

PAPER

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14, 2244High conversion of methane to methyl ester at
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To establish an aerobic oxidation of methane to produce methanol with a high yield under ambient conditions is one of the dreams of researchers in academia and industry. However, although a lot of progress has been made on methane functionalization for several decades, it is still a great challenge to break through the selectivity-conversion limit in the aerobic oxidation of methane to methanol or methyl ester especially at room temperature. Herein, we report a simple visible-light driven reaction of CH₄/O₂ with CF₃CO₂H (HTFA) to CH₃-O-COCF₃ (MTFA) at 298 K, just using catalytic NaNO₂ in an aqueous HCl/HTFA solution. In a batch reaction of CH₄/O₂ (1:5, 0.4 MPa), the yield of MTFA is over 90%. In a 7-day continuous experiment using CH₄/O₂ (2:1, 0.1 MPa), the MTFA selectivity and methane conversion are over 90% based on the methane input. The turnover frequency (TOF) is 2.5 mol_{MTFA} mol_{NaNO₂}⁻¹ h⁻¹, and the turnover number (TON) is over 400. A reasonable reaction mechanism is suggested and partially confirmed by experiments, involving NOCl as a crucial species in the two-phase aerobic oxidation of methane to methyl ester. Methanol could be obtained with a commonly used hydrolysis of MTFA at 298 K. Neither metal catalysts nor special reagents are necessary in this two-step conversion of methane to methanol.

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Introduction

Methane is a thermodynamically stable greenhouse gas under ambient conditions.^{1–4} As the main component of natural gas (70–90% methane)⁵ and biogas (50–75% methane),⁶ the conversion of methane to some liquid chemicals such as methanol or methanol derivatives by a practical and commercial approach is greatly desired, not only for its storage, transportation and use as a fuel or a carbon feedstock^{7,8} but also for the reduction of carbon dioxide emission due to its flaring in upstream oil and gas operations.⁹ However, although a lot of progress in the functionalization of methane has been made for over five decades,^{2,10,11} to break through the selectivity-conversion limit of the aerobic oxidation of methane, *i.e.*, to obtain methanol or methyl ester with a high yield (over 80%), is still a great challenge,^{12–24} especially at room temperature (293–298 K)^{25–29} under normal or low pressure (0.1–1.6 MPa).^{25–27,30} Although some reaction systems show a high catalytic efficiency, over-oxidation has not been avoided.^{31,32}

Normally, to establish effective oxidation of methane with dioxygen to give methanol or methyl ester with a high yield

under ambient conditions, it is necessary to determine: 1) a more effective catalytic species to cleave an inert C–H bond of methane (BDE = 439 kJ mol⁻¹),¹ 2) a reasonable way to generate methyl-oxygen intermediates using dioxygen or dioxygen activation, and 3) a chemical environment to guarantee that the product survives completely. However, because almost all the traditional powerful species, including metal complexes, non-metal compounds and enzymes, used to cleave the C–H bonds of methane are carried out in the liquid-phase or on the gas–solid interface, good solubility of solvent to methane, high partial pressure of methane, poor coordination of product molecule with reactive species and special operations in the current oxidations of methane are often required. This indicates that methane and its products are in the same phase during the whole process, which creates a dilemma between enhancing methane transformation and reducing side reactions such as oxidation of methanol rather than methane under reaction conditions (Scheme 1a). Thus, it is necessary to design a two-phase process for the conversion of methane, in which methane should undergo an aerobic oxidation in the gas-phase, and its target product must be in the liquid-phase without over-oxidation happening (Scheme 1a).

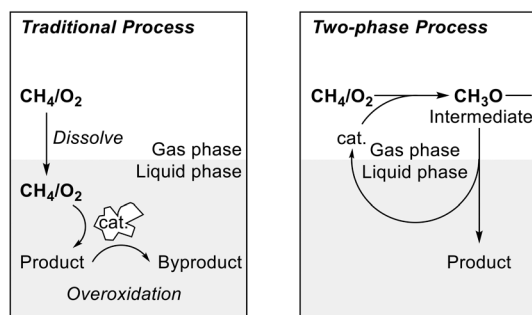
It is well known that in the gas-phase under light at room temperature, a chlorine radical (Cl·) can abstract a hydrogen from methane to form a methyl radical (CH₃·) in the radical chlorination of methane with chlorine (Cl₂).³³ Moreover, as the most readily available gas-phase oxidant, dioxygen (O₂)

