Methane transformation by photocatalysis

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Abstract | Methane hydrate and shale gas are predicted to have substantial reserves, far beyond the sum of other fossil fuels. Using methane instead of crude oil as a building block is thus a very attractive strategy for synthesising valuable chemicals. Because methane is so inert, its direct conversion needs a high activation energy and typically requires harsh reaction conditions or strong oxidants. Photocatalysis, which employs photons operated under very mild conditions, is a promising technology to reduce the thermodynamic barrier in direct methane conversion and to avoid the common issues of overoxidation and catalyst deactivation. In this Review, we cover the development of photocatalysts and co-catalysts, including the use of inorganic materials and polymeric semiconductors, and explain how the use of batch or flow reaction systems affects the reaction kinetics and product selectivity. We also discuss efforts to understand the underlying reaction mechanisms from both a photophysical and a chemical perspective. Finally, we present our view of the challenges facing this field and suggest potential solutions.

[H1] Introduction

With the declining reserve of crude oil and the predicted substantial reserve of methane hydrate and shale gas, there is a real need to utilise methane instead of oil as a building block for chemical synthesis in the next decades.[1,2] According to the International Energy Outlook 2019 (U.S. Energy Information Administration, Sept 2019), natural gas production in the whole world will increase enormously from 133.1 to 191.6 quadrillion British thermal units by 2050, indicating the importance of efficient methane conversion and utilisation.[3] Although the direct conversion of methane to high-energy-density fuel and chemicals is desirable, it is not yet possible at commercial scale. Owing to the inert nature of methane—arising from its symmetrical tetrahedral geometry, low polarizability, and high C-H bond energy of 439 kJ mol^{-1}—its conversion traditionally requires harsh reaction conditions and/or strong oxidants, and is energy-intensive with excess CO_2 emissions.[2,4] Rapid accumulation of cokes and sintering of catalysts often happen under such harsh conditions, leading to the deactivation of catalysts.[5,6] Furthermore, the serious impact of direct methane emission into the atmosphere as a greenhouse gas must be mitigated.[7] Thus there are clear financial and environmental incentives for academia and industry to develop effective and green approaches to directly convert methane into valuable chemicals.

Photocatalysis, a promising alternative to traditional thermocatalysis, employs photons instead of thermal energy to drive chemical processes and is mostly operated under ambient conditions. Unlike methane conversion by thermocatalysis, which requires a large activation energy due to methane's inertness, photocatalysis generates very energetic charge carriers that pre-activate methane and substantially reduce the activation energy. This pre-activation process even allows uphill (thermodynamically unfavourable) reactions to proceed at room temperature, overcoming the conventional thermodynamical barrier (Figure 1a). Furthermore, for those reactions often carried out at very high temperatures (such as non-oxidative coupling of methane (NOCM) or non-oxidative methane dehydroaromatistaion (MDA) at >673 K, sometimes even >1273 K), the product yield by thermocatalysis at room temperature is estimated to be about 0.0002% and 0.000007%, respectively, due to thermodynamic equilibrium;[8,9] the special function of photons can break the limitation of thermodynamic equilibrium, leading to a 100-to-10000-times improvement in yield. In addition, photocatalytic reactions are theoretically expected to avoid harsh reaction conditions, overoxidation and catalyst deactivation. The heat generated by the reaction can also be readily dissipated. At the same time, the spatial separation of redox reaction sites within one photocatalyst can to some extent further prevent unnecessary collision of radicals. All these factors contribute to the advantage of photocatalytic methane conversion in the control of high selectivity. Thus almost all the products of interest can find a photocatalytic system with a selectivity of >90% and even 100% (Supplementary Table 1).

In particular, the past five years have witnessed an explosion of various products photocatalytically synthesised from methane, such as methanol,[10–12] formaldehyde,[13] ethanol,[14] ethane and ethylene,[15–17] acetone,[18] benzene[8] and syngas.[19] Many photocatalysts and co-catalysts have been developed to improve yield and/or selectivity by either enhanced light harvesting, charge separation or C-H activation. The reaction system itself, including the reactor setup, can also heavily affect the reaction yield and selectivity. Solid progress has also been made in understanding the underlying mechanism, although still far behind the discovery of catalysts owing to the complicated hardware required and the time-consuming nature of mechanistic studies.

This Review covers the development of photocatalysts and co-catalysts, with an aim to comprehensively examine the strategies to improve selectivity and yield for desired products and catalyst stability. We also compare the design and performance of batch and flow reaction systems, and discuss efforts to understand the photophysical and surface chemical reaction mechanisms. Finally, we present key challenges in photocatalytic methane conversion and offer blueprints for future research.

[H1] Principles of photocatalytic methane conversion

The basic mechanism of photocatalysis[20,21] is illustrated in Figure 1b. When irradiated by a light source with proper wavelength, a photocatalyst harvests photons and the electrons populate the conduction band, leaving holes in the valence band. Some recombination of electrons and holes produces thermal energy, while the other photo-generated carriers migrate to the surface to initiate chemical reactions with reactants.

The reaction between charges and methane can take several different pathways (Figure 1c). The C-H bond can be directly activated by photoholes, photoelectrons, or energetic carriers from plasmonic metals. In the direct activation by photoholes, a metal oxide semiconductor such as TiO_2[10] or ZnO[22] generates photoholes (or lattice O^- species) with high oxidative power (approximately +3 V vs. standard hydrogen electrode)[23,24] to abstract hydrogen from the C-H bond. Photoholes are not only from the classic semiconductors; some pure silica materials with active nonbridging oxygen hole centres ($\equiv Si-O\cdot$), for instance, can also react with methane to generate methyl radical under high-energy UV light.[25] The activation by photoelectrons was only recently reported, in which the C-H bond was reduced and cleaved by the photoelectrons. This result was supported by density functional theory calculations and in situ diffuse reflectance infrared spectroscopy in a NOCM reaction, and the as-formed methyl anion was proposed as a possible intermediate species for the further generation of ethane.[26] A plasmonic metal such as Cu, Ag, or Rh can also activate the C-H bond. When the metal is under irradiation, the localized surface plasmon resonance (LSPR) induces enhanced light absorption and thus the efficient generation of energetic hot carriers.[19] The injection of either energetic carriers or energy into the molecular orbital of the methane molecule can weaken and activate the strong C-H bond.[27,28]

The C-H bond can also be indirectly activated by $\cdot OR$ radicals or through a chemical loop process by mediates. In the first case, the most frequently observed intermediate is the hydroxyl radical ($\cdot OH$), which is easily generated in the presence of surface hydroxyl ions, adsorbed water or added hydrogen peroxide (H_2O_2). Hydroxyl radicals can abstract a hydrogen atom from methane to generate methyl radicals,[29] owing to their high oxidative potential ($E^{\ominus}$=2.73 V).[30] The high-energy electrophilic alkoxy radical ($\cdot OR$) functions similarly.[31] In the chemical loop process,[32,33] a mediate such as a metal cationic species or lattice oxygen is used to carry out photocatalytic methane oxidation by two interconnected steps: first, the interaction between methane and the photocatalyst at the expense of the mediate to generate the products with high selectivity, followed by the regeneration of reduced mediate species with oxidants (O_2, H_2O) to complete the catalytic cycle.

Methane can be used to synthesise diverse products through different reaction pathways by photocatalysis or thermocatalysis, and the major processes are listed in Table 1. These products include methanol (CH_3OH) and ethanol (CH_3CH_2OH) through partial oxidation of methane (POM), ethane (C_2H_6) and ethylene (C_2H_4) through oxidative coupling of methane (OCM) and non-oxidative coupling of methane (NOCM), benzene (C_6H_6) through non-oxidative methane dehydroaromatistaion (MDA), syngas (CO and H_2) through steam reforming of methane (SRM) and dry reforming of methane (DRM), and carbon dioxide (CO_2) through total

oxidation. It should be noted that some reactions are thermodynamically feasible only with the assistance of oxygen (Table 1, entries 3-4, 7, 9-10, 13-14) while the others do not require oxygen. Furthermore, these reactions are always accompanied by thermodynamically favourable but unexpected side reactions, no matter whether under aerobic conditions (for example, CO_2, entry 14) or anaerobic conditions (for example, cokes, entry 15), making the development of a catalyst with high yield and high selectivity very challenging.

