## Perspective

# Photocatalytic conversion of methane: catalytically active sites and species

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## SUMMARY

The development of direct routes for catalytic functionalization of methane would accelerate the chemical utilization of this abundant carbon resource to produce value-added chemicals or easily transportable fuels. However, the selective transformation of methane remains highly challenging due to the dilemma between the activation of inert C–H bond and the keeping of vulnerable target products from over-oxidation or deep dehydrogenation. A number of studies have been devoted to selective methane transformations by heterogeneous photocatalysis. Unlike a comprehensive review of the field, this article focuses on the insights into the catalytically active sites/species, which are usually overlooked in photocatalysis, and offers the strategies that may facilitate selective methane conversions by manipulating the active sites/species at surface/interface regions. The key factors that determine not only the C–H activation but also the selectivity control are discussed. The future opportunities for photocatalytic methane conversions by rationally controlling catalytic active sites/species are analyzed.

Key words: methane, photocatalysis, C−H activation, active site, active species, selectivity control, semiconductor

## INTRODUCTION

As an abundant carbon resource widely contained in natural gas, shale gas, coal-bed gas, methane hydrate (also known as combustible ice) and biogas, methane is mainly combusted directly for heat or electricity. The anticipation is increasing to utilize this $C_1$ molecule as a building block for the synthesis of a variety of high-value chemicals or easily transportable fuels.[1] Actually, the functionalization of $CH_4$ with only inert C−H bonds has long been regarded as a "holy grail" in chemistry.[2] However, the chemical utilization of $CH_4$ is still limited to the indirect route via syngas ($H_2$/CO), which is highly energy-consuming. The direct route for selective transformation of $CH_4$ suffers from low product selectivity at a considerable $CH_4$ conversion, because a high reaction temperature is usually required for thermocatalytic activation of the inert C−H bond, which inevitably leads to consecutive conversions of the target product such as methanol or ethylene to thermodynamically more stable $CO_2$ or coke.[3-5] Many studies including not only thermocatalysis but also electrocatalysis and photocatalysis have been devoted to developing new systems that can selectively transform $CH_4$ under mild conditions.[6,7]

Photocatalysis, which harnesses solar energy for chemical transformations under mild conditions, has attracted particular attention for $CH_4$ conversions in the past decade.[7-13] Generally, the heterogeneous photocatalysis proceeds through the absorption of light irradiation by a semiconductor to generate high-energy charge carriers, *i.e.*, electrons and holes, and the charge carriers migrating to the surface may induce reductive and oxidative reactions

depending on the energy level of conduction band (CB) or valance band (VB) of the semiconductor and the redox potential of the half reaction. The research efforts in semiconductor-based photocatalysis have mostly been put into accelerating the light-absorption and charge-carrier separation processes. The elucidation of active sites/species, which is a main research goal in heterogeneous catalysis, is often overlooked in photocatalysis for environmental remediation and $H_2$ evolution, the most intensively investigated photocatalytic reactions, where the activation of reactants and the control of product selectivity are usually not vital. On the other hand, for photocatalytic transformation of $CH_4$, whose activation and selective functionalization play decisive roles, the insights into the active sites/species become very crucial in improving the performance and designing efficient catalysts.

The transformation of $CH_4$ typically involves two consecutive steps, *i.e.*, the C−H cleavage and the subsequent functionalization to form products (Figure 1A). The cleavage of C−H bond via direct electron transfer is usually difficult due to the inertness of C−H bond and the symmetric structure of $CH_4$. This emphasizes the crucial roles of photocatalyst surfaces in $CH_4$ activation and the subsequent transformation. Different from molecular photocatalysts, semiconductor-based heterogeneous photocatalysts enable the co-existence of multiple active sites on the surface.[14] Further, the *in situ* generated active species, most of which are radicals with limited diffusion distances, are mainly localized near the surface, and their properties may be tuned by manipulating the surface structure. Therefore, in heterogeneous photocatalytic systems, the cleavage of C−H bonds usually proceeds through the adsorption/activation of $CH_4$ on active sites or the reaction with active species. The surface active sites and species, which are generated from photogenerated charge carriers with high energy (Figure 1B), can be highly reactive, and thus can drive the activation of C−H bond under mild conditions. In addition, the surface active sites with unique electronic configurations may play important roles in the adsorption and stabilization of intermediates, and the subsequent formation and desorption of products. The multiple catalytic active sites and active species constitute the sophisticated surface reaction region, and it is expected that the interactions between the surface sites/species with $CH_4$/reaction intermediates at the surface region play key roles in the C−H activation and the selectivity control (Figure 1A).

Several comprehensive reviews have been devoted to photocatalytic conversions of $CH_4$.[7−13] Different from these reviews, the present Perspective article sheds lights on the issues related to active sites and species for $CH_4$ selective transformations on heterogeneous photocatalysts. Strategies that facilitate light absorption and charge-carrier separation are not in the scope of this article. Instead, this Perspective aims to disentangle the complicated functions of different catalytically active sites/species in photocatalytic conversions of $CH_4$. On the one hand, the surface region with rich sites and species holds great potential for the activation and transformation of $CH_4$ to various products; on the other hand, the complexity exerts difficulty in comprehensively understanding the reaction mechanism at a molecular level and in precisely controlling the product selectivity. The properties and the roles of hole-localized active sites, electron-localized active sites, surface-bonded active species, and near-surface active species (Figure 1B) in both the C−H activation and selectivity control steps are analyzed. The interactions of $CH_4$/reaction intermediates with the active sites/species as well as the correlation between the active sites/species and performances are discussed. The article also offers perspectives for the photocatalytic $CH_4$ transformation to useful products.

