



Electrothermal Conversion of Methane to Methanol at Room Temperature with Phosphotungstic Acid

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Abstract: Traditional methods for the aerobic oxidation of methane to methanol frequently require the use of noble metal catalysts or flammable H_2 - O_2 mixtures. While electrochemical methods enhance safety and may avoid the use of noble metals, these processes suffer from low yields due to limited current density and/or low selectivity. Here, we design an electrothermal process to conduct aerobic oxidation of methane to methanol at room temperature using phosphotungstic acid (PTA) as a redox mediator. When electrochemically reduced, PTA activates methane with O_2 to produce methanol selectively. The optimum productivity reaches $29.45 \mu\text{mol g}_{\text{PTA}}^{-1} \text{h}^{-1}$ with approximately 20.3 % overall electron yield. Under continuous operation, we achieved $19.90 \mu\text{mol g}_{\text{PTA}}^{-1} \text{h}^{-1}$ catalytic activity, over 74.3 % methanol selectivity, and 10 hours durability. This approach leverages reduced PTA to initiate thermal catalysis in solution phase, addressing slow methane oxidation kinetics and preventing overoxidations on electrode surfaces. The current density towards methanol production increased over 40 times compared with direct electrochemical processes. The in situ generated hydroxyl radical, from the reaction of reduced PTA and oxygen, plays an important role in the methane conversion. This study demonstrates reduced polyoxotungstate as a viable platform to integrate thermo- and electrochemical methane oxidation at ambient conditions.

Introduction

Industrial production of methanol (CH_3OH) from methane (CH_4) relies on a two-step high temperature, high pressure process via syngas (Figure S1a).^[1] In comparison, the direct one-step oxidation of CH_4 to CH_3OH is difficult because of CH_4 's stable C–H bonds and CH_3OH 's susceptibility to overoxidation.^[2] Chemical looping processes have been developed to oxidize CH_4 to CH_3OH , preventing direct contact between O_2 and CH_4 to reduce overoxidation, but these face issues like high heat requirements, coke deposition, and catalyst sintering.^[2a,3] Researchers have also reported single-step CH_4 activation using metal species like $\text{Pt}^{(\text{II})}$, $\text{Pd}^{(\text{II})}$ and $\text{Pb}^{(\text{IV})}$ in sulfuric acid/trifluoroacetic acid solvent^[4] at temperatures of 80–220 °C (Figure S1b). Irrespective of the mechanistic details, these metal species activate the C–H bond of CH_4 , followed by reductive elimination that generates CH_3OH and a lower valent metal species. This sequence requires the addition of chemical oxidants such as H_2O_2 , O_2 , $\text{K}_2\text{S}_2\text{O}_8$, or peroxytrifluoroacetic acid to reoxidize reduced metal species.^[4b] Moreover, H_2O_2 is used to oxidize CH_4 to oxygenates under mild and non-corrosive conditions at 50–180 °C (Figure S1b).^[5] To address the issue of overoxidation by excessive amount of H_2O_2 , the in situ synthesis of H_2O_2 from H_2/O_2 mixtures, catalyzed by AuPd bimetallic nanoparticles, has been integrated into CH_4 oxidation processes.^[6] Nonetheless, the cost of catalysts/oxidants and the employment of hazardous chemicals have limited the utility of those process.

Recently, electrocatalytic conversion of CH_4 has been reported, bringing advantages like mild reaction condition and innovative reaction pathway.^[7] Studies have demonstrated that CH_4 can be directly activated on the electro-

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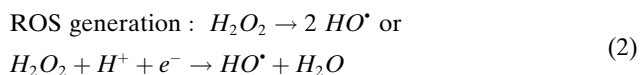
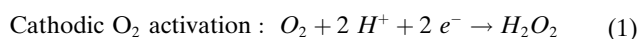
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catalyst surface such as NiO/Ni^[8] and TiO₂/RuO₂/V₂O₅,^[9] showing 13–97 % CH₃OH selectivity (Table S1). However, the electrocatalysis was highly restricted by the low electrochemical surface area and gas transport of CH₄ to the electrode surface (Figure S1c), resulting in very low current density (< 40 μA cm⁻², with effective current density for CH₃OH production less than 10 μA cm⁻²) and hard-to-avoid overoxidation by anodic potential.^[10,11] Besides generating active oxygen species from H₂O, CO₃²⁻ was also developed as an oxygen donor on the anodic electrode surface.^[12] ZrO₂, NiCo₂O₄, NiO/ZnO, Fe₂O₃ and CuO/CeO₂ were shown to produce O* from CO₃²⁻, which then facilitated the breaking of C–H bonds in CH₄. The activated CH₃* was subsequently electrochemically transformed into valuable products, including ethanol, propanol and propionic acid.^[12b–f] The isotope labeling experiment confirmed that the carbon and oxygen in these products originate from CH₄ and CO₃²⁻, respectively.^[12c–f]

