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Room-temperature coupling of methane with singlet oxygen†

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Owing to emission of methane (CH₄) causing global warming and waste of resources, conversion of CH₄ to value-added chemicals can mitigate environmental sustainability and energy concerns. Direct room-temperature coupling of CH₄ to form ethane (CH₃CH₃) challenges chemists owing to the strong C-H bonds requiring high temperature (>700 °C) for dehydrogenation of CH₄. Oxidative coupling is a promising approach for CH₄ conversion to C₂H₆ using solar energy at room temperature. To achieve high efficiency of C₂H₆ formation, using an appropriate oxidant is a potential strategy to avoid overoxidation during the CH₄ coupling process. Singlet oxygen (¹O₂) has typically manifested a mild redox capacity with a high selectivity to attack organic substrate CH4. Here, we report a synergistic photocatalytic-oxidative route for direct CH₄ coupling. Under solar light irradiation, a high CH_3CH_3 generation rate of 647 μ mol g^{-1} h⁻¹ is achieved at 25 °C. Our work demonstrates that the solar-oxidative route can result in new and useful C1-based catalytic behaviors.

Taking into account the environmental pollution and global warming caused by the use of traditional fossil energy and the shortage of its reserves, increasing the use of natural gas mainly composed of methane (CH₄) is an inevitable trend, since methane has the advantage of being abundant and relatively inexpensive and clean. However, methane itself is also a greenhouse gas whose greenhouse effect is about 25 times that of carbon dioxide of the same mass.2 Thus, methane emissions contribute to global warming. On the other hand, the direct use of natural gas as a fuel will also cause environmental pollution and waste of resources, since methane storage

Environmental significance

Owing to emission of methane (CH₄) causing global warming and waste of resources, conversion of CH4 to value-added chemicals can mitigate environmental and energy concerns. Direct room-temperature coupling of CH₄ to form ethane (CH₃CH₃) challenges chemists owing to the strong C-H bonds requiring high temperature (>700 °C) for dehydrogenation of CH4. Oxidative coupling is a promising approach for CH4 conversion to C2H6 using solar energy at room temperature. To achieve high efficiency of C2H6 formation, using an appropriate oxidant is a potential strategy to avoid overoxidation during the CH₄ coupling process. Singlet oxygen (1O₂) has typically manifested a mild redox capacity with a high selectivity to attack organic substrate CH4. Here, we report a synergistic photocatalyticoxidative route for direct CH4 coupling. Under solar light irradiation, a high CH₃CH₃ generation rate of 647 μmol g⁻¹ h⁻¹ is achieved at 25 °C. Our work demonstrates that the solar-oxidative route can result in new and useful C1-based catalytic behaviors.

transportation are difficult and it is prone to leakage. These factors have made scientists invest a lot of energy in the research and development of simple and feasible technologies for converting methane into value-added chemical raw materials.

However, a high temperature (>700 °C) is required for thermodynamic dehydrogenation of CH₄ due to the strong C-H bonds (434 kJ mol⁻¹), leading to energy consumption and low selectivity of CH₄ conversion.³ Photocatalytic methane conversion is a safe, low-energy and environmentally friendly strategy for the direct conversion of methane, since the dissociation of methane at room temperature can be achieved by means of photocatalytic methods using the light energy of sunlight and a suitable photocatalyst. Photocatalytic oxidation is also a promising approach for coupling of CH4 to form C2H6 using solar energy at room temperature.4 Nevertheless, the major challenge of CH₄ coupling via the photocatalytic route is insufficient yield of target CH3CH3 and large production of byproducts, e.g., HCOOH, CO, and CO2. Furthermore, noble metal co-catalysts, such as Au, Pd, and Pt, were generally used for promoting the efficiency of coupling of CH₄.5 Developing oxidative-coupling and noble-metal-free catalyst systems, thus,

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is highly desirable for photocatalytic CH₄ coupling at room temperature.