## C−H ACTIVATION

Methane, possessing strong and localized C−H bonds, has no filled orbitals of high energy (HOMO: −10.6 eV) or empty orbitals of low energy (LUMO: +1.99 eV) that could readily participate in chemical reactions (Figure 2A).[11] The energy level of molecular orbitals of $CH_4$ suggests that the direct removal of electrons from or donation of electrons to a $CH_4$ molecule is extremely difficult. The active sites/species at the surface region derived from the photogenerated charge carriers function for the activation of C−H bond, and we roughly classify these into the following four groups: hole-localized active sites; electron-localized active sites; concerted electron-hole pairs, and active species. Here, the properties of these active sites/species are analyzed together with their functioning mechanisms for a better understanding of the underlying chemistry.

**Hole-Localized Active Sites**. Photogenerated holes can migrate to the surface and be localized on surface sites. These surface sites have empty orbitals and hold the potential to accept

electrons from the occupied σ orbital of $CH_4$, and thus can drive the C−H bond cleavage (Figure 2A). The hole-induced active site may be composed of either a coordinatively unsaturated metal site ($M^{\delta+}$) (Figure 2B) or a surface electron-deficient oxygen ($O^-$) site on metal oxides (Figure 2C). The carbon atom in $CH_4$ with partially negative charges may be bonded onto $M^{\delta+}$ (Figure 2B), while the hydrogen atom with partially positive charges may be adsorbed onto $O^-$ (Figure 2C).

The coordinatively unsaturated metal site can be generated on plasmonic metal-semiconductor composites under light irradiation. In such a plasmonic metal-semiconductor system, hot electrons derived from light excitations by the metal can be injected to the CB of the adjacent semiconductor. The Schottky barrier formed at the metal-semiconductor interface prevents the back transfer of hot electrons, leaving $M^{\delta+}$ at an electron-deficient state on the surface. The $M^{\delta+}$ facilitates the adsorption of $CH_4$ by binding to the C atom ($\delta C = -0.185$).[11] The C−H bond can be activated by transferring electrons to the electron-deficient orbital of $M^{\delta+}$ (Figure 2B). The activation of $CH_4$ over some photocatalysts including noble metals/mesoporous silica,[15] $Rh/TiO_2$,[16] and $Pt/Ga_2O_3$[17] might proceed *via* this mechanism. In addition to the *in situ* generated $M^{\delta+}$ site on plasmonic metal/semiconductor, the electron-deficient metal site responsible for C−H bond activation could also be generated *ex situ*. For example, $Ag^+$ highly dispersed on a heteropolyacid−$TiO_2$ composite was capable of activating $CH_4$ into methyl radical, but this stoichiometric reaction led to inactive metallic Ag. The light irradiation of metallic Ag in air at ambient temperature regenerated the active $Ag^+$ site, forming a photochemical looping for photocatalytic $CH_4$ conversion to $C_2H_6$.[18]

Many studies demonstrated that the photogenerated holes on metal oxide semiconductors such as ZnO,[19-23] $TiO_2$,[24-27] and $CuO_x$[28] could drive the activation of C−H bond in $CH_4$. The CB and VB of these metal oxide semiconductors are often composed of a number of closely spaced molecular orbitals hybridized from atomic orbitals of metal cations and $O^{2-}$.[14] The band edges of VB predominantly consist of O 2p states, and thus the photogenerated holes are mainly localized on oxygen atoms, turning $O^{2-}$ to $O^-$. The single occupied $O^-$ 2p orbital may extract hydrogen with an electron from C−H bond of $CH_4$ (Figure 2C). Most metal oxides possess high oxidation potential due to the low VB position of O 2p orbitals, indicating strong C−H activation ability. However, the C−H activation by $O^-$ might lead to the over-oxidation of $CH_4$ and the consumption of lattice oxygen. The loading of transition metal atoms on metal oxides, for example single-atom Pd on $TiO_2$, could reduce the contribution of O 2p in the VB edge by incorporating metallic d orbitals, mitigating the over-oxidation and increasing the catalyst durability.[29]

**Electron-Localized Active Sites.** Electron-localized active sites mainly involve electron-rich metal sites (Figure 2D) and partially reduced metal cations (Figure 2E). Although the mechanism of C−H activation on electron-localized sites is less understood as compared to that on hole-localized sites, the donation of electrons from the electron-rich site to the empty σ* anti-bonding orbital of $CH_4$ is generally involved, rendering $CH_4$ to be vulnerable (Figure 2A).