The combination of electro- and thermo- catalysis has led to an indirect electrochemical CH₄ activation process.^[7a,13] As shown in Figure S1d, applying potentials upward of 1.6–2.2 V versus Hg₂SO₄/Hg produces high-valent metal cations at the anode, which react with CH₄ and H₂SO₄ to produce methyl bisulfate. This method eliminates the use of hazardous oxidants and is more controllable.^[4d,14] Similarly, electrochemical processes have been tested with trifluoroacetic acid solvent, Pd^(IV) trifluoroacetate oxidant, and potassium trifluoroacetate electrolyte. While versatile for various gaseous alkanes, its Faradaic efficiency (FE) for CH₄ was just about 2 %.^[15]

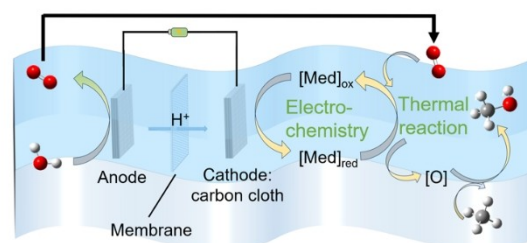
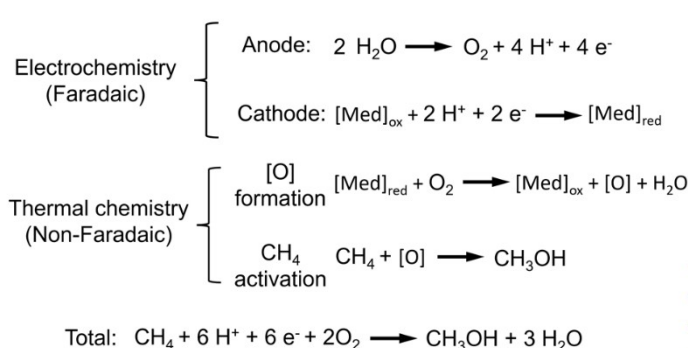
Furthermore, cathodic aerobic activation employing in situ generated H₂O₂ from a two-electron oxygen reduction reaction was introduced. Due to the low solubility of CH₄ in water and the low selectivity of reactive oxygen species (ROS, as detailed in Eq. 1–3), the total electron yield towards organooxygen compounds rarely surpassed 12 %. The primary oxygenates' selectivity, including CH₃OH and CH₃OOH, remained under 20 % for cathodic methane conversion.^[16] Electrochemical imitation of CH₄ monooxygenase (MMO) process^[17] was also developed using solution phase with iron-tungsten oxide as electrolyte, from which light hydrocarbons were aerobically oxidized to various

oxygenates in electrolyte near the cathode following an inner sphere electron transfer mechanism.^[18] Nonetheless, the oxidation of CH₄ was sluggish with a FE of around 0.7 % and no CH₃OH or CH₃OOH was detected in the final products. In light of these earlier findings, developing a strategy for the direct and selective generation of CH₃OH from CH₄ without using corrosive acid, H₂ and noble metals is highly demanded.^[18b]



Polyoxometalates (POMs), such as phosphomolybdic (PMA) and phosphotungstic acid (PTA), have been utilized as catalysts in various reactions due to their acidity and redox properties.^[19] CH₄ can be activated by POM-based catalysts in conjunction with noble metals.^[20] For instance, Pd supported on PMA offered considerable activity for CH₄ to CH₃OH in the presence of a H₂-O₂ mixture.^[21] A disadvantage of the work, however, is the use of noble metal Pd and the requirements of H₂ as co-feed. Built upon our earlier work on the facile electron transfer between electrode and POMs,^[22]

here, we intend to design an electrothermal process (Scheme 1) to convert CH₄ into primary oxygenates (CH₃OH and CH₃OOH, or combined as CH₃O_xH with *x* = 1,2) at room temperature under aerobic conditions without the use of noble metals and H₂. Since CH₃OOH can be converted to CH₃OH easily (see details in Conversion of CH₃OOH to CH₃OH in Supporting Information, Figure S2), we considered CH₃OOH as a(an) variant/intermediate of CH₃OH. Specifically, we employ the cathodic potential to reduce the POMs. Then O₂ and subsequently CH₄ was activated by reduced POM to CH₃O_xH with up to 100 % selectivity and 20.3 % electron yield (EY, refer to Supporting Information for definitions). PTA was chosen as a model compound for study due to its redox reversibility and its stability.



- Room temperature
- Noble metal & H₂ & highly corrosive acid free system
- High CH₃OH productivity and selectivity
- Mild applied potential (avoid overreaction)

Scheme 1. Proposed strategy for electrothermal CH₄ activation to CH₃OH via several redox cycles.

