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Oxygen-Promoted Methane Activation on Copper

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ABSTRACT

The role of oxygen in the activation of C-H bonds in methane on clean and oxygen pre-covered Cu(111) and Cu₂O(111) surfaces was studied with combined in situ near-ambient-pressure scanning tunneling microscopy and X-ray photoelectron spectroscopy. Activation of methane at 300 K and “moderate pressures” was only observed on oxygen pre-covered Cu(111) surfaces. Density functional theory calculations reveal that the lowest activation energy barrier of C-H on Cu(111) in the presence of chemisorbed oxygen is related to a two-active-site, four-centered mechanism, which stabilizes the required transition-state intermediate by dipole-dipole attraction of O-H and Cu-CH₃ species. The C-H bond activation barriers on Cu₂O(111) surfaces are large due to the weak stabilization of H and CH₃ fragments.

INTRODUCTION

Conversion of methane to value-added commodity chemicals is highly desirable in industry^{1,2}. One critical step in these processes is the activation of C-H bonds due to their high molecular stability and the relatively large bond energy (440kJ/mol)^{3,4}. For instance, the chemical vapor deposition of graphene on metals^{5,6}, semiconductors^{7,8} or dielectric surfaces^{9,10} by using methane as the carbon feedstock requires high temperature pyrolysis or assistance of plasma enhancement to break the C-H bond¹¹. The calculated activation energy of the initial reaction rate from CH₄ to CH₃ on Cu(111) surface is 1.77 eV (170.8 kJ/mol)¹². However, in the presence of oxygen, the activation energy for the initial step in dissociation of methane decreases to 125 kJ/mol with an oxygen coverage of 0.5 ML on the Cu(100) surface¹³. Density functional theory (DFT) calculations show that adsorbed oxygen shifts the highest occupied molecular orbital (HOMO) peak of CH₃ closer to the Fermi level of Cu, Ag, and Au, and hence these surfaces with pre-covered oxygen promote CH₄ dissociation dramatically¹⁴. Theoretical studies suggest that chemisorbed oxygen species or lattice oxygen in metal oxides, such as CuO, can abstract the hydrogen from C-H and lower the activation energy barrier¹⁵. The presence of O*- and OH*- species can promote C-H activation of methane on noble metal surfaces with barriers that are 0.4-1.5eV lower than on clean metals¹⁶. The formation of CH₃* and OH*, instead of CH₃* and H*, during O-promoted C-H activation leads to lower activation barriers¹⁷. Furthermore, the presence of oxygen on copper foil surfaces can passivate active sites and decrease nucleation density during graphene synthesis, which facilitates the growth of large-scale crystalline graphene and changes the growth kinetics from edge-attachment-limited to diffusion-limited¹⁸. The continuous supply of oxygen during chemical vapor deposition of graphene on copper can also accelerate its growth rate to 60μm/s¹⁹. Oxygen can also intercalate between the 1st graphene layer and the copper substrate, and then promote the diffusion of carbon atoms underneath the 1st layer to form large domains of the 2nd layer²⁰. However, the growth mechanism and the role of oxygen played during the methane decomposition on copper is still in dispute^{21,22}. Thus, gaining a fundamental understanding of the methane activation process and of the role that oxygen plays during methane dissociation is crucial in controlling graphene growth.

Although direct coupling of methane either in the absence of oxygen (pyrolysis)²³, or in the presence of oxygen (oxidative coupling)²⁴ has been extensively studied, the active surfaces, and the selectivity leading to different species²⁵, as well as the mechanism governing each processes have not been fully clarified. Oxidized copper clusters supported in zeolites have been suggested to be active species in partial oxidation of methane to methanol²⁶. Copper catalysts are quite easily to be oxidized in atmosphere; therefore, the study of the activation of alkanes on oxidized copper is of high relevance. It is also necessary to bridge the gap between the controlled experiments in ultra-high vacuum (UHV) and the studies aiming to capture the intermediates in real working conditions²⁷. Moreover, different preparation approaches also generate various copper oxides which exhibit distinct activities, and hence the understanding at atomic scale is required to reveal the underlying mechanism. In this study, by using in-situ ambient-pressure scanning tunneling microscopy (AP-STM), X-ray photoelectron spectroscopy (XPS), combined with theoretical calculations, we studied the processes of methane adsorption and decomposition on clean and oxygen pre-covered Cu(111) and Cu₂O(111) surfaces. The Cu₂O(111) surface was used as a reference to compare the role of different copper-oxygen clusters in methane activation.