Electron-rich metal sites have been proposed by plasmonic excitation. For example, a plasmonic bimetallic catalyst consisting of Cu nanoparticles (NPs) with sparsely distributed Ru single atoms exhibited high efficiency for the dry reforming of $CH_4$ ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$).[30] Cu NPs were plasmonically active and thus could harvest visible light and produce hot carriers. DFT calculation illustrated that hot electrons from plasmonic excitation of Cu NP may migrate and be localized on Ru states. Electron-rich Ru single atoms were believed to be active sites for C−H activation.[30] More specifically, hot electrons localized on Ru 4d states with high energy could be donated to the empty orbital of $CH_4$, elongating the C−H bond, and subsequently the H atom gained a considerable negative charge upon dissociation, being adsorbed on the metal surface (Figure 2D).[30]

Partially reduced metal cations have been found to be generated under irradiation on some photocatalysts and can work for C−H activation. Typical examples are systems with $Zn^+$ as the active site for photocatalytic $CH_4$ transformations.[31,32] The $Zn^{2+}$ cation with an empty 4s orbital dispersed on ZSM-5 zeolite or $CeO_2$ surfaces was demonstrated to be capable of accepting a photogenerated electron under light irradiation and was reduced to $Zn^+$. The electron in the 4s orbital of $Zn^+$ was highly reactive and could be transferred to the empty $CH_4$ σ* anti-bonding orbital.[32] The generated $Zn^+$ on surfaces of ZSM-5 zeolite or $CeO_2$ could work for the activation of C−H bond of $CH_4$, forming $Zn−H−CH_3$[31] or $Zn−CH_3−H$[32] intermediates (Figure 2E). It is

noteworthy that only some metal cations can facilitate the conversion of $CH_4$. For example, the incorporation of *n*-type dopants (Nb, W, Mo, Ta) could enhance the activity of $TiO_2$ for the activation of C−H bond of $CH_4$ to form $C_2H_6$ as the predominant product *via* methyl radical, whereas such an enhancement was not observed by doping *p*-type dopants (Cu, Fe, Ga) into $TiO_2$.[25] It was revealed that the *n*-type dopant could provide extra electrons onto the catalyst surface, which were shallowly localized in the neighborhood of the doped atom, rendering the electron-rich active site for C−H activation.[25]

**Concerted Electron-Hole Pairs**. Electron-localized and hole-localized active sites may co-exist on a photocatalyst and work concertedly for C−H activation. Studies have revealed that even though two types of active sites function together, typically one type of active site plays the major role while the other active site plays the auxiliary role in the charge transfer and C−H activation (Figure 3A and 3B). For example, the electron-localized $Zn^+$ site on $CeO_2$ played key roles in the activation of C−H bond by charge transfer, and the hole-localized $O^-$ site interacting with H atom of $CH_4$ helped the dissociation of the C−H bond at the same time (Figure 3A).[32]

The co-existence of electron-localized and hole-localized pair sites may induce electric field to polarize $CH_4$. The symmetrical tetrahedral structure of $CH_4$ with four equal C−H bonds results in the non-polar feature of $CH_4$ molecule and further difficulty in its activation. The polarization of $CH_4$ holds the potential to decrease the activation energy for C−H activation and cleavage. For example, $CH_4$ molecule on GaN nanowires could be polarized into $CH_3^{\delta-}$ and $H^{\delta+}$ by interaction with surface $Ga^{3+}$ and $N^{3-}$ sites, and the longer Ga−N bond length (1.95 Å) as compared to the C−H bond length (1.09 Å) may be beneficial to the stretching of the C−H bond.[33] The polarized $CH_4$ molecule was then split heterolytically into $CH_3^-$ and $H^+$ upon UV irradiation, and the photogenerated electrons and holes migrated to the surface and participated in the reduction of $H^+$ into H• and the oxidation of $CH_3^-$ into •$CH_3$, respectively (Figure 3C).

The $CH_4$ molecule may also be polarized by the localized surface plasmon resonance (LSPR) effect. Under light irradiation, the LSPR effect induces positive and negative charges on the local surface of plasmonic metals. This triggers electromagnetic fields and symmetrical molecules like $CH_4$ can be partially polarized by the electromagnetic field (Figure 3D). An increase in the activity was observed for the dry reforming of $CH_4$ operating under light irradiation at room temperature with an increase in the electromagnetic field induced by the LSPR effect over metal/oxide catalysts.[34,35] It is noteworthy that the dry reforming of $CH_4$ is a strong endothermic reaction ($\Delta G_{298K} = +171$ kJ mol$^{-1}$) that performs at 800−900 °C in the current thermocatalytic technology.[36]