Traditionally, chemical oxidants, including O2, H2O2, and CO₂, have been proven to be important in oxidative activation of CH₄ to hydrocarbons, such as methanol.⁶ Actually, these oxidants potentially generate reactive oxygen species (ROS), such as the superoxide radical anion (O2'-), hydroxyl radical ('OH), sulfate radical (SO_4 ' and singlet oxygen (1O_2), which are crucial in activation of CH₄.⁷ In particular, the ¹O₂-based system typically manifested a mild redox capacity (2.2 V) with a high selectivity to attack organic substrates, compared to other free radicals such as SO_4 (2.5-3.1 V) and 'OH (2.7 V) (see Fig. 1).8

Peroxymonosulfate (P) as an excellent alternative oxidant has been confirmed to be the main source of ${\rm HSO_5}^-$ which can produce ¹O₂, 'OH, and SO₄' radicals. 9 In particular, P can be utilized for selective oxidation of organic substances during which 1O2 is generated and serves as a mild oxidant with distinct reactivity towards different substrates. 10 Importantly, the HSO₅⁻ molecule has a higher oxidizing potential (1.82 V) than H₂O₂ (1.76 V), and is thus more promising for activation of CH₄.7 Therefore, P is often applied as an electron acceptor in photocatalytic degradation of organic pollutants.11 Nevertheless, P has never been studied for selective activation of CH₄.

Herein, we develop a TiO_2 - 1O_2 system for the photocatalytic-oxidative route for CH4 coupling to form CH₃CH₃ with solar light at room temperature. Other oxidants, including O2, H2O2, and CO2, have been investigated to illustrate the important role of HSO₅⁻ in selectively controlling the coupling of CH₄ to form C₂H₆. Further, an ¹O₂ involving radical-mediated pathway is proposed to explain the high activity of C₂H₆ formation from CH₄. This work provides an alternative new approach for effective coupling of CH₄ to form C_2H_6 at room temperature.

The XRD patterns of TiO2 in Fig. S1a† show the typical anatase and rutile diffraction peaks. The particle morphology with the size range of 10-30 nm and crystalline structure have been clearly indicated by the TEM and HRTEM images of TiO₂, respectively (Fig. S1b and c†). Fig. 1 shows the band structure of TiO₂ and the redox potentials of H₂O₂/'OH, H₂O/'OH, O₂/O₂'-, $^{1}O_{2}/O_{2}$, $^{-}$, $^{-}$ /HSO $_{5}$, and $^{-}$ /SO $_{4}$, $^{-}$. 12,13 Based on these band and redox positions, the TiO2 material is expected to present enhanced performance for radical generation and activation of CH4.

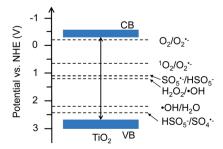


Fig. 1 Band structure of TiO₂ (Degussa P25) and redox potentials of reactive oxygen species.

In order to reveal the photocatalytic performance of the TiO₂-¹O₂ system, we first made a comparison of control experiments based on different reaction conditions, including light, catalyst, and HSO₅⁻ (see Fig. 2a). Under solar light irradiation, TiO2 with HSO5 as oxidant gave rise to an excellent performance for selective generation of C₂H₆, with a rate of 647 μmol $g^{-1} h^{-1}$, much higher than the 180 and 89 μ mol $g^{-1} h^{-1}$ for the two by-products CH₃OH and HCOOH, respectively, leading to a calculated C₂H₆ selectivity up to 75%. Notably, HSO₅ can be independently activated by solar light with the corresponding reaction: $HSO_5^- \rightarrow SO_4^{--} + OH^{-14}$ The 'OH radical enables activation of CH4 to produce 'CH3 species which are essential for C₂H₆ and CH₃OH generation. Under these conditions only a little C2H6, CH3OH, HCOOH, and CO were detected, as displayed in Fig. 2a. For TiO₂ as catalyst, the photo-generated carriers reacting with HSO5 generate more 1O2 which activates CH₄ to generate 'CH₃ species, thus accelerating the coupling of ${}^{\cdot}CH_3$ to form C_2H_6 .