EXPERIMENTAL AND CALCULATION DETAILS

Sample preparation: Clean Cu(111) was prepared by several cycles of Ar⁺ sputtering (1.2keV, 15min) and annealing (800°C, 10min). The well-ordered Cu₂O(111) surface was prepared by exposing the Cu(111) surface to 5×10^{-7} mbar O₂ at 300 °C for 20 min²⁸. The clean sample was interrogated by XPS and STM to ensure that the surface was clean with large terraces. AP-STM measurements were performed at room temperature in batch mode with a commercial Leiden Probe Reactor Microscopy STM²⁹. The reactor cell is sealed by an inert fluoroelastomer ring, which allows increasing the pressure to several bars. This setup allows switching the reactor cell between high-pressure conditions to UHV ($\sim 10^{-8}$ mbar). All the STM images were acquired in the constant-current mode with a top-to-down scan direction³⁰. The scanning parameters are indicated in the figure captions. XPS experiments were performed with a SPECS XPS system at a base pressure of 2×10^{-10} mbar. The chamber is equipped with a hemispherical energy analyzer and a twin anode (Mg and Al) X-ray source. The O1s core levels were excited by Al K α radiation (1486.6 eV). All the spectra were recorded at 300 K.

DFT calculations: The DFT calculations were carried out using the program package Cambridge Sequential Total Energy Package (CASTEP) with a plane-wave basis set in the Materials Studio (MS) software³¹. The Perdew-Wang-91 (PW91) functional with the generalized gradient approximation was employed to deal with the electronic exchange and correlation³². The kinetic wave cutoff energy was set at 400 eV to describe the electronic wave functions. The Brillouin-zone integration was sampled using a 3×3×1 Monkhorst-Pack k-points grid with a Methfessel-Paxton smearing of 0.1eV. The convergence criteria for configuration optimization was set to the tolerance for self-consistent field (SCF), energy, maximum force and a maximum displacement of 2.0×10^{-6} eV/atom, 2.0×10^{-5} eV/atom, 0.05 eV/Å and 2.0×10^{-3} Å.

The transition states (TSs) were explored by means of the complete LST/QST method for the elementary reactions³³. In addition, for validating the TSs in the reactions, the Dmol3 program was employed to calculate the frequency of the transition state, and TS confirmation was performed to ensure that every transition state could lead to the desired reactants and products. Although addition of vdw correction is warranted for the calculation of methane adsorption, previous reports have shown that this correction has negligible effect on the trend of activation barriers for C-H bond scission^{14,34}

The adsorption energies for all species on the surfaces were calculated as follows:

$$E_{ads} = E_{adsorbates} + E_{surface} - E_{adsorbates/surface} \quad (1)$$

Where $E_{adsorbates}$ is the energy of the free adsorbates in the gas phase, $E_{surface}$ is the energy of the surface, and $E_{adsorbates/surface}$ is the total energy of the surface together with the adsorbates.

For a reaction such as $AB \rightarrow A + B$ on the surfaces, the reaction energy (ΔH) and energy barrier (E_b) were calculated on the basis of the following formulas:

$$\Delta H = E_{(A+B)/surface} - E_{AB/surface} \quad (2)$$

$$E_b = E_{TS/surface} - E_{AB/surface} \quad (3)$$

where $E_{(AB)/surface}$ is the total energy of the adsorbed AB, $E_{(A+B)/surface}$ is the total energy of the co-adsorbed A/B on the metal surface, and the $E_{TS/surface}$ is the total energy of the transition state on the metal surface.

