Understanding (photo)electrocatalysis for the conversion of methane to valuable chemicals through partial oxidation processes

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Methane (CH₄) with sp³ hybridization is known as a main constituent of natural gas, and has been utilized as a fuel and a hydrogen reservoir for power plant and transportation applications. Along with the complete oxidation of CH₄ to CO₂ to retard global warming, the partial oxidation toward the generation of liquid fuels is a big challenge because oxygenated products are more prone to oxidation than CH₄. Therefore, the control of the charge carriers and radical species is critical to prohibit the unwanted reaction, in other words, to maximize the formation of desired products. Photo and electrocatalysis are clean and sustainable techniques for CH₄ conversion, which do not require extreme experimental conditions (i.e., high temperature and pressure), and indeed, the reaction can be driven under sunlight (i.e., charge carriers generated by light absorption or photovoltaic-assisted electricity). In this review, we discuss how

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to design catalysts to overcome the bottlenecks in the photo and electrocatalytic partial oxidation of CH$_4$ with focus on (i) an interfacial charge transfer process, (ii) strategies for surface engineering of catalysts, (iii) key factors affecting the reaction mechanism and rate-determining step, and (iv) a systematic investigation of the reaction conditions to lift up the catalytic performance. Finally, we propose the milestone to guide not only the preparation of catalysts that can effectively generate charge carriers and intermediates with a mild oxidation behavior but also the design of reactors for scale-up to prevent undesired reaction pathways.

1. Introduction

Depending on the aspect of climate change and energy crisis, the conversion of methane (CH$_4$), the largest component of natural gas (70–90%), should lead toward the complete oxidation to carbon dioxide (CO$_2$) and partial oxidation to valuable oxygenates and (halo)hydrocarbons, respectively. With an environmental perspective, CH$_4$ is considered as one of the greenhouse gases, whose global warming potential (GWP, a measure of how much heat is trapped by each greenhouse gases in the atmosphere relative to CO$_2$) is 25 times higher than that of CO$_2$ over a 100 year period. Indeed, CH$_4$ is a major source for rising tropospheric ozone level, damaging human health and plant growth. Therefore, many countries pledged to cut CH$_4$ emission by 30% by 2030 under the Paris agreement. CH$_4$ emission occurs from both nature and human activities, and the main sources in the latter are natural gas harvesting, petroleum industry, enteric fermentation, landfills, manure management, and coal mining (Fig. 1a). Due to the inevitable emission of CH$_4$, concerted efforts to cut it down in agriculture and industry has been made for achieving the goals of the climate agreement. From an energy security standpoint, the discovery of a vast storehouse of methane hydrate as well as the advance of gas-well drilling and hydraulic fracturing technologies make CH$_4$ more readily available in the exothermic combustion of vehicular fuels and thermal power generation. The production of liquid hydrocarbons and oxygenates through the conversion of CH$_4$ is of major interest due to it being more usable as a basic building block for manufacturing diverse products, a high volumetric energy density (e.g., 37.8 J L$^{-1}$ for CH$_4$ versus 17.8 MJ L$^{-1}$ for methanol at 15 °C under 1 bar), and relatively low transportation/storage cost as well. Accordingly, it has received attention to develop low-cost, ecofriendly, and highly-efficient methods for the direct conversion of CH$_4$ to desired compounds.

CH$_4$ with sp$^3$ hybridization is known as a stable molecule in terms of the intrinsic inertness for C–H activation; thus, an energy intensive step requiring a high temperature and pressure is required to convert it to the desired products. In the industry, the steam methane reforming process (CH$_4$(g) + 0.5O$_2$(g) → CO(g) + 2H$_2$(g); CH$_4$(g) + H$_2$O(v) → CO(g) + 3H$_2$(g)) operating at 700–1000 °C and 3–25 bar generates hydrogen (H$_2$) and carbon monoxide (CO), which are utilized as not only fuel in fuel cell vehicle but also precursors to synthesize a wide range of products, a high volumetric energy density (e.g., 37.8 J L$^{-1}$ for CH$_4$ versus 17.8 MJ L$^{-1}$ for methanol at 15 °C under 1 bar), and relatively low transportation/storage cost as well. Accordingly, it has received attention to develop low-cost, ecofriendly, and highly-efficient methods for the direct conversion of CH$_4$ to desired compounds.

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**Fig. 1** (a) Source of methane emission in U.S. in 2019. (b) Enthalpy change of the sequential oxidation of CH$_4$ at 298 K. Redrawn with permission. Copyright 1991, Elsevier.
of chemicals and polymers. In order to produce value-added chemicals and fuels via the direct conversion of CH₄, reaction with a limited amount of oxygen (i.e., partial oxidation with less than the stoichiometric oxygen content) should be employed for prohibiting the oxidation of CH₄ into CO₂ and H₂O (CH₄(g) + 2O₂(g) → CO₂(g) + 2H₂O(v), ΔH₂₉₈ = −802.6 kJ mol⁻¹). However, it is unavoidable that a huge amount of CO₂ is released as a byproduct, and the process is not energetically favorable relative to complete oxidation (e.g., CH₄(g) + 0.5O₂(g) → CH₃OH(g), ΔH₂ₙ₉₈ = −126.4 kJ mol⁻¹; CH₄(g) + O₂(g) → HCHO(g) + H₂O(v), ΔH₂ₙ₉₈ = −276 kJ mol⁻¹) (Fig. 1b).

Photo and electricity-assisted conversion of CH₄ to valuable chemicals and liquid fuels is a future-oriented technology since the reaction proceeds under mild conditions (i.e., room temperature and atmospheric pressure) and renewable energy stemming from sunlight, wind, biomass, etc., is likely to replace fossil fuels. Moreover, the system does not require a complex and centralized infrastructure, which makes it suitable for remote location applications such as offshore drilling rigs, shale gas extraction facilities, and landfills. On the other hand, the bottleneck in the partial oxidation process of CH₄ mainly comes from a poor selectivity toward the target products as well as low reactivity owing to the activation energy barrier. The physicochemical property of CH₄, including a high homolytic bond dissociation energy for H-abstraction (440 kJ mol⁻¹), weakly-polarized symmetric sp³ geometry, weak acidity, and poor solubility should be considered to develop active catalysts.

Given the relatively effective dissociation behavior of CH₄ in thermocatalysis, a wide range of transition metal-based catalysts such as zerovalent metals, metal oxides, metal complexes, single metal atoms, and metal-exchanged zeolites have been revisited to be utilized as photo, electro, or cocatalysts. Furthermore, as part of methodologies to overcome such a high energy barrier, the addition of hydrogen peroxide (H₂O₂) facilitates its partial and complete oxidation depending on the experimental conditions. In photocatalysis, photogenerated electron–hole pairs are manipulated within one particle, whose conduction/valence band position thermodynamically determines whether an interfacial charge transfer occurs or not.

However, in electrocatalysis, the driving force can be controlled by applying the potential, where the reduction and oxidation reactions are separated by a membrane (Fig. 2b). The problems associated with poor mass transfer and low solubility of CH₄ should be avoided to optimize the cell performance. In this regard, a membrane electrode assembly (MEA) with outperforming typical H-type cells is suggested, where each cathode and anode catalyst layer is coated on the front and back side of a separator or membrane, respectively. The gas diffusion layer (GDL) coated on the outside of the catalyst layers dramatically improves the mass transport limitation of CH₄ and gas phase products. Furthermore, the overoxidation can be avoid by the set-up of the flow cell that is able to collect liquid oxygenates from the electrolyte. When designing anode catalysts, it is critical to selectively oxidize CH₄ instead of oxygenate products. Indeed, the competitive oxygen evolution reaction and the performance deterioration caused by ohmic, mass transport, and kinetic losses should be under control, especially when the cell voltage or the current density is high. For example, to meet the economic viability for the conversion of CH₄ to methanol, the selectivity should be at least 70% under the conditions (the overpotential <1 V and the current density >100 mA cm⁻² at 100–250 °C). A photoelectrochemical (PEC) cell is a combined system of photocatalysis and electrocatalysis; the operation is possible under bias-free conditions.
without electricity) and the oxidation/reduction reaction can be separated via the proper configuration of cells (Fig. 2c). Because of the deep valence band position of O\textsubscript{2p} and N\textsubscript{2p} in metal oxides and nitrides, respectively, photogenerated holes with strong oxidation power are feasible to stimulate the oxidation of CH\textsubscript{4}. Under an applied external bias or using a tandem PEC cell, a prolonged lifetime of charge carriers is achieved as a result of the band bending of the depletion layer, hence increasing the driving force for interfacial hole transfer to CH\textsubscript{4}.

In this review, we overview the state-of-the-art strategies that have been well established for the partial oxidation of CH\textsubscript{4} by means of photocatalysis, electrocatalysis, PEC cells, and advanced oxidation process (AOP)-related radical reaction, and discuss the geometric and electronic parameters of catalysts, reactor engineering, and the effect of the surroundings contributing to the activity and selectivity. Understanding the mechanistic pathway of electron- and hole-mediated reactions correlated with the formation of intermediates and products will offer a rational solution to overcome the bottleneck and optimize the catalytic performance as well. Rather than describing the synthesis of new materials and their characterizations, we focus on the surface engineering of catalysts affecting the interfacial charge transfer processes in the microenvironment and key factors changing the reaction mechanism and rate-determining step. At the end, we outline the milestones to lead researchers into the right path for not only the design of promising catalysts but also the engineering of reactors for scale-up.