Table 1 Change of ΔG^0 (298 K) for various methane conversion reactions

Entry	Main product	Reaction name	Chemical equation	ΔG^0 (298 K) kJ mol^{-1}
1	Syngas	Steam reforming of methane (SRM)	$CH_4 + H_2O \rightarrow CO + 3H_2$	142.1
2		Dry reforming of methane (DRM)	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	170.7
3		Partial oxidation of methane (POM)	$2CH_4 + O_2 \rightarrow 2CO + 4H_2$	-173
4	CH_3OH	POM	$2CH_4 + O_2 \rightarrow 2CH_3OH$	-222.6
5		Methane to methanol with water	$CH_4 + H_2O \rightarrow CH_3OH + H_2$	117.3
6	C_2H_5OH	Methane to ethanol with water	$2CH_4 + H_2O \rightarrow C_2H_5OH + 2H_2$	161.7
7	HCHO	POM	$2CH_4 + O_2 \rightarrow 2HCHO + 2H_2$	-103.6
8	CH_3COCH_3	Methane to acetone with CO_2	$2CH_4 + CO_2 \rightarrow CH_3COCH_3 + H_2O$	114.1
9	C_2H_4/C_2H_6	Oxidative coupling of methane (OCM)	$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$	-287.6
10		OCM	$4CH_4 + O_2 \rightarrow 2C_2H_6 + 2H_2O$	-320
11		Non-oxidation coupling of methane (NOCM)	$2CH_4 \rightarrow C_2H_6 + H_2$	68.6
12	C_6H_6	Non-oxidative methane dehydroaromatistation (MDA)	$6CH_4 \rightarrow C_6H_6 + 9H_2$	433.9
13		Oxidative aromatization of methane	$12CH_4 + 9O_2 \rightarrow 2C_6H_6 + 18H_2O$	-3247
14	CO_2	Total oxidation	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	-800.9
15	Carbon	Pyrolysis	$CH_4 \rightarrow C + 2H_2$	50.7

[H1] Development of photocatalytic materials

Photocatalytic materials are at the core of achieving decent yield and selectivity for methane conversion. Many materials have been reported over the past few decades (Figure 2). The photocatalytic materials consist of a substrate semiconductor that absorbs light and generates redox pairs (e$^-$/h$^+$), and a co-catalyst on which the thermodynamic barrier of methane activation is lowered and the selectivity to target products is manipulated. We review representative photocatalysts and co-catalysts, in particular focusing on those developed over the past five years (Table 2; for a full table please see Supplementary Table 1).

Table 2 Representative photocatalysts used for methane conversion to various products

Co-catalyst/photo catalyst	Experimental conditions	Methane conversion	Main products	Product rate	Product selectivity		AQY[b]
[a]TiO_2[38]	Batch reaction, Hg lamp (λ > 320 nm), 100 mg catalyst, 0.097 Torr CH_4, 0.152 Torr O_2, room temperature to 623 K, reaction time 1.5 h	-	C_2H_6	1.61 mol h^{-1}	ca. 27.6%		-
[a]Pt/TiO_2[41]	Batch reaction, 1.6 kW Xe lamp, 100 mg catalyst, 20 mL 2 M NH_4Cl solutions, reaction time 64 h	-	Amino acids	~0.0078 µmol h^{-1}	-		-
Pt/black TiO_2[122]	Flow reaction, 150 W Xenon lamp (λ > 420 nm), 15 mg catalyst, H_2O:CH_4 = 1:1, GHSV = 80000 mL g^{-1} h^{-1}, 773 K	-	H_2	2.775 mmol h^{-1}	-		60% (λ > 420 nm, 773 K)
FeO_x/TiO_2[10]	Batch reaction, 300 W Xe lamp (λ < 710 nm), 10 mg catalyst, 20% CH_4, 80% Ar, 6 mL H_2O, 4 mL 2 mM H_2O_2, 298 K, reaction time 3 h	15%	CH_3OH	3.5 µmol h^{-1}	90%		-
Au/TiO_2[26]	Flow reaction, 300 W Xe lamp, 5 mg catalyst, 10% CH_4, 90% Ar, GHSV = 120000 mL g^{-1} h^{-1}, room temperature	-	C_2H_6	0.41 µmol h^{-1}	95.9%		-
Pt-CuO_x/TiO_2[93]	Flow reaction, 40 W 365 nm LED, 100 mg catalyst, CH_4:O_2 = 400:1, 10% CH_4, GHSV = 2400 h^{-1}, 313 K	-	$C_2H_4$and C_2H_6 CO_2	6.8 µmol h^{-1}	60%		0.5% (365 nm)
Zn-$H_3PW_{12}O_{40}/TiO_2$[34]	Batch reaction, 400 W Xe lamp, 100 mg catalyst, 0.3 MPa CH_4, 0.1 MPa air, room temperature, reaction time 6 h	-	CO	42.9 µmol h^{-1}	84%		7.1% (362 nm)
Ag-$H_3PW_{12}O_{40}/TiO_2$[32]	Batch reaction, 400 W Xe lamp, 100 mg catalyst, 0.3 MPa CH_4, room temperature, reaction time 7 h	-	C_2H_6	2.3 µmol h^{-1}	90%		3.5% (362 nm)

Catalyst	Conditions	Conversion	Products	Rate	Selectivity		Quantum efficiency
SiO_2-Al_2O_3 (20 mol%Al) [17]	Batch reaction, 250 W Xe lamp, 1 g catalyst, 200 μmol CH_4, ca. 310 K, reaction time 6 h	-	C_2H_6	0.0167 μmol h^{-1}	100%		-
[a]MoO_3(5wt%)/SiO_2 [13]	Flow reaction, 200 W Hg lamp, 25 mg catalyst, CH_4: O_2: He = 6:2:25, GHSV = 10000 h^{-1}, 493 K	-	HCHO CH_3OH	5.8 μmol h^{-1} 0.2 μmol h^{-1}	96.7% 3.3%		-
[a]Cu/CdS-TiO_2/SiO_2 [18]	Flow reaction, 125 W Hg lamp, 10 g catalyst, CH_4: CO_2 = 1:1, GHSV = 200 h^{-1}, 373 K	1.47%	CH_3COCH_3	-	92.3%		-
Ga-ETS-10-0.2 [60]	Batch reaction, 150 W Hg lamp, 200 mg catalyst, 200 μmol CH_4, room temperature, reaction time 5 h	14.9%	C_2H_6	2.178 μmol h^{-1}	73.9%		-
V-MCM-41 [11]	Batch reaction, 100 W leg lamp (λ > 270 nm), 150 μmol CH_4 per g catalyst, CH_4: NO=1, 295 K, reaction time 5 h	7%	CH_3OH CO_2	1.6 μmol h^{-1} g^{-1} 0.4 μmol h^{-1} g^{-1}	80% 20%		-
Ag/ZnO [22]	Batch reaction, 300 W Xe lamp, 500 mg catalyst, CH_4 100 ppm, N_2 78.9%, O_2 21.1%, room temperature, reaction time 2.5 h; Flow reaction, 300 W Xe lamp, 500 mg catalyst, CH_4 100 ppm, N_2 78.9%, O_2 21.1%, GHSV = 3000 mL g^{-1} h^{-1}, room temperature	100% (batch reaction); 98.5% (flow reaction)	CO_2	-	100%		8% (<400 nm) 0.1% (~470 ± 12 nm)
Au/ZnO [43]	Batch reaction, 300 W Xe lamp, 10 mg catalyst, 2 MPa CH_4, 0.1 MPa O_2, 100 mL H_2O, 298 ± 2 K, reaction time 2 h	-	CH_3OOH CH_3OH HCHO	61.7 μmol h^{-1} 20.6 μmol h^{-1} 43.2 μmol h^{-1}	46.9% 15.7% 32.8%		11.7% (368 nm)
[a]$CuMoO_4$ [12]	Flow reaction, 1000 W Xe lamp, 400 mg catalyst, CH_4:O_2=9:1, 373 K	-	CH_3OH	6 μmol h^{-1}	~100%		-
Rh/$SrTiO_3$ [82]	Flow reaction, 150 W Hg-Xe lamp, 5 mg catalyst, CH_4 1%, CO_2 1%, Ar 98%, GHSV = 120000 mL g^{-1} h^{-1}	52%	CO H_2	270 μmol h^{-1} 264 μmol h^{-1}	Ratio (H_2/CO) =~ 1		5.9%