**Active Species.** Photo-excited charge carriers with energies of several eVs have the potential to generate high-energy species, typically radicals (denoted as X•), which can serve as active species to extract H from the C−H bond, forming X•−H−$CH_3$ transition state. Most of the generated radical species may be located on the photocatalyst surface or diffuse inside a region near the surface. As an example, the hydroxyl radical (•OH) has been identified as a key active species in many photocatalytic systems.[27,37-39] •OH could be generated by the oxidation of $H_2O$ with holes, the decomposition of $H_2O_2$, or the reduction of $O_2$. The generation of •OH *via* several different approaches under photocatalytic conditions has been reviewed by Tang and co-workers.[12] The superoxide radical species (•$O_2^-$) formed by the reduction of $O_2$ with photogenerated electrons has also been proposed to drive the C−H activation.[40] Chlorine intermediates, which can be generated under photo-[41] or electro-conditions[42,43], have exhibited high efficiencies in promoting selective C−H activation in $CH_4$.[41,42] Most chlorine-based systems for photochemical conversion of $CH_4$ do not involve the participation of heterogeneous photocatalysts.[12] For example, $Cl_2$ from the electrochemical oxidation of KCl electrolyte was decomposed under 254 nm irradiation, producing •Cl to mediate the conversion of $CH_4$ to $CH_3OH$, $CH_3Cl$, and $CH_2Cl_2$.[41] Recently, BiOCl was discovered as an efficient photocatalyst for chlorine evolution, and $Cl_2$ generated from synthetic seawater was directly used for $CH_4$ functionalization in one pot under UV lamp irradiation.[44] Diethyl ether was formed with high selectivity of over 90% after 2 h irradiation. Unfortunately, mechanistic studies have not been conducted for this system, and whether the $CH_4$ functionalization by chlorine intermediates over BiOCl is a heterogeneous catalysis or a photolysis process remains elusive.[44] Similar to •Cl, other radical species such as •OR have also been identified as active species for C−H activation in homogenous photocatalytic systems but have not yet been reported in heterogeneous ones.[12] The development of heterogeneous catalytic systems for $CH_4$ conversion

via different types of active species is a promising approach to achieving high activity and unique selectivity.

Besides the radicals like •OH that can diffuse away from the surface, some surface-bonded active species have also been reported for the C−H activation. For example, the surface silyloxyl radical (Si−O•), which was generated from the surface silanol group on silica or zeolite by deep UV (165 or 185 nm) irradiation, was found to be efficient for the C−H activation, forming $C_1$ oxygenates or $C_2H_6$ as major products depending on the presence of $O_2$ or not.[45] Another example is the dry reforming of $CH_4$ by $CO_2$ over Ru/SrTiO$_3$ under light irradiation, where hot electrons on Ru reduced $CO_2$ to CO, while the remaining $O^{2-}$ ion trapped in the SrTiO$_3$ lattice together with the photogenerated holes worked for $CH_4$ conversions.[36]

## SELECTIVITY CONTROL

The intermediate formed by the activation of C−H bond of $CH_4$ can be converted into a variety of products in the subsequent step (Figure 1A). The products mainly include multi-carbon ($C_{2+}$) alkanes ($C_2H_6$, $C_3H_8$), olefins ($C_2H_4$, $C_3H_6$), aromatics ($C_6H_6$), $C_1$ and $C_2$ organic oxygenates ($CH_3OH$, $CH_2O$, $C_2H_5OH$, $HOCH_2CH_2OH$) as well as CO. To tune reaction pathways by controlling active sites or active species is essential to achieving selectivity control. Here, some strategies to manipulate and improve product selectivity will be analyzed. The representative systems that demonstrate high selectivity of a specific product are summarized in Table 1.

**Control of Active Sites.** $C_2H_6$ is the most often reported product in photocatalytic conversion of $CH_4$, in particular under non-oxidative conditions. The non-oxidative dehydrogenation of $CH_4$ to $C_2H_6$ is thermodynamically limited and requires a very high temperature in thermocatalysis (typically >900 °C).[5] Thus, photocatalysis offers an alternative and promising approach to achieving coupling products from $CH_4$ under mild conditions. $C_2H_6$ is normally formed by the coupling of •$CH_3$ from the C−H activation of $CH_4$, but the adsorbed •$CH_3$ may also undergo side reactions such as deep dehydrogenation to coke or oxidation to CO or $CO_2$ depending on the catalyst employed and the reaction atmosphere. Further, the formed $C_2H_6$ molecule, if adsorbed strongly on the catalyst surface, may also face side reactions such as the reverse reaction of C−C bond breakage or the uncontrollable deep dehydrogenation to coke. Several strategies to modify the active sites have been proposed to enhance $C_2H_6$ selectivity by suppressing these side reactions. For example, the incorporation of Nb into hierarchical porous $TiO_2$–$SiO_2$ increased the energy required for C−C bond cleavage and facilitated the desorption of $C_2H_6$, therefore achieving a high selectivity of $C_2H_6$.[25] The presence of electron-rich metal cation centers, *e.g.*, the electron-localized Nb single atom and $Zn^+$ sites,[25,32] may help the stabilization of •$CH_3$, thus preventing •$CH_3$ from deep dehydrogenation by forming M−C bonds. The dispersion of active sites is also a crucial factor for selectivity control. For example, it was claimed that the intermediate, $CH_x$, formed during $CH_4$ activation on Ru island located on Cu tended to undergo oligomerization to coke, whereas the atomically dispersed Ru site favored the subsequent selective conversion.[30]