2. Mechanistic view for methane conversion to desired products

As CH\textsubscript{4} is pyrolyzed above 700 °C, hydrocarbons can be produced by autocatalysis following the sequential processes (CH\textsubscript{4} \rightleftharpoons C\textsubscript{2}H\textsubscript{2} \rightleftharpoons C\textsubscript{2}H\textsubscript{4} \rightarrow C\textsubscript{2}H\textsubscript{6} \rightarrow aromatic hydrocarbons and coke), which is initiated by the radical species (CH\textsubscript{4} \rightleftharpoons CH\textsubscript{3} + H\textsuperscript{+}).\textsuperscript{24} Likewise, C\textsubscript{2} and C\textsubscript{3} products are obtained by the chain propagation (e.g., 2CH\textsubscript{3} \rightarrow C\textsubscript{2}H\textsubscript{6}; CH\textsubscript{3} + C\textsubscript{2}H\textsubscript{4} \rightarrow C\textsubscript{2}H\textsubscript{2} + CH\textsubscript{4}; C\textsubscript{2}H\textsubscript{6} \rightarrow C\textsubscript{2}H\textsubscript{4} + H\textsuperscript{+}; CH\textsubscript{3} + C\textsubscript{2}H\textsubscript{4} \rightarrow C\textsubscript{2}H\textsubscript{2} + CH\textsubscript{4}; C\textsubscript{2}H\textsubscript{3} \rightarrow C\textsubscript{2}H\textsuperscript{2} + H\textsuperscript{+} for C\textsubscript{2} hydrocarbons and CH\textsubscript{3} + C\textsubscript{2}H\textsubscript{4} \rightarrow n-C\textsubscript{3}H\textsubscript{7}; n-C\textsubscript{3}H\textsubscript{7} \rightarrow C\textsubscript{3}H\textsubscript{6} + H\textsuperscript{+}; CH\textsubscript{3} + C\textsubscript{2}H\textsubscript{4} \rightarrow C\textsubscript{3}H\textsubscript{3} + CH\textsubscript{4}; C\textsubscript{3}H\textsubscript{3} \rightarrow C\textsubscript{3}H\textsubscript{4} + H\textsuperscript{+} for C\textsubscript{3} hydrocarbons). In the presence of O\textsubscript{2}, diverse oxygenates can also be generated by both CH\textsubscript{3} and OH\textsubscript{2} radicals (CH\textsubscript{4} + O\textsubscript{2} \rightarrow CH\textsubscript{3} + OH\textsubscript{2}), which are involved in the formation of acetic acid, methanol, formaldehyde, etc. (e.g., CH\textsubscript{3} + O\textsubscript{2} \rightarrow CH\textsubscript{2}O\textsubscript{2}; CH\textsubscript{3}O\textsubscript{2} + CH\textsubscript{4} \rightarrow CH\textsubscript{2}COOH + CH\textsubscript{3}; CH\textsubscript{2}O\textsubscript{2} + CH\textsubscript{3} \rightarrow CH\textsubscript{2}OH + CH\textsubscript{2}O; CH\textsubscript{2}O\textsubscript{2} + CH\textsubscript{3} \rightarrow HCHO + OH\textsuperscript{+}).\textsuperscript{25} However, the problem is that the yield is extremely low.

The introduction of oxidants (e.g., nitrogen oxide, H\textsubscript{2}O\textsubscript{2}, O\textsubscript{2}, and water) or/heterogeneous catalysts sheds light on the solution to enhance the yield and selectivity since the activation energy can be effectively reduced. For example, the reactive radical species (CH\textsubscript{3} + CH\textsubscript{2}O\textsubscript{2}, etc.) can appear through the attack of nitrogen dioxide (NO\textsubscript{2}) (e.g., CH\textsubscript{4} + NO\textsubscript{2} \rightarrow CH\textsubscript{3} + HNO\textsubscript{3}; CH\textsubscript{3} + NO\textsubscript{2} \rightarrow CH\textsubscript{2}O\textsubscript{2} + NO). Over the surface of heterogeneous catalysts at low temperature, it is proposed that the C–H bond is cleaved by two mechanistic pathways. One is dehydrogenation involving electrophilic oxygen atoms (M–O sites) as a result of the formation of CH\textsubscript{3} + H\textsuperscript{+} following a radical-mediated oxidation process with a formal oxidation state (FOS) of C\textsuperscript{+I} for CH\textsubscript{2} (i.e., CH\textsubscript{3} \rightarrow CH\textsubscript{2} + H\textsuperscript{+}) in Fig. 3a. The other is deprotonation stemming from the dissociative adsorption of CH\textsubscript{4} (i.e., CH\textsubscript{4} \rightarrow CH\textsubscript{3} + H\textsuperscript{+}) following an instant coordination onto unsaturated metal centers to form the C–M σ-bond (Fig. 3b).\textsuperscript{26} The C–M σ-bond is formed when CH\textsubscript{4} is activated over metal centers. The formation of active site is balanced to optimize the performance of the catalysts. Photo and electrocatalysis over transition metal oxides can assist the (re)generation of active sites on the catalyst surface. In regard to the deprotonation process, the presence of proton acceptors on the surface of catalysts facilitates the reaction kinetics, and surface oxidizing M–O species that are able to be formed by photo and electrocatalysis may play an important role as a proton acceptor.

The study of CH\textsubscript{4} conversion in heterogeneous photocatalysis has mainly focused on gas phase systems, where the overoxidation of CH\textsubscript{4} was caused by the lattice and surface adsorbed oxygens, which consequently led to the formation of CO and CO\textsubscript{2}. The cleavage of the C–H bond initiated by the
trapped hole \( \text{M}^{2+} - \text{O}^2^+ + \text{h}^+ \rightarrow \text{M}^{3+} - \text{O}^+ \) in metal oxides), \('\text{OH}', \text{or other electrophilic oxygen species} is crucial for the partial oxidation. In contrast, the formation of reactive oxygen species (ROS) should be minimized in order to increase the selectivity for the non-oxidative coupling of CH\(_4\). As such, the manipulation of proper oxidants and radical species determines whether to synthesize oxygenates or hydrocarbons as the final products. In an aqueous system, the activation of CH\(_4\) may be more favorable by mobile \('\text{OH}' rather than by the trapped hole (or surface bound \('\text{OH}' in that the solubility of CH\(_4\) is extremely low and the adsorption of CH\(_4\) on the surface of catalysts is difficult under mild conditions (Fig. 4a)).\(27^{-31}\) The opposite outcome was also reported, i.e., mobile \('\text{OH}' stimulates the formation of C\(_2\)H\(_6\), whereas the reaction of surface-bound \('\text{OH}' with CH\(_4\) selectively produces methanol (Fig. 4b)).\(32\) The true mechanism of photocatalytic CH\(_4\) conversion is still a mystery. Nevertheless, it should be noted that the handling of time-dependent \('\text{OH}' concentration is important to improve the catalytic performance. The design of flow-type reactors is one of the strategies for not accumulating the oxidative radical species (i.e., to prevent overoxidation).\(33\) In addition, the photo-Fenton process is another approach to supply \('\text{OH}' in terms of the activation of H\(_2\)O\(_2\) \(\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}; \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{H}_2\text{O}\) (Fig. 4c).\(34^{,35}\) In spite of much efforts, the issue that the relatively high quantum yield and selectivity are obtained when the conversion of CH\(_4\) is extremely low is still unsolved in photocatalysis.