$Cu_{19.8}Ru_{0.2}$[19]	Flow reaction, supercontinuum laser 19 W cm^{-2}, 1.5 mg catalyst, CH_4 50%, CO 50%, GHSV = 640000 mL g^{-1} h^{-1}, room temperature	-	CO H_2	2970 µmol h^{-1} 2970 µmol h^{-1}	Ratio (H_2/CO) =~ 1		-
GaN[8]	Batch reaction, 300 W Xe lamp, 0.35 mg catalyst, 150 µmol CH_4, 278 K, reaction time 12 h	0.98%	Benzene	0.019 µmol h^{-1}	96.5%		ca. 0.72% (290-380 nm) based on production of benzene
Cu-0.5/polymeric carbon nitride (PCN)[14]	Batch reaction, 500 W Xe lamp, 20 mg catalyst, 25 mL H_2O, CH_4:N_2= 1:9, total flow rate 100 mL min^{-1}, room temperature, reaction time 1 h	-	C_2H_5OH	2.12 µmol h^{-1}	-		-

The majority of the processes were operated at room temperature, while the reactions [a] were carried out at elevated temperatures. The controlled high-temperature experiments indicated that photon energy was still the major driving force in these reactions, because all of them could not proceed under identical temperatures without light irradiation, whereas heating could accelerate these reactions under light irradiation. [b] Although apparent quantum yield (AQY) is one important index to evaluate the photocatalytic efficiency, not all the studies in Table 2 reported it.

[H2] Semiconductor materials

The semiconductor photocatalyst is the most basic component of a photocatalytic system. Theoretically, a photohole in the valence band or the highest occupied molecular orbital of a photocatalyst with an oxidation potential (>+1.75 V vs. SHE) is required to activate the inert C-H bond in a methane molecule.[32] Other activation pathways have also been reported, as mentioned earlier. In principle, a semiconductor that exhibits high activity in equivalent photocatalytic processes (water splitting, CO_2 conversion and nitrogen reduction, for instance) could be theoretically applicable in methane conversion, including oxides and nitrides.

[H3] Binary metal oxides

TiO_2 is the most studied semiconductor photocatalyst and has been used for NOCM, OCM, POM, DRM and SRM.[27,34–37] The first use of TiO_2 in photocatalytic methane activation dates back to 1978, where the main product obtained was CO_2.[38] Later, methane activation and water splitting were combined, which simultaneously produced H_2, CO, CO_2, C_2H_4 and C_2H_6, although with a relatively low selectivity toward the desired products and a low yield rate (at the level of 2 µmol h^{-1}).[39,40] Proper design of TiO_2 with a specific structure can enhance the interactions between the catalyst surface and reactants, as shown by an ordered hierarchical porous microarray of TiO_2 synthesised for NOCM by using polystyrenes as a soft template,[16] resulting into a conversion rate of 0.41%. This significant improvement was attributed to the ordered pores, which largely increased the residence time of methane molecules. Apart from hydrocarbons, various products

have also been achieved over TiO_2 with the precise design of an appropriate reaction process, such as the photosynthesis of amino acids with ammonia water over Pt/TiO_2,[41] and the production of acetic acid by the conversion of CH_4 and CO_2 using phthalocyanine-modified TiO_2.[42] TiO_2 also displayed an excellent synergistic effect as a photo-redox support for noble metals in the photocatalytic SRM reaction.[27,39,40]

Compared with TiO_2, ZnO has a similar band structure and has drawn attention in recent years with its unusual asymmetric polar crystal structure.[15,22,43,44] Owing to the intrinsic inner electric field formed by non-uniform charge distribution, ZnO has a large spontaneous polarization of 0.047 C m^{-2} along the [0001] direction.[45,46] This structure not only facilitates charge separation but also provides polar facets to activate the highly symmetrical methane. The impact of polar facets was investigated by conducting a photocatalytic methane oxidation reaction over single-crystalline ZnO (0001)-dominated nanosheets and (01$\bar{1}$0)-dominated nanorods.[47] The rate constant for ZnO nanosheets was ten times larger than that of ZnO nanorods, verifying the positive effect of polar facets in methane conversion. Using this material as a base, a series of heterojunctions, such as Ag/ZnO,[22] CuO/ZnO,[44] and $ZnO/La_{0.8}Sr_{0.2}CoO_3$,[48] have been constructed for photocatalytic oxidation of greenhouse gas CH_4. The best performance was obtained by Ag/ZnO, reaching 100% removal of 100 ppm CH_4 at a 25 mL min^{-1} flow rate. Facet-tailored ZnO nanosheets with {001} planes with a gold co-catalyst were used for NOCM, exhibiting a C_2H_6 yield rate of about 0.0113 µmol h^{-1},[15] and a similar Au/ZnO catalyst showed excellent performance (125 µmol h^{-1} yield rate and >95% selectivity) in selective photocatalytic oxidation of methane to oxygenates with O_2 in water.[43]

WO_3 is also widely used for methane activation, especially in the presence of water under visible light. The first example of photocatalytic partial oxidation of methane over WO_3 was presented in 1997 by visible light.[49] After that, many studies were carried out with the focus evolving from the light source to scavengers, radical generators and amount of catalysts.[35,50–53] However, the selectivity for desired products was still moderate, owing to non-selective intermediate species such as the hydroxyl radical (·OH). In an attempt to control this active radical, the performances of fluorinated WO_3 and pure WO_3 were compared.[54] Most of the generated methanol (94%) was found to be related to the hydroxyl radicals on WO_3, whereas the free ·OH radicals in the solution had a detrimental effect on the selectivity. The introduction of lanthanum to mesoporous WO_3 increased the density of OH groups on the surface, resulting in an improvement of selectivity from 22% to 47%.[55] In a breakthrough result, mesoporous WO_3 loaded with amorphous FeOOH achieved a methane conversion rate of 4.77 µmol h^{-1} with high selectivity of 91.0% to methanol.[56] Interestingly, H_2O_2 was indispensable for the generation of methanol in this process, and FeOOH played an important role in reacting with H_2O_2 to generate hydroxyl radicals.

Inorganic porous materials, such as silica, alumina, and zeolites with highly dispersed metal oxide species on their surfaces, are another important group of these photocatalysts. The attempt to use silica-related materials for NOCM started with photocatalytic materials such as V/SiO_2,[38] Ag/zeolite Y,[57] Mo/SiO_2,[58] and the first example of a pure silica-alumina material without deposited transition metals was reported in 1998.[59] A ~5% yield of coupling products (for example, C_2H_6, C_2H_4, C_3H_8) was obtained using this silica-alumina material under UV irradiation for 18 h. Other pure silica materials, such as MCM-41 and FSM-16, were later found active in photocatalytic NOCM to ethane (0.019 µmol h^{-1}).[25] Silica was also loaded with dispersive cation species of Ce, Mg, Ga, Ti, Zr, or Zn for photocatalytic NOCM,[60–69] and among them, Ga^{3+}-modified titanosilicate exhibited the highest methane conversion rate, 5.96 µmol h^{-1} over 200 mg catalyst.[60] The key to this relatively high activity was the polarisation of C-H bonds by Ga^{3+} at the extra framework. In addition, when V and Bi were co-loaded on a zeolite framework and the acid-base properties tuned,[69] a methanol selectivity of 100% could be obtained under deep UV. Following the development of these inorganic porous materials, it is easy to find that their roles gradually shifted from active photo-redox centre to others, such as a support and promoter. Their use as a support or promoter is more suited to these materials and also consistent with their roles widely reported in thermocatalytic methane conversion.[70–72]

Some large band-gap oxides, such as Ga_2O_3, MgO and ZrO_2, have also been tested in DRM or NOCM.[65,73–78] However, these oxide photocatalysts had limited light absorption (< 300 nm) and thus low activity.

