High conversion of methane to methyl ester at 298 K

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ABSTRACT: To establish an aerobic oxidation of methane to produce methanol in high yield under ambient conditions is one of dreams to researchers in both academia and industry. However, although a lot of progress has been made on methane functionalization for several decades, it is still a grand 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 visiblelight driven reaction of CH_4/O_2 with CF_3CO_2H (HTFA) to CH_3 -O-COCF₃ (MTFA) at 298 K, just using catalytic NaNO₂ in aqueous HCl/HTFA solution. In a batch reaction of CH_4/O_2 (1:5, o.4 MPa), the yield of MTFA is over 90%. In a 7-day continuous experiment of CH_4/O_2 (2:1, o.1 MPa), both the MTFA selectivity and the methane conversion are over 90% based on the input methane. 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 partial confirmed by experiments, involving NOCl as a crucial species in the two-phase aerobic oxidation of methane to methyl ester. Methanol could be obtained by a common hydrolysis of MTFA at 298 K. Neither metal catalysts nor special reagents are necessary in this two-step conversion of methane to methanol.

Methane is a thermodynamically stable and greenhouse gas under ambient conditions ¹⁻³. As the main component of natural gas (70~90% methane) ⁴ and biogas (50~75% methane) ⁵, methane converted to some liquid chemicals such as methanol or methanol derivatives by a practical and commercial approach is strongly desired, for not only its storage, transportation and use as a fuel or a carbon feedstock, ^{6,7} but also the reducing of carbon dioxide emission due to its flaring in upstream oil and gas operations.⁸ However, although a lot of progress in the functionalization of methane has been made for over five decades, ^{2,9,10} to break through the selectivity-conversion limit of the aerobic oxidation of methane, i.e., to obtain methanol or methyl ester in high yield (over 80%), is still a grand challenge, ¹¹⁻²² especially under normal or low pressure (0.1~1.6 MPa) ²³⁻ ²⁶ at room temperature (293~298 K). ²⁴⁻²⁹

Normally, to establish an effective oxidation of methane with dioxygen to give methanol or methyl ester in high yield under ambient conditions, it is necessary to find out 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 by use of dioxygen or by dioxygen activation, and 3) a chemical environment to guarantee product surviving completely. However, since almost all traditional powerful species including metal complexes, non-metal compounds and enzymes to cleave C-H bonds of methane are carried out in the liquid-phase or on the gas-solid interface, it is often required that good solubility of solvent to methane, high partial pressure of methane, poor coordination of product molecule with reactive species and special operation in the current oxidations of methane. It indicates that methane and its products are in the same phase during the whole process, which makes a dilemma between enhancing methane

transformation and reducing side reactions such as an oxidation of methanol rather than methane under the reaction conditions (Scheme 1a). Thus, it should be 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, chlorine radical (Cl•) can abstract hydrogen of methane to form methyl radical (CH₃•) in the radical chlorination of methane with chlorine (Cl₂). Moreover, as the most readily available gas-phase oxidant, dioxygen (O₂) has been already widely used in the conversions of methane (Figure S1, Table S1), and especially CH₃-OO• species could be formed from CH₃• with O₂ in the gas-phase. However, there are few reports to disclose how to convert CH₃-OO• species to methanol or methyl ester exclusively, to prevent over-oxidations of methanol or methyl ester happening in the liquid-phase, and to make a chlorine catalytic system for the aerobic oxidation of methane under the radical reaction conditions.

Here we report that a two-phase reaction of methane/dioxygen (CH₄/O₂) with trifluoroacetic acid (HTFA, CF₃CO₂H) affords methyl trifluoroacetate (MTFA, CH₃OCOCF₃) in high yield under visible-light at 298 K (25 °C), which breaks through the selectivity-conversion limit of the aerobic oxidation of methane successfully. Furthermore, MTFA is also hydrolyzed to give methanol (CH₃OH) easily at room temperature to complete the two-step conversion of methane to methanol under ambient conditions (Scheme 1b). In the aerobic oxidations, sodium nitrite (NaNO₂) is just employed in a catalytic amount in aqueous HCl/HTFA solution without any metal complexes or special additives. In a batch reaction of CH₄/O₂(1:5, 35 mL, 0.4 MPa) with 2.4 mol% NaNO₂ based on methane, MTFA was obtained in 91.3% yield with the methane conversion up to 100% in 3 days. On the other hand, to keep the constant pressure of gases in the reactor, CH_4/O_2 (2:1, 35 mL, 0.1 MPa) was used as a buffer gas with 2.3 µmol NaNO₂ during a continuous experiment. The external CH_4/O_2 (2:1, 42 mL, 0.1 MPa) was inputted within 7 days. MTFA was produced in 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 mol_{MTFA} mol_{NaNO2}⁻¹ h⁻¹, and the turnover number (TON) was over 400.