The electrocatalytic conversion of CH\(_4\) to value-added chemicals is driven by an anodic pathway, where active sites generated by applying positive bias \(\text{M} - \text{O}^2^- \rightarrow \text{M} - \text{O} + 2e^-\) or
MO₂ + H₂O → MO₂(‘OH) + H⁺ + e⁻; MO₂(‘OH) → MO₂⁻ + H⁺ + e⁻oxidizes CH₄. Along with the applied electrode potential, the local chemical environment influenced by adsorbates, supports, electrolyte constitutes, 3D chemical surroundings, temperature, pressure, etc., would also change the CH₄ oxidation process. The oxygen evolution reaction (OER) is a predominant process when a high voltage is applied for transition metal oxide catalysts such as Co₅O₄, NiO, and RuO₂, which is known as a competitive reaction for the oxidation of CH₄ in aqueous media. Fig. 5a compares the Gibbs free energy of transition metal oxides for water oxidation (O* + H₂O → *OOH + H⁺ + e⁻) and CH₄ activation (O* + CH₄ → *O–CH₄ → *(HO–CH₃)). Through the reaction steps, molecular oxygen (*OOH → * + O₂ + H⁺ + e⁻) and methanol (*HO–CH₃) → *CH₂OH → * + CH₃OH) are produced as the final product. In both the reactions, the dehydrogenation of *OH (‘OH → *O + H⁺ + e⁻) that is formed by single electron transfer process (‘H + H₂O → ‘OOH + H⁺ + e⁻) creates the adsorbed active oxygen atom (O*) as a transient species. In order to overcome the OER, the design of catalysts with a high Gibbs free energy for water oxidation but with a low one for CH₄ activation is highly required, and V₂O₅, TiO₂, SnO₂, PtO₂, and RhO₂ meet the conditions well. Theoretically, the operation in potentials close to 1.23 V₉Hₑ is amenable to suppress the OER. The emergence of high-valent metal oxidation states and the change in the surface free energy would increase the coverage of active M–O sites and modify the reaction pathway. Regarding TiO₂/RuO₂ composites, the introduction of V₂O₅ switches the reaction pathway as follows. Two ruthenium redox couples, Ru⁴⁺/⁶⁺ and Ru³⁺/⁴⁺, in RuO₂ participate in the production of oxygenates and modify the reaction pathway. Regarding TiO₂/RuO₂ surface free energy would increase the coverage of active M sites and modify the reaction pathway. Regarding TiO₂/RuO₂, the conversion of ruthenium (Ru⁶⁺) to Ru⁴⁺ to Ru³⁺ following the reactions CH₄ + 2RuO₂²⁻ → Ru⁴⁺–O–CH₂–O–RuO²⁻ → HCOOH + 2RuO²⁺. However, in the presence of V₂O₅ on RuO₂, the redox couple of vanadium (V⁵⁺/⁴⁺) may not donate enough electrons to form a double bond for formaldehyde and formic acid; thus, the selectivity toward methanol increases (CH₄ + V₂O₅→ CH₃–V₂O₄⁴⁻ + H⁺; CH₃–V₂O₄⁴⁻ + H⁺ → CH₃OH + V₂O₂²⁻). Transition metal ions also can be utilized as a redox couple in a homogeneous system, where metal centers of organometallic complexes dissolved in the electrolyte turn into a high-valent state by applying anodic bias. As shown in Fig. 5b, the Pt⁴⁺ of chloroplatinate accepts CH₄ by electrophilic addition reaction, and deprotonation produces the Pt²⁺–CH₃ complex, which is further oxidized into the Pt⁴⁺–CH₃ complex by virtue of the oxidation by the electrochemically-formed [Pt⁴⁺Cl₆]²⁻ (i.e., the Shilov cycle catalyzed by the redox cycle of [Pt⁴⁺Cl₆]²⁻ and [Pt⁴⁺Cl₆]⁴⁻). When H₂O or HCl exists, the Pt⁴⁺–CH₃ complex leads to the formation of methanol or methyl chloride, respectively. The mechanistic pathway based on the PEC oxidation of CH₄ is quite analogous to the electrochemical system. The surface-bound *OH on the (010) facet of the WO₃ photoanode can oxidize in situ formed methanol, resulting in the selective formation of ethylene glycol (Fig. 5c). A wide range of strategies to improve the active site and the activation of CH₄ toward the production of desired products will be discussed in the following section.

3. Selective oxidation of methane into oxygenates via light- and electricity-driven processes over heterogeneous catalysts

3.1. Photocatalytic CH₄ conversion

Photocatalysis is a tool to utilize photonic energy as a driving force for photocatalytic (∆G° < 0: downhill process) and photosynthetic (∆G° > 0: uphill process) reactions. As mentioned before, the oxidation of CH₄ is a downhill process; thus, the Gibbs free energy for partial oxidation to obtain oxygenates is more unfavorable than that for the complete oxidation to CO₂ (e.g., ∆G°(CH₂OH) = −115 kJ mol⁻¹; ∆G°(CH₃OH) = −296 kJ mol⁻¹; ∆G°(CO₂) = −818 kJ mol⁻¹).

Fig. 6 (a) Simplified photocatalytic process. (b) Diverse factors influencing the photocatalytic performance. IPCE and QE refer to ‘incident-photon-to-electron conversion efficiency’ and ‘quantum efficiency’, respectively. Reproduced with permission. Copyright 2017, American Chemical Society.
Although the schematic diagram representing the generation of electron–hole pairs and the interfacial charge transfer is simply depicted (Fig. 6a), understanding the detailed photophysical and photochemical processes is very difficult. Indeed, various factors should be considered to design highly active photocatalysts (Fig. 6b). Takanabe articulates the mechanistic pathway of photogenerated electron–hole pairs with considering time scale in his review article.\textsuperscript{44} The photocatalytic performance is governed by (i) photon absorption, (ii) exciton separation, (iii) carrier diffusion, (iv) carrier transport, (v) catalytic efficiency, and (vi) mass transfer of reactants and products. The excitation of the electron from the valence band to the conduction band (\textit{cf.}, from HOMO to LUMO in homogeneous photocatalysts) and the relaxation of the electron and hole to the band edge level occur in femtoseconds and in the range of femto to picosecond time scale, respectively.\textsuperscript{45} Free charge carriers separated from excitons in nano to microseconds are delivered to the surface, which participate in the redox reaction within milliseconds to seconds. Therefore, the optimization of the electronic structure of the photocatalyst can improve the photon absorption, exciton separation, carrier diffusion, and carrier transport, which is a descriptor of how efficiently generation and transfer of the charge carriers to the surface take place. In particular, the introduction of catalytically active sites on the surface of photocatalysts such as defect sites, functional groups, and cocatalysts would help to facilitate C–H activation in terms of the dehydrogenation and deprotonation of CH\textsubscript{4}. The control of the materials’ morphologies and the design of reactors can solve the mass transfer problems of CH\textsubscript{4} and gas phase products.

Some factors influencing the redox reaction such as experimental conditions, nature of the oxidants, sacrificial reagents, morphology, and surface properties of the photocatalysts should be considered for the effective conversion of CH\textsubscript{4}.\textsuperscript{46,47} Photocatalytic partial oxidation of CH\textsubscript{4} can be achieved under relatively low temperature and pressure.\textsuperscript{20,48} Contrary to thermocatalysis, the mild experimental conditions make it the systematic build-up of reactors much more easy. On the other hand, the addition of oxidants including H\textsubscript{2}O\textsubscript{2}, nitric oxide (NO), and O\textsubscript{2} could accelerate the photocatalytic activation of CH\textsubscript{4} by means of the emergence of highly active radical species such as \textsuperscript{1}OH or \textsuperscript{1}O\textsubscript{2}.\textsuperscript{49–51} The introduction of suitable sacrificial reagents can also boost up the reaction kinetics with scavenging either photogenerated electrons or holes. Accordingly, more charge carriers survived against the recombination possibly accelerate the activation of CH\textsubscript{4}.\textsuperscript{52} The dehydrogenation of CH\textsubscript{4} can be achieved by photogenerated holes directly, and the addition of electron acceptors such as Cu\textsuperscript{2+}, Ag\textsuperscript{+}, Fe\textsuperscript{3+}, and methyl viologen (MV\textsuperscript{2+}) may facilitate the kinetics since they are endowed with prolonged lifetime of holes.\textsuperscript{20,22,53} The concept is analogous to a three-electrode system in electrochemical cells. Consistent with many other studies, the morphology and surface functionality of photocatalysts have significant impact on the photocatalytic oxidation of CH\textsubscript{4}.\textsuperscript{20,46}

A systematic investigation on the parameters influencing the partial oxidation of CH\textsubscript{4} to CH\textsubscript{3}OH was conducted using...
The CH4 conversion and CH3OH production rate was 0.8% and 22.3, 59.7, and 18.1%, respectively. The lowest CH3OH production rate, which might be due to the photocatalytic process with Bi2WO4, whereas the lower selectivity toward C2H6 (9.0%) was observed. When the temperature increased from 55 to 90 °C, the formation of C2H6 was almost negligible and the CH3OH production rate was barely affected. Introducing Fe3+ as a more effective electron scavenger greatly accelerated the evolution of CO2, which was probably due to the enhanced charge separation and the overoxidation of CH4 by •OH (Fig. 7a). Interestingly, the higher selectivity toward CH3OH (below 10%) was obtained in spite of the sharp increase in the total conversion (~7%). The blank test with Fe3+ solution showed the oxidation of CH4 to CH3OH, CO2, and C2H6 and was attributed to hydroxyl radicals produced in the photo-Fenton process under UV light irradiation. The fabrication of Bi2WO5/TiO2 and BiVO4 was carried out to investigate the effect of the ability of charge separation and the conduction band energy level on CH4 oxidation, respectively (Fig. 7b). Among the three samples, Bi2WO5/TiO2 showed the highest CO2 production rate and lowest CH3OH production rate, which might be due to the production of more •OH. Despite such a low CH4 conversion, the selectivity (i.e., higher CH3OH, lower CO2, and C2H6 production) makes BiVO4 a promising material.

Noceti et al. synthesized La- and Pt-doped WO3 and carried out the photocatalytic activity test in the presence of MV2+ as an electron acceptor. This allowed photogenerated holes to oxidize H2O to •OH effectively instead of the recombination with electrons (Fig. 7c). •OH induced the dehydrogenation of CH4 to ‘CH3, and CH3OH was generated by the reaction between ‘CH3 and water (or •OH). The electron transfer from the conduction band to protons mediated by MV2+/+ led to the production of H2. The La-doped WO3 showed a relatively good catalytic activity (cf., about 4% of CH4 conversion) under mild conditions (at 94 °C and under a constant gas flow of CH4), where by-products including CO, H2, and O2 appeared (Fig. 7d). In the presence of H2O2 as a source to make •OH, the loading of FeOOH on WO3 significantly improved the photocatalytic conversion of CH4. However, an excess amount of H2O2 significantly reduced the production of the desired products (i.e., a poor selectivity) owing to overoxidation. The introduction of NO2− as an electron scavenger in the BiVO4-dispersed solution lifted up the formation of •OH in terms of the concomitant water oxidation by holes. Consequently, the selectivity of CH4 to CH3OH reached up to 93.0% but the low conversion problem still remained.