RESULTS AND DISCUSSION

1. Methane Activation on the Oxygen pre-covered Cu(111)

Molecular oxygen dissociates after adsorption on Cu(111) at 300 K with a barrier of $\sim 0.1\text{--}0.2$ eV³⁵. The dissociated O atoms chemisorb on the surface and induce a reconstruction. STM images in Figure 1A and B (supporting information Figure S1) display the initial stages of Cu(111) under exposure to 10^{-2} mbar O₂, where it is observed that Cu atoms from step edges and terraces are incorporated during the growth of the surface oxide. Branched islands form along the steps and on the terraces. The oxidation of Cu(111) has been extensively studied by experimental^{36,37} and theoretical methods³⁸. The surface dynamics and kinetics, as well as the final surface oxide strongly depend on the oxygen pressure and substrate temperature³⁹. The two most common copper oxides are cuprous oxide, Cu₂O, and cupric oxide, CuO. The former is favored at low temperature and pressure, while the latter dominates at high temperature and pressure⁴⁰. The Cu₂O phase forms more readily than CuO from a thermodynamic point of view and it is the most commonly observed structure upon oxidation⁴¹. In the current case, room temperature exposure of Cu(111) to 10^{-2} mbar oxygen leads to the generation of amorphous copper structures with preferred faceting orientation as shown in the enlarged STM image (Figure 1C), which include both Cu₂O and CuO domains⁴². Figure S2 demonstrates the progression in the ordering of the Cu₂O domains upon annealing.

Figure 1. (A) to (C) AP-STM image of the Cu(111) surface under 10^{-2} mbar O_2 at 300 K for 2min. (D) to (F) after evacuating the reactor cell to UHV and during subsequent exposure to 1bar methane; (G) AP-STM image of a bare Cu(111) surface after exposure to 10^{-2} mbar O_2 at 300 K for 15min; (H) and (I) introducing 1bar methane into the reactor cell in presence of O_2 . Scanning parameters (Sample bias: V_s ; tunneling current: I_t between 1.0-1.2 nA) are (A) and (B) -1.0V; (C) -0.2 V; (D) to (F) -0.1 V; (G) and (H) -0.5 V; (I) -0.1V.

In order to investigate the effect of oxygen coverage on the surface of Cu(111) and the activation of methane, we monitored the variation of the surface morphology during oxygen exposure. After the initial exposure to oxygen, which leads to the partial oxidation of Cu(111) (Figure 1B), we evacuated the reactor cell, and introduced 1bar methane at 300 K (Figures 1D-F). As shown in Figures 1D to F, no significant surface morphology changes were detected during sequential scans of the same area. At this point, the reactor cell was evacuated to UHV, and the modified copper surface was further exposed to 10^{-2} mbar oxygen leading to a surface fully covered by clusters induced by further oxidation (Figure 1G). The images were taken in situ at

10^{-2} mbar O_2 . An additional one bar methane (2 bar in total) gas was introduced into the reactor cell together with 10^{-2} mbar O_2 . As shown in Figure 1H and the enlarged STM image of Figure 1I, the entire surface becomes further decorated by smaller clusters with an average size of 2.2nm.

2. Oxygen adsorption and methane exposure on $Cu_2O(111)$

As discussed above, Cu_2O is the most stable surface oxide under vacuum conditions⁴⁰. We proceeded to compare the methane activation on Cu_2O surfaces which were prepared by different methods, *i.e.*, room temperature exposure of clean $Cu(111)$ to O_2 leading to amorphous structures (see Fig. 1), and annealing $Cu(111)$ in O_2 atmosphere at $350^\circ C$ leading to ordered structures⁴³. We conducted AP-STM studies on the oxygen adsorption on $Cu_2O(111)$ and methane adsorption on the freshly prepared and O_2 treated surfaces, respectively. Figure 2A is the freshly prepared $Cu_2O(111)$ taken in vacuum. The periodic rows with a spacing of ~ 0.6 nm (supporting information Figure S3) and XPS data (next section) show the typical structure of $Cu_2O(111)$ ⁴³.