To reveal the crucial role of ¹O₂ in selective conversion of CH₄ to C₂H₆, a control experiment was conducted using different oxidants for the conversion of CH4. Fig. 2b summarizes the results of CH₄ oxidation with various oxidants (${}^{1}O_{2}$, H₂O₂, O₂, and CO₂) under solar light irradiation. Apart from a little bit of CH₃OH, trace amounts of C₂H₆ were found for H₂O₂, O₂, and CO₂ as oxidants, as shown in Fig. 2b. In contrast, the reaction with 1O2 as oxidant remarkably promotes the conversion of CH₄ and selective generation of C₂H₆. Therefore, we conclude that ¹O₂ possesses superiority in view of the photocatalytic activity and selectivity for C2H6 generation. This is probably attributed to the specific band structure of TiO2 and more positive redox potential of HSO₅⁻/SO₄[•]-, thus favouring

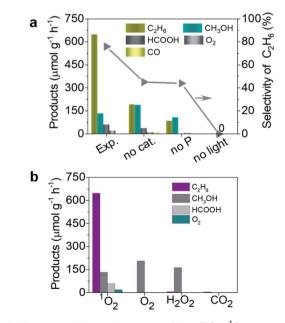


Fig. 2 Photocatalytic performance of the $TiO_2-{}^1O_2$ system under solar light irradiation: (a) comparison of this work (Exp.) and control experiments by varying conditions (no light, no P, and no cat.); (b) products obtained with different oxidants (¹O₂, O₂, H₂O₂, and CO₂).

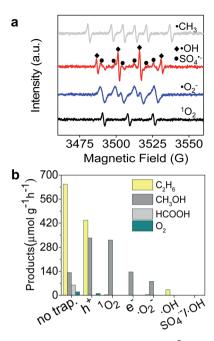


Fig. 3 (a) ESR spectra of 'CH₃, 'OH, SO_4 '-, and 'O²- radicals produced after photocatalytic reaction for 10 min. (b) Products of CH₄ conversion after adding scavengers *para*-quinone, $K_2Cr_2O_7$, $Na_2C_2O_4$, and salicylic acid in the reaction system for trapping 'O²-, e⁻, h⁺, and 'OH, respectively.

generation of $^{1}O_{2}$, as shown in Fig. 1. Additionally, to further understand the ability of $^{1}O_{2}$, we controlled the amount of P which is the source of $^{1}O_{2}$ (Fig. S2a†). As the amount of P was increased from 0 to 0.10 mmol, more $C_{2}H_{6}$ was selectively produced in addition to two other products $CH_{3}OH$ and HCOOH. Meanwhile, much more over-oxidation by-products (HCOOH, CO_{3} and CO_{2}) were generated as it increased to 0.4 mmol, as displayed in Fig. 3a and b. This is presumably owing to the over-oxidation of CH_{4} . It is possible that excessive P may undergo a photoreaction ($HSO_{5}^{-} \rightarrow SO_{4}^{-} + {}^{+}OH$) and produce $^{+}OH_{3}$, leading to the formation of $CH_{3}OH$ and subsequent over-oxidization to HCOOH.

Therefore, excessive P normally results in formation of other by-products, leading to less C_2H_6 . This result further suggests that an appropriate amount of P contributes to selective

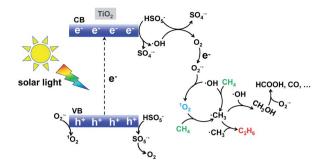
conversion of CH_4 to C_2H_6 . Importantly, such a noble-metal free catalyst system presents remarkable coupling of CH_4 to form CH_3CH_3 compared to the various reported noble metal-based catalysts (see Table 1).