BiVO4 with unique morphologies was also investigated for CH4 conversion. Zhu et al. compared the photocatalytic activity of BiVO4 with different morphologies, and concluded that the bipyramid BiVO4 with (102) and (012) surface facets was favorable for the production of CH3OH relative to the platelet-type one with (001) facets. The selectivity toward CH3OH reached up to 85% and the mass activity was recorded as 112–134 μmol

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**Fig. 8** (a) Time-dependent formation of CO2, CO, and CH3OH for g-C3N4@Cs0.33WO3 sample under irradiation. (b) Trapping of the radical species; herein, K2Cr2O7, para-quinone, salicylic acid, and Na2C2O4 were used as sacrificial reagents for electrons, O2−, •OH, and holes, respectively. (c) Proposed mechanism for the conversion of CH4. Reproduced with permission. Copyright 2019, American Chemical Society.
The high selectivity is probably originated from not only the effective interfacial hole transfer but also the adjusted surface energy for the activation of the C–H bond.

Carbon nitride (C₃N₄), consisting of only carbon and nitrogen, is one of cost-effective visible light-active photocatalysts, and its preparation is also quite easy. Li et al. observed that CO and CO₂ were the main products when bare g-C₃N₄ was utilized, indicating that the overoxidation of CH₄ was severe. However, it could be overcome by the fabrication of mace-like g-C₃N₄-decorated Cs₀.₃₃WO₃ (g-C₃N₄@Cs₀.₃₃WO₃) nanocomposites. As seen in Fig. 8a, the selectivity of CH₄ (1000 ppm) to CH₃OH, CO, and CO₂ was estimated to be 51.59%, 12.08%, and 36.33%, respectively, where the concentration of CH₃OH increased linearly with the irradiation time. Cs₀.₃₃WO₃ was likely to protect the overoxidation of CH₃OH. According to the screening test result (Fig. 8b), it was concluded that both O₂⁻ and e⁻ are a main source to activate CH₄ (i.e., the C–H bond activation via the reductive pathway mediated by O₂⁻) (Fig. 8c), which is in contrast to the result of other studies. The in situ EPR measurement should be helpful to determine the ROS mainly involved as well as to monitor the structure change of the catalysts during the reaction.

In the presence of H₂O₂, the selective conversion of CH₄ to CH₃OH was accomplished by virtue of the fabrication of highly dispersed iron species on TiO₂ photocatalysts. In pristine TiO₂, CH₄ conversion and its selectivity toward CH₃OH during 3 h irradiation was 10.9% and 36%, respectively. As seen in Fig. 9a and b, the loading of noble metals on TiO₂ adversely affected the photocatalytic performance because zerovalent metals are known as a catalyst for the oxidation of CH₄ to CO and CO₂. Notably, the loading of 0.33 wt% iron species on TiO₂ enhanced the CH₄ conversion and the selectivity toward CH₃OH. By counting the formation of CH₃OH as the by-product, the total conversion to alcohols was estimated to be 97%. The control experiment clearly supports that the conversion of CH₄ mainly proceeded by the photocatalytic activation of H₂O₂ (Fig. 9c). Indeed, the labelling experiment using 13CH₄ revealed a new peak at m/z = 33, which indicates the formation of 13CH₃OH⁺ from the photocatalytic process (Fig. 9d).

Considering the X-ray absorption spectroscopy data, it was confirmed that FeOₓ consisted of FeOOH and Fe₂O₃, whose oxidation state was close to +3. Along with the enhanced electron transfer process from the TiO₂ conduction band to FeOₓ, the effective activation of H₂O₂ through a concomitant electron transfer improved the photocatalytic performance (Fig. 9e). As a result, it was proposed that the reaction between CH₃ and CH₃OH produced CH₃OH; the formation of O₂⁻ should be prohibited to avoid the overoxidation of CH₃OH to CO₂ (Fig. 9f). ZnO is an UV light active photocatalyst, whose bandgap size is almost identical to TiO₂ (about 3.2 eV). Without adding oxidants or cocatalysts, the photocatalytic conversion of CH₄ to CH₃OH was almost negligible, indicating that the proper modification of ZnO is highly required. The loading of cocatalysts (e.g., Pt, Pd, Au, or Ag) on ZnO showed the good photocatalytic conversion of CH₄ to CH₃OH and CH₃OOH under aerobic conditions. For instance, 0.1 wt% Au/ZnO resulted in a high photocatalytic activity of 125 μmol h⁻¹ for oxygenates with selectivity over 95%. The isotope experiment exhibited that the...
oxygen in CH3OH and CH3OOH stemmed from dissolved O2 in water. The result supports the proposed mechanism that CH3 formed by the dehydrogenation of CH4 with holes and CH3OOH generated by the oxygen reduction with electrons are combined together and then turned into CH3OH and CH3OOH. It should be noted that water oxidation was not considered in the overall reaction. Therefore, the balance between the reductive and oxidative pathways is critical to increase the selectivity. The different mechanism was also proposed in the Au/ZnO photo-catalyst.\textsuperscript{69} The dehydrogenation of CH4 to CH3 by OH can proceeded through both reductive and oxidative pathways; consequently, the reaction of CH3 with either OH or O2\textsuperscript{−} produced CH3OH. In here, both H2O and O2 were involved in the reaction.

3.2. Electrocatalytic CH4 conversion

The electrocatalytic activation of CH4 is able to be driven by either active oxygen on the surface electrode directly or free radicals formed at the electrode/electrolyte interface indirectly. In general, the cell performance is governed by the overpotential, surroundings, and the collision frequency, which are closely related to the activation energy, the ease of forming an active surface oxygen, and mass transfer of CH4 and products, respectively.\textsuperscript{61} In order to optimize the partial oxidation of CH4 to the desired products, efforts on catalyst discovery, electrolyte engineering, and reactor design should be made considering the three factors shown in Fig. 10. To date, not only diverse electrocatalysts but also the engineering of electrolytes and reactors have been investigated for the partial oxidation of CH4. The electrochemical system can be classified as (i) heterogeneous and homogeneous reaction, (ii) high and low temperature process, (iii) cathodic and anodic reaction, (iv) solid oxide and liquid electrolyte, and (v) fuel cell and electrolyzer type cell. 

In previous review articles, the effects of electrocatalysts, reaction conditions, and cell configurations on the formation of final products have already been well discussed and summarized in tables.\textsuperscript{20,26,63–73} In this review, we mainly focused on the theoretical approach to interpret the CH4 partial oxidation process on active sites in mild conditions, and overviewed the recent research results.

**Transition metal oxides.**\textsuperscript{74} The electrocatalytic oxidation of CH4 on transition metal oxides proceeds through the physical adsorption of CH4, followed by the activation of the C–H bond. Fig. 11a shows the products obtained from the oxidation of CH4 over various transition metal oxide catalysts. CO2 evolution was only observed both for TiO2, IrO2, and PbO2 in phosphate buffer and for PtO2 in KCl electrolyte. The inactivity of PtO2 in phosphate buffer was due to the poisoning of Pt covered by phosphate ions. The physical adsorption of CH4 transformed the tetrahedral symmetry of CH4 to the distorted structure \((D_{2d})\) with the H–C–H bond angle of about 120°, which scaled with the electrostatic interaction between CH4 and transition metal oxides. Therefore, the experimentally measured CH4 binding energy linearly increased with the Madelung potential of the metal in transition metal oxides (Fig. 11b). TiO2, IrO2, PbO2, and PtO2, classified as active catalysts, have a higher CH4 binding energy (>0.23 V) and a lower Madelung potential (<–40 V). The inactivity of ZrO2 and SnO2, despite satisfying the condition, was ascribed to the poor electrical conductivity and a small number of active sites, respectively. The introduction of Cu2O on TiO2 resulted in 6% faradaic efficiency at 0.35 mA cm\(^{-2}\) current density for the production of CH3OH, in which \(*\text{OH}\) was provided from Cu to \(*\text{CH}_3\)-populated TiO2. Cu has a lower energy barrier for the reaction of \(*\text{CH}_3\) with \(*\text{OH}\) and is resistant to the overoxidation of CH3OH (Fig. 11c). The DFT-predicted reaction profile for OER is depicted for the fully reduced state (Fig. 11d) and fully oxidized one (Fig. 11e) according to the reaction pathway (\(*\text{H}_2\text{O} \rightarrow *\text{OH} + 0.5\text{H}_2; *\text{OH} \rightarrow *\text{O} + 0.5\text{H}_2; *\text{O} + \text{H}_2\text{O} \rightarrow * + \text{O}_2 + \text{H}_2\)). OER was favorable for the under-coordinated metal sites of SnO2, TiO2, and IrO2 but on the
bridging O site of PbO$_2$. Fig. 11f shows the reaction profile for CH$_4$ oxidation following five steps: 1st: *CH$_4$ → *CH$_3$ + 0.5H$_2$; 2nd: *CH$_3$ → *CH$_2$ + 0.5H$_2$; 3rd: *CH$_2$ → *CH + 0.5H$_2$; 4th: *CH + H$_2$O → *CO + 1.5H$_2$; 5th: *CO + H$_2$O → *CO$_2$ + H$_2$.