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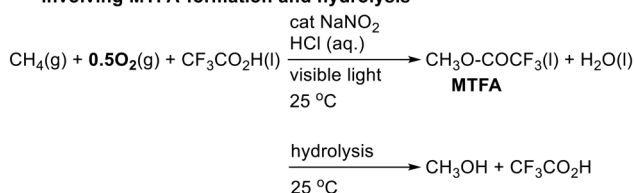
[†] Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4cy00048j>



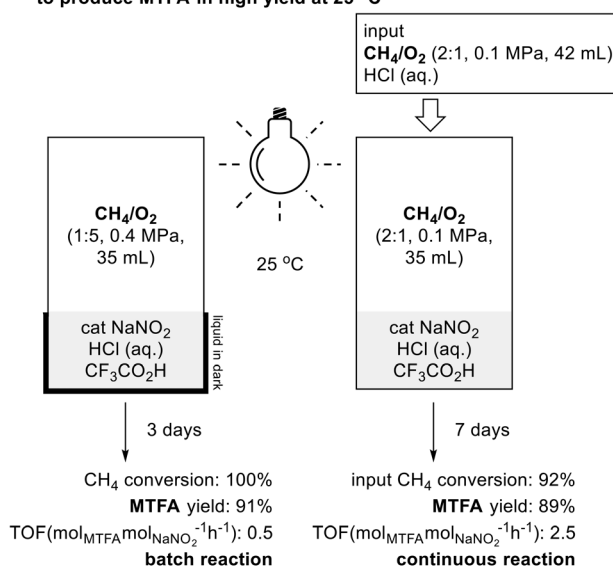
(a) Traditional process vs two-phase process for the aerobic oxidation of methane



(b) Two-step conversion of methane to methanol involving MTFA formation and hydrolysis



(c) Visible-light driven aerobic oxidation of methane to produce MTFA in high yield at 25 °C



Scheme 1 Aerobic oxidation of methane used in this work. (a) Traditional process vs. a two-phase process for the aerobic oxidation of methane. (b) Two-step conversion of methane to methanol involving MTFA formation and hydrolysis. (c) Visible-light driven aerobic oxidation of methane to produce MTFA with a high yield at 25 °C.

has already been widely used in conversions of methane (Fig. S1, Table S1†), and $\text{CH}_3\text{-OO}\cdot$ species could be formed from $\text{CH}_3\cdot$ with O_2 in the gas-phase. Using the chlorine radical to give $\text{CH}_3\text{-OO}\cdot$ species, Ohkubo and co-workers obtained a high yield of methane oxides, mainly as formic acid.^{34,35} However, there are few reports which disclose how to convert $\text{CH}_3\text{-OO}\cdot$ species to methanol or a methyl ester exclusively,^{36,37} to prevent over-oxidations of methanol or methyl ester happening in the liquid-phase and to devise a chlorine catalytic system for the aerobic oxidation of methane under radical reaction conditions.

Herein, we report a two-phase reaction of methane/dioxygen (CH_4/O_2) with trifluoroacetic acid (HTFA, $\text{CF}_3\text{CO}_2\text{H}$), which gives methyl trifluoroacetate (MTFA, $\text{CH}_3\text{OCOCF}_3$) with a high yield under visible-light at 298 K (25 °C), which successfully breaks through the selectivity-conversion limit of the aerobic oxidation of methane. Furthermore, MTFA is hydrolyzed to easily give methanol (CH_3OH) at room temperature to complete the two-step conversion of methane to methanol under ambient conditions (Scheme 1b). In aerobic oxidations, sodium nitrite (NaNO_2) is employed in a catalytic amount in aqueous HCl /HTFA solution without any metal complexes or special additives. In a batch reaction of CH_4/O_2 (1:5, 35 mL, and 0.4 MPa) with 2.4 mol% NaNO_2 based on methane, MTFA was obtained with a 91.3% yield with the methane conversion up to 100% in 3 days. Conversely, to keep the constant pressure of gases in the reactor, CH_4/O_2 (2:1, 35 mL, and 0.1 MPa) was used as a buffer gas with 2.3 μmol NaNO_2 during a continuous experiment. The external CH_4/O_2 (2:1, 42 mL, and 0.1 MPa) was input within 7 days. MTFA was produced with an 88.6%

yield (96% selectivity), and the methane conversion was 92% based on the external CH_4/O_2 under ambient conditions in this reaction (Scheme 1c). The turnover frequency (TOF) was 2.5 $\text{mol}_{\text{MTFA}} \text{mol}_{\text{NaNO}_2}^{-1} \text{h}^{-1}$, and the turnover number (TON) was over 400.