Figure 2. AP-STM images of Cu_2O freshly prepared, oxygen covered and after methane exposure. (A) freshly prepared $Cu_2O(111)$; (B) Cu_2O while exposed to 10^{-2} mbar O_2 for 5min.; (C) zoom in scan showing the clusters after O_2 exposure; (D) while subsequent exposure to 1bar methane; (E) Cu_2O exposure to 10^{-2} mbar O_2 for 20mins; (F) zoom in scan from E showing the clusters spanned over the surface; (G) while subsequent exposure to 1bar methane; (H) high-resolution AP-STM image taken in the mixture of 1bar methane and 10^{-2} mbar O_2 . Scanning parameters (Sample bias: V_s ; tunneling current: I_t) are (A) -1.5 V, 1 nA; (B) -0.5 V, 1 nA; (C) and (D) -0.1 V, 1 nA; (E) and (F) -1.5 V, 1 nA; (G) and (H) -0.1V, 1 nA.

After introducing 10^{-2} mbar O_2 , clusters with an average size of 2.5nm randomly dispersed on Cu_2O . This phenomenon is different from that observed on the bare Cu(111), on which large areas of surface oxide were formed under similar conditions. Before exposing the modified Cu_2O surface to methane gas, the reactor cell was evacuated to UHV. Figure 2D is an in situ AP-STM image taken in 1bar methane. We further exposed the Cu_2O surface to 10^{-2} mbar oxygen for a longer time. As shown in Figure 2E and F, the whole surface was covered by clusters after 10 minutes of exposure to O_2 . When no further morphology changes on the surface were observed, we added 1bar methane. Figure 2G and H are in-situ AP-STM images taken in 1bar methane. Clusters with an average size of 2.1nm assembled into a short-range ordered hexagonal pattern on the flat area (dim part), which is similar to the clusters that were formed during high oxygen exposure on the bare Cu(111) surface (Fig. 1). In both cases the entire surface was covered by clusters with sizes between 2.1-2.5nm, however after exposure to methane (Figures 2G and 2H) these clusters form short-range ordered arrays on $Cu_2O(111)$ while randomly disperse on Cu(111).

3. XPS characterization

Figure 3A shows the C1s XPS region acquired after the AP-STM studies on the Cu(111) surface described in the previous section. The black spectra were taken after exposure to 1 bar CH_4 on clean Cu(111) for 15 min., where a very weak peak at 282.9 is observed. No C1s peaks were observed after the exposure of 10^{-2} mbar O_2 on the bare Cu(111). The top line (red) in Figure 3A was taken after the AP-STM study displayed in Figure 1, with more than four hours of exposure to 1 bar methane. An asymmetric feature with a peak at 282.9 eV can be distinctly identified. The shoulder at higher energies is consistent with CH features ~ 283.6 eV, while the main peak at 282.9 eV can be assigned to CH_3 species, suggesting the decomposition of methane after adsorption on the oxygen-activated copper surface⁴⁴. In contrast, C1s peaks were barely visible on the Cu_2O surface (Figure 3C) after the exposure of methane directly on bare or oxygen activated Cu_2O surfaces displayed in Figure 2.

Figure 3. (A) C 1s and (B) O 1s XPS spectra after exposure to 1 bar methane of oxygen-modified Cu(111) surfaces. 10^{-2} mbar O₂, and first O₂ then 1 bar methane, from bottom to top; (C) C 1s and (D) O 1s XPS spectra from Cu₂O(111) after exposure to methane.