The C–H bond activation was energetically advantageous for TiO$_2$, IrO$_2$, and PbO$_2$; however, SnO$_2$, with a lower M–O site, encountered a higher energy barrier. According to reactant-impulse chronoamperometry (RIC) and open circuit potential (OCP) changes along with DFT calculation, the reaction mechanism proposed that CH$_4$ oxidation proceeded through the formation of *CH$_x$ and *CH$_x$O($y$) intermediates at lower and higher potentials, respectively (Fig. 11g).

2D transition metal carbides (MXenes). The DFT calculation of the electrocatalytic CH$_4$ oxidation on various 2D carbides (MXenes) offers important clues to understand the relation among the stability of active oxygen, the reactivity of C–H bond activation, and the selectivity toward specific oxygenates. Under applied anodic potential, the O-terminated surface was predominant rather than both metal-terminated and OH-terminated surface. The C–H bond was activated by an active oxygen (O*) derived from water oxidation (i.e., hydroxylation adsorption: H$_2$O + * → OH* + H* + e$^-$; deprotonation: OH* → O* + H* + e$^-$). As the lower limit of electrochemical potential to form active oxygen ($U_{form}$, derived from $\max[\Delta G_{O*}/e]$/C0) is lower than the dissociation potential of active oxygen ($U_{diss}$, calculated by $[\Delta G_{OOH*}/e]$/C0), O* can be accumulated on the surface of the catalysts. As shown in Fig. 12a, the OER follows a volcano curve; thus, the MXenes at the right and left side of the volcano curve are suitable for CH$_4$ oxidation and OER, respectively. The change in C–H bond activation ($\Delta E_{a,TS} = E_{a,TS} - E_{CH4*}$) for the affinity energy of proton ($\Delta E_{OH*}/e$) indicates that MXenes with a high proton affinity tend to stimulate the activation of the C–H bond (Fig. 12b). A Sabatier-like relation was observed between the stability of active oxygen and the reactivity of C–H bond activation. The active oxygen in Hf$_2$CO$_2$ and Zr$_2$CO$_2$ is too active but the stabilized O* in Ta$_2$CO$_2$, NbC$_2$O$_2$, and V$_2$CO$_2$ is too inert, consequently lowering the CH$_4$ conversion yield. Contrary to MXenes composed of single

Fig. 11 (a) CH$_4$ oxidation products and faradaic efficiency over diverse transition metal oxides in 0.1 M potassium phosphate buffer (pH = 7). The result of PtO$_2$ was obtained in 1 M KCl (pH = 7) because of inactivity in 0.1 M potassium phosphate buffer. (b) Scaling relationship between the measured binding energy of *CH$_4$ and the Madelung potential of metal in transition metal oxides. (c) Faradaic efficiency of methanol oxidation to CO$_2$ over TiO$_2$ with applied potential in the presence/absence of Cu$_2$O$_3$. Reaction profile (d) for OER on the undercoordinated metal sites, (e) for CH$_4$ oxidation on the undercoordinated metal sites in transition metal oxides. (g) Possible reaction pathways for CH$_4$ oxidation and OER in an aqueous electrolyte. Reproduced with permission. Copyright 2021, National Academy of Sciences.
metals, CrHf2CO2 and TaHfCO2 are energetically favorable for CH4 activation. Depending on the applied potential for TaHf2C2O2, the formation of intermediates, known as relatively stable species, was changed (i.e., CH3O*, CO*, and CO2* at 1.4, 1.8, and 2.4 V, respectively) (Fig. 12c). On TaHf2C2O2, the production of oxygenates was preferred to that of hydrocarbons (inset in Fig. 12c), which is supported by the calculation based on the projected density of states (PDOS) and projected crystal orbital Hamilton population (pCOHP). For the Hf (5d2) with a few d electrons in TaHf2C2O2, the Hf–O bond is stronger than the Hf–C bond; therefore, the formation of oxygenates is predominant (Fig. 12d). The observation that only hydrocarbons, CO, and CO2 were produced on metallic Pt in a previous study would be due to a strong interaction between Pt and C. The electrons in Pt–C that are able to occupy the anti-bonding orbital are fewer than those in Pt–O (Fig. 12e).

Only few research articles have reported the electrocatalytic partial oxidation of CH4 at room temperature. The introduction of V2O5 in TiO2/RuO2 composites increased the current density and selectivity toward CH3OH when a gas diffusion electrode (GDE) cell was utilized in 0.1 M Na2SO4. The redox couple of V5+/4+ would not give electrons to form a double bond; thus, the selectivity toward CH3OH increased against HCHO and HCOOH. Park’s group reported the partial oxidation of CH4 to oxygenates using Co3O4/ZrO2 nanocomposites, Co3O4-incorporated ZrO2 nanotubes, and ZrO2/NiCo2O4 nanowires.

Fig. 12 (a) Free energies of the OH*, O*, and OOH* formation steps in OER as functions of ΔEOH* – ΔEO*. (b) The energy barrier of C–H bond activation (ΔEa,TS; TS means transition state) as a function of ΔEOH* – ΔEO*. (c) Free energy diagram of stable products in methane oxidation at different electrode potentials (1.40, 1.80, and 2.40 V vs.HRE). Inset: schematic diagram of the electrocatalytic conversion of CH4 on TaHf2C2O2 and blue arrows mean the energetically favorable route. Band filling of oxygen and carbon adsorbed on (d) TaHf2C2O2 and (e) metal Pt. Reproduced with permission. Copyright 2021, Elsevier.
using the typical single cell reactor. The Co₃O₄/ZrO₂ nanocomposites led to the formation of acetaldehyde as a major intermediate in the first 3 h, and finally turned into 1- and 2-propanol as the main products after 12 h in 0.5 M Na₂CO₃ (Fig. 13a). It was proposed that the electrochemically formed carbonate radicals would initiate the dehydrogenation of CH₄.
and the addition reaction of $^1\text{CH}_3$ to acetaldehyde generated C3 products. Herein, the role of ZrO$_2$ was assigned as a promoter to adsorb carbonates. In the control experiment, no increase in the LSV curve was observed for pristine Co$_3$O$_4$ regardless of CH$_4$ purging. With increasing ZrO$_2$ content, the current density increased and then decreased, supporting that the optimal ratio of ZrO$_2$ to Co$_3$O$_4$ should be considered to design highly-efficient electrocatalysts (Fig. 13b). The electrocatalytic performance was further enhanced either by the morphology control of Co$_3$O$_4$/ZrO$_2$ with Co$_3$O$_4$ nanoparticles embedded on the surface of ZrO$_2$ nanotubes or ZrO$_2$/NiCo$_2$O$_4$ quasi-solid solution nanowires, which improved the mass transfer problem of CH$_4$.

The electrocatalytic conversion of CH$_4$ to C$_2$H$_5$OH was investigated on NiO/Ni and Rh/ZnO catalysts. The NiO/Ni electrode in the potential range from 1.37 to 1.43 V$_{RHE}$ produced C$_2$H$_5$OH, whose selectivity was recorded to be about 81–89% in 0.1 M NaOH. Counting the formation of CH$_3$OH as a byproduct, the selectivity toward oxygenates was estimated to be over 90%. The yield of C$_2$H$_5$OH and CH$_3$OH increased up to 1.40 V, and then decreased with applied potential (Fig. 13c). The DFT calculation revealed that the formation of C$_2$H$_5$OH is more favorable than that of CH$_3$OH, and the proposed reaction pathway follows the sequential steps ($\text{i.e.}$, CH$_4$* $\rightarrow$ CH$_3$* + H*; CH$_3$* $\rightarrow$ CH$_2$* + H*; CH$_2$* + OH* $\rightarrow$ CH$_3$OH*; CH$_3$* + CH$_2$OH* $\rightarrow$ CH$_3$CH$_2$OH*) (Fig. 13d). Regarding Rh/ZnO nanosheets, the conversion, faradaic efficiency, and selectivity toward C$_2$H$_5$OH was measured as 789 $\mu$mol $g_{cat}^{-1}$ h$^{-1}$, 22.5%, and 85%, respectively, at 2.2 V$_{RHE}$ in 0.1 M KOH. It was suggested that Rh nanoparticles on ZnO nanosheets accelerated the adsorption of CH$_4$ and the formation of active oxygen species. The operando analysis is a powerful tool to understand the real-time process involved in the activation and conversion of CH$_4$. Hahn et al. investigated the activation of CH$_4$ on the Pt catalyst at room temperature using attenuated total reflectance-surface enhanced infrared absorption spectroscopy (ATR-SEIRAS), and it was confirmed that the intermediates –CHO (aldehyde) and –COOH (acid) were formed during the oxidation of CH$_4$. Furthermore, the intermediates were detected by in situ linear potential sweep-Fourier transform infrared spectroscopy (LPS-FTIRS). Together with CO$_2$ (2345 cm$^{-1}$), CO (2020 cm$^{-1}$), and H$_2$O (1650 cm$^{-1}$) peaks, a broad peak (1750 cm$^{-1}$) was observed due to the formation of aldehydic and ketonic species with the –CO moiety. At 1.46 V, the intermediate peaks for –CHO (1719 cm$^{-1}$) and –COOH (2027 cm$^{-1}$) were measured on the Pt electrode surface. The electrochemical oxidation of CH$_4$ over Pt/C, Pt/C-ATO, Pd/C, and Pd/C-ATO electrocatalysts was also confirmed by in situ ATR-Fourier transform infrared (ATR-FTIR) spectroscopy. Herein, the intermediates –CHO and CO were...
observed in the potential range from 0.05 to 1.2 V, which were clarified as intermediates for the production of CO₂.