Results

Initially, we investigated the catalytic NaNO_2 /acid system for the aerobic oxidation of methane under ambient conditions, which had been used successfully in our aerobic chlorination and bromination of alkanes under visible-light at room temperature previously.^{33,38,39} In the presence of 2.4 mol% NaNO_2 based on CH_4 in HCl (12 M) solution, only a trace of CH_3OH and methyl nitrate ($\text{CH}_3\text{-ONO}_2$) were detected by $^1\text{H-NMR}$ analysis in the reaction of CH_4/O_2 (2:1, 0.1 MPa) under irradiation by a 23 W LED at 298 K after 24 hours. It seemed that the oxidation of methane did not proceed very well because the catalytic NaNO_2 was fixed in CH_3ONO_2 to stop the reaction. Then, HTFA was added into the solution to transfer CH_3ONO_2 to MTFA and HNO_3 under same conditions. As expected, no CH_3ONO_2 was detected, and methyl chlorides $\text{CH}_3\text{Cl}/\text{CH}_2\text{Cl}_2$ were major products (92% selectivity) with a 39.7% yield based on methane. Notably, MTFA with a 2.7% yield and HCO_2H with a 0.8% yield were also found in the products. In contrast, when NaNO_2 loading was reduced to 0.024 mol%, only MTFA was produced with a 2.7% yield without any other products, and the TON was over 100 in 24 hours. This implies that the amount of NaNO_2 could significantly affect the selectivity of MTFA, and the modified catalytic

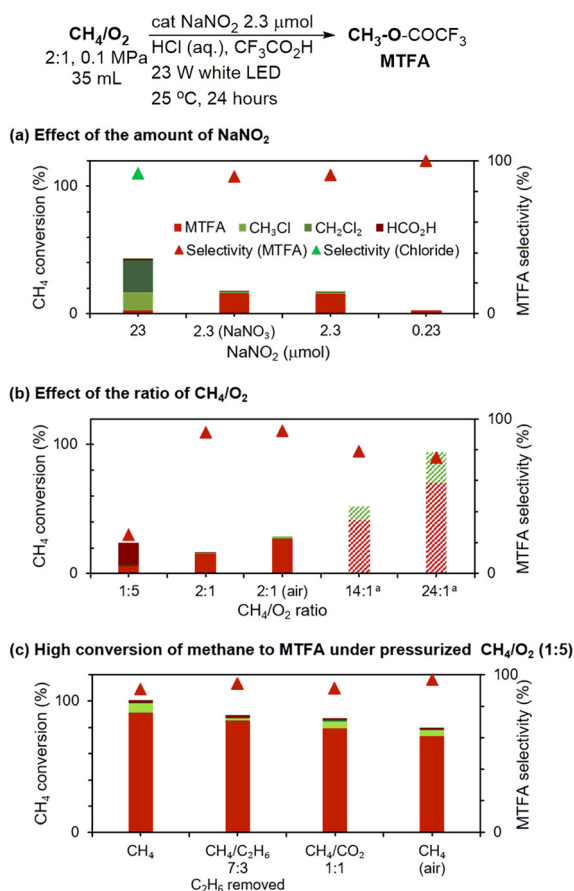


system of $\text{NaNO}_2/\text{HCl}/\text{HTFA}$ should be effective for the conversion of methane to MTFA in an aerobic oxidation of methane under ambient conditions. Using just 0.24 mol% of NaNO_2 (2.3 μmol) in HCl (12 M, 0.18 mL)/HTFA (0.7 mL) solution, it was found that MTFA could be produced as the major product with a 15.7% yield from CH_4/O_2 (2:1, 0.95 mmol/0.48 mmol, 35 mL, and 0.1 MPa) under 23 W LED at 25 °C after 24 hours. The selectivity of MTFA was 91% with just a small amount of CH_3Cl (5%) and HCO_2H (4%). No other byproducts including formaldehyde, nitromethane or carbon dioxide were detected by $^1\text{H-NMR}$ and IR analyses. The turnover frequency (TOF) was 2.8 $\text{mol}_{\text{MTFA}} \text{mol}_{\text{NaNO}_2}^{-1} \text{h}^{-1}$ in this batch experiment. The performance of sodium nitrate NaNO_3 was not different from NaNO_2 in the aerobic oxidation (Scheme 2a, Table S3†). However, if HCl was replaced by hydrobromic acid (HBr) or in the absence of HTFA, O_2 or light, no methyl ester was detected. If using 2.3 μmol NaNO_2 under normal pressure in the same reactor (Table S5†), we also found that air was available to give MTFA with a 92% selectivity