Results

Initially, we investigated the catalytic NaNO₂/acid system for the aerobic oxidation of methane under ambient conditions, which was used successfully in our aerobic bromination of alkanes under visible-light at room temperature before. ³⁰ In the presence of 2.4 mol% NaNO₂ based on CH₄ in HCl (12 M) solution, only a trace of CH₃OH and methyl nitrate (CH₃ONO₂) were detected by ¹H NMR analysis in the reaction of CH₄/O₂ (2:1, 0.1 MPa) under irradiation by 23 W LED at 298 K after 24 hours. It seems that the oxidation of methane did not proceed very well since the catalytic NaNO2 was fixed in CH3ONO2 to stop the reaction. Then, HTFA was added into the solution to transfer CH₃ONO₂ to MTFA and HNO₃ under the same conditions. Of course, no CH₃ONO₂ was detected, and methyl chlorides CH₃Cl/CH₂Cl₂ were the major products (92% selectivity) in 39.7% yield based on methane. Notably, MTFA in 2.7% yield and HCO₂H in 0.8% yield were also found in the products. In contrast, when NaNO2 loading was reduced to 0.024 mol%, only MTFA was produced in 2.7% yield without any other products and the TON was over 100 in 24 hours. It implies that the amount of NaNO2 could affect the selectivity of MTFA seriously, and the modified catalytic system of NaNO₂/HCl/HTFA should be effective to the conversion of methane to MTFA in an aerobic oxidation of methane under ambient conditions. Just by use of 0.24 mol% NaNO₂(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 in 15.7% yield from CH₄/O₂ (2:1, 0.95 mmol/0.48 mmol, 35 mL, 0.1 MPa) under 23 W LED at 25 °C after 24 hours. The selectivity of MTFA was 91% just with a small amount of CH₃Cl (5%) and HCO₂H (4%). No other byproducts including formaldehyde, nitromethane and carbon dioxide were detected by ¹H NMR and IR analysis. The turnover frequency (TOF) was 2.8 mol_{MTFA} mol_{NaNO2}⁻¹ h⁻¹ in this batch experiment. The performance of sodium nitrate NaNO₃ was not different from NaNO₂ in the aerobic oxidation (Figure 1a, Table S3). However, if HCl was replaced by hydrobromic acid HBr or in the absence of HTFA, O2 or light, no methyl ester was detected. In the cases of using 2.3 µmol NaNO₂ under normal pressure in the same reactor (Table S5), we also found that air was available to give MTFA in 92% selectivity and CH₃Cl, and the TOF was 2.1 mol_{MTFA} mol_{NaNO2}⁻¹ h⁻¹. If the ratio of CH₄/O₂ was up to 24:1, O₂ could be consumed almost completely in 24 hours. The yields of MTFA and CH₃Cl based on O₂ were 70.7% and 23.6% respectively. On the other hand, when the ratio of CH_4/O_2 was down to 1:5, HCO₂H as the major product and MTFA (~3:1) were formed in total 24% yield, and no methyl chlorides were

found (Figure 1b). These results shows that the formation of byproducts was related to the ratio of CH_4/O_2 , i.e., methyl chlorides were generated easily in the lack of O_2 , but HCO_2H was formed quickly in the rich of O_2 .

In the studies on enhancing the yield of MTFA, we found that in the reaction of CH₄/O₂ (2:1, 0.1MPa) 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 both the amount and ratio of NaNO₂ (as a catalytic species)/CH₄/O₂ in a reactor can affect not only the product yield and selectivity but also the reaction rate and lifetime especially in a long reaction time. For example, in the presence of 2.4 mol% NaNO₂ (23 µmol) with CH₄/O₂ (1:5, 35 mL, 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 CH₃Cl (7.3%), CH₂Cl₂ (0.2%) and HCO₂H (2%). (Table S13). In this case, both more NaNO₂ and O₂ could enhance the yield of MTFA with a high selectivity. Under the similar conditions, the feed gases containing an inert gas such as nitrogen (CH4/air O2/air N2, 1:5:19) or carbon dioxide (CH₄/O₂/CO₂, 1:5:1) could also produce MTFA in over 73% yield with over 90% selectivity. (Figure 1c, Table S13) However, other alkanes such as ethane or cyclohexane are not available in this aerobic oxidation. Over 10% ethane in methane (C₂H₆/CH₄, 1:10) would block the reaction. However, ethane in the mixed gases (C_2H_6/CH_4 , 3:7) could be converted to ethyl bromides almost completely by an aerobic bromination system (catalytic NaNO₂/HBr/solvent) under visible-light at room temperature, and methane was just lost in less than 5% at the same time. The remaining gas like pure CH₄ could undergo the aerobic oxidation smoothly to produce MTFA in 85.4% yield based on methane (Figure 1c). For the reactions under low pressure, keeping the liquid-phase out of the light was beneficial to reduce byproducts (Table S14), which means the aerobic oxidation proceeds in the gas-phase and radical reactions of products may occur in the liquid-phase.

A 4-day continuous reaction could be established for a reactor containing CH₄/O₂ (2:1, 35 mL, 0.1 MPa) with 0.24 mol% NaNO₂ (2.3 µmol) in HCl/HTFA solution. To 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 CH_4/O_2 consumed is very close to 2:1. Thus, at the end of the continuous reactions, the amount of the input gas could be equal to that of the consumed gas during the reaction. Based on the input $CH_4/O_2(2:1, 21 \text{ mL})$, 0.1 MPa), the yield of MTFA was 85% with the selectivity of 90% in the 4-day continuous reaction. It was proved that the ratio of CH_4/O_2 (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 selectivity with the TOFs close to 2.2 mol_{MTFA} $mol_{NaNO_2}^{-1}$ h⁻¹ (Figure 2a, Table S15).