### 3.3. Photoelectrochemical CH₄ conversion

When the Fermi level of the semiconductor and the chemical potential of the electrolyte (chemical species) are at equilibrium, ‘band-bending’ occurs depending on n-type and p-type materials. Under applied external bias or by the configuration of the tandem cell, photogenerated electron–hole pairs are separated, and the recombination is significantly retarded. In the n-type photoanode, the photogenerated holes transferred to the electrolyte/semiconductor interface initiate the oxidation. At the same time, the electrons collected on the counter electrode begin the reduction reaction. Ideally, the photogenerated holes oxidize CH₄ to oxygenates, while the electrons transferred to the cathode produce H₂. As mentioned before, ROS formed by water oxidation can attack and activate the stubborn C–H bond in terms of lowering the energy barrier, accompanying the dehydrogenation of CH₄ through a radical process. The technical advantages of the PEC cells including the controllable selectivity and production rate by applied potential, tunability of the electrode properties with the cocatalyst, and the facile fabrication of the cells are visible. However, it has failed to overcome a low efficiency and selectivity problem for the oxidation of CH₄. Due to limited studies, we discuss the PEC conversion of CH₄ to oxygenates and hydrocarbons as well.

Amano et al. reported the activation of CH₄ on WO₃ photoanode with a high quantum efficiency under visible light irradiation at room temperature. Applying external bias enabled the use of photogenerated electrons for H₂ production and the deeper depletion layer formed in WO₃ suppressed the recombination of charge carriers. In order to solve the low solubility and mass transport problems of CH₄, a bimodal (meso and macro) porous WO₃ photoanode was fabricated via the deposition of WO₃ nanoparticles on the microporous 3D Ti microfiber. The concentration of protons between the photoanode and cathode chambers was balanced by the assembly with Nafion membrane (Fig. 14a and b). Since the valence band maximum of WO₃ is more positive than the standard electrode potential of CH₄ oxidation (CH₄ +h⁺→ CH₃ + H⁺ + e⁻; E^' (CH₃/CH₄) = 2.06 V_{SH}) (Fig. 14a and b), the photogenerated holes can dehydrogenate CH₄ into a methyl radical (CH₃). Consequently, the homogeneous coupling of CH₃ brought about the production of C₂H₆ (CH₃ + CH₃ → C₂H₆). The gas–electrolyte–solid triple-phase boundary significantly improved the oxidation of the inert
C–H bond of CH₄ and led to the formation of CO₂ and C₂H₆. When the concentration of CH₄ was reduced in the feed (i.e., the stream of Ar with 10% CH₄ and 3 vol% H₂O), the production of C₂H₆ was negligible (Fig. 14c). In reverse, as the concentration of CH₄ fed increased, C₂H₆ production steadily increased. Under 97/3 vol% of CH₄/H₂O stream, the selectivity and the faradaic efficiency toward C₂H₆ reached up to 53.5% and 12%, respectively. These results indicate that the access of gaseous CH₄ to the surface of the WO₃ photoanode is important for preferential C–H bond activation by photogenerated holes. The selectivity toward C₂H₆ could be improved by making the surface of WO₃ hydrophobic for the effective adsorption of CH₄ instead of water.

Ma et al. optimized the reactivity of ’OH on WO₃ via facet tuning to produce ethylene glycol (EG) under mild conditions without adding any oxidants.⁴² Three WO₃ photoanodes with different (010) facet ratios including WO₃ nanobar arrays (WO₃NB), WO₃ nanoplate arrays (WO₃NP), and WO₃ nanoflake arrays (WO₃NF) were fabricated for comparison (Fig. 15a). Among them, WO₃NB with a predominant (010) facet revealed a superior CH₄ conversion performance. To confirm the production of ’OH on the catalysts with different facets, electron paramagnetic resonance (EPR) spectroscopy was measured using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a spin-trapping agent. The signal for DMPO−’OH on WO₃NB was stronger than that of other WO₃ structures. Based on the result that no H₂O₂ formation was observed during the experiment, it was expected that the oxidation of water was the only source to provide ’OH. Consequently, the EG production rate, selectivity, and solar-to-fuel efficiency in WO₃NB were recorded to be 0.47 μmol cm⁻² h⁻¹, 66%, and 0.12% at 1.3 V_RHE, respectively (Fig. 15b). The in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) data support that EG was steadily produced on the PEC cell (Fig. 15c). The typical peaks of EG at 2853 and 2924 cm⁻¹ (cf., assigned to methylene (CH₂) symmetric C–H stretching and antisymmetric C–H stretching, respectively) were measured, which increased with the irradiation time. Moreover, the emergence of methyl (CH₃) symmetric C–H stretching at 2879 cm⁻¹ and antisymmetric C–H stretching of CH₃OH at 2957 cm⁻¹ indicate that CH₃OH was formed as an intermediate during the PEC process. Therefore, the mechanism can be explained as follows: CH₃OH was formed by the
reaction between \(^{`OH}\) and \(^{`CH_3}\), which was further attacked by \(^{`OH}\), finally producing the EG (Fig. 13d).

It should be worth highlighting other metal oxide candidates for PEC cell applications. Fe\(_2\)O\(_3\) (hematite) has a suitable valence band minimum for CH\(_4\) oxidation and an ideal visible light absorption with n-type property, whose band gap energy was about 2.1–2.2 eV.\(^{85,86}\) Iron oxide is abundant in nature, cheap, and non-toxic, and the hematite-based photoanode is very stable during OER in an alkali electrolyte.\(^{87}\) BiVO\(_4\) with a bandgap of 2.4 eV shows an excellent PEC OER performance and is relatively stable in neutral pH.\(^{88,89}\) Metal chalcogenide, C\(_x\)N\(_y\), and metal carbide are also good candidates for visible light PEC CH\(_4\) oxidation because the outstanding photocatalytic activity was already reported for the partial oxidation of CH\(_4\) in slurry-type systems.\(^{90,91}\) The modification of the bulk and surface properties of semiconducting materials and cocatalysts or the introduction of highly active photocatalysts and electrocatalysts in PEC systems should be helpful to advance the design of the PEC device with high performance under sunlight.

### 3.4. Activation of oxidants for radical-assisted CH\(_4\) conversion

While the direct interaction between the surface-active site of heterogeneous (photo)electrocatalysts and CH\(_4\) stimulates the activation of CH\(_4\) in terms of the dehydrogenation and deprotonation processes, free-standing radical species (especially, \(^{`OH}\) and \(^{`Cl}\)) floating in the solution enable the extraction of hydrogen from CH\(_4\). Like Shi1ov cycle (Fig. 5b), the supply of \(^{`OH}\) can be maintained by the Fenton process unless H\(_2\)O\(_2\) is completely consumed. The ferric/ferrous redox cycle is regenerated by the electron transfer induced by photo and electrocatalysis. Under anaerobic conditions, a hole-mediated oxidation or an anodic reaction of water or chloride is the only way to produce active radical species. However, under aerobic conditions, the reductive pathway (i.e., electron-mediated reactions) produces H\(_2\)O\(_2\) and further electron transfer to \textit{in situ} formed H\(_2\)O\(_2\) generates \(^{`OH}\). Since an excessive amount of \(^{`OH}\) leads to the overoxidation of CH\(_4\), it is essential to establish the optimized experimental condition in order to increase the selectivity of the desired products.

