectively) and Cu(II)-OH groups (from 3655 cm<sup>-1</sup> to 3645 cm<sup>-1</sup>) with  $v_{O-H}/v_{18O-H}$  of ~1.003. That is, the active hydroxyls can undergo fast isotope exchange with water. Feeding methane to the <sup>18</sup>O-exchange Cu-CHA led to the formation of <sup>18</sup>O-carboxyl group (band at 2105 cm<sup>-1</sup>,  $v_{C-O}/v_{C-18O} = 1.024$ ) on Cu<sup>+</sup> sites, in accordance with the appearance of <sup>13</sup>C-carboxyl group at 2107 cm<sup>-1</sup> upon feeding <sup>13</sup>CH<sub>4</sub> to Cu-CHA ( $v_{C-O}/v_{13C-O} = 1.023$ ).

### Reaction mechanism of methane-to-methanol

Following nature particulate MMO (pMMO), the dicopper sites in zeolites have been proposed for methane oxidation to methanol via a chemical looping process. However, it has been recently argued that the pMMO contains only mononuclear copper centers (41). Experimentally, there were no signs of dicopper sites in our Cu-CHA under all

conditions employed (Fig. 4a). The dicopper sites, even if might exist under certain conditions, would undergo hydrolysis to monomeric copper species in excess water. A series of Cu-CHA samples with different copper loadings were further prepared and their specific activity was compared. As shown in Fig. S33, the site specific methanol yields were in the similar high level of 400~600 mmol/mol<sub>Cu</sub>/h at copper loadings of 0.6~2.3 wt.% while the methanol yield decreased to <300 mmol/mol<sub>Cu</sub>/h with further increasing copper loading to 3.5 wt.%. In this context, it is rational to propose monomeric copper species, i.e. Cu(II)-OH observed by FTIR spectroscopy (Fig. 5), as the catalytically active sites for MTM, although the formation of dicopper sites could not be fully excluded.



**Figure 6. Reaction mechanism from DFT calculations. (a):** Proposed reaction mechanism for the methane oxidation to methanol reaction on Cu-CHA involving CuOOH intermediate; **(b):** Energy profile of methane selective oxidation to methanol catalyzed by CuOH monomer in CHA at 0 K; **(c):** Energy profile of methane selective oxidation to methanol catalyzed by CuOH dimer in CHA at 0 K.

Finally, the complete reaction mechanism for MTM conversion was proposed from spin-polarized density functional theory (DFT) calculations to rationalize the above experimental observations. As shown in Fig. 6a, CuOH monomer or dimer was set as the intrinsic active sites for MTM conversion. Regarding the structure evolution and the energy variation at CuOH monomer (Fig. 6b, Fig. S34), the activation of methane (**TS-A**, 90 kJ/mol) and the subsequent adsorption of water resulted in the formation of mobilized  $\text{CH}_3\text{Cu}[\text{OH}_2]_2$  cation in the cage of CHA zeolite (**M3**). Dioxygen molecule was demonstrated to chemically adsorb on  $\text{Cu}^+$  center to form four-coordinated Cu complex (**M4**). Interestingly, the framework-bound methoxide ( $\text{ZCH}_3$ ) could be obtained via demethylation (**TS-B**) accompanied by the formation of two-coordinated  $\text{H}_2\text{OCuO}_2$  complexes (**M5**). Methanol could then be produced by the typical methylation (**TS-C**) between methoxide and adjacent  $\text{H}_2\text{O}$ , leaving H atom to  $\text{H}_2\text{OCuO}_2$ . The energy barriers in both steps were 101 and 50 kJ/mol, respectively. The adsorbed dioxygen was found to play an important role to maintain the coordination structure of Cu complex and facilitate the formation of methanol from water. Framework-bound CuOOH or hydrated CuOOH (**M7**) was identified as the key intermediate in the MTM reaction pathway catalyzed by CuOH. The CuOOH was also active for methane (**TS-D**, 99 kJ/mol) to produce methanol and regenerate CuOH active center. Dioxygen served as the explicit oxidant for C-H activation in these steps. In the case of CuOH dimer evolution (Fig. 6c, Fig. S35), one CuOH was assumed to follow the aforementioned CuOH monomer pathway, generating CuOOH in close proximity to another CuOH site in zeolites. If appropriate in distance, more stable binuclear Cu complex (**D2**) could be formed. The feasible breaking of O-OH bond in CuOOH (**TS-E**, 82 kJ/mol) led to the formation of immobilized  $\text{OHCuOCuOH}$  complex (**D3**). The activation of methane by