Results and Discussion

The electrochemical properties of PTA were investigated by a cyclic voltammetry (CV) curve as shown in Figure S3a, with the half wave potential ($E_{1/2}$) of first and second electron transfer occurring at -33.5 and -310 mV versus Ag/AgCl (approximately 268.5 and -8 mV versus RHE, the pH ~ 1.84 for 5 mM PTA solution (Figure S4)), respectively, consistent with previous reports.^[23] The subsequent reduction of PTA, while in principle possible (green rectangular marker in Figure S3a), is limited by the electrochemical stability of water and convoluted by concomitant hydrogen evolution even on relatively poor HER catalysts like carbon^[24] and was thus not further considered in our study. One-/two-electron reduced PTA (PTA_{1e} and PTA_{2e}) was readily obtained from chronoamperometry at constant negative potential within 15 min under inert atmosphere in a divided electrochemical cell (Figures 1a and S3b–d) using a carbon cloth electrode. Hydrogen evolution was suppressed and the color of the electrolyte changed from colorless to dark blue due to the formation of reduced PTA – so called “heteropoly blues” (Figure S3d).^[25] The efficiency of electro-reduction was analyzed by the total number of electrons

transferred into PTA molecules via X-ray photoelectron spectroscopy (XPS) (Figure 1b). The XPS samples were obtained from freeze dryer, stored in glove box, and transferred into XPS instrument using a vacuum transfer module (see details in Characterization). A new symmetric pair of peaks located at 37.0 and 34.9 eV appeared for the PTA_{red} sample corresponding to $W^{(V)} 4f_{5/2}$ and $W^{(V)} 4f_{7/2}$, respectively.^[26] The $W^{(V)}$ proportions for PTA_{1e} and PTA_{2e} were 9.0% and 17.7% , aligning with estimates for one and two electron-reduction scenarios, respectively. We did not observe the formation of $W^{(IV)}$ species, suggesting the composition of PTA is $[PW^{(VI)}_{10}W^{(V)}_2O_{40}]^{5-}$ in the two-electron reduced state. The structure of PTA remained intact after reduction, inferred from the virtually identical X-ray diffraction (XRD) patterns and Fourier transform infrared (FTIR) spectra (Figures S5a, S5b). Concurrently, the most abundant mass-to-charge ratio (m/z) of PTA_{red} locates at 1439.1 , 1439.6 and 1440.1 , respectively, for original PTA (PTA_{ox}), PTA_{1e} and PTA_{2e} (the additional charges are countered by protons from solution (Figure S4)), as revealed by electrospray ionization mass spectrometry (ESI-MS, Figure 1c). These confirmed the facile electrochemical