In the presence of H\(_2\)O\(_2\) under mild conditions (below 100 °C), (i) iron-based catalysts (e.g., single iron atoms confined in graphene,\(^{92}\) ferric chloride (FeCl\(_3\)),\(^{93}\) Fe–Cu-ZSM-5,\(^{94}\) Fe/ZSM-5,\(^{95,96}\) Fe/Fe\(_x\)C,\(^{15}\) N-doped carbon supported iron species,\(^{97}\) etc.), (ii) atomic metals or metal nanoparticles embedded/loaded on metal oxides (e.g., single atomic Rh/ZrO\(_2\),\(^{98}\) AuPd/TiO\(_2\),\(^{99}\) single atomic Cr/TiO\(_2\),\(^{100}\) Rh/CoO\(_2\),\(^{101}\) single atomic Cu/CoN\(_4\),\(^{102}\) etc.), and (iii) bimetallic materials (e.g. Pd@Pt core–shell nanoparticles,\(^{103}\) Au–Pd alloys,\(^{104}\) AuPd@colloids,\(^{105}\) etc.) have been investigated for the partial oxidation of CH\(_4\). For example, graphene-confined single Fe sites (FeN\(_4\)/graphene nanosheets (GNs)) (Fig. 16a) effectively oxidized CH\(_4\) to C1 oxidated products including CH\(_3\)OH, CH\(_3\)OOH, HOCH\(_2\)OOH, and HCOOH in the liquid phase, whose turnover frequency (TOF) reached to 0.47 h\(^{-1}\) at room temperature.\(^{92}\) The labelling experiment using \(^{13}\)CH\(_4\) revealed that C1 oxidated products were originated from the partial oxidation process instead of the self-oxidation of graphene (Fig. 16b). As the Fe content increased from 1.5 to 4.0 wt%, the yield of C1-oxidated products increased from 27 to 100 μmol; however, the turnover number (TON) peaked at 2.7 wt% Fe and then decreased with Fe wt%. While more active sites emerged with the increase in the Fe content, the agglomeration among excess Fe species adversely affected the catalytic performance. Besides, with longer reaction time, the C1-oxidated products were prone to mineralization into CO\(_2\). Under the optimized conditions, the selectivity of C1-oxidated products and CO\(_2\) was 94 and 6%, respectively. Based on \textit{in operando} time-of-flight mass spectrometry (TOF-MS) data, it was confirmed that the formation of CH\(_3\)OH and CH\(_3\)OOH was predominant in the first 300 min, whereas HOCH\(_2\)OOH and HCOOH markedly increased in the last 300 min (Fig. 16c). The DFT calculation supports that the active oxygen atom can be easily formed by the adsorption and decomposition of H\(_2\)O\(_2\) on the Fe site (Fig. 16d). The methyl radical generated through CH\(_4\) activation over O–Fe\(_x\)N–0 would attack the hydroxide and hydroperoxide groups, which produced CH\(_3\)OOH and CH\(_3\)OOH, and the further oxidation of CH\(_3\)OH allowed to form HOCH\(_2\)OOH and HCOOH (Fig. 16e). As FeCl\(_3\) was utilized as a homogenous catalyst in the presence of H\(_2\)O\(_2\), the yield of CH\(_3\)OH and HCOOH was recorded as 1.97 and 33.3 mmol g\(_{-}\)cat\(^{-1}\) with a TOF of 5.7 h\(^{-1}\), respectively.\(^{99}\) It was proposed that the hydrated ferryl ion, [(H\(_2\)O)\(_5\)FeIVO\(_2\)]\(^{2+}\), that originated from the reaction with H\(_2\)O\(_2\) (i.e., Fe\(_{3+}\) + H\(_2\)O\(_2\) → [Fe\(_{5+}\)O\(_{2+}\) + OH + H\(_2\)O, or Fe\(_{3+}\) + H\(_2\)O\(_2\) → [Fe\(_{5+}\)O\(_{2+}\) + H\(_2\)O\(_2\)]) led to the activation of CH\(_4\) and consequently the formation of CH\(_3\)OH. On the other hand, \(^{`OH}\) provided by the Fenton process brought about the production of HCOOH, CO, and CO\(_2\).

On irradiating UV light with a wavelength below 380 nm, the direct photolysis of H\(_2\)O\(_2\) drove the formation of \(^{`OH}\), which promoted the oxidation of CH\(_4\) to CH\(_3\)OH and HCOOH.\(^{101}\) With an excess amount of H\(_2\)O\(_2\), the consumption of \(^{`OH}\) by H\(_2\)O\(_2\) (H\(_2\)O\(_2\) + \(^{`OH}\) → \(^{`OH}\) + H\(_2\)O; \(^{`OH}\) + H\(_2\)O → O\(_2\) + H\(_2\)O) decreased the CH\(_4\) conversion. Although the overoxidation of CH\(_4\) was inevitable, the complete mineralization to CO\(_2\) was significantly retarded by establishing the steady state condition that H\(_2\)O\(_2\) was added at a constant and relatively low rate. To overcome the drawback, especially a need for energy-intensive UV light and low quantum yield, the activation of H\(_2\)O\(_2\) on diverse photocatalysts (e.g., WO\(_3\),\(^{95,51}\) g-C\(_3\)N\(_4\),\(^{47}\) TiO\(_2\),\(^{104}\) iron clusters anchored on carbon aerogel,\(^{106}\) and BiVO\(_4\)\(^{55}\)\(^e\)) and its correlation with the oxidation of CH\(_4\) has been carried out. Under simulated solar light irradiation, the system containing TiO\(_2\), Fe\(_3\)O\(_4\), and H\(_2\)O\(_2\) transformed CH\(_4\) to CH\(_3\)OH, whose yield and selectivity reached up to 471 μmol g\(^{-1}\) h\(^{-1}\) and 83%, respectively.\(^{34}\) The conduction and valence band energy levels of TiO\(_2\) are suitable for the redox reaction of ferric/ferrous ions and the formation of \(^{`OH}\) by virtue of either water oxidation or H\(_2\)O\(_2\) activation (Fig. 17a). Compared with the cases (e.g., TiO\(_2\) + Fe\(^{3+}\) + light; TiO\(_2\) + H\(_2\)O\(_2\) + light; Fe\(^{3+}\) + H\(_2\)O\(_2\)), a higher yield and selectivity toward CH\(_3\)OH was achieved (Fig. 17b). The screening test using K\(_2\)Cr\(_2\)O\(_7\), \textit{para}-quinone, salicylic acid, and Na\(_2\)C\(_2\)O\(_4\) as scavengers of e\(^{-}\), O\(_2\), \(^{`OH}\), and h\(^+\), respectively, supports (i) the regeneration of Fe\(^{3+}\) is induced by the electron...
transfer, (ii) the activation of H$_2$O$_2$ produces ROS, and (iii) the oxidation of CH$_4$ proceeds through photogenerated holes and ROS (Fig. 4c and 17c).

The positively charged iron clusters anchored on 3D porous carbon aerogel, denoted as 0.75FeCA800-4, has a good activity for the partial oxidation of CH$_4$ to CH$_3$OOH. The 3D porous carbon aerogel with a high electrical conductivity is a good support; therefore, iron clusters with size from 0.25 to 0.45 nm were uniformly dispersed (Fig. 17d). Under simulated solar light irradiation, the production rate and selectivity toward CH$_3$OOH were 13.2 mmol g$_{Fe}$ h$^{-1}$ and almost 100% in the presence of H$_2$O$_2$ (2 mmol), respectively (Fig. 17e). The trend that an excess amount of H$_2$O$_2$ significantly cut down the selectivity owing to the overoxidation of CH$_3$OOH to CO$_2$ was also observed. The in situ DRIFTS and in situ EPR are powerful tools to understand the real-time reaction mechanism during photocatalysis. As seen in Fig. 17f, new peaks observed at 1306/1348, 1453, and 1550 cm$^{-1}$, assigned to $^*$C–H, $^*$C–O, and $^*$CH$_3$–O groups, respectively, increased with the irradiation time. Indeed, Fig. 17g demonstrates that the intensity of both the high spin state Fe$^{3+}$ at 200 G and the low spin state Fe$^{2+}$ at 3750 G was markedly enhanced with the irradiation time, which indicates that Fe$^{3+}$ gave electrons to the carbon atoms. The proposed mechanism is as follows: (i) photoexcitation of carbon atoms in 0.75FeCA800-4, (ii) electron transfer from Fe$^{3+}$ to C$^*$, (iii) formation of C$^*$, (iv) production of CH$_4$ via the electron transfer from C$^*$ to CH$_4$, (v) generation of Fe$^{3+}$–CH$_3$ with $^*$OH formed by the activation of H$_2$O$_2$, (vi) formation of Fe$^{3+}$–CH$_3$O$^*$ intermediates, (vii) reaction of Fe$^{3+}$–CH$_3$O$^*$ with $^*$OH, and finally, (ix) the production of CH$_3$OOH (Fig. 17h).

Scheme 1 A schematic representation of photocatalytic (PC), electrocatalytic (EC), photoelectrochemical (PEC), and advanced oxidation process (AOP)-based activation of methane as a tool to detour the energy-intensive process. Partial oxidation processes driven by clean and sustainable technologies are one of the most promising ways to obtain valuable products directly from methane.
The introduction of a relatively excess amount of oxidants and their activation to ROS with high oxidation power may damage the membrane in electrochemical cells. Therefore, oxygen reduction reaction (ORR) catalysts should promote 4e− transfer \((O_2 + 4H^+ + 4e^- \rightarrow 2H_2O)\) with suppressed 2e− transfer \((O_2 + 2H^+ + 2e^- \rightarrow H_2O_2)\) to be utilized for a proton exchange membrane fuel cell \((\text{PEMFC})\).\(^{107}\) Although no studies have been reported so far except for one paper, the cathodic activation of \(H_2O_2\) for \(\text{CH}_3\text{OH}\) production in a \(\text{PEMFC}\),\(^{108}\) the recent research work provides a profound insight into the feasibility of producing and handling reactive species for electrocatalytic \(\text{CH}_4\) conversion.\(^{109}\) The cobalt–nickel mixed spinels of \(\text{Co}_2\text{Ni}_3\text{O}_4\) consisting of tetrahedral \(\text{Ni}^{2+}\) and octahedral \(\text{Co}^{3+}\) and \(\text{CoNi}_2\text{O}_4\) composed of octahedral \(\text{Ni}^{2+}\) and tetrahedral \(\text{Co}^{3+}\) (Fig. 18a) were favorable for generating active chlorine species \((*\text{Cl})\), which promoted the production of \(\text{CH}_3\text{Cl}\) under an applied potential. The surface adsorbed \(*\text{Cl}\) as an intermediate of the chlorine evolution reaction \((\text{CIER})\) stimulated the cleavage of the C–H bond and overoxidation could be avoided by the release of gaseous \(\text{CH}_3\text{Cl}\) from the electrolyte. In 0.5 M \(\text{Na}_2\text{SO}_4\) electrolyte, the current density in the LSV curve was quite low due to a high energy barrier, and only \(\text{CO}_2\) was evolved (Fig. 18b). However, when an excess amount of \(\text{Cl}^-\) was present \((5.4\ \text{M NaCl})\), the current density at 2.3 V rose up to 19.5 mA cm\(^{-2}\) and the CIER-assisted pathway prevailed on the OER-assisted one. The \(\text{in situ}\) EPR experiment confirmed the formation of \(*\text{Cl}\) and subsequently \('\text{Cl}_2\) where \(\text{DMPO–Cl}\), \(\text{DMPO–OH}\), and \(\text{DMPO–OCl}\) were simultaneously observed (Fig. 18c). Regarding the conversion of \(\text{CH}_4\) to \(\text{CH}_3\text{Cl}\), a higher overpotential to make active oxygen atoms \((\text{Ni–O}^\bullet)\) is required; thus, the overoxidation of liquid oxygenates is inevitable (Fig. 18d).