[H3] Ternary metal oxides

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A variety of ternary metal oxides with a chemical formula of $A_xB_yO_z$ (where A and B = metal) also exhibit activity in photocatalytic methane conversion. A classic group of them are bismuth-based materials, such as $BiVO_4$ and Bi_2WO_6.[79] However, they often suffer from poor selectivity (<50%) to methanol owing to the generation of highly oxidative hydroxyl radicals by their deep valence bands. Using nitrite ions as a hydroxyl radical scavenger can significantly increase the selectivity (>90%).[80] The selectivity towards methanol over $BiVO_4$ can also be manipulated by the facets,[81] indicating that precise control over catalyst synthesis may be an avenue to control its selectivity, illustrating an importantcorrelation between structure and property. $SrTiO_3$ is another efficient photocatalyst that can activate methane to produce different products with various co-catalysts.[82,83] The $Rh/SrTiO_3$ catalyst efficiently promoted methane reforming under UV irradiation with a conversion >50% even at mild temperatures below 473 K, beyond the thermodynamic constraints.[82] Moreover, the accumulation of cokes and aggregation of nanoparticles, which often happen in thermocatalysis, were not observed during the long-term experiment.

[H3] Nitrides

Nitrides are emerging as materials for photocatalytic methane conversion, boasting an expanded scope of products. For instance, the first and only example of photocatalytic methane conversion to benzene was achieved by a GaN nanowire with 97% of m-planes under UV irradiation at room temperature.[8] A yield rate of 0.019 μmol h^{-1} with a decent selectivity (96.8%) to benzene could be obtained over the optimal sample of Si-doped n-type GaN. However, the reaction mechanism was unclear. Graphitic carbon nitride, the most popular and intensively studied polymeric photocatalyst for water splitting, has gradually been reported in photocatalytic methane conversion. Different modifications of this polymer were adaptive to different processes, such as the product Ru/Zn-graphitic-C_3N_4 for methane coupling with CO_2,[84] Cu/graphitic-C_3N_4 for methane coupling and CO_2 reduction,[85] Cu/polymeric carbon nitride for methane oxidation to ethanol,[14] La/graphitic carbon nitride tubes for DRM,[86] and graphitic carbon nitride for partial oxidation of methane to methanol with H_2O_2.[87] The example of methane to ethanol is an interesting process, because this kind of alcohol was seldom reported using inorganic photocatalysts.[14] Benefiting from the synergy of Cu species and the adjacent C atom in the framework of graphitic C_3N_4, the as-formed hydroxymethyl on Cu could combine with methoxy groups on the C atom to generate ethanol at a yield rate of 2.12 μmol h^{-1}. However, the participation of carbon atoms from the polymeric framework could not be ruled out without the ^{13}C isotope experiment.

[H2] Non-semiconductor materials

Other materials have been proven active in methane conversion. Noble metal nanoparticles can be used to induce surface plasmons to enhance light absorption, in particular in the visible or near-IR regions, or as a co-catalyst to facilitate charge separation and create new active sites (which we discuss in the below section). Plasmonic nanoparticles such as Ni,[88–91] Au,[92] and CuRu[19] have demonstrated promise in photocatalytic DRM For instance, the decoration of single-Ru atomic sites on Cu nanoparticles led to an efficient photocatalytic DRM process under low temperature. Under white light irradiation, the surface temperature of the photocatalyst increased owing to the photothermal effect. The conversion of methane was always higher by photocatalysis than by thermocatalysis at the same temperature, with the largest difference reaching nearly a factor of three, and high selectivity (>99%) to H_2/CO was also observed for a long-term run (50 h) without the notable formation of cokes. Quantum mechanical studies revealed that photocatalysis promoted a different activation process from thermocatalysis—through the suppression of the reverse water-gas shift reaction—leading to a higher selectivity than thermocatalysis.

Homogenous photocatalytic organic synthesis through ligand-to-metal transfer is booming in modern photoredox catalysis, which is an emerging area in CH_4 conversion. Interested audiences are recommended to read this reference[31] as it is not the focus of this Review.

[H2] Co-catalysts

The co-catalyst not only facilitates the separation of photo-generated electrons and holes, but is also the active site that lowers the thermodynamic barrier in methane activation. As such, both noble metals and non-precious transition-metal-based species have been extensively used.

[H3] Noble metals

Due to appropriate work functions, noble metals are considered ideal electron sinks in photocatalysis, and photo-induced electrons and holes can be separated to suppress charge recombination.[22,39,40,93,94] The selectivity of methane conversion can also be manipulated by co-catalysts. For example, modification of commercial ZnO nanoparticles with various noble metals (Pt, Pd, Au and Ag) strongly enhanced ZnO's activity in POM.[43] Interestingly, the selectivity toward liquid products (CH_3OH and CH_3OOH) can vary with the type of co-catalyst. Compared with Au and Ag, Pt and Pd co-catalysts were found to shift the selectivity to CH_3OH: namely Au and Ag co-catalysts were efficient in the two-electron oxygen reduction reaction to produce H_2O_2 or CH_3OOH, whereas Pd and Pt were more selective in the four-electron oxygen reduction reaction that forms H_2O or CH_3OH.

The same co-catalyst can also have different functions in different processes. For instance, the function of Rh can change according to the wavelength of the light source. In a photocatalytic SRM, the surface plasmon resonance effect of Rh nanoparticles dominated under visible light, providing hot electrons to the substrate TiO_2.[27] Then, the Rh nanoparticles became positively charged to accept σ electrons of methane, facilitating C−H bond cleavage. In contrast, in a photocatalytic DRM reaction under UV light, Rh acted as an electron acceptor to promote the CO_2 reduction half-reaction.[82] A similar dependence on light source was observed in a Ag/TiO_2 catalyst.[95]

[H3] Non-precious metals

The selection of an appropriate non-precious metal co-catalyst depends on the reaction process. For example, highly dispersed iron species can act as a high-performance co-catalyst to promote the photocatalytic methane conversion to methanol over TiO_2.[10] After the decoration of Fe species, methanol production was enhanced by a factor of four, leading to extremely high selectivity to methanol (>90%).The iron species were found not only to accept electrons to promote charge separation but also to lower the activation barrier for H_2O_2 reduction, thus facilitating both reduction of H_2O_2 to ·OH radicals and oxidation of methane to CH_3· radicals. The universality of the iron species in this type of reactions was further confirmed in an FeOOH/WO_3 photocatalyst.[56] A copper species on graphitic carbon nitride promoted a similar mechanism of H_2O_2 activation,[14] but the copper also functioned as an active site for methane adsorption and activation in this case. In another example, Ga^{3+} deposited on a titanosilicate zeolite material significantly increased the conversion of methane from nearly 0 to 15%.[60] Surprisingly, the polarization of the C-H bond could happen at room temperature over Ga^{3+}, weakening the C-H bond and making the abstraction of protons by the photogenerated radicals easier. Methane activation can also be improved by enhancing methane's adsorption on the non-precious co-catalyst. For example, $SrCO_3$ improved the methane adsorption capacity of $SrTiO_3$ by an acid-base interaction ($SrCO_3$: basic oxide, CH_4: Lewis acid).[83] This explanation was further supported by a study, in which the photocatalytic methane combustion performance of TiO_2 was enhanced by $SrCO_3$.[37]

Unlike conventional methane conversion, photocatalytic methane conversion must take into account the photophysical process as well as the catalytic process. Therefore, if one co-catalyst is not sufficient to achieve an ideal result, it may be effective to introduce different co-catalysts with complementary functions to work synergistically. When Pt nanoparticles and CuO_x clusters were decorated together on anatase TiO_2 for photocatalytic OCM,[93] the metallic Pt species acted as electron acceptors to efficiently separate charge carriers, while copper species accepted photoholes and lowered their oxidation potential to avoid overoxidation of target C_2 products. In SRM over $K_2Ti_6O_{13}$-based photocatalysts,[94] metallic Rh and Rh_2O_3 nanoparticles were used as electron and hole acceptors, respectively, to promote reduction (hydrogen production) and oxidation (methane oxidation) reactions.