The design of active sites may also cause selective dehydrogenation of intermediates to form more valuable olefins or aromatics, although the uncontrollable dehydrogenation leads to coke formation. For example, a Pd-modified ZnO−Au catalyst achieved ~40% selectivity of $C_2H_4$ with a formation rate of 102 µmol g$^{-1}$ in 8 h.[20] The other products were $C_2H_6$ with a selectivity of 55% and minor $C_3H_8$ and $C_3H_6$. The Pd site incorporated into Au lattice was demonstrated to function as the active site for dehydrogenation and was the key to implementing the $CH_4 \rightarrow$ methoxy $\rightarrow$ ethoxy $\rightarrow C_2H_4$ reaction pathway.[20] Briefly speaking, on the ZnO−PdAu catalyst, $CH_4$ was first dissociated into methoxy species under light irradiation and Pd catalyzed the subsequent dehydrogenation of methoxy species, followed by the coupling between the dehydrogenated methoxy and methyl radical to form ethoxy species. Pd further facilitated the dehydrogenation of ethoxy species, offering $C_2H_4$.[20]

Li *et al.* reported an interesting photocatalytic system based on GaN nanowires with a rationally constructed *m*-plane for the direct conversion of $CH_4$ to benzene.[33] Benzene was formed with 96.5% selectivity at room temperature under UV illumination and the $CH_4$ conversion rate reached 725 µmol g$^{-1}$ h$^{-1}$.[33] The strong polarization effect and the longer bond length of the $Ga^{3+}$−$N^{3-}$ on the *m*-plane of GaN nanowires were proposed to contribute to the activation of C−H bond. Ethylene, which was formed by the dehydrogenation of ethane, was probably the intermediate for benzene formation through cyclization and dehydrogenation.[33] However, more

in-depth insights into the active sites for cyclization and selective dehydrogenation over GaN nanowires remain elusive.

Photocatalysis would also contribute to the simultaneous activation of $CH_4$ and $CO_2$, two most stable $C_1$ molecules, under mild conditions using solar energy instead of thermal energy. The design of active sites for the activation of both $CH_4$ and $CO_2$ molecules is expected to be crucial. Besides dry reforming of $CH_4$ with $CO_2$ to syngas at ambient or moderate temperatures,[34-36] recent studies also demonstrated that photocatalysis could accomplish the coupling of $CH_4$ and $CO_2$ to $C_2$ oxygenates. For example, a Ru-loaded Zn-doped g-$C_3N_4$ was found to be an efficient catalyst for the synthesis of $CH_3CHO$ and $C_2H_5OH$ from $CH_4$ and $CO_2$ at 80 °C under UV-vis light irradiation.[49] The selectivity and formation rate of these two $C_2$ oxygenates reached >70% and >600 µmol $g^{-1}$ $h^{-1}$. It is proposed that $CO_2$ may be activated on Ru sites to *CO by the photogenerated electrons, while $CH_4$ is activated on g-$C_3N_4$ by the photogenerated holes.[49] The coupling of *CHO formed from *CO and •$CH_3$ would lead to the formation of $CH_3CHO$, which was subsequently hydrogenated to $C_2H_5OH$, and thus the cooperation of the active sites for $CH_4$ and $CO_2$ activation should play key roles in the formation of $C_2$ oxygenates.[49]

**Control of Active Species.** The control of active species is a powerful strategy for the selective functionalization of $CH_4$, in particularly to organic oxygenates. The active species often reported for photocatalytic $CH_4$ conversions are radicals (*e.g.*, •OH and •OOH) and other excited or high-energy chemical species (Figure 4). Some strategies have been developed to control the properties, concentrations and locations of active species to tune the product selectivity in $CH_4$ conversions (Figure 4).

Some radicals, in particular •OH, are known to be capable of activating $CH_4$ and forming $CH_3OH$ through the coupling between •$CH_3$ and •OH. The employment of $H_2O_2$ as an oxidant with a proper catalyst could generate •OH facilely for $CH_4$ oxidation under mild conditions.[7] Recent studies showed that photocatalysis facilitated the generation of •OH from $H_2O_2$ for the oxidation of $CH_4$. For example, Xie *et al.* found that an FeO$_x$/$TiO_2$ catalyst showed higher activity and selectivity than bare $TiO_2$ and noble-metal/$TiO_2$ catalysts for the transformation of $CH_4$ to $CH_3OH$ by $H_2O_2$ under light irradiation.[27] The presence of FeOOH or $Fe_2O_3$ enhanced the formation of •OH radical and suppressed the generation of $O_2$•$^-$. The •OH radical was proposed to be the active species for the formation of $CH_3OH$, whereas $O_2$•$^-$ was assumed to be responsible for the formation of $CO_2$ in this system.[27] Another example is that the addition of the Fenton reagent ($Fe^{2+}$ + $H_2O_2$) into a photocatalytic system composed of $TiO_2$ significantly accelerated the conversion of $CH_4$ to $CH_3OH$ owing to the enhanced generation of •OH.[50]