To gain a better understanding of the mechanism of the photocatalytic process for selective conversion of CH₄ to C₂H₆, we used electron spin resonance (ESR) characterization and performed trapping experiments of active species, where 5dimethyl-1-pyrroline-N-oxide (DMPO) was used as a trapping reagent to detect 'CH3, SO4'-, 'OH, and O2'- species. 2,2,6,6-Tetramethylpiperidine (TEMP) was used for detection of ¹O₂. As shown in Fig. 3a, the typical 'CH₃, SO₄'-, 'OH, O₂'-, and ¹O₂ radical species were obviously formed during the photocatalytic process. To verify the distinctive roles of these species in selective conversion of CH₄, we carried out trapping experiments using the corresponding scavengers, as displayed in Fig. 2a. The detailed reactions between scavenger reagents and active species are described in the ESI.† In Fig. 3b, the generation of C₂H₆ was significantly suppressed after trapping the ¹O₂ in Fig. 2b, while CH₃OH production was slightly promoted during this process. This result suggests that 102 remarkably facilitates the formation of C2H6 and the 'OH radical prefers to activate CH4 for generation of CH3OH. However, a fraction of C₂H₆ was still detectable even after trapping 'OH in the reactive system, which is probably attributed to the remaining 102 radicals. Apart from a certain amount of CH3OH, C2H6 was never found in the absence of O₂. active species (see Fig. 3b). This indicates that O2. also remarkably determined the selective formation of C2H6 which is related to the formation of ¹O₂. The e⁻ was also essential for the selective conversion as it initiated the ¹O₂ generation through chain reactions, which was proven by the absence of C₂H₆ in products after elimination of photogenerated electrons. On the other hand, h⁺ only partially controlled the formation of C2H6 based on an h+ trapping experiment.

Based on the above experimental analysis, we proposed a plausible mechanism. As displayed in Scheme 1, photo-induced electrons reacted with ${\rm HSO_5}^-$ and generated ${\rm SO_4}^-$ and 'OH radicals (eqn (1) and (2)).²⁴ Meanwhile, direct light irradiation accelerated the generation of ${\rm SO_4}^-$ and 'OH radicals (eqn (3)).⁷ ${\rm O_2}$ was formed based on the reactions described by eqn (4)–(6),⁷ which agrees well with the trace amount of ${\rm O_2}$

 $\textbf{Table 1} \quad \text{Comparison of photocatalytic conversion of } \ \text{CH}_{4} \ \text{to } \ \text{CH}_{3} \ \text{CH}_{3} \ \text{over reported noble-metal-based catalysts}$

Catalysts	Light source	Temperature (°C)	C_2H_6 ($\mu mol\ g^{-1}\ h^{-1}$)	Ref.
6.0 wt% Ag-HPW/TiO ₂	Xe lamp 400 W (200 < λ < 1000 nm)	30	20.3	15
1.0 wt% Pt/HGTS	Xe lamp 300 W	60	0.63	16
11.7 wt% Au/m-ZnO	Xe lamp 300 W (solar light)	30	11.3	17
AuPd/ZnO (Pd, 1.0 wt%)	Xe lamp 300 W (solar light)	30	17.7	18
0.5 wt% Pd/Ga ₂ O ₃	Xe lamp 300 W ($\lambda = 254 \text{ nm}$)	45	0.28	19
WO_3 , H_2O_2 (2 mM)	Mercury-vapor lamp (UVC-visible light)	55	3.40	20
HBEA	Hg lamp 450 W	70	14.3	21
$Cu_{0.1}Pt_{0.5}/PC-50$	LED 40 W ($\lambda = 365 \text{ nm}$)	40	68.0	22
Au-ZnO/TiO ₂	Xenon lamp 300 W (300 < λ < 500 nm)	26	188	23
TiO ₂ , ¹ O ₂	Xe lamp 300 W (solar light)	25	647	This wor



Scheme 1 Singlet oxygen involving radical-pathway mechanism for conversion of methane to ethane with the $TiO_2 - {}^1O_2$ system.