and CH_3Cl , and the TOF was 2.1 $\text{mol}_{\text{MTFA}} \text{mol}_{\text{NaNO}_2}^{-1} \text{h}^{-1}$. If the ratio of CH_4/O_2 was increased up to 24:1, O_2 could be consumed almost completely in 24 hours. The yields of MTFA and CH_3Cl based on O_2 were 70.7% and 23.6%, respectively. In contrast, when the ratio of CH_4/O_2 was decreased down to 1:5, HCO_2H was the major product and MTFA (~3:1) was formed with a total yield of 24%, and no methyl chlorides were found (Scheme 2b). These results show that the formation of byproducts was related to the ratio of CH_4/O_2 , i.e., methyl chlorides were generated easily in the absence of O_2 , but HCO_2H was formed quickly with a rich O_2 .

Based on studies on enhancing the yield of MTFA, we found that in the reaction of CH_4/O_2 (2:1 and 0.1 MPa) the yield of MTFA could be over 30% in 48 hours (Table S8†), but after that, it increased slowly with the reaction time and/or with the amount of CH_4/O_2 consumed in the reactor. It is reasonable to believe that the amount and ratio of NaNO_2 (as a catalytic species)/ CH_4/O_2 in a reactor can affect not only the product yield and selectivity but also the reaction rate and lifetime especially with a long reaction time. For example, in the presence of 2.4 mol% of NaNO_2 (23 μmol) with CH_4/O_2 (1:5, 35 mL, and 0.4 MPa), the yield of MTFA was 91.3% based on methane after 3 days. The methane conversion was 100%, and the byproducts were CH_3Cl (7.3%), CH_2Cl_2 (0.2%) and HCO_2H (2%). (Table S13†). In this case, an increase of NaNO_2 and O_2 could enhance the yield of MTFA with a high selectivity. Under similar conditions, feed gases containing an inert gas such as nitrogen ($\text{CH}_4/\text{air O}_2/\text{air N}_2$, 1:5:19) or carbon dioxide ($\text{CH}_4/\text{O}_2/\text{CO}_2$, 1:5:1) could also produce MTFA with greater than 73% yield with over 90% selectivity (Scheme 2c, Table S13†). However, other alkanes such as ethane or cyclohexane are not available in this aerobic oxidation. Over 10% of ethane in methane ($\text{C}_2\text{H}_6/\text{CH}_4$, 1:10) would block the reaction. However, ethane in mixed gases ($\text{C}_2\text{H}_6/\text{CH}_4$, 3:7) could be converted to liquid ethyl bromides almost completely by an aerobic bromination system (catalytic $\text{NaNO}_2/\text{HBr}/\text{solvent}$) under visible-light at room temperature before the beginning of methane conversion to methyl ester. A remaining gas, such as pure CH_4 , could undergo aerobic oxidation smoothly to produce MTFA with an 85.4% yield based on methane (Scheme 2c). For reactions under low pressure, keeping the liquid-phase out of the light was beneficial to reduce byproducts, which means that the aerobic oxidation proceeds in the gas-phase. If the liquid phase was irradiated by light, the selectivity of MTFA and methane conversion decreased greatly (Tables 1 and S14†). This indicates that side reactions in the liquid phase could occur and interrupt the desired reaction in the gas phase. For example, alkane chlorination and nitrosation proceeded without oxygen in the solution to block the catalytic cycle, resulting in NO_x catalyst loss.³³

A 4 day continuous reaction could be established for a reactor containing CH_4/O_2 (2:1, 35 mL, and 0.1 MPa) with 0.24 mol% of NaNO_2 (2.3 μmol) in a HCl/HTFA solution. To



Scheme 2 Methane conversion and MTFA selectivity in aerobic oxidations. (a) Effect of the amount of NaNO_2 (NaNO_2 0.23–23 μmol). (b) Effect of the ratio of CH_4/O_2 (CH_4/O_2 1:5–24:1; ^a conversion based on O_2). (c) High conversion of methane to MTFA under pressurized CH_4/O_2 (1:5) (total pressure 0.4–2.0 MPa; NaNO_2 23 μmol ; liquid kept in the dark; 72 hours).