Prior to O₂ exposure, no peaks were observed in the O1s region (Figure 3B, black line) on Cu(111). Exposure to 10⁻² mbar O₂ for 1 hr on the Cu(111) surface leads to an XPS peak at 530.2 eV which can be accounted for the formation of surface Cu oxides⁴⁵. The O1s peaks have been extensively studied in the literature and assigned to various components⁴⁶. A peak around 529.9 eV has been assigned to chemisorbed atomic oxygen⁴⁷. Peaks at around 532.5 and 284.5 eV can be related to small water and hydrocarbons contamination traces in the chamber or gas cylinder⁴⁸. Tahir et al. reported that the O 1s peak is different in CuO and Cu₂O, with the former at 529.9 and the later at 530.8 eV⁴⁹. It is obvious that the O1s peak intensity in Figure 3B is dramatically reduced after exposure to 1 bar methane, accompanied with broadening that can be fitted with a new peak at ~530.7 eV. CH₄ effectively removes the oxygen adatoms *via* C–H bond activation on an oxygen site that converts the O adatom to a hydroxyl intermediate, which may desorb as H₂O in sequential steps⁵⁰. The broadening O1s peak towards higher binding energies could also be related to oxygen from OCH_x species⁵¹.

In comparison, the O 1s spectra taken on the Cu₂O surface under different conditions are shown in Figure 3D. The dominating peak, located at 530.0–530.2 eV is assigned to oxygen from a surface oxide⁴⁵. Upon exposure to oxygen, the O 1s peak from the Cu₂O(111) film became stronger and symmetric, but no change of the peak position was observed. Furthermore, the O1s peak reserved the original feature after exposing O₂/Cu₂O to 1 bar methane. This phenomenon is in stark contrast to the O₂/Cu(111) surface case, which saw a significant decrease in the O1s signal after methane exposure. In order to elucidate these remarkable differences of methane activation on oxygen pre-covered surfaces, we performed DFT calculations.

4. DFT calculations

4.1 Adsorption of CH₄, CH₃, and other constituents on clean and O-covered Cu (111) and Cu₂O (111) surfaces

To determine the optimal adsorption structures of methane, methyl and other potential intermediates during methane dissociation, we calculated the geometries and adsorption energy at their most stable adsorption sites on Cu(111) and Cu₂O(111) surfaces (Figure 4). Table 1 lists the calculated values of adsorption energy (E_{ads}) and key geometric parameters. The CH₄ molecule physisorbs at the top site on Cu(111) with a negligible value of E_{ads} (-0.03 eV). After introducing O adatoms on Cu(111) surface, the oxygen prefers to reside at the hollow site which bonds with neighboring three copper atoms with E_{ads} of -4.28 eV and $d_{\text{O-Cu}}$ of 1.88 Å. However,

the co-adsorption of oxygen has minor effect on the adsorption of methane, as evidenced by the minimal adsorption energy increase of 0.01eV. In the case of Cu₂O(111), a CH₄ molecule physisorbs at the top O_{surface} site (O_{surface} is the outer-most surface oxygen atom, supporting information Figure S4) with a hydrogen atom pointing toward substrate. The adsorption energy is only -0.02 eV. As seen from the lower right of Figure 4, although the oxygen still resides at the hollow site, but it stays closer to the coordinately saturated Cu (Cu_{CSA})site. Furthermore, the nonplanar Cu₂O(111) surface forces the lattice oxygen to stay above the copper atoms, thus, the chemisorbed oxygen atom is much farther away from the adsorbed CH₄ than in the case of bare Cu(111). Finally, the adsorption energy of methane only marginally increases to -0.05eV after the co-adsorption of oxygen. In the case of CH₃, it preferably anchors on the fcc top site on Cu(111) forming a C-Cu bond with a bond length of 2.2Å. The adsorption energy is -2.03eV, which is in agreement with the previously reported value⁵². On the Cu₂O (111) surface, both the CH₃ and H atoms preferably adsorb at the top O_{surface} site with significant lower adsorption energies than on Cu(111). The lower adsorption energies reflect the weak interaction and nonstable transition states on Cu₂O (111).

Table 1 The adsorption sites, adsorption energies and key parameters for related species on clean Cu (111) and Cu₂O (111) surfaces.