Besides the employment of $H_2O_2$, •OH can also be generated during the oxidation of $H_2O$ by holes and has been observed in many photocatalytic systems, but it is often considered to be too reactive to be suitable for selective oxidation.[51] One useful strategy to enhance the selectivity of organic oxygenates is the control of the concentration or density of •OH (Figure 4A). In addition to regulating the light-absorption and charge-transfer abilities of a semiconductor photocatalyst, the density of active sites on its surface may also control the concentration of •OH. For example, the modification of the surface of beta zeolite with V or Bi−V might block a part of the Si−OH sites, which were assumed to be responsible for the formation of •OH under light irradiation, thus enhancing the selectivity of $CH_3OH$ by suppressing $CO_2$ formation.[52] Another example is the introduction of Cu species onto a polymeric carbon nitride (PCN) to control the generation of •OH by a two-step route instead of the direct oxidation of $H_2O$ to •OH.[37] In brief, the oxidation of $H_2O$ into $H_2O_2$ by the photogenerated holes occurred in the first step and then the formed $H_2O_2$ was converted to •OH by the low-valence Cu species. This two-step route was proposed to be capable of limiting the concentration of •OH, favoring the selectivity of organic oxygenates during photocatalytic $CH_4$ oxidation.[37] Besides these examples of modification of catalysts, the addition of a small amount of •OH scavenger such as nitrite ion ($NO_2^-$) into a $BiVO_4$-based photocatalytic system was found to enhance the formation of $CH_3OH$ during $CH_4$ oxidation due to the optimized •OH concentration.[53]

Another strategy to tune the selectivity of •OH-based photocatalytic conversion of $CH_4$ is to manipulate the location of •OH radicals (Figure 4A). Villa *et al.* found that the modification of $WO_3$ by $F^-$ significantly decreased the formation rate of $CH_3OH$ during the oxidation of $CH_4$ under UVC-vis light irradiation.[54] It was proposed that the •OH radical generated by $H_2O$ activation was mainly adsorbed on $WO_3$ surfaces and the •OH$_{ads}$ could efficiently react with

the •CH$_3$ formed by CH$_4$ activation to yield CH$_3$OH. On the other hand, on the F$^-$-modified WO$_3$ surface, the •OH radical was mainly formed as the free radical in the aqueous solution, and the •OH$_{free}$ could activate CH$_4$ but gave C$_2$H$_6$ rather than CH$_3$OH as the major product.[54] Zeng and co-workers pointed out that the •OH generated on the surface of single-atom Au-loaded black phosphorus (Au$_1$/BP) via the photocatalytic activation of O$_2$ in the presence of H$_2$O could react directly with the nearby *CH$_3$ on the Au site to form CH$_3$OH with > 99% selectivity.[55]

Only a few studies have disclosed the formation of C$_2$ oxygenates by photocatalytic conversions of CH$_4$.[37,48] The Cu-modified PCN could catalyze the formation of CH$_3$CH$_2$OH with a formation rate of 106 µmol g$^{-1}$ h$^{-1}$ and 81% selectivity during photocatalytic conversion of CH$_4$ with H$_2$O under UV-vis light illumination.[37] As already discussed, •OH formed by the two-step activation of H$_2$O via H$_2$O$_2$ is the key active species in this system. It is assumed that CH$_3$OH is an intermediate product, and CH$_3$CH$_2$OH might be formed either via *CH$_2$CH$_3$, an intermediate through the coupling of *CH$_3$ and *OCH$_3$, or via the direct coupling of *OCH$_3$ and *CH$_2$OH, two intermediates from CH$_3$OH through cleavage O−H and C−H, respectively.[37] Although more evidence is needed to understand the true mechanism, it is clear that the formation of CH$_3$CH$_2$OH requires the participation of multiple reactive intermediates. Xiong and co-workers recently demonstrated the direct conversion of CH$_4$ to ethylene glycol (EG), another attractive C$_2$ oxygenate for the production of poly(ethylene terephthalate), under light irradiation with an aid of applied potentials (photoelectrochemical conditions).[48] Solar energy-driven synthesis of EG from C$_1$ chemicals such as CH$_4$ or CH$_3$OH represents a new and sustainable route for the synthesis of bulk chemicals and has recently attracted much attention.[56,57] In their recent work, Xiong and co-workers pointed out the crucial roles of the optimization of the reactivity of •OH radicals by controlling the facet of WO$_3$ nanocrystals. The WO$_3$ photoanode with a high fraction of {010} facet showed an EG selectivity of 66% and formation rate of 0.47 mmol cm$^{-2}$ h$^{-1}$ under light irradiation and a moderate applied potential of 1.3 V versus reversible hydrogen electrode.[48] It was revealed that the distance of the two adjacent •OH radicals bonded on {010} facet was significantly longer than that on other facets. This was claimed to enhance the activity of •OH, because the formation of hydrogen bonding between •OH radicals with such a long distance became impossible. The formation of EG was proposed to proceed via the coupling between •OH and •CH$_3$ from CH$_4$ activation to CH$_3$OH, the C−H activation of CH$_3$OH to •CH$_2$OH, and the coupling of •CH$_2$OH.[48] This suggests once again that the formation of C$_2$ oxygenates involves multiple steps and intermediates. Therefore, the control of the selectivity of C$_2$ oxygenates would require the cooperation of multiple surface species (Figure 4A) and is a very challenging task.