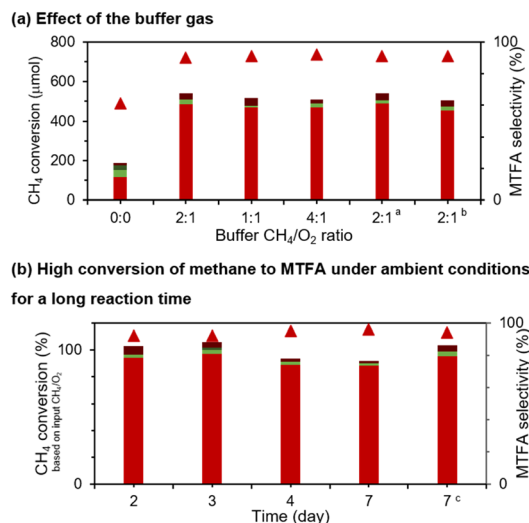
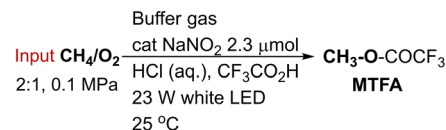
Table 1 Effect of different irradiated phases on selectivity

$\text{CH}_4/\text{O}_2 \xrightarrow[\text{25 } ^\circ\text{C, 72 hours}]{\text{cat NaNO}_2 \text{ 23 } \mu\text{mol}, \text{HCl (aq.)}, \text{CF}_3\text{CO}_2\text{H}} \text{CH}_3\text{-O-COCF}_3$ $\text{1:5, 0.4 MPa} \quad \text{MTFA}$ 35 mL		
Irradiated phase	CH ₄ conv. (%)	Selectivity of ester (%)
Gas phase	100	91
Both	56	79
Liquid phase	49	34

Reaction conditions: CH₄/O₂ (1:5, 0.4 MPa, 1 equiv., in a Schlenk tube), NaNO₂ (1.59 mg, 23 μmol, and 2.4 mol%), HCl (12 M and 1.8 mL), HTFA (7 mL), 23 W white LED bulb, 298 K, partly covered, 72 hours. Yields determined by NMR with MeNO₂ as an internal standard.

keep the reaction system stable, the external CH₄/O₂ (2:1, 0.1 MPa) was added into the reactor every 24 hours. The initial gas in the reactor may be as the buffer gas, and the external gas added is called the input gas here. When the selectivity of MTFA and CH₃Cl is very high (over 90%), the ratio of CH₄/O₂ consumed is very close to 2:1. Thus, at the end of continuous reactions, the amount of the input gas could be equal to that of the consumed gas during the reaction. Based on the input of CH₄/O₂ (2:1, 21 mL, and 0.1 MPa), the yield of MTFA was 85% with a selectivity of 90% in the 4-day continuous reaction. It was proved that the ratio of CH₄/O₂ (1:1–4:1) in the buffer gas, and the amount of the input gas (15–30 mL) did not greatly affect the MTFA production and gave a selectivity with the TOF close to 2.2 mol_{MTFA} mol_{NaNO₂}^{−1} h^{−1} (Scheme 3a, Table S15†).