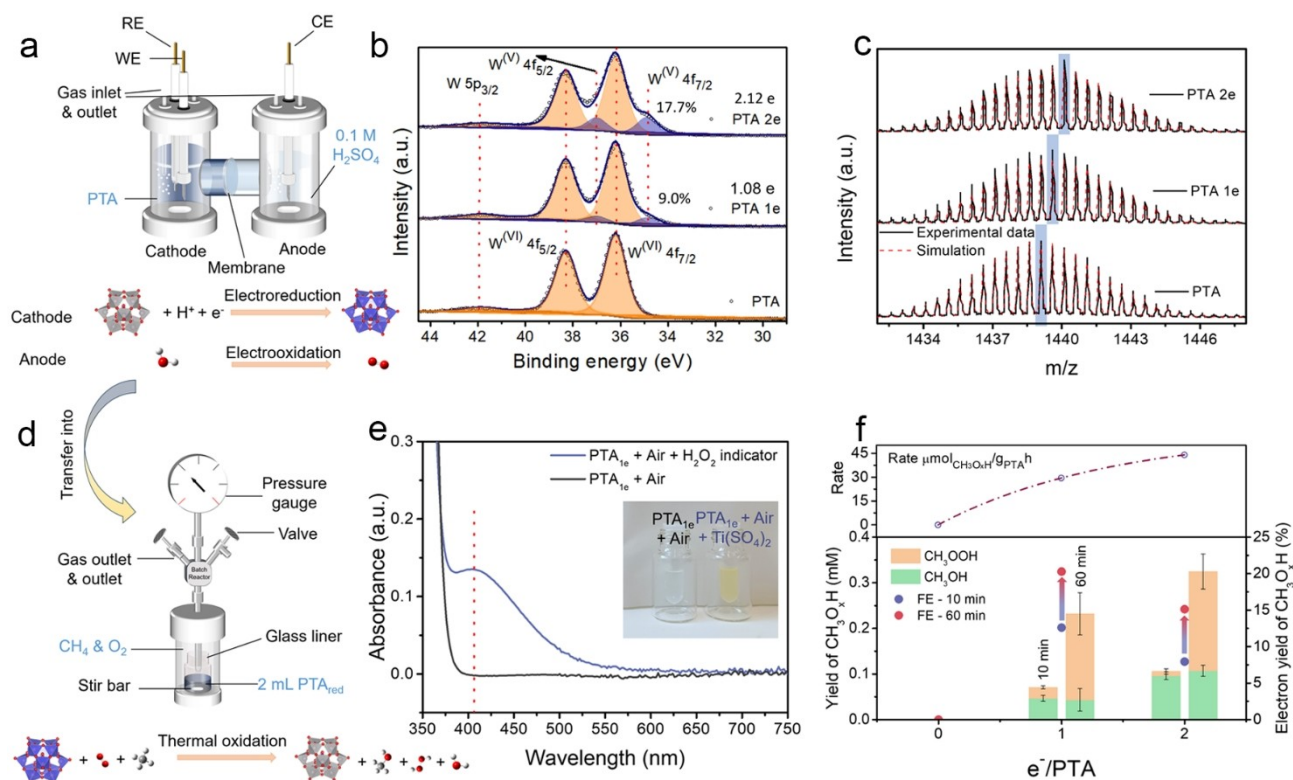


Figure 1. Electrochemically reduced phosphotungstic acid (PTA_{red}) and its reaction with air and CH₄. a, d) The illustration of electroreduction process and thermal reaction procedure. RE, CE and WE represent reference, counter and working electrode, respectively. b, c) X-ray photoelectron spectroscopy (XPS) and electrospray ionization mass spectrometry (ESI-MS) of original PTA, one-/two- electron reduced PTA (PTA_{1e} and PTA_{2e}), respectively. e) ultraviolet-visible spectrum (UV/Vis) of solution (after reoxidation) with titanium (IV) sulfate (H₂O₂ indicator), and f) the reaction performance of original 5 mM PTA, PTA_{1e} and PTA_{2e} under 60 bar of CH₄ and 1 bar of air. Typically, 2 mL of a 5 mM PTA_{red} solution was stored in a batch reactor (33 mL gas volume, as illustrated in d), stirred at 800 rpm at room temperature for reaction time of 10 and 60 min. The average values reported here are repeated three times. EY represents electron yield.

reduction of PTA on carbon electrodes and the structural stability of reduced PTA in aqueous solutions.

Following electroreduction, 2 mL of the deep blue PTA solution was moved to a batch reactor with a stirrer and subjected to 60 bar of CH_4 and 1 bar of air (Figure 1d). After reaction, the liquid phase was analyzed by ultraviolet-visible spectroscopy (UV/Vis) (Figures 1e, S6 and S7) and ^1H nuclear magnetic resonance (NMR) spectroscopy (typical ^1H NMR spectra are shown in Figures S8–S10, using CH_3CN as the interior standard and calibration curves are shown in Figure S11), while the gas phase was characterized by gas chromatograph (GC) coupled to a methanizer and a flame ionization detector (see details in Characterization). Importantly, we observed the formation of CH_3OH and CH_3OOH , demonstrating the feasibility of aerobic CH_4 oxidation by PTA_{red} (Figure 1f). Reaction rates of $\text{PTA}_{1\text{e}}$ and $\text{PTA}_{2\text{e}}$ system, determined by the yield after 10 min of reaction (broadly in line with the average values, as outline in Supplementary Note I and Figure S12), were 29.5 and 44.0 $\mu\text{mol}_{\text{CH}_3\text{OxH}}\text{g}_{\text{PTA}}^{-1}\text{h}^{-1}$, respectively, comparable to other catalytic systems in previous reports (Table S1). The electron yield towards CH_3OxH in the one-electron reduced PTA system was relatively high, at 12.61 % initially and 20.27 % towards the end. In contrast, a 30–40 % drop was noted under the $\text{PTA}_{2\text{e}}$ condition which is due to the $\text{PTA}_{2\text{e}}$ promoted the overreduction of O_2 to H_2O . Reasons such as the higher reducing ability (Figures S13a, S13b), the pH effect (Figures S4 and S13c) and reaction kinetics may account for the observed overreduction by $\text{PTA}_{2\text{e}}$ (details can be found in supplementary Note II). Thus, maintaining the 1e reduction state of PTA during electroreduction is preferable. No carbon-based products were detected using non-reduced PTA (PTA_{ox}), highlighting the importance of PTA's reduction state for methane oxidation.