Besides •OH radicals, other active species have also been proposed to work for the selective formation of organic oxygenates in photocatalytic conversions of CH$_4$ (Figure 4B). For example, Ye and co-workers proposed that the hydroperoxyl radical (•OOH), which was a relatively mild species formed on ZnO through the activation of O$_2$ in the presence of H$_2$O, was the active species for the selective conversion of CH$_4$ to CH$_3$OOH, CH$_3$OH and HCHO.[21] The loading of a proper noble metal (Pt, Pd, Au, or Ag) as a co-catalyst accelerated the activation of O$_2$ to •OOH, and thus enhanced the formation of C$_1$ oxygenates.[21] The Au/ZnO photocatalyst demonstrated the best performance; the selectivity of C$_1$ oxygenates was ~95% and the amount of liquid oxygenates reached 250 µmol with 10 mg catalyst in 2 h under UV-vis irradiation.[21] For the WO$_3$-catalyzed photocatalytic oxidation of CH$_4$, in addition to the •OH radical, which functioned as the key active species in some studies,[48,54] the surface O$^-$ was also proposed as the active species for the formation of organic oxygenates.[47] Actually, the O$^-$ site could also be viewed as the hole-localized surface site. In other words, under UV-vis light irradiation, the lattice oxygen on WO$_3$ was excited to O$^-$ by photogenerated holes, which was responsible for the activation of C−H bond.[47] It is of interest that HCHO was obtained with a selectivity of >99% and a HCHO formation rate of ~23 µmol g$^{-1}$ h$^{-1}$ was achieved on a cubic WO$_3$.

## OUTLOOK

Photocatalysis driven by solar energy represents one of the most attractive research areas for the chemical utilization of CH$_4$ under mild conditions. As described in the present article, some useful insights into the active sites/species have been gained and some interesting photocatalytic systems with unique selectivity of a high-value product such as C$_2$H$_4$, benzene, ethanol or EG have been presented. However, the product formation rate and the quantum yield are still too low to be of industrial interest. The photocatalytic systems for the selective transformation of CH$_4$ to high-value olefins and organic oxygenates are still limited and the

reproducibility of some excellent selectivity results is also needed. Furthermore, in many cases, $C_2H_6$ instead of high-value olefins is the major product for the photocatalytic conversion of $CH_4$ without an additional oxidant, while the over-oxidation to $CO_2$ also occurs when an oxidant is added to obtain organic oxygenates. The control of active sites/species has shown some successes in tuning the product selectivity, but such studies are still at their early stage. We point out the following important research directions for photocatalytic conversions of $CH_4$ in the future.

First, one important future research direction is the design and fabrication of photocatalysts containing multiple functionalities such as C−H activation on hole-localized surface sites and selective dehydrogenation on noble or transition metals with controllable sizes (*e.g.*, single atoms, clusters or nanometers). These active sites with different functionalities should be assembled in a spatially controlled sequence to accomplish the synthesis of high-value olefins from $CH_4$. There is much to learn from thermocatalytic conversions of $CH_4$ including not only the heterogeneous catalytic systems but also the homogeneous catalytic systems, where the C−H activation and product selective formation can also proceed under mild conditions.[58] Future efforts could also be put into using some established strategies from thermo- or electro-catalytic systems for controlling the properties of active sites. Strategies such as vacancy engineering[59] and ligand modification[60], which have not yet been investigated for the photocatalytic conversion of $CH_4$, can be powerful tools to modulate the geometric and electronic configuration of active sites. Further, the design of active sites can be inspired by hybrid photocatalysts comprising biomimetic complexes and semiconductors, and such artificial photosynthetic systems have been proven to be efficient in photocatalytic $CO_2$ reduction and $H_2$ evolution.[61] The design of such a photocatalytic biomimetic system for the conversion of $CH_4$ remains unexplored. The photocatalytic systems composed of semiconductors and methane monooxygenase can be expected to bring about some unique performances for the selective transformation of $CH_4$ to $CH_3OH$.

Second, more active species including radicals and excited species that may be generated under photocatalytic $CH_4$ conversion conditions and more strategies that can manipulate the reactivity of active species should be pursued. The studies reported to date suggest the crucial roles of •OH radicals, but the rational design and intentional generation of other types of active species that may be selective for the formation of high-value products are needed. Further, although a few studies have pointed out the distinct features of active species in the bulk phase and on the catalyst surface, the nature of such differences and how to control the generation of bulk-phase or surface-bonded active species remain unexplored. The manipulation of the concentration or density, the location, the vicinity and the distribution of these active species should be investigated to enrich the toolbox for controlling the active species and establishing the correlation with activity and selectivity.

Third, the solvent effect on active sites/species, which has been overlooked so far, represents an important research theme in photocatalytic $CH_4$ conversions. Solvents constitute a major part of surface reaction environments in batch systems. However, the effects of solvents in the photocatalytic conversion of $CH_4$ have not been systematically investigated. Kinetic solvent effects of many synthetically valuable radical reactions are significant.[62] The solvent may tune the reaction channel by tuning the hydrophilic/hydrophobic properties of the surface active site and the adsorption behavior towards intermediate species. For example, the tuning of polarity of solvents may help regulate the product from non-polar $C_2H_6$ to organic oxygenates.