when ¹O₂ is used as oxidant in Fig. 2b. This O₂ further generated the O_2 radical according to the reactions described by eqn (7). Consequently, ¹O₂ was finally produced as a result of the presence of the O2. - radical (see eqn (8) and (9)). 25 The synthesized ¹O₂ was able to selectively dehydrogenize CH₄ and generate the 'CH₃ radical which further underwent coupling, hence producing CH₃CH₃ (eqn (10)-(13)). It is noted that an increasing amount of 'CH₃ prefers to form C₂H₆,²⁶ which is competitive with the CH₃OH generation ('CH₃ + 'OH → CH₃OH).^{27,28} Therefore, when more 'OH or O2' was present, CH3OH could be generally produced. This well indicates that the dominant product was CH₃OH when radicals H₂O₂ and O₂ were selected as oxidants in Fig. 2b. Taken together, ¹O₂ favoured selective production of CH₃CH₃, in comparison with H₂O₂ or O₂-based systems. Apart from the products CH₃CH₃ and CH₃OH, overoxidation by-products such as HCOOH, CO, and even CO2 could also be formed (see eqn (14) and (15)) in the presence of the O2' radical.29

$$HSO_5^- + e^- \to OH^- + SO_4^{--}$$
 (1)

$$HSO_5^- + e^- \rightarrow OH + SO_4^{2-}$$

$$HSO_5^- \rightarrow 'OH + SO_4'^-$$

$$2HSO_5^- + 2'OH \rightarrow 2SO_4^- + 2H_2O + O_2$$
 (4)

$$HSO_5^- + h^+ \rightarrow H^+ + SO_5^{\bullet -}$$
 (5)

$$SO_5^{\cdot -} + SO_5^{\cdot -} \rightarrow 2SO_4^{\cdot -} + O_2$$
 (6)

$$O_2 + e^- \rightarrow O_2^{\bullet -} \tag{7}$$

$$O_2^{*-} + h^+ \rightarrow {}^1O_2$$
 (8)

$$^{\circ}OH + O_{2}^{\bullet -} \rightarrow {}^{1}O_{2} + OH^{-}$$
 (9)

$${}^{1}O_{2} + CH_{4} \rightarrow {}^{\cdot}CH_{3}$$
 (10)

$$CH_4 + OH \rightarrow CH_3 + H_2O$$
 (11)

$$^{\circ}CH_3 + ^{\circ}OH \rightarrow CH_3OH$$
 (12)

$${}^{\cdot}\text{CH}_3 + {}^{\cdot}\text{CH}_3 \to \text{C}_2\text{H}_6$$
 (13)

$$CH_3OH + O_2^{-} \rightarrow HCOOH$$
 (14)

$$\text{HCOOH} + \text{O}_2^{\bullet -} \rightarrow \text{CO} + \text{CO}_2$$
 (15)

Conclusions

Solar-light driven selective conversion of methane to ethane has been achieved through a photocatalytic reaction at room temperature. By introducing HSO₅⁻ into a TiO₂-based photocatalytic system, enhanced yields and selectivity of CH₃CH₃ are obtained largely due to the presence of ¹O₂ provided by HSO₅⁻. Solar light stimulates the TiO2 catalyst to produce charge carriers (excited electrons and holes) which further activate HSO₅⁻ to generate ¹O₂. Detection and trapping experiments of active species further prove that the photocatalytic TiO2-1O2 system involves the 1O2 radical pathway mechanism. This report opens up a new possibility for efficient conversion of methane to ethane with solar energy at ambient temperature.

Author contributions

Anhua Huang and Jingsheng Wang prepared the samples, carried out the experiments, analysed the data and prepared the paper; Xingyang Wu and Hangchen Liu assisted with the characterization and photocatalytic tests; Jun Cai and Guo Qin Xu reviewed and edited the manuscript; Song Ling Wang supervised this work and reviewed/edited the manuscript; all authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