[H1] Reaction system design

The reaction system, especially the type of reactor, is a key way to manipulate the reaction rate and selectivity (Figure 3). Compared with the development of the catalysts themselves, far less attention has been paid to this aspect in photocatalysis.

[H2] Batch systems

The majority of the reactors used for photocatalytic methane conversion are slurry batch reactors, in which gas is purged through a reactor containing a catalyst before the reaction or during the reaction.[8,10,14,16] In these reactors, products cannot be removed as they are generated, increasing the possibility of over-reaction, especially overoxidation. Nearly all the products of methane conversion reactions are easier to be activated than methane itself. Thus, thermodynamically obtaining the desired products with a high yield and selectivity is very challenging in a batch reactor. This type of simple system can only be employed to initially screen photocatalysts, and there are limited parameters that can be optimised to improve the yield and selectivity. In addition, adsorption of methane and desorption of products mainly rely on spontaneous gas diffusion in these batch reactors, especially in a gas-solid two-phase reaction such as NOCM, owing to the lack of strong forces to facilitate the mass transfer. This phenomenon implies that mass transfer, rather than photocatalytic efficiency itself, is likely one limiting factor for the low yield rate.

Some strategies have been introduced to improve the conversion and/or yield in batch systems. The reactant gas can be circulated in the batch reactor to improve the mass transfer to some extent, leading to an improved catalytic process (Figure 3a).[39,40] Using such a circulation process, the highest C_2 product yields (2.08 µmol h^{-1} over Pt/TiO$_2$ and 2.13 µmol h^{-1} over Pd/TiO$_2$, respectively) were reported among all TiO$_2$-based photocatalysts in atmospheric batch reactors. Increasing the pressure of the reaction system is another way to enhance the interaction between reactants and catalysts. For example, the influence of pressure on the direct oxidation of methane to oxygenates was investigated over a Au-loaded ZnO photocatalyst (Figure 3b).[43] With increasing CH$_4$ pressure, the solubility of methane in water also increased, leading to a higher yield of desired products. It is interesting to note that the yield of CO$_2$ increased only slightly with the increasing pressure, and thus the selectivity of oxygenated liquid products was very high (>95%). This in part indicates the influence of mass transfer on the performance of the photocatalysts.

[H2] Flow systems

Developing the knowledge learnt from the batch reactor, a flow system can be an effective way to improve mass transfer. A flow reactor can adjust the residence time of methane and products and control the interaction between molecules and catalysts. The single-run conversion rate can be evaluated, which is a very valuable reference for subsequent applications. Moreover, unlike the uneven distribution of reactants in batch reactors, the reactant molecules are dispersed evenly in a flow system. Given these advantages, it is clearly important to assess photocatalytic activity in a flow system, and so far, flow reactors have been used mainly in photocatalytic methane reforming[19,82] and methane degradation.[22]

In an example of a continuous flow photocatalytic process, OCM was performed over modified TiO$_2$ at room temperature and atmospheric pressure in a flow reactor (Figure 3c).[93] The reactor enables a readily tuned ratio of CH$_4$ to O$_2$ with a relatively evenly distributed gas stream through the catalyst bed, and accurate online product analysis. Benefiting from the promoted mass transfer and controlled reaction time in a flow system, the optimised CuPt/TiO$_2$ photocatalyst represented the highest yield of C_2 products (6.8 µmol h^{-1}) among all TiO$_2$-based photocatalytic methane conversions . Moreover, the C_2 selectivity was as high as 60%, comparable to that of a traditional thermal catalyst (such as Li/MgO) at high temperature (>943 K). In a similar flow reactor strategy, photocatalytic NOCM was carried out over Pd/Ga$_2$O$_3$.[73] The selectivity to ethane could be improved by increasing the flow rate. The fast flow promoted the migration of methyl radicals for coupling, rather than further oxidation by holes to unexpected products (for example, cokes). In addition, the shorter contact time decreased the possibility of successive coupling reactions to other products, such as propane. All these results indicate the superiority of a flow system over a batch system.

[H2] Other reaction systems

To further improve the selectivity of the desired products, some clever designs have also been employed. For example, a two-phase system of perfluorohexane and water was used for the photooxidation of CH$_4$ with chlorine dioxide radical (ClO$_2$•) and molecular oxygen (Figure 3d).[96] Although this reaction is photochemical rather than photocatalytic, the two-phase strategy may be useful for the latter. Owing to the more inert nature of perfluorohexane than CH$_4$, the generated CH$_3$ and Cl radicals prefer to attack CH$_4$. Moreover, the gas reactants, CH$_4$ and O$_2$, have high solubility in perfluorohexane, whereas the oxygenated products, CH$_3$OH and HCOOH, are more soluble in water. The oxygenation of CH$_4$ proceeded in perfluorohexane and the

products transferred to water, avoiding further oxidation, and resulting in a 99% conversion of methane without CO or CO_2 production. A similar concept was tested in other photocatalytic reactions, such as the photocatalytic synthesis of H_2O_2.[97]

Another strategy is to use a chemical loop in which methane conversion and regeneration of catalysts are two separate steps. This type of loop was used for stoichiometric methane conversion to ethane on Ag-$H_3PW_{12}O_{40}$/TiO_2 (Figure 3e).[32] The photoelectrons were consumed by Ag^+ species to form metallic Ag, while CH_4 was activated by the photoholes to generate $CH_3\bullet$, which coupled into C_2H_6. The production of C_2H_6 stopped after the Ag^+ species were completely reduced. The metallic Ag species were then recovered into their original oxidation state through UV irradiation in the presence of air. The Ag^+/Ag^0 redox couple served as an important mediator to separate O_2 reduction from the methane oxidation step, and overoxidation was effectively avoided. This strategy alleviates the uncontrollable radical oxidative process. Similarly, in a photocatalytic methane conversion to ethane and ethylene over AuPd/ZnO, methane reacted with the lattice oxygen of ZnO, producing C_2H_4 and H_2O.[33] 3.68% of the total lattice oxygen was consumed after photocatalytic reaction for 8 hours. The oxygen vacancies formed could be easily compensated by subsequent water rinsing. So far, the chemical loop strategy has only been applied in a batch reactor. Combining a flow reactor with a chemical loop is an attractive approach for future studies.

[H1] Techniques for mechanistic understanding
Mechanistic study of photocatalytic methane conversion has significantly lagged behind catalyst development. Photocatalytic methane conversion can typically be understood by two interlinked processes, the photophysics and the chemistry.

[H2] Photophysics
In photocatalysis, the lifetime of the charge carriers should be longer than the timescale of relevant surface reactions. The time-resolved spectroscopies provide a powerful way to monitor the generation and lifetime of photo-induced carriers. Three complementary technologies can be useful in this regard: time-resolved resonance Raman spectroscopy (TRRS), transient absorption spectroscopy (TAS), and time-resolved infrared (TRIR) spectroscopy (Figure 4).[98–101] Using these techniques together may allow observation of charge carriers and reaction intermediates, and elucidate fundamentals of the photophysical processes. However, few studies have actually applied these spectroscopies to photocatalytic methane conversion. Thus, in addition to describing those few examples, we also describe the use of these techniques in related photocatalytic processes to show their potential in the methane conversion field.