4. Conclusions and outlook

Photocatalysis, electrocatalysis, PEC cell, and radical-mediated AOP techniques are capable of bypassing energy-intensive processes \((\text{i.e.},\ \text{high temperature and pressure})\) but are available to utilize the photonic energy \((\text{cf.},\ \text{ideally, direct absorption of solar light or PV-powered electrolyzer})\) as a driving force for the activation of the C–H bond (Scheme 1). The major hurdle of \(\text{CH}_4\) partial oxidation refers to (i) low conversion yield of \(\text{CH}_3\), (ii) a competitive OER process, (iii) poor selectivity induced by the overoxidation, (iv) mass transfer problem of \(\text{CH}_4\) and the final products, (v) separation of the desired products from the electrolytes, (vi) scale-up issue, and (vii) a mysterious reaction mechanism, which should be overcome and verified for practical applications.

Photocatalysis follows a series of processes including (i) photon absorption, (ii) exciton separation, (iii) carrier diffusion, (iv) carrier transport, (v) catalytic efficiency, and (vi) mass transfer of the reactants and products. Therefore, the overall reaction kinetics are governed by the most sluggish step, which means that all the six factors should be optimized in order to increase the photocatalytic activity. In addition, the electronic structure of the photocatalyst \((\text{i.e.},\ \text{the bandgap, conduction and valence band position, energy level of the trapping sites for charge carriers, and Fermi level equilibrium})\) is associated with the thermodynamics that determine whether the reaction proceeds or not. When focusing on not only interfacial charge transfer but also the activation of the C–H bond, the direct dehydrogenation of \(\text{CH}_4\) likely proceeds by photogenerated holes over the surface of the photocatalysts. On the other hand, \('\text{OH}\) provided from the cleavage of \(\text{in situ}\) formed \(\text{H}_2\text{O}_2\) by electron transfer or hole-mediated water oxidation enables to abstract hydrogen from \(\text{CH}_4\) in the proximity of the catalysts. The formation of \('\text{OH}\) and \(\text{O}_2^\bullet\) is adjusted by the addition of \(\text{H}_2\text{O}_2\) or by the reaction under aerobic conditions. The combination of \(\text{CH}_4\) with \('\text{OH}\) produces oxygenates, and the selectivity toward the desired products can be improved by controlling the concentration of \('\text{OH}\) by suppressing the over-oxidation. One of the strategies will be the introduction of a proper scavenger of \('\text{OH}\); for example, carbonate \((\text{CO}_3^{2–})\) effectively quenches \('\text{OH}\) \((k(\text{HCO}_3^-) = 8.5 \times 10^6 \ \text{M}^{-1} \ \text{s}^{-1}\) and \(k(\text{CO}_3^{2–}) = 3.9 \times 10^8 \ \text{M}^{-1} \ \text{s}^{-1}\))\(^{110}\) resulting in the formation of \(\text{CO}_3\) with a higher standard reduction potential \((E(\text{CO}_3^{2–}/\text{CO}_2) = 1.63 \ \text{V})\).\(^{111}\) Likewise, such a high oxidation power of \('\text{OH}\) would be systematically reduced by electron transfer from the halide ions \((E(\text{Cl}^-/\text{Cl}) = 2.5 \ \text{V}; E(\text{Cl}_2^-/\text{Cl}) = 2.2 \ \text{V}; E(\text{Br}^-/\text{Br}^-) = 2.0 \ \text{V}; E(\text{Br}_2^-/\text{Br}^-) = 1.7 \ \text{V})\).\(^{112}\) Another approach is the control of the HOMO and LUMO energy levels in terms of the synthesis and modification of transition metal complexes. Not only the change in the oxidation potential of \('\text{OH}\) by redox couples but also the emergence of high-valent transition metal ions may assist C–H bond activation and increase the yield and selectivity. Beyond the utilization of \(\text{H}_2\text{O}_2\), persulfate \((\text{peroxymonosulfate and peroxydisulfate})\), periodate, hypochlorous acid, \(\text{etc.},\) are also good candidates to supply the radical species through the photocatalytic process. As a non-radical reaction pathway, the influence of singlet oxygen \((\text{O}_2\) formed \(\text{via}\) the conversion of the singlet excited state to the triplet excited state on the photocatalytic oxidation of \(\text{CH}_4\) needs to be proven.

The electrocatalytic partial oxidation of \(\text{CH}_4\) to oxygenates under mild conditions is still at quite an early stage, and very limited studies have been undertaken so far. The design of appropriate electrocatalysts and electrochemical cells in consideration of factors such as an electrode configuration, a membrane, an electrolyte, a surrounding condition, \(\text{etc.},\) is critical to increase the conversion of \(\text{CH}_4\) and its selectivity to desired products. In general, high selectivity is achieved at a low current density \((\text{i.e.},\ \text{a low conversion yield due to a small number of electrons involved})\), and as the current density rises, the selectivity significantly decreases due to not only the overoxidation of the target products but also the competitive reaction with OER. To overcome the competitive OER, the development of catalysts with a high Gibbs free energy for water oxidation but with a low one for \(\text{CH}_4\) activation is highly required. Under an applied bias, active M–O sites on transition metal oxides promote the dehydrogenation of \(\text{CH}_4\) in which the catalyst with a high \(\text{CH}_4\) binding energy but a low Madelung potential leads to a higher performance. In the presence of proton acceptors, the deprotonation pathway drives the activation of the C–H bond as well. Therefore, materials that can simultaneously stimulate the dehydrogenation and deprotonation will be favorable for the conversion of \(\text{CH}_4\), where more
precise control of the active sites is essential to optimize the selectivity. To better understand the reaction mechanism, real-time spectroscopy is necessary to monitor the change of (i) the oxidation states and electronic structures of transition metal-based catalysts, (ii) reorientation of surface atoms and defects, (iii) electrode surface pH and interaction with electrolyte ions confined in the microenvironment, (iv) the formation of transient species and intermediates, and their correlation with DFT calculation. Through either by the fabrication of MEAs or the modulation of cells by stacking, the size of the device can be scaled-up; thus, the productivity increases to meet the demand of industries. The development of membranes that enable the desired products to be transported from the anode to the cathode chamber, and electrolyte engineering that may help to stabilize oxygenates by solvation (e.g., ionic liquid and H2SO4) may effectively retard the overoxidation process. As proposed in photocatalysis and electrocatalysis, the same strategy may be valid to optimize the performance of PEC cells.

The radical-mediated AOP technique looks similar to a double-edged sword because ROS formed by the activation of oxidants accelerate the oxidation of CH4 but the excess amount drives the complete mineralization into CO2. Indeed, the prolonged reaction time overoxidizes the desired products. Therefore, the addition of H2O2 at regular time intervals to maintain a steady state condition may be more advantageous to reach a higher selectivity. The activation of oxidants into ROS occurs via heterogeneous catalysis, whereas the dehydrogenation of CH4 by ROS is proceeded in the homogeneous phase. Ideally, if ROS are instantaneously produced (i.e., 100% conversion of H2O2 to OH within a few seconds) and the concentration of dissolved CH4 is enough to consume all OH, overoxidation will be suppressed due to the termination of the radical reaction in the second scale. The concept is quite similar to burst nucleation to synthesize uniform-sized metal nanoparticles.11 Under atmospheric pressure, micro or nanobubbling of CH4 would increase the solubility of CH4 as well as the collision probability of ROS. In order to commercialize the electrocatalytic CH4OH production directly from CH4, the conversion efficiency should reach up to 70% by satisfying the operation condition (i.e., cell area ≥200 cm², current density ≥100 mA cm⁻², and applied bias ≤1 V).23 Although it may seem like a distinct future when it comes to realization under mild conditions, it is a promising research topic and rapid scientific progress will advance the deployment of self-standing reactors at commercial scales.

Author contributions


Conflicts of interest

There are no conflicts to declare.

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Notes and references