- 1 H. Herzog, B. Eliasson and O. Kaarstad, Capturing greenhouse gases, Sci. Am., 2000, 282, 72-79.
- 2 H. Song, X. Meng, Z.-j. Wang, H. Liu and J. Ye, Solar-energymediated methane conversion, Joule, 2019, 3, 1606-1636.
- 3 Y. Zeng, H. C. Liu, J. S. Wang, X. Y. Wu and S. L. Wang, Synergistic photocatalysis-Fenton reaction for selective conversion of methane to methanol at room temperature, Catal. Sci. Technol., 2020, 10, 2329-2332.
- 4 L. Yuliati and H. Yoshida, Photocatalytic conversion of methane, Chem. Soc. Rev., 2008, 37, 1592-1602.
- 5 L. Yu, Y. Shao and D. Li, Direct combination of hydrogen evolution from water and methane conversion in a photocatalytic system over Pt/TiO2, Appl. Catal., B, 2017, 204, 216-223.

- 6 Y. Kang, Z. Li, X. Lv, W. Song, Y. Wei, X. Zhang, J. Liu and Z. Zhao, Active oxygen promoted electrochemical conversion of methane on two-dimensional carbide (MXenes): from stability, reactivity and selectivity, *J. Catal.*, 2020, 393, 20–29.
- 7 F. Ghanbari and M. Moradi, Application of peroxymonosulfate and its activation methods for degradation of environmental organic pollutants, *Chem. Eng. J.*, 2017, 310, 41–62.
- 8 S. Zhu, X. Li, J. Kang, X. Duan and S. Wang, Nonradical oxidation in persulfate activation by graphene-like nanosheets (GNS): differentiating the contributions of singlet oxygen ($^{1}O_{2}$) and sorption-dependent electron transfer, *Environ. Sci. Technol.*, 2019, 53, 307–315.
- 9 D. Dai, Z. Yang, Y. Yao, L. Chen, G. Jia and L. Luo, Persulfate activation on crystallographic manganese oxides: mechanism of singlet oxygen evolution for nonradical selective degradation of aqueous contaminants, *Catal. Sci. Technol.*, 2017, 7, 934–942.
- 10 Y. Zhou, J. Jiang, Y. Gao, J. Ma, S.-Y. Pang, J. Li, X.-T. Lu and L.-P. Yuan, Activation of peroxymonosulfate by benzoquinone: a novel nonradical oxidation process, *Environ. Sci. Technol.*, 2015, 49, 12941–12950.
- 11 M. Ahmadi, F. Ghanbari and M. Moradi, Photocatalysis assisted by peroxymonosulfate and persulfate for benzotriazole degradation: effect of pH on sulfate and hydroxyl radicals, *Water Sci. Technol.*, 2015, **72**, 2095–2102.
- 12 Y. Shiraishi, Y. Ueda, A. Soramoto, S. Hinokuma and T. Hirai, Photocatalytic hydrogen peroxide splitting on metal-free powders assisted by phosphoric acid as a stabilizer, *Nat. Commun.*, 2020, **11**, 3386.
- 13 J. Lim, Y. Yang and M. Hoffmann, Activation of Peroxymonosulfate by Oxygen Vacancies-Enriched Cobalt-Doped Black TiO₂ Nanotubes for the Removal of Organic Pollutants, *Environ. Sci. Technol.*, 2019, 53, 6972–6980.
- 14 M. G. Antoniou, A. A. de la Cruz and D. D. Dionysiou, Degradation of microcystin-LR using sulfate radicals generated through photolysis, thermolysis and e-transfer mechanisms, *Appl. Catal.*, B, 2010, 96, 290–298.
- 15 X. Yu, V. L. Zholobenko, S. Moldovan, D. Hu, D. Wu, V. V. Ordomsky and A. Y. Khodakov, Stoichiometric methane conversion to ethane using photochemical looping at ambient temperature, *Nat. Energy*, 2020, 5, 511–519.
- 16 S. Wu, X. Tan, J. Lei, H. Chen, L. Wang and J. Zhang, Gadoped and Pt-loaded porous TiO₂–SiO₂ for photocatalytic nonoxidative coupling of methane, *J. Am. Chem. Soc.*, 2019, **141**, 6592–6600.
- 17 L. Meng, Z. Chen, Z. Ma, S. He, Y. Hou, H.-H. Li, R. Yuan, X.-H. Huang, X. Wang and X. Wang, Gold plasmon-induced photocatalytic dehydrogenative coupling of