Surfaces	Species	Configurations	Bond lengths/Å	Adsorption energies/eV
Cu(111)	CH ₄	top, away from the surface	d (C-Cu) = 3.49	-0.03
	CH ₃	fcc, C-bound	d (C-Cu) = 2.21	-2.03
	OH	O-bound	d (O-Cu) = 2.03	-2.85
	O	O-bound	d (O-Cu) = 1.88	-4.28
	H	H-bound	d (H-Cu) = 1.72	-2.57
O-Cu(111)	CH ₄	top, away from the surface	d (C-Cu) = 3.40	-0.04
Cu ₂ O(111)	CH ₄	top, away from the surface	d (C-Cu) = 3.40	-0.02

	CH ₃	top, C-bound	d (C-O) = 1.47	-1.28
	H	top, H-bound	d (H-O) = 0.98	-1.72
O-Cu ₂ O(111)	CH ₄	top, away from the surface	d (C-Cu) = 3.40	-0.05

Due to the high electronegativity of oxygen, there is significant electron transfer from the Cu atoms to the O adatom. The O adatom itself and its bonded neighboring Cu atoms were perturbed, inducing the work function change and surface dipole. The highest adsorption energy (-4.28eV) of oxygen on Cu(111) and the bond length (1.88Å) indicate some degree of ionic character in this Cu-O bond^{38,53}. Hydrogen adatoms adsorb at the fcc site of Cu showing the shortest bond distance of 1.72Å with a bond energy of -2.57 eV. The diffusion barrier of single H atom on Cu is quite low, implying that the H adatoms diffuse rapidly, so we did not consider the effect of H atoms from CH₄ dissociation to CH₃⁵⁴.

Figure 4. Geometric structures of CH₄, CH₃ and other reaction intermediates during the dehydrogenation on Cu(111) and Cu₂O(111). Light orange, grey, red and white represent copper, carbon, oxygen and hydrogen respectively. The adsorbed oxygen on Cu₂O is highlighted with green color.

4.2 Dissociation of CH₄ on clean and O-covered Cu(111) and Cu₂O (111) surfaces

In this section, we present the probable reaction pathways for the dissociation of the first C-H bond of CH₄ on the four different surfaces. Table 2 lists the energy barriers and reaction energetics. Figure 5 depicts the geometries of the transition states on different surfaces. Dissociation of CH₄ to CH₃ on clean Cu(111) has an energy barrier of 1.77 eV, with an endothermic value of 1.07 eV, as seen from the geometry of TS2 in Figure 5. The chemisorbed oxygen at the hollow site abstracts one hydrogen atom from methane with cooperative assistance from the surface copper atom, generating surface O-H and CH₃ species. The calculated activation energy barrier of 137 kJ/mol is in good agreement with the previously reported value of 133.1 kJ/mol and the experimentally determined values of 123 ± 27 kJ/mol¹³. The reaction energy is reduced to 0.91 eV on O-modified Cu(111) compared to 1.07 eV on the clean Cu(111) surface, suggesting that the adsorbed oxygen atoms can promote the dissociation of methane on Cu(111).

Table 2 Energies of CH₄ dissociation reaction on clean and O-covered Cu (111) and Cu₂O (111) surfaces (eV).

Surfaces	Reactions	TS	E(b) _f /eV	ΔH/eV	C-H bond [#] length/Å
Cu (111)	CH ₄ → CH ₃ + H	TS1	1.77	1.07	1.71
O-Cu (111)	CH ₄ +O → CH ₃ + OH	TS2	1.42	0.91	1.54
Cu ₂ O (111)	CH ₄ → CH ₃ + H	TS3	4.59	1.33	2.38
O-Cu ₂ O (111)	CH ₄ +O → CH ₃ + OH	TS4	3.83	-0.94	2.38

E(b)_f is the energy barrier of the forward reaction; ΔH is the reaction energy.

represents the broken C-H bond in the transition states.

Figure 5. The transition states and final states in CH₄ dissociation reaction on clean and O-covered Cu (111) and Cu₂O (111) surfaces. Color scheme same as Figure 4.