After the reaction, the solution changed back to colorless suggesting reoxidation of PTA (Figure 1e). Meanwhile, the structure simultaneously reverted to PTA_{ox} (Figure S5c). However, reacting with CH_4 alone does not lead to color change. Adding titanium (IV) sulfate to the PTA_{red} solution in the presence of air, the color changed to yellow. These suggest that electrons were transferred from PTA_{red} to oxygen resulting in the formation of H_2O_2 (as shown in Table S1) and H_2O ,^[27] following an outer-sphere mechanism which has been demonstrated by stopped-flow techniques and Marcus theory.^[28]

Rates of reoxidation of PTA_{red} in the presence of O_2 were determined by UV/Vis spectroscopy. The intensity decrease of the peaks at 750 and 495 nm—attributed to metal-to-metal intervalence charge transfer (IVCT) and d-d transition band, respectively (Figure S14),^[29]—were measured over time at different O_2 partial pressures. We observed a pseudo first order relationship between PTA_{red} reoxidation and the concentrations of PTA and O_2 (Figures S15 and S16). The CH_3OxH generation rates increased 4.2 folds when O_2 partial pressure increased from 50 mbar to 1 bar, peaking at 72.5 $\mu\text{mol}_{\text{CH}_3\text{OxH}}\text{g}_{\text{PTA}}^{-1}\text{h}^{-1}$ at 1 bar O_2 . No other carbon-containing products were detected at O_2 pressures below 0.2 bar. However, formaldehyde (HCHO), an over-oxidation product, appeared after 30 min reaction at 1 bar

O_2 (Figure S17). Despite this, the final yields of CH_3OxH (approximately 0.25 mM) and H_2O_2 (approximately 0.7 mM) remained unchanged (Figures 2a and b). On the other hand, the product selectivity changed from H_2O_2 to CH_3OxH when reaction progresses. More specifically, the electron yield of CH_3OxH and FE of H_2O_2 changed from 14.3 % and 39.8 % to 21.7 % and 26.4 % for initial and final reaction stage, respectively, suggesting that H_2O_2 generation and CH_4 activation may be consecutive steps. The concentration of PTA_{red} influenced the electron transfer rate from PTA_{red} to O_2 , affecting the FE of H_2O_2 (from 34.3 % to 4.9 %), but having little effect on the electron yield of CH_3OxH (approximately 20 %, Figures 2c and d). As a consequence, the reaction kinetics towards CH_3OxH production normalized by the amount of PTA remained unchanged during the reaction. These results indicated the existence of competitive reactions like H_2O_2 decomposition, corresponding to the observation of a slight acceleration of the oxidation rate of PTA_{red} at higher concentrations (Figure S18b, and magenta and orange fitting curves in Figure S16c). Over a

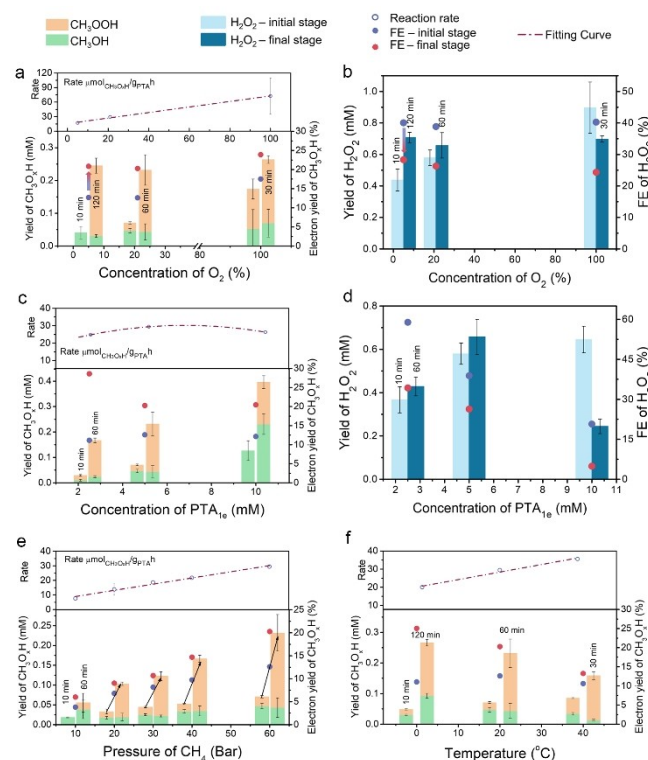


Figure 2. CH_4 activation by reduced PTA (PTA_{red}) and air in batch reactor. The influence of a, b) concentration of O_2 , c, d) PTA_{red} , e) pressure of CH_4 and f) temperature on the reaction kinetics, yield and selectivity towards methyl derivatives (CH_3OxH) and H_2O_2 for the initial (10 min) and final reaction stage (typically 60 min, but 120 min and 30 min for 50 mbar and 1 bar O_2 or 0°C and 40°C experiment, respectively). The typical reaction conditions were 60 bar of CH_4 , 1 bar of air, and 2 mL of a 5 mM $\text{PTA}_{1\text{e}}$ solution in a batch reactor (33 mL), stirred at 800 rpm at room temperature for reaction time of 10 and 60 min. All reported data collected from at least three independent trials, and the average values are reported here. EY represents electron yield, analogous to Faradaic efficiency (FE) in the context of faradaic processes (H_2O_2 production).