However, in a 7 day continuous reaction, external HCl (12 M) was also necessary to be added several times with the input gas, which effectively maintained the TOF at 2.5 mol_{MTFA} mol_{NaNO₂}^{−1} h^{−1} (Table S16†). One of reasons for this, is that a lot of MTFA accumulated in the solution can block the reaction, but adding more HCl (12 M) will partially overcome this problem (Table S12†). In this reaction, the yield of MTFA was 88.6% based on the input CH₄/O₂ (2:1, 42 mL, and 0.1 MPa) or 48.3% based on CH₄/O₂ (2:1, 77 mL, and 0.1 MPa), with a concentration of MTFA of ~510 mmol L^{−1} in the resultant solution. In other continuous experiments for 2, 3 or 4 days, the methane conversion and MTFA selectivity were greater than 90% based on the input CH₄/O₂ (2:1), and the TOFs were 2.2–2.3 mol_{MTFA} mol_{NaNO₂}^{−1} h^{−1} (Scheme 3b, Table S17†). Meanwhile, the ratio of CH₄/O₂ in the reactors was always around 2:1 as the initial state. This indicates that the aerobic oxidation of methane can proceed very well and produces methyl ester with an excellent selectivity under stable conditions, including temperature, light, pressure, acidity, and the ratio of CH₄/O₂. Furthermore, CH₃OH was obtained with an 85.2% yield by hydrolysis of MTFA under non-optimized conditions at room temperature after 4 hours (Table S19†) to complete the two-step conversion of methane to methanol under ambient conditions.

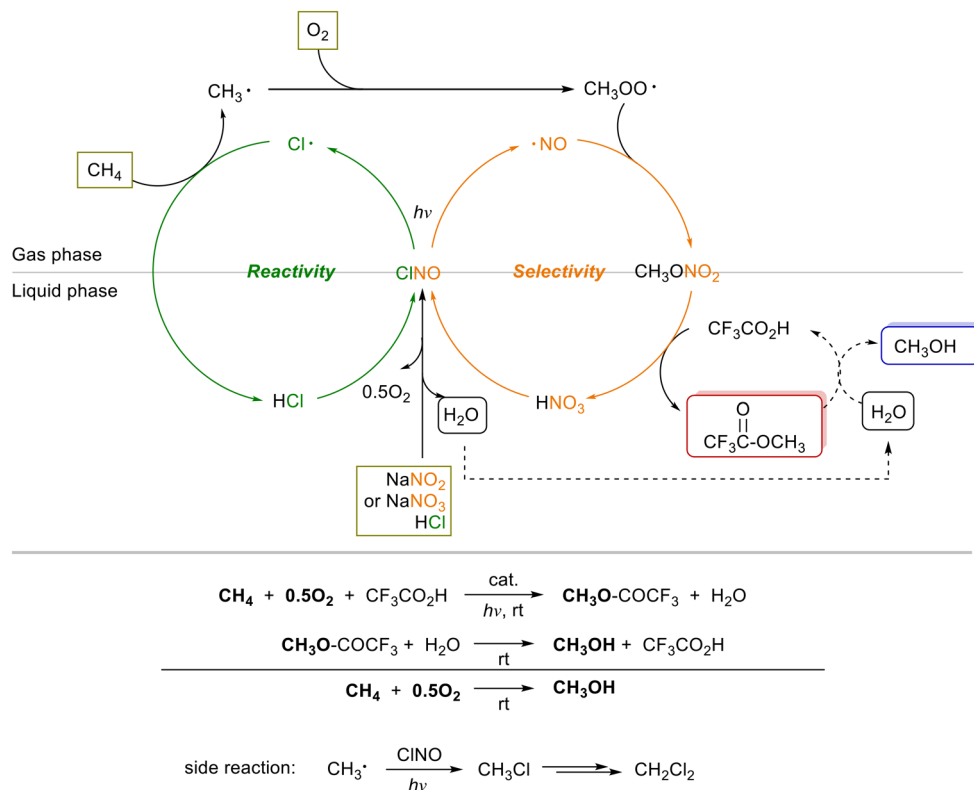


Scheme 3 Methane to MTFA in continuous experiments. (a) Effect of the buffer gas (buffer CH₄/O₂ 0:0–4:1, 0 or 0.1 MPa; input CH₄/O₂ 21 mL; 4 days. ^a Input CH₄/O₂ 15 mL. ^b Input CH₄/O₂ 30 mL). (b) High conversion of methane to MTFA under ambient conditions for a long reaction time (input CH₄/O₂ 10–42 mL; input HCl aq. 0.18–1.08 mL. ^c Input CH₄/O₂ 18 mL; NaNO₂ 1.0 μmol).