Furthermore, the innovation of photocatalytic $CH_4$ utilization reactions is also an important future research direction. For example, $CH_4$ can be used as an alkylation reagent to react with electrophiles for organic synthesis.[63] The studies can be benefited from the collaborations with machine learning and DFT calculations.[64] The joint work of computations, machine learning and *operando* characterizations would be highly valuable in particular for the innovation of complicated photocatalytic systems.

## AUTHOR CONTRIBUTIONS

All authors contributed to writing and editing the manuscript.

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**Figure 1. Schematic illustration of two-step processes and active sites/species for CH₄ conversions by heterogeneous photocatalysis**

(A) Two steps of C−H activation and functionalization.

(B) Potential active sites/species generated from photogenerated charge carriers at surface/interface regions of semiconductors. "A" refers to active species.

"*" before chemicals denotes surface-bonded/adsorbed species.

**Figure 2. Schematic illustration of hole- and electron-localized active sites for the activation of C−H bond**

(A) The energy diagram of the molecular orbitals of CH₄; illustration of an empty orbital from the hole-localized active site that can accept an electron, and an orbital with an extra electron from the electron-localized active site that can donate an electron.

The values of HOMO (-10.6 eV) and LUMO (+1.99 eV) are from

http://sites.science.oregonstate.edu/~gablek/CH334/Chapter1/methane_MOs.htm

(B) Hole-localized coordinatively unsaturated metal site ($M^{\delta+}$) for C−H activation.

(C) Hole-localized electron-deficient oxygen ($O^−$) site for C−H activation.

(D) Electron-localized metal sites ($M^{\delta-}$) for C−H activation.

(E) Electron-localized partially reduced metal cations ($M^+$) for C−H activation.

**Figure 3. Concerted electron-hole pairs for the activation of C−H**

(A) The electron-localized active site works concertedly with the electron-deficient site.

(B) The hole-localized active site works concertedly with the electron-rich site.

(C) C−H bond is cleaved heterolytically over a polarized surface.

(D) LSPR-induced electromagnetic field facilitates the polarization and activation of CH₄.

**Figure 4. Representative examples for the control of active species for selective functionalization of CH₄**

(A) Control of the reactivity of •OH radicals for selective CH₄ transformations.

(B) Other active species for selective CH₄ transformations.

**Table 1. Representative photocatalytic systems that have achieved high selectivity of specific products in methane transformations**

| No.[a] | Catalyst | Reaction systems and conditions | Major product and selectivity | Key in selectivity control | Ref. |
|---|---|---|---|---|---|
| 1 | Nb-TiO₂-SiO₂ | 1 mL CH₄; 0.1 g catalyst; 300W Xe lamp; 4 h | $C_2H_6$ (containing minor $C_3H_8$): 100% | Nb: reducing C−C cleavage and facilitating the desorption of $C_2H_6$; stabilizing •CH₃ to avoid deep dehydrogenation | 25 |
| 2 | ZnO-AuPd | 44.6 mmol CH₄; 2 mg catalyst on FTO; 300W Xe lamp; 8 h | $C_2H_4$: 39.7% $C_2H_6$: 54.9% | Pd: dehydrogenative active site | 20 |
| 3 | GaN nanowire | 0.15 mmol CH₄; 0.35 mg catalyst; 300 W Xe lamp; 12 h | $C_6H_6$: 96.5% | The *m*-plane of GaN nanowires has strong polarization ability for C−H activation, dehydrogenation, and cyclization | 33 |
| 4 | FeOₓ/TiO₂ | CH₄-saturated H₂O (6 mL); 2 mM H₂O₂ (4 ml); 10 mg catalyst; 300 W Xe lamp ($\lambda < 710$ nm); 3 h | $CH_3OH$: 90% | Photocatalytically generated •OH from $H_2O_2$ is responsible for $CH_3OH$ formation, whereas $O_2$•⁻ may lead to $CO_2$ | 27 |
| 5 | Zn-HPW/TiO₂ | CH₄ 0.3 MPa; Air 0.1 MPa; 100 mg catalyst; 400 W Xe lamp; 6h | CO: 84% | CH₄ was activated on Zn-O site to form Zn-methyl species as an intermediate | 46 |
| 6 | WO₃ | 7 bar O₂; 13 bar CH₄; 150 mL H₂O; 10 mg catalyst; Xe lamp illumination of 150 mW cm⁻²; 3 h | HCHO: 99% | Surface $O^−$ species functions as the active species | 47 |
| 7 | WO₃ photoanode | 0.1 M Na₂SO₄ aqueous solution saturated with CH₄; simulated solar illumination of 100 mW cm⁻²; applied potential: 1.3V vs. reversible hydrogen electrode | $HOCH_2CH_2OH$: 66% | •OH radicals adsorbed on the (010) facet are separated | 48 |
| 8 | Cu-0.5/PCN | H₂O saturated with CH₄ (25 mL); 20 mg catalyst; 500 W Xe lamp; 1 h | $C_2H_5OH$: 81% | Synergistic interactions between Cu and the adjacent C atom in PCN | 37 |

[a]Examples 1-3 are illustrated in the section of *Control of Active Sites*. Examples 4-8 are illustrated in the section of *Control of Active Species*.