wide range of 10–60 bar CH_4 pressures, the reaction followed a pseudo-first-order kinetics (Figure 2e). This is consistent with previous reports ascribing this trend to CH_4 activation being a rate-determining step.^[14b] The rate of electron transfer from PTA_{red} and the yield of H_2O_2 remained largely invariant with CH_4 pressure (Figures S18c and S18d), demonstrating that CH_4 does not affect dioxygen activation.

When reaction temperature increased, the $\text{CH}_3\text{O}_x\text{H}$ production rate (calculated from 10 min reaction, Figure 2f), electron transfer rate (Figure S18e) and H_2O_2 productivity

(Figure S18f) increased at the expense of $\text{CH}_3\text{O}_x\text{H}$ selectivity (as observed at the end of the reaction). This could be explained by lower CH_4 solubility or the acceleration of 2-electron O_2 reduction accompanied by lower ROS generation efficiency at higher temperatures. As such, electron yields increased to around 25 % when the reaction was conducted at 0°C . Notably, the ratio between CH_3OH and CH_3OOH increased with higher concentration of PTA_{red} but decreased with temperature, a fact that will be discussed in more detail in a later section. No significant oxidation of CH_3OH was observed in this two-step reaction process (Figure S19), which may be attributed to the lower concentration of CH_3OH and the protective effect of PTA_{red} .

We propose that the partial oxidation of CH_4 by PTA_{red} and O_2 follows a three-step process, including oxygen activation, ROS production, and CH_4 activation. We first investigated the oxygen source for the reaction by isotope labelling experiments using $^{18}\text{O}_2$ and H_2^{18}O (Figure 3a). Two major peaks at $m/z=31$ and $m/z=29$ representative $[\text{CH}_3^{16}\text{O}]^+$ and $[\text{CH}^{16}\text{O}]^+$ (the fragments of $\text{CH}_3^{16}\text{OH}$ and HCH^{16}O , the overoxidation product under prolonged operation, Figure 5d), were formed in the presence of $^{16}\text{O}_2$, regardless of whether H_2^{16}O or H_2^{18}O was used. In contrast, the two peaks shift to $m/z=33$ and $m/z=31$, respectively,

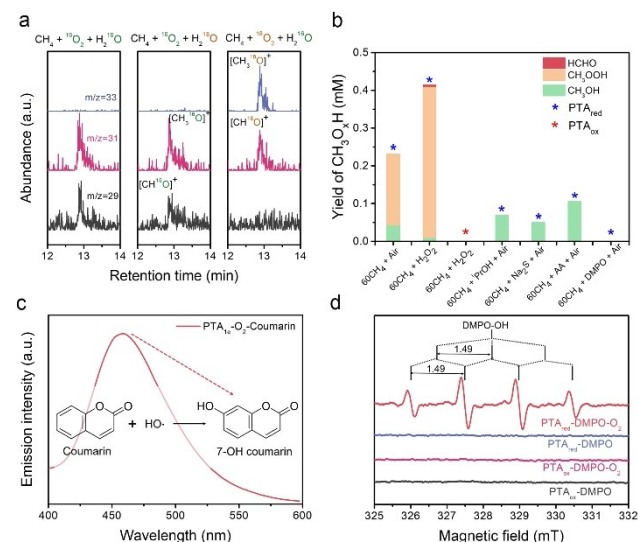


Figure 3. Mechanism understanding of CH_4 partial oxidation by PTA_{red} and air. Control experiments under a) different isotope-labelled reactants, b) different reaction conditions. c) Fluorescence spectra of coumarin with PTA_{red} and air, d) electron paramagnetic resonance (EPR) spectra of PTA_{ox} (black), PTA_{red} (blue), $\text{PTA}_{\text{ox}}/\text{air}$ (pink) and $\text{PTA}_{\text{red}}/\text{air}$ (red) system.

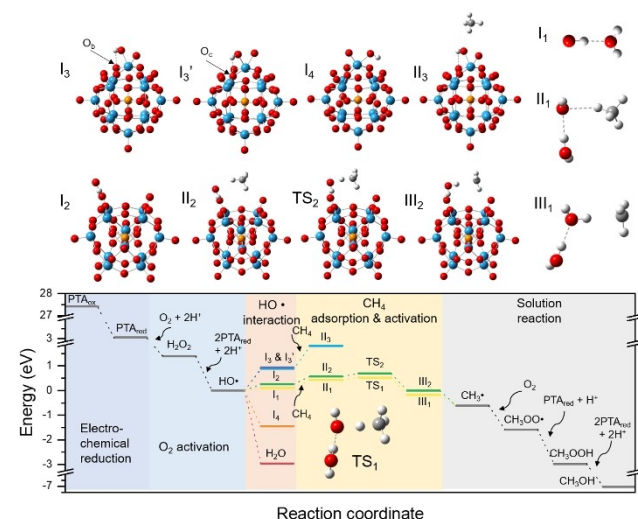


Figure 4. Illustration of structure intermediates and related energy profile.