TAS is widely used to observe the photo-induced electrons and holes, determine their lifetimes and compare the charge dynamics with a wide timescale, ranging from picoseconds to milliseconds in many photocatalytic processes (Figure 4a and 4c).[102–105] In a typical example, TAS revealed the mechanism of photocatalytic SRM over Rh/TiO_2 under visible light illumination.[27] The Rh/TiO_2 exhibited a significantly faster rise of transient absorption after excitation than those of Rh/ZrO_2 and Rh/SiO_2, indicating the promotion of ultrafast charge separation. Through fitting the absorption spectra, the lifetimes of hot electrons were determined, which were remarkably prolonged by the Schottky junction. TAS, together with the manipulation of experimental conditions can also help identify the timescale of interfacial reactions, such as measuring the lifetime of holes and the kinetics of the reactions between photoholes and water.[103] The lifetime of holes could be directly observed and more importantly, they could be changed by the addition of different scavengers, such as Ag^+ or Pt. O_2 evolution was then found to be at a timescale of seconds over oxide photocatalysts. These results provide solid evidence that extending the lifetime of holes can promote photocatalysis, thus guiding the material design. However, there is a lack of in-depth understanding of the reaction kinetics for photocatalytic methane conversion.

The probes of TAS are usually located at the visible-to-near-IR region, making it difficult to monitor species with featureless absorption spectra in this region, such as the vibrations of reactants and intermediates.[98,106] TRIR spectroscopy is thus a powerful complementary tool to cover the mid-IR range (Figure 4a and 4d). It has been also used to trace the kinetics of photo-induced carriers in homogeneous and heterogeneous systems.[98,107–109] For example, since the photoelectrons trapped in shallow states absorb IR light, TRIR

spectroscopy can monitor the electron decay in TiO_2 and Pt/TiO_2 under O_2/H_2O atmosphere.[109] The introduction of water vapour significantly slowed the decay of transient IR absorbance at 2000 cm^{-1} and the lifetime of photoelectrons was extended up to 0.9 s, which was attributed to the abstraction of holes by hydroxyl anions, thus mitigating charge carrier recombination. Moreover, the timescale (10 – 100 µs) of superoxide radical generation was also monitored by this technique. Taking into account the important role of the superoxide radicals in photocatalytic methane conversion, TRIR shows a strong potential to observe the reaction mechanism involved with oxygen, although it has seldom been used so far for this process.

For short-lived intermediates and electronically excited states that have a complex or negligible IR response, TRRS provides a complementary means to visualize the molecular fingerprint, where the Raman operational window spreads from the deep UV to the visible region and can be monitored at the middle-far IR region (Figure 4a and 4b). The UV region, which is important for conjugated catalysts, is particularly attractive given the surge in polymeric photocatalysts and potential conjugated products. A combination of TAS and TRRS was used to investigate the homogeneous photoredox reaction of an anthraquinone derivative.[110] In the TAS spectra, the transient species exhibited absorbance at 383 and 430 nm with a first-order kinetic decay. However, the absorption spectra were broad, and little structural information could be acquired. TRRS was able to extract structural information, revealing that the transient species overlapped with the Raman bands of the triplet excited state of the anthraquinone derivative at 1570 cm^{-1}. The transient ketyl radical species of this anthraquinone derivative could be analysed after comparison of the spectra at 200 ns with the modelled spectra, demonstrating the effectiveness of TRRS.

[H2] Reaction steps and surface chemistry
From a chemical perspective, in order to reveal the reaction pathway, both the catalytic surface and interaction between the surface and the reactants have to be paid particular attention. In most cases, significant effort was devoted to the activation of the first C-H bond in the CH_4 molecule to form methyl radicals, but it is not always the most important rate-determining step in the full catalytic cycle.[111] So far, only those photocatalytic reactions with a limited number of elementary steps are fully understood. For example, in NOCM and OCM, the coupling of as-formed methyl radicals after C-H activation produces the final products.[26,93,112] In contrast to these simple processes, when too many active radicals are involved in the process, it is hard to rationalise a consistent reaction pathway. Using one photocatalytic methane conversion reaction to methanol as an example, the intermediate hydroxyl radicals may react with methyl groups to form methanol[10,56,113] or may act as the active species to abstract H from methane.[53,114] Even the generation of hydroxyl radicals involves different pathways according to different catalytic processes: they could be directly generated by photoholes with water[115]; by the reaction between photoelectrons and H_2O_2, which could either be from external addition or formed in situ[14,56]; or by the reaction between singlet oxygen and water[113]. Thus, it is difficult to establish a unified pathway for each route, although the intermediates might be similar. For the reactions that involve multiple elementary steps and/or multi-carbon products, such as the generation of C_{2+}, the mechanisms have mostly been based on speculation without solid experimental evidence. Therefore, to draw the full picture of each photocatalytic methane conversion process, operando or at least in situ characterisation must be used to monitor the active catalytic sites at the molecular level, investigate their interactions with molecules and possible transformations, and observe the different intermediates (Table 3).

Table 3 State of art in-situ or operando technologies (either static or time-resolved mode) used to study methane conversion

Technology	Species	Information	Representative references
[a]Infrared spectroscopy (IR)	Vibrational modes of molecules and functional groups (e.g., C-H, O-H, C-O)	Capture intermediates; Reveal reaction pathways	14,15,118,22,34,44,53,83,84,95,117
[a]Electron paramagnetic resonance spectroscopy (EPR)	Radicals (e.g., O_2•-, OH•, CH_3•); transition metal ions (e.g., Ti^{3+})	Determine active sites; Identify active species; Explore activation mechanism	33,43,115

[a]X-ray photoelectron spectroscopy (XPS)	Composition (elements); chemical states	Determine active sites; Investigate interface reactions; Correlate the structure with performance of catalysts	[10,56,121]
X-ray absorption spectroscopy (XAS)	Composition (elements); chemical states and environments	Determine active sites; Investigate interface reactions; Resolve coordination environments; Acquire atomic level interaction	[71,120]
Time-of-flight mass spectrometry (TOF-MS)	Molecules; radicals	Capture intermediates; Reveal reaction pathways; Identify catalytic cycle	[116]

[a]Only these technologies have been used to study photocatalytic methane conversion; the others have been extensively applied to study conventional thermal catalytic processes.

In situ IR spectroscopy has been widely used in photocatalytic methane conversion to observe species on the catalysts' surface.[14,15,22,34,44,53,83,84,95] Owing to the organic nature of this reaction, many vibrational modes are sensitive to IR, such as C-H, O-H, C-O, CH_3-O, and C=O, which helps reveal the mechanism behind the surface chemistry. The intensity of typical ν(C-H) vibration modes of methane at around 3015 cm^{-1} can be readily monitored during methane conversion, whereas the other bands can vary from one process to another. For example, the decreasing intensities of ν(C-H) accompanied by the gradual growth of CO_2 under irradiation could be observed, along with the increasing bands attributed to chemisorbed H_2O.[22] More telling was a newly formed band corresponding to the δ(CHO) of chemisorbed aldehyde, which slowly increased during the reaction, unlike other products. Based on this, CH_4 was proposed to react with O_2 at first to form HCHO and H_2O, then the intermediate HCHO further reacted with O_2 to form CO_2. We emphasise the advance of coupling in situ FTIR spectroscopy with isotopic labelling to study the role of lattice oxygen in metal oxides during photocatalytic methane conversion. These lattice oxygen species were found to activate methane and be regenerated through a mechanism like the Mars-van Krevelen mechanism (a chemical loop) when the reactants contain oxygen atoms (O_2 or CO_2, for instance).[34,82] However, this reaction pathway cannot be applied to the continuous selective generation of hydrogen and hydrocarbons in NOCM over metal oxide photocatalysts.[15,16]

In situ electron paramagnetic resonance (EPR) spectroscopy is able to monitor active species that contain unpaired electrons, such as transition metal ions in paramagnetic valence states and radicals, either on photocatalysts or in the reaction intermediates. The most common species observed by in situ EPR in photocatalytic methane conversion include superoxide radicals ($O_2 \bullet^-$), hydroxyl radicals (OH$\bullet$) and methyl radicals ($CH_3 \bullet$).