Turning to the Cu₂O(111) surface, the dissociation of CH₄ to CH₃ has the highest barrier of 4.59 eV and the largest endothermic energy of 1.33 eV. The CH₄ decomposition is neither thermodynamically nor kinetically favorable on the Cu₂O surface. Co-adsorption of O atoms can significantly decrease the energy barrier to 3.83 eV, and induce the reaction to be exothermic with an energy of -0.94 eV. However, comparing with that on the Cu(111) surfaces, the energy barrier is still too high to activate the CH₄ dissociation at moderate temperatures. Although plain Cu₂O(111) is inactive for methane dissociation, it is an excellent support for CeO₂ to dissociate methane to C, CH_x fragments and CO_x species at room temperature. As reported by Zuo *et al.*, they found that the oxygen center at the interface of CeO₂ and Cu₂O can break the C-H bond⁵⁵.

Figure 6. Potential energy profiles of CH_4 dissociation on clean and O-covered Cu(111) and Cu_2O (111) surfaces.

The potential energy profiles (Figure 6) of the CH_4 dissociation on the four different conditions distinctly revealed that the pre-adsorbed O atoms can promote the C-H bond dissociation and that the CH_4 decomposition on O-precovered Cu(111) is kinetically favorable. This finding is in agreement with the experiment results. Methane activation at 300 K can only be detected on the O-covered Cu(111) surface.

DISCUSSION:

One-site-three-centered vs Two-site-four-centered activation mechanism

The transition-state for the first C-H bond activation in CH_4 on the clean Cu(111) surface, shown in Figure 7A (TS1), represents a one-site-three-centered mechanism. Similar transition-state structures have also been reported for CH_4 activation on Pd(111)⁵⁶ and Pt(111)⁵⁷. The active Cu center acts as both electrophile and nucleophile which can shuttle electrons via the donation from CH_4 to Cu and back donation from Cu to $\sigma_{\text{C-H}}$ antibonding states, forming a three centered $\text{CH}_3\cdots\text{Cu}\cdots\text{H}$ complex¹⁵. Therefore, both the H adatom and CH_3 group receive extra electrons from the Cu atom, resulting in a repulsive interaction between them (see detail in Table S1 for the calculated charge on each atom). Consequently, the unstable TS in a copper one-site-three-centered process leads to a high activation barrier for methane dissociation.

Figure 7. Transition state (TS) for the dissociation of CH_4 on clean and O-covered $\text{Cu}(111)$ and $\text{Cu}_2\text{O}(111)$ surfaces via two different mechanisms. (A) Cu single-site three-centered mechanism on clean $\text{Cu}(111)$; (B) Cu and O two-site four-centered mechanism on chemisorbed oxygen/ $\text{Cu}(111)$; (C) lattice O single-site three-centered mechanism on bare $\text{Cu}_2\text{O}(111)$; (D) lattice O and adsorbed oxygen two-site three-centered mechanism on oxygen precovered $\text{Cu}_2\text{O}(111)$. The active sites and three/four reaction centers are indicated by the numbers. The calculated charges on the CH_3 and H group are highlighted.

In the case of the involvement of chemisorbed oxygen in the dissociation of methane on $\text{Cu}(111)$, there are two active sites (oxygen and copper) and thus four reaction centers (O, Cu, H and CH_3), as shown in Figure 7B (TS2). The oxygen atom located at the fcc hollow site can abstract a hydrogen from methane, forming an OH group, and a CH_3 radical. The CH_3 radical simultaneously anchors on the neighboring Cu. Finally, the CH_3 group gains charge from copper, while the hydrogen atom loses charge. Therefore, a dipole-dipole interaction can be expected between the CH_3 ($-0.35e$) and H ($0.21e$) species ($\text{CH}_3^{\delta-} \cdots \text{H}^{\delta+}$). Additionally, according to the activation strain model (ASM), the potential energy surface along the reaction coordinate is

composed of strain of the reactants that deformed during the reaction, and the interaction between these deformed reactants⁵⁸. The smaller strain and stronger interactions can result in a lower activation barrier. In the current case, the shorter C-H bond between dissociated hydrogen and the CH₃ group on O-covered Cu(111) implies less strain than on the clean surface. The dipole-dipole interaction stabilizes the TS, and further lowers the strain. Consequently, the dissociation of CH₄ on an oxygen modified Cu(111) surface has a much lower activation energy barrier than on clean copper.