OHCuOCuOH (**TS-F**) only needed to overcome a low barrier of ~59 kJ/mol to produce methanol and to regenerate CuOH dimer. Comparing the kinetics in Cu monomer and dimer pathways (**TS-D** versus **TS-F**), it seemed that HOCuOCuOH might be more active than CuOOH for methane activation. Herein, we would like to highlight that CuOH and the previous proposed active species like Cu(II), CuOCu, CuOOCu could be readily interconverted by the participation of methane or water (Fig. 6a, Figs. S36-39). The proposed reaction pathway originated from CuOH provides an alternative to produce methanol without dihydrogen (Fig. 3b) and reveals the direct role of dioxygen in MTM conversion. In the experiments, the fast redox cycle of  $\text{Cu}^{2+}$ - $\text{Cu}^+$ - $\text{Cu}^{2+}$  during MTM reaction was clearly identified (Fig. 4) and the presence of  $\text{Cu}^+$  was proved to be necessary for the chemisorption of dioxygen by theoretical calculations (Fig. 6). That is, the fast redox cycle of  $\text{Cu}^{2+}$ - $\text{Cu}^+$ - $\text{Cu}^{2+}$  is the origination of the high activity of Cu-CHA under our reaction conditions. According to theoretical calculations, the oxygen in methanol might come from both water and dioxygen (see dioxygen labelling in Fig. 6a), while the fast oxygen isotope exchange between CuOH and water (Fig. 5c) made water as the apparent oxygen source of methanol (Fig. 2c, 2d). Water is known as a must for the methane-to-methanol conversion while it plays an important role in the catalytic route by hydrolyzing the Cu-O bond, which resulted in the formation of mobilized  $\text{CH}_3\text{Cu}[\text{OH}_2]_2$  cations from framework-bound species and the transformation of dicopper species (CuOCu, CuOOCu) to monomeric copper species (CuOH).

## Conclusions

A catalytic route of methane selective oxidation to methanol in the presence of water and dioxygen was demonstrated, and the specific roles of water and dioxygen were clearly explicated. With the elaborate optimizing of catalyst and reaction parameters, a state-of-the-art methanol space-time yield of 543 mmol/mol<sub>Cu</sub>/h with methanol selectivity of 91 % was achieved at 573 K with a Cu-CHA catalyst. The reaction pathway of MTM was established by kinetic analyses with isotope labelling. The apparent oxygen and hydrogen source of hydroxyls in methanol was determined to be water while dioxygen indeed participated in the reaction through reducing to water,

resulting in the unique process of water-involved methane oxidation by dioxygen. The fast redox cycle of  $\text{Cu}^{2+}$ - $\text{Cu}^+$ - $\text{Cu}^{2+}$  was identified by in situ spectroscopy under certain reaction conditions and revealed to be closely related to the high catalytic activity of Cu-CHA.

On the basis of all the experiment fragments, a detailed mechanism of MTM was interpreted via density functional theory calculations. Both CuOH monomer and dimer in Cu-CHA could catalyze the selective oxidation of methane to methanol, with CuOOH as the key intermediate. The previous proposed active species like Cu(II), CuOH, CuOCu and CuOOCu could be readily interconverted with the participation of methane or water under reaction conditions. These findings have addressed most misconceptions in MTM reaction over copper-zeolites (42) and will make a major step forward in methane oxidative functionalization.

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### **Author Contributions**

L.S. and Y.W. conducted material preparations, performance tests and spectroscopic analyses. C.W. and Z.X. contributed to theoretical calculations and directed the theoretical section. N.G. analyzed the data and provided helpful discussions. L.L. directed and supervised the project. L.S., C.W. and L.L. prepared the manuscript.

### **Competing Interests**

The authors declare no competing financial interests.

### **Additional information**

**Supplementary Materials** is available for this paper, including Materials and Methods, Figures S1-S39, Tables S1-S2.

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