As a complementary technique, in situ X-ray photoelectron spectroscopy (XPS) provides information about the composition and chemical environment of the catalytic sites, acquiring rich information and understanding of the dynamic process. Only a few studies of photocatalytic methane conversion have used in situ XPS so far.[10,56] In an investigation of highly dispersed iron species on TiO_2 during photocatalytic selective oxidation of methane to methanol,[10] both Fe $2p_{3/2}$ and $2p_{1/2}$ peaks shifted to lower binding energy upon light irradiation, indicating the role of iron species as the electron acceptor during the photocatalytic methane conversion.

In situ X-ray absorption spectroscopy (XAS) can extract quantitative chemical and structural information of a photocatalyst, in order to reveal the correlations between catalyst activity and its structure. Although it has not yet been reported for photocatalytic methane conversion, an example of its application to thermal

methane conversion is discussed here to illustrate its potential for photocatalysis. With selective methane conversion to methanol over a copper-exchanged zeolite as the reaction of interest, in situ XAS was used to observe the reaction mechanism at Cu^{II} oxide centres.[71] The intensity of the peak assigned to Cu^{I} increased after the introduction of CH_4 at 473 K, indicating the interaction between Cu^{II} and methane. As water vapour was introduced to regenerate Cu^{II}, the intensity of the Cu^{I} peak decreased. Moreover, a new peak attributed to the hydrated Cu^{II} species appeared. In this way, the in situ XAS data helped to unravel the methane oxidation and regeneration processes over Cu^{II} active sites.

The above techniques primarily examine surface species, surface structure and composition under in situ conditions, which are simulated reaction conditions. Compared with in situ technologies, operando measurements characterise catalysts under actual reaction processes (exactly the same reaction conditions, in the same reactor system). Operando tests can provide rich and accurate information on the catalytic process in real time, such as active intermediates, reaction pathways and the full catalytic cycle, which helps to correlate the activity and selectivity of the catalyst with its structure. Operando time-of-flight mass spectrometry (TOF-MS), in which a capillary reactor was coupled to a mass spectrometer, was used to track the evolution of methane to liquid products during a high-pressure reaction.[116] Given an initial increase in signals assigned to CH_3OH and CH_3OOH, followed by a marked increase in $HOCH_2OOH$ and $HCOOH$ signals in the last 300 minutes, it was determined that CH_4 was first oxidised to the first two products and then further oxidised to the latter two. Diffuse reflectance FT-IR spectroscopy (DRIFTS) is another accessible technique to elucidate heterogeneous catalytic reactions under operando conditions.[117] For example, it was used to investigate the active sites and enhanced coke resistance of Ni-Ru catalysts in the thermocatalytic DRM reaction.[118] Because DRIFTS can directly observe and analyse the important intermediates online under consistent catalytic kinetic conditions, it revealed that the presence of Ru promoted the carbon gasification and alleviated the dissociation of CO.

In addition to observing transformations of substances and reaction intermediates, operando technologies are also widely used to understand the details of a catalyst's structural transformation.[119] An operando XAS experiment was able to abstract the nature of active Pd species under the genuine condition of methane combustion.[120] Through the simultaneous observation of the Pd K edge spectra and the monitoring of methane conversion, the temperature-dependent active species (Pd oxide species below 950 K and reduced Pd above 950 K) could be clearly resolved. Similarly, an operando NAP-XPS technique determined the surface composition of a bimetallic CuNi catalyst during methane decomposition.[121] From the Ni $2p_{3/2}$ and Cu $2p_{3/2}$ spectra, it was concluded that Ni propagates to the surface during the reaction even if the surface is rich in Cu at the beginning.

[H1] Challenges and outlook

Although substantial progress has been made in the development of photocatalytic methane conversion to various products, we believe at least five challenges face this field.

[H2] Development of photocatalysts

The highest apparent quantum yield (AQY) reported in photocatalytic methane conversion has been 60% over Pt/black TiO_2,[122] but the majority of photocatalysts have exhibited a much lower AQY, some even less than 10%. In contrast, a high AQY is commonly reported in other photocatalytic processes, in particular for water splitting (up to 96%, $350 < \lambda < 360$ nm),[123] indicating that significant improvement is needed for photocatalytic methane conversion.

There are a few strategies to address this problem, beginning with the optimisation of the most promising photocatalysts reported for analogous processes (water splitting, CO_2 conversion, nitrogen reduction) for methane conversion. Types of photocatalysts other than inorganic materials can also be explored. Emerging polymeric photocatalysts, including graphitic carbon nitride, covalent triazine frameworks, and covalent organic frameworks, have already shown enormous potential owing to their light absorption properties, band structure, and surface characteristics, which can all be easily tuned by molecular engineering.[124] Based on the needs of the specific experiment, the catalyst structure can also be modified through the construction of hierarchical structures, facet control, size adjustments and interface chemistry.[125]

Different photocatalysts can also be constructed into junctions that inherit the advantages of each individual component. Possible heterojunctions, for example, include conventional type-II heterojunctions, p-n heterojunctions, Z-scheme heterojunctions,[126] and even tandem design.[127] In addition, machine learning has already been applied to the design of hydrogen evolution photocatalysts, electrocatalysts, and even methane conversion thermocatalysts,[128–131] hinting that artificial intelligence techniques could help design methane conversion photocatalysts in the near future.

[H2] Development of co-catalysts

Co-catalysts play a pivotal role in manipulating products' yield and selectivity. Although the reported co-catalysts cover a wide field, including nanoparticles, clusters and single atoms, the function of the real active sites and the reaction steps on each type of active site are still ambiguous. Understanding the function of single-atom materials in both photocatalytic and thermocatalytic reactions is expected to assist the development of economical co-catalysts for photocatalytic methane conversion; a few examples of single-atom co-catalysts have been reported in photocatalytic methane conversion, such as single Ru atoms on plasmonic Cu for DRM.[19] On the other hand, a single component co-catalyst may not meet the requirement of organic synthesis from methane owing to the diversity of the products. Therefore, the field is trending towards combining multiple components with complementary functions. Mixing single Pt atoms with Pt_n clusters provides balanced activity and durability for the water-gas shift reaction,[132] for example, suggesting that such combination may be an attractive strategy for co-catalyst design in methane conversion.

[H2] Design of appropriate reaction systems

The development of reaction systems is equally and perhaps even more important than progress in photoactive materials. Most of the reactors reported are batch reactors. Flow systems are undoubtedly more effective, but flow reactors are challenging to design and use, considering the complex methane conversion process, the cost, and safety issues.

Most of these challenges can be overcome if more effort is devoted to this subject. The relatively mature flow systems in thermocatalysis, especially those that have been successfully adopted in industry, are excellent references. The limited flow systems reported for photocatalytic methane conversion have mainly been applied to gas-solid two-phase reactions. A system involving a liquid phase, such as a gas-liquid-solid three-phase reaction, will be important for synthesizing liquid products from methane or using liquid water as the reactant. The design of a flow reactor itself is also pertinent, and research should not be limited to the simple fixed-bed reactors, but also extend to more sophisticated reactors such as membrane reactors and fluidised reactors.

[H2] Understanding mechanisms

Compared with the fast development of the catalyst materials, still little is known about the mechanism behind every methane conversion reaction, including the photophysics and photochemistry. Moreover, the mechanistic investigation of chemical processes has mainly focused narrowly on the activation of the first C-H bond, but studying the full catalytic cycle, especially the elementary reactions in the gas phase, is equally important.

Using complementary time-resolved spectroscopies in cooperation, rather than one technique alone, is highly recommended to monitor the generation and transportation of photo-induced carriers and, more importantly, their interaction with the adsorbed reactant molecules. Although in situ spectroscopies remain the most frequently employed techniques to gain understanding of active sites and intermediates, operando characterisation can acquire more convincing evidence of the process under real reaction conditions. Investigating the mechanism in the gas phase is equally important to studying it on the catalyst surface. Advanced techniques such as vacuum ultraviolet soft photoionization molecular-beam mass spectrometry can monitor the intermediates and resolve the elementary steps in the gas phase,[72] which can then help design more efficient photocatalysts and control the selectivity to higher-value chemicals. Simulations are another effective way to investigate those transient intermediates.