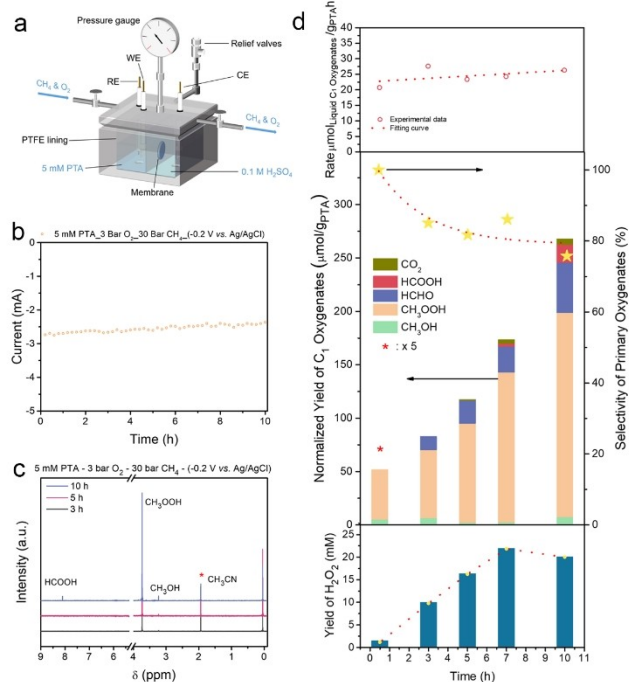


Figure 5. Continuous operation of electrothermal process for CH_4 partial oxidation. a) Scheme illustration of high-pressure H-type electrolytic cell, b) durability test of the electrothermal process under 30 bar CH_4 , 3 bar O_2 at -0.2 V versus Ag/AgCl , c) the ^1H nuclear magnetic resonance (NMR) spectrum with distinct reaction time and d) electrothermal kinetics and products analysis. The typical reaction conditions were 30 bar of CH_4 , 3 bar of O_2 , and 10 mL of a 5 mM PTA_{ox} electrolyte (cathodic compartment) in a high-pressure electrochemical cell ($\sim 100\text{ mL}$), stirred at 1200 rpm under room temperature with a potential of -0.2 V versus Ag/AgCl .

when using $^{18}\text{O}_2$, indicating the formation of ^{18}O -labelled methanol ($\text{CH}_3^{18}\text{OH}$) and formaldehyde (HCH^{18}O), proving that oxygen in organic compound comes exclusively from O_2 . Then, experiments using H_2O_2 rather than O_2 as terminal oxidant were conducted with PTA_{red} or PTA_{ox} . While catalytic performance comparable to that in the presence of O_2 was observed for PTA_{red} , PTA_{ox} still did not yield any $\text{CH}_3\text{O}_x\text{H}$ products in the presence of H_2O_2 (Figure 3b). This sharp contrast demonstrates the significance of employing reduced PTA even beyond the formation of H_2O_2 from O_2 .

To uncover the active species, a fluorescein-based probe molecule like coumarin was employed to detect the potential $\text{HO}^\bullet$ in the solution. A peak located at 455 nm was observed after the reaction with electrolyte containing PTA_{red} and O_2 , indicating the formation of 7-OH coumarin (Figure 3c).^[30] Concurrently, the electron paramagnetic resonance (EPR) experiments using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) radical trapping agent were implemented. In contrast to the EPR-silent PTA_{ox} system and our previous Mo-based polyoxometalate catalyst, the appearance of characteristic quadruple peaks (1:2:2:1) for trapped $\text{HO}^\bullet$ radicals in $\text{PTA}_{\text{red}}/\text{O}_2$ system clearly indicated the production of such species during the reaction (Figure 3d).^[31] To mitigate the interference from superoxide anions/hydroperoxyl radicals ($\text{O}_2^{\bullet-}/\text{HOO}^\bullet$) in $\text{HO}^\bullet$ detection, dimethyl sulfoxide (DMSO)^[32] was introduced during the EPR testing (refer to Supplementary Note III for details). The absence of DMPO signals (Figure S20) confirms the production of $\text{HO}^\bullet$ in $\text{PTA}_{\text{red}}/\text{O}_2$ system. While $\text{O}_2^{\bullet-}/\text{HOO}^\bullet$ radicals^[28] are significant intermediates in O_2 reduction, they are not readily detectable due to kinetic limitations (Supplementary Note III). Thus, the focus remains on the role of $\text{HO}^\bullet$ radicals in the reaction. Subsequently, experiments of CH_4 oxidation were conducted in the presence of $\text{HO}^\bullet$ radical scavengers, such as iso-propanol ($^i\text{PrOH}$), sodium sulfide (Na_2S), ascorbic acid (AA) and DMPO. The yield of CH_3OOH dropped in the presence of all four inhibitors (Figure 3b), strengthening the active role of $\text{HO}^\bullet$ in CH_4 activation.^[16,33] The formation of CH_3OH , however, remained constant in the presence of Na_2S or even increased for $^i\text{PrOH}$ and AA, respectively (Figure 3b). The increase in CH_3OH could be related to changes in the lifetime of PTA_{red} (Figure S21) analogous to what we found for catalysis with PMA.^[21] The generated PTA_{red} promoted the formation of $\text{HO}^\bullet$ radicals in solution, counteracting the consumption effects of the sacrificial reaction. Additionally, the increased or maintained PTA_{red} concentration facilitated the conversion of CH_3OOH to CH_3OH (Figure S2), aligning with the observed effects of PTA_{red} as well as temperature on reaction performance. Notably, the use of DMPO as a scavenger completely suppressed the oxidation of CH_4 , highlighting the significant role of $\text{HO}^\bullet$ in this process.^[20a] The possibility of reactions occurring on the surface of PTA was also considered. Since electron transfer between $\text{O}_2/\text{H}_2\text{O}_2$ and PTA_{red} occurs through an outer-sphere mechanism,^[28,34] and no reaction was observed in the $\text{O}_2/\text{H}_2\text{O}_2$ and PTA_{ox} system, we explored the potential for CH_4

activation via the formation of W–O bonds between $\text{HO}^\bullet$ and $\text{PTA}_{\text{ox}}/\text{PTA}_{\text{red}}$.

As shown in Figure 4, PTA_{red} is electrochemically produced from PTA_{ox} , with an absolute Gibbs free energy change (ΔG) of -4.059 eV (192.2 mV versus RHE, Supplementary Note IV), consistent with the results shown in Figure S3a. PTA_{red} then acts as the active species, facilitating the generation of $\text{HO}^\bullet$ through a 3-electron O_2 reduction reaction. Three interaction scenarios involving $\text{HO}^\bullet$ radicals are explored: 1) hydrogen bonding with H_2O or PTA_{ox} (Structures I_1 and I_2 , respectively); 2) W–O bonding with PTA_{ox} (Structures I_3 and I_3') or PTA_{red} (Structure I_4); and 3) electron transfer from PTA_{red} , leading to overreduction and the formation of H_2O .

The formation of Structures I_3 and I_3' results in increases in enthalpy (ΔH , Figure S22) and ΔG (Figure 4) of $0.47/0.52$ eV and $0.85/0.90$ eV, respectively, indicating that W–O bond formation between $\text{HO}^\bullet$ radicals and PTA_{ox} is energetically unfavorable. While W–O bond formation with PTA_{red} is energetically possible, it is less advantageous compared to the overreduction process. Additionally, formation of Structure I_4 causes a change in spin multiplicity (from doublet to singlet), complicating subsequent C–H activation. Consequently, capturing free radicals through structural changes in the $\text{PTA}_{\text{ox/red}}$ cluster is considered less effective. Therefore, we believe that the reaction predominantly proceeds via the solution pathway.

$\text{HO}^\bullet$ has been reported to be active in the solution phase abstraction of H atoms from CH_4 to form $\text{CH}_3^\bullet$ (positive order in CH_4).^[35] Two viable scenarios involving hydrogen bonding between radicals and H_2O ^[36] or PTA_{ox} are proposed. The relatively small free energy barriers (0.53 eV for TS_1 and 0.69 eV for TS_2) indicate that the H abstraction reaction is feasible at room temperature.^[37] Methyl radicals ($\text{CH}_3^\bullet$) produced in the reaction rapidly combines with dissolved O_2 to form CH_3OOH .^[6b,38] CH_3OOH then reacts with PTA_{red} and protons in the solution to produce CH_3OH . Direct termination of $\text{CH}_3^\bullet$ by $\text{HOO}^\bullet$ or $\text{HO}^\bullet$ is also considered, but due to the high reactivity and low concentration of radicals, such collisions are highly unlikely (Figures S23–S25, Supplementary Note IV), rendering these pathways kinetically infeasible. Nevertheless, increasing the pressure of CH_4 , as well as the concentrations of $\text{HO}^\bullet$ and PTA_{red} , will