Figure 7C (TS3) shows the TS for methane dissociation by the lattice oxygen in Cu₂O (111) surface, suggesting a one-site (oxygen) and three-center (O, CH₃ and H) pathway. A lattice oxygen instead of a copper atom is the active site. The resulting CH₃ fragment prefers to attach atop of the lattice oxygen rather than to a copper atom, and thus the dissociated CH₃ and H species cannot be stabilized by any surface atoms as shown in Figure TS3. In contrast to the case in the clean Cu(111) surface, the dissociated H atom is also unable to interact with the CH₃ group due to the large distance (2.38 Å) from the free radical species. As such, this one-site-three-centered pathway results in a high activation energy barrier for methane dissociation. A similar situation is observed for the oxygen-modified Cu₂O(111). The chemisorbed oxygen can abstract the hydrogen atom from CH₄, forming an OH group with the H towards the CH₃ group. The CH₃ species adsorbs atop of the lattice oxygen, showing an amount of electron depletion to oxygen, leading to a partially positive polarization of CH₃. Thus, there will be a dipole-dipole repulsion between (O^{δ-}-CH₃^{δ+}) and (O^{δ-}-H^{δ+}). Although the presence of oxygen facilitates the abstraction of hydrogen, this dipole-dipole repulsion dramatically increases the activation energy in comparison to the case of O-covered clean Cu(111).

CONCLUSION

Clean Cu(111) or Cu₂O(111) surfaces are inert towards methane activation at 300 K, but oxygen-modified Cu(111) surfaces obtained by exposure to 10⁻² mbar of O₂ lead to reactive structures towards methane. In-situ AP-STM images demonstrate that both the Cu(111) and Cu₂O(111) surface are fully covered by clusters with an average size of ~2.1 nm, but showing different packing structures after exposure to oxygen. No morphology variations have been observed on these surfaces after exposures up to 1 bar of methane at 300 K. DFT calculations

suggest two potential mechanisms for methane dissociation on clean and oxygen pre-covered Cu and Cu₂O. The dissociation of methane on clean Cu(111) proceeds by a single active site (Cu) three-centered (CH₃, H, Cu) mechanism, which leads to a high activation energy barrier of 170 kJ/mol. On oxygen pre-covered Cu(111) surfaces, the oxygen and copper atoms form two active sites, and the dissociated CH₃ and hydrogen are associated with a four-centered transition state which is stabilized by a dipole-dipole attraction, exhibiting a relatively low activation energy barrier of 137 kJ/mol. However, on an ordered Cu₂O(111) surface, CH₄ adsorbs on lattice oxygen atom instead of copper, and the hydrogen abstraction by the neighboring copper is the only accessible pathway, with the highest reaction barrier found in this study (442 kJ/mol). Although co-adsorbed oxygen on the neighboring Cu atom of Cu₂O(111) can facilitate the hydrogen abstraction from methane, the weak stabilization of CH₃ and the repulsive interaction between O-H and O-CH₃ make the corresponding TS unstable, leading to a relatively high activation energy of 369 kJ/mol. The reported effect of co-adsorbed oxygen species studied here could be extended to other transition metal surfaces and used for the growth of single-crystal graphene over large areas.

ASSOCIATED CONTENT

Supporting information. AP-STM images of Cu(111) at the initial stage of oxygen adsorption (Figure S1), and during annealing after exposing to 10⁻² mbar O₂ (Figure S2). The atomic resolution STM image showing the structure of Cu₂O(111) surface (Figure S3). Calculated charge of each atom of the transition states during methane dissociation on Cu(111) and oxygen modified Cu(111) (Table S1). Optimized structural model of the Cu(111) and Cu₂O(111) surface used for DFT calculations (Figure S4). This material is available free of charge via the Internet at <http://pubs.ac.org>.

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Notes

The authors declare no competing financial interest

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