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[H2] Reliability and reproducibility

Photocatalytic methane conversion can be evaluated by a library of criteria. A standard set of experimental conditions and evaluation criteria should be established in order to make fair comparisons between systems.

A combination of selectivity to the desired product, conversion rate, and AQY provides a relatively comprehensive toolkit to fairly evaluate the performance of a photocatalyst. Taking the criteria used in thermocatalysis—for example, C_{2+} selectivity should be over 88% with single-pass conversion over 35% in the OCM reaction[133]—a high conversion of methane is less attractive if a high selectivity cannot be achieved, and vice versa. Considering the influence of light intensity, AQY determines how energy-efficient a catalytic process is.

Particular attention should be paid to the stability of a photocatalyst. Although many of the methane conversion photocatalysts reported are stable during their corresponding cyclic tests or continuous runs, most of the durability tests are too short (<50 hours or <10 cycles) to give a comprehensive view of their stability, especially compared with those in thermocatalysis (for example, Ni-Mo/MgO in DRM is stable for 850 hours[4]). An economic model to work out the feasibility of photocatalytic DRM even used an average catalytic lifetime of 3 years.[134] Although coke formation is a universal issue in thermocatalysis at high temperatures, it has seldom been observed in photocatalysis owing to the merits of mild, low-temperature reaction conditions. However, cokes could become a problem in photocatalysis with long-term runs, along with the possible photo-corrosion of catalysts[23] and surface oxidation of the nanoparticles.[135] It is thus critical to run long-term observations for an efficient photocatalyst. Encapsulating photocatalysts and co-catalysts with stabilisers, synthesising co-catalysts with selectivity against poison products such as cokes, and designing reactors to manipulate the reaction conditions (for example, high space velocity to avoid deep dehydrogenation), may also help develop more durable photocatalysts.

The carbon source of products should also be scrutinised. The simulated methane gas used in a laboratory always contains impurities such as ethane. Thus, one should be careful to identify the carbon source of products using isotope-labeled CH_4 gas when long-chain products are observed (for example, C_{2+}). This issue is more serious in a batch system with continuous methane purging, as the impurities will accumulate and be readily converted to long-chain chemicals.

Apart from improving the photocatalytic performance, scientific models should be set up to evaluate the economics of methane conversion processes, facilitating the translation of these studies from laboratories to demo systems and contributing to net zero carbon emission industrial processes. A systematic economic model that considered a series of parameters, including use of sunlight, selection of catalysts, scale of production, cost of feedstock, and capital expenditure,[134] suggested that photocatalytic DRM exhibited a bright future for commercialisation. This report also highlighted the important fact that the mimimal lifetime of future photocatalysts should be greater than a few months. As for the photocatalytic methane conversion processes currently without a reliable scientific model to be evaluated by, we recommend taking the common heterogeneous catalysis as a gold standard: the yield rates should reach the level of 1 μmol cm^{-3} s^{-1} or the turnover frequency at least around 1 s^{-1}.[136] This yield rate is an important reference for the commericalisation of a photocatalytic process.

Although photocatalytic methane conversion is at a very early stage, the integration of multidisciplinary knowledge across materials science, characterisation techniques, and chemical reaction engineering will rapidly develop this area. The scope of products will also expand from simple hydrocarbons to long chain C_n products.

Figure captions

Figure 1 | **The fundamentals of photocatalysis and methane conversion**. **a** | The top and bottom graphs show thermodynamically unfavourable (ΔG>0) and favourable (ΔG<0) reaction pathways for methane conversion operated at room temperature, respectively. Photocatalysis can reduce the activation energy (E_a)

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of the reaction compared with thermocatalysis. NOCM: non-oxidative coupling of methane, SRM: steam reforming of methane, DRM: dry reforming of methane, MDA: non-oxidative methane dehydroaromatistaion, OCM: oxidative coupling of methane, POM: partial oxidation of methane. **b |** The principle of photocatalysis involves (Step 1) illumination, (Step 2) excitation of electrons from the valence band to the conduction band, (Step 3) charge separation and transportation to the reaction sites, (Step 4) surface reactions and (Step 5) charge recombination on the surface. A: electron acceptor, D: electron donor. **c |** Methane can be activated by different mechanisms photocatalytically. The C-H bond can be directly activated by photoholes, photoelectrons, or energy from localized surface plasmon resonance; or indirectly activated by RO· radicals such as ·OH or $CH_3O·$, or chemical loop processes through mediates, such as metal cationic species or lattice oxygen.

Figure 2 | **Key developments in photocatalytic methane conversion.** The timeline covers initial attempts, development of valuable products, representative yields and selectivity, and advanced reaction systems. NOCM: non-oxidative coupling of methane, SRM: steam reforming of methane, POM: partial oxidation of methane, DRM: dry reforming of methane, OCM: oxidative coupling of methane.

Figure 3 | **Representative reaction systems in photocatalytic methane conversion**. **a |** A batch reactor is equipped with a circulation pump to improve the mass transfer of methane. [40] **b |** The influence of reactants' pressure on the direct oxidation of methane to oxygenates was investigated over Au-loaded ZnO photocatalyst. The increasing methane pressure led to the increased conversion and selectivity to C1 oxygenates against CO_2.[43] c | A flow reactor was first reported for the photocatalytic OCM reaction. The flow system facilitated the mass transfer and reaction time, resulting in decent C_2 yield rate and selectivity.[93] **d |** A two-phase reaction system was used for photooxidation of CH_4 by $NaClO_2$. The as-formed oxygenates in the fluorous phase (perfluorohexane) could be transferred to the aqueous phase (water), avoiding further oxidation to CO or CO_2.[96] **e |** A chemical loop was used for stoichiometric methane conversion to ethane over Ag-$H_3PW_{12}O_{40}$/TiO_2. The photoelectrons were consumed by Ag^+ species to form metallic Ag, while CH_4 was activated by the photoholes to couple into C_2H_6. The Ag^+ species were then regenerated through oxidation of metallic Ag species with air under UV irradiation. The separation of methane activation and catalyst regeneration avoids the co-existence of methane and oxygen, mitigating overoxidation to CO_2..[32] Panel **a** is reprinted with permission from ref. [40], Elsevier. Panel **b** is reprinted with permission from ref. [43], ACS. Panel **c** is adapted from ref. [93], CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/). Panel **d** is reprinted with permission from ref. [96], Wiley. Panel **e** is reprinted from ref. [32], Springer Nature Limited.

Figure 4 | **Complementary time-resolved spectroscopies to probe photophysical and photochemical processes in photocatalysts**. a. The operation and observation windows, time scales and subjects of time-resolved infrared spectroscopy (TRIR), transient absorption spectroscopy (TAS), and time-resolved Raman spectroscopy (TRRS). In a semiconductor (ellipse), trapped states (short blue bars) located in the bandgap between the minimum conduction band (CB) and the maximum valence band (VB) act as extra energy levels for the capture of photo-induced electrons and holes. The red arrows and navy blue arrows represent observation of trapped states by TRIR and TAS, respectively. b. Schematic representation of time-resolved Raman spectra after excitation. The experiments (solid lines) are conducted at a wide range of timescales to observe the temporal changes of the vibrations of a molecular structure of a photocatalyst or surface species, validated by simulation (dotted line) to identify these species. c. Schematic representation of TAS spectra: the lifetime and dynamics of photo-induced carriers over different photocatalysts (A, B, and C) can be determined with an appropriate fitting. d. Schematic representation of TRIR spectra: the peaks corresponding to the absorbance of products, intermediates, and reactants keep changing as the reaction proceeds. The lifetimes of active intermediates and reactants could also be monitored at the applied timescale, providing useful information for the determination of reaction kinetics.

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