However, in a 7-day continuous reaction, the external HCl (12 M) was also necessary to be added in several times with the input gas, which could effectively maintain the TOF at 2.5 $mol_{MTFA} mol_{NaNO_2}$ ⁻¹ h⁻¹ (Table S16). One of reasons is that a lot of MTFA accumulated in the solution can block the reaction, but more HCl (12 M) added will overcome this problem partially (Table S12). In this reaction, the yield of MTFA was

88.6% based on the input CH₄/O₂ (2:1, 42 mL, 0.1 MPa) or 48.3% based on all CH₄/O₂ (2:1, 77 mL, 0.1 MPa) with a concentration of MTFA of ~510 mmol L⁻¹ in the resultant solution. In other continuous experiments for 2, 3 and 4 days, both the methane conversion and the MTFA selectivity were over 90% based on the input CH₄/O₂ (2:1), and the TOFs were 2.2~2.3 mol_{MTFA} mol_{NaNO₂}⁻¹ h⁻¹ (Figure 2b, Table S17). Meanwhile, the ratio of CH₄/O₂ in the reactors was always around 2:1 as the initial state. It indicates that the aerobic oxidations of methane can proceed very well to produce methyl ester in an excellent selectivity under the stable conditions, including temperature, light, pressure, acidity, and the ratio of CH₄/O₂, et al.

Furthermore, CH₃OH was obtained in 85.2% yield by a hydrolysis of MTFA under non-optimized conditions at room temperature after 4 hours (Table S19), and HTFA could also be recovered probably to complete the two-step conversion of methane to methanol involving an aerobic oxidation and a hydrolysis under ambient conditions.

Discussion

A possible reaction mechanism is suggested based on our studies and previous reports (Scheme 2). The first step is nitrosyl chloride NOCl is released into the gas-phase from the acidic solution of catalytic NaNO2 or NaNO3 with HCl at room temperature. ³¹ Then 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). ³² In the gas-phase, CH₄ is attacked by Cl• to give methyl radical CH₃• and HCl, and CH₃• combines with O₂ to generate methyl peroxide species CH₃-OO• subsequently, which is partially confirmed by an isotopic ¹⁸O test to find CH₃¹⁸O species (Scheme S1). On the other hand, methyl chloride CH3-Cl could also be produced from the reaction of CH3• with NOCl, especially when O2 is insufficient and more NaNO2 is used (Table S5). Meanwhile, another byproduct, formic acid HCO₂H will be generated in the further reactions of CH₃-OO• species readily ^{33,34}. Fortunately, CH₃-OO• can also react with NO to give CH₃-OO-NO quickly 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 the same conditions, ^{33,35,36} which is a key step for the product selectivity. It 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 ¹H NMR analysis in the reaction as mentioned above. When CH₃ONO₂ was used instead of NaNO₂, the reaction could still proceed 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 provides not only Cl• to cleave 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 on both reactivity and selectivity. Moreover, a large amount of Cl₂ generated rather 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. Since the main reactions are carried out in the gasphase, including the breaking of CH₃-H bond and the formation of CH₃-O bond, it is unnecessary to demand good solubility of either CH₄ or O₂ in the liquid solvent. Some factors to hamper the formation of NOCl should be eliminated. For example, with the amount of MTFA increasing, the rate of transesterification of CH₃O-NO₂ with HTFA was slow down. Thus, more HCl added 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)³⁷ in the reactor, a classical radical nitrosation occurs easily at a very low O₂ concentration. ³⁸ Acetic acid or caprolactam was formed after oxime rearrangements in the liquid-phase, resulting in the loss of NO to stop the catalytic cycle.

Overall, we establish a very convenient visible-light driven aerobic oxidation of methane with HTFA to MTFA at room temperature, 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 form MTFA and NOCl effectively. This is a novel two-phase methane conversion without any special catalysts or reagents. MTFA could be obtained in a high yield (over 80%) based on CH₄ in both batch and continuous experiments. Especially, 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 CH_4/O_2 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 to be a practical and commercial process in industry after further exploration and improvement.

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

Yangquan Coal Industry (group) Co., Ltd. is gratefully acknowledged.

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Scheme 1. Aerobic oxidation of methane in this work. (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.



Figure 1. Methane conversion and MTFA selectivity in the aerobic oxidations. (a) Effect of the amount of NaNO₂. (NaNO₂ 0.23~23 µmol.) (b) Effect of the ratio of CH₄/O₂. (CH₄/O₂

1:5~24:1; ^a Conversion based on O₂.) (c) High conversion of methane to MTFA under pressured CH₄/O₂ (1:5). (Total pressure 0.4~2.0 MPa; NaNO₂ 23 μ mol; liquid in dark; 72 hours.)



Figure 2. 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

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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 μ mol.)



Scheme 2. A proposed mechanism.