Discussion

A possible reaction mechanism is suggested based on our studies and previous reports (Scheme 4). The first step is that nitrosyl chloride (NOCl) is released into the gas-phase from the acidic solution of catalytic NaNO₂ or NaNO₃ with HCl at room temperature.^{40,41} Then, a chlorine radical Cl· and nitric oxide (NO) are formed from NOCl under visible-light. The effective wavelengths of LED light are 350–450 nm (Table S9†).⁴² In the gas-phase, CH₄ is attacked by Cl· to give a methyl radical (CH₃·) and HCl, and CH₃· subsequently combines with O₂ to generate methyl peroxide species (CH₃-OO·), which is partially confirmed by an isotopic ¹⁸O test to find CH₃¹⁸O species (Scheme S1†). Conversely, methyl chloride (CH₃-Cl) could also be produced from the reaction of CH₃· with NOCl under light, especially when O₂ is insufficient and more NaNO₂ is used (Table S5†) or the radical reactions were concentrated in the liquid phase (Tables 1 and S14†). Meanwhile, another byproduct, formic acid (HCO₂H) will be readily generated in the further reactions of CH₃-OO· species.^{34,35,43} Fortunately, CH₃-OO· can also react with NO to quickly give CH₃-OO-NO in the gas-phase, and CH₃-OO-NO could be isomerized to methyl nitrate (CH₃O-NO₂) as a protected species to prevent over-oxidations happening under same conditions,^{44,45} which is a key step for product selectivity. This implies that the selectivity of methyl ester in the gas-phase depends on the ratio of NOCl/CH₄/O₂, and NOCl is from NO₂[−] or NO₃[−] with HCl in the liquid-phase. In the absence of HTFA, CH₃O-NO₂ was detected by





Scheme 4 Proposed mechanism.

¹H-NMR analysis in the reaction as mentioned previously. When CH₃ONO₂ was used instead of NaNO₂, the reaction still proceeded very well (Table S21†). Finally, CH₃O-COCF₃ (MTFA) and HNO₃ are produced by the transesterification of CH₃O-NO₂ with HTFA in the presence of HCl in the liquid-phase (Table S22†). NOCl is also regenerated from HNO₃ and HCl in the solution. Actually, NOCl provided not only Cl· to cleave the inert CH₃-H bond but also NO to form CH₃O-NO₂ under visible-light at room temperature. Thus, it is a gas catalytic species for the total catalysis of reactivity and selectivity. Moreover, if Cl₂ generated more than NOCl is not good to produce methyl ester selectively in the aerobic oxidation of methane, like under the reaction conditions for the visible-light driven oxidative chlorination of alkanes. Because the main reactions are carried out in the gas phase, including the breaking of the CH₃-H bond and formation of the CH₃-O bond, it is unnecessary to demand good solubility of either CH₄ or O₂ in the liquid solvent. Some factors which hamper the formation of NOCl should be eliminated. For example, as the amount of MTFA increases, the rate of transesterification of CH₃O-NO₂ with HTFA slowed down. Thus, addition of more HCl to enhance the acidity is beneficial to release HNO₃ from CH₃O-NO₂ for the regeneration of NOCl in the continuous reactions. If there is another alkane with weaker C-H bonds, such as ethane (BDE = 420 kJ mol⁻¹)¹ or cyclohexane (BDE = 416 kJ mol⁻¹),⁴⁶ in the reactor, a classical radical nitrosation occurs easily at a very low O₂ concentration.⁴⁷ Acetic acid or caprolactam was formed after oxime rearrangements in

the liquid-phase, resulting in the loss of NO to stop the catalytic cycle.

Conclusions

Overall, a visible-light driven aerobic oxidation of methane with HTFA to MTFA at room temperature has been established, involving the gas-phase oxidative reactions of CH₄/O₂ with NOCl to give CH₃O-NO₂/HCl selectively, and the liquid-phase transform reactions of CH₃O-NO₂/HCl with HTFA to effectively form MTFA and NOCl. This is a novel two-phase methane conversion without any special catalysts or reagents. MTFA could be obtained with a high yield (over 80%) based on CH₄ in batch and continuous experiments. In particular, in the continuous reactions under ambient conditions, MTFA could be produced smoothly, and its selectivity is over 90% in 7 days. The ratio of initial and input CH₄/O₂ is 2 : 1 in these reactions, which is not only consistent with the aerobic oxidation of methane to methanol but also beyond the explosion limit of methane. MTFA is more easily hydrolyzed to afford methanol at room temperature. It is feasible that this reaction will become a practical and commercial process in industry after further exploration and improvement.

Author contributions

The manuscript was written with contributions from of all authors.



Conflicts of interest

There are no conflicts to declare.

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