- methane to ethane on polar oxide surfaces, *Energy Environ. Sci.*, 2018, **11**, 294–298.
- 18 W. Jiang, J. Low, K. Mao, D. Duan, S. Chen, W. Liu, C.-W. Pao, J. Ma, S. Sang and C. Shu, Pd-Modified ZnO–Au Enabling Alkoxy Intermediates Formation and Dehydrogenation for Photocatalytic Conversion of Methane to Ethylene, *J. Am. Chem. Soc.*, 2020, **143**, 269–278.
- 19 S. P. Singh, A. Anzai, S. Kawaharasaki, A. Yamamoto and H. Yoshida, Non-oxidative coupling of methane over Pdloaded gallium oxide photocatalysts in a flow reactor, *Catal. Today*, 2020, 375, 264–272.
- 20 K. Villa, S. Murcia-López, T. Andreu and J. R. Morante, Mesoporous WO₃ photocatalyst for the partial oxidation of methane to methanol using electron scavengers, *Appl. Catal.*, B, 2015, 163, 150–155.
- 21 S. Murcia-López, M. C. Bacariza, K. Villa, J. M. Lopes, C. Henriques, J. R. Morante and T. Andreu, Controlled photocatalytic oxidation of methane to methanol through surface modification of beta zeolites, ACS Catal., 2017, 7, 2878–2885.
- 22 X. Li, J. Xie, H. Rao, C. Wang and J. Tang, Platinum-and CuO_x-Decorated TiO₂ Photocatalyst for Oxidative Coupling of Methane to C₂ Hydrocarbons in a Flow Reactor, *Angew. Chem., Int. Ed.*, 2020, **59**, 19702–19707.
- 23 S. Song, H. Song, L. Li, S. Wang, W. Chu, K. Peng, X. Meng, Q. Wang, B. Deng, Q. Liu, Z. Wang, Y. Weng, H. Hu, H. Lin, T. Kako and J. Ye, A selective Au-ZnO/TiO₂ hybrid photocatalyst for oxidative coupling of methane to ethane with dioxygen, *Nat. Catal.*, 2021, 4, 1032–1042.
- 24 X. Chen, W. Wang, H. Xiao, C. Hong, F. Zhu, Y. Yao and Z. Xue, Accelerated TiO₂ photocatalytic degradation of Acid Orange 7 under visible light mediated by peroxymonosulfate, *Chem. Eng. J.*, 2012, **193**, 290–295.
- 25 X. Li, J. Liu, A. I. Rykov, H. Han, C. Jin, X. Liu and J. Wang, Excellent photo-Fenton catalysts of Fe–Co Prussian blue analogues and their reaction mechanism study, *Appl. Catal.*, *B*, 2015, **179**, 196–205.
- 26 S. Murcia-López, K. Villa, T. Andreu and J. R. Morante, Partial oxidation of methane to methanol using bismuthbased photocatalysts, ACS Catal., 2014, 4, 3013–3019.
- 27 K. Sahel, L. Elsellami, I. Mirali, F. Dappozze, M. Bouhent and C. Guillard, Hydrogen peroxide and photocatalysis, *Appl. Catal.*, *B*, 2016, **188**, 106–112.
- 28 M. Hayyan, M. A. Hashim and I. M. AlNashef, Superoxide ion: generation and chemical implications, *Chem. Rev.*, 2016, **116**, 3029–3085.
- 29 J. Xie, R. Jin, A. Li, Y. Bi, Q. Ruan, Y. Deng, Y. Zhang, S. Yao, G. Sankar and D. Ma, J. Highly selective oxidation of methane to methanol at ambient conditions by titanium dioxide-supported iron species, Tang, *Nat. Catal.*, 2018, 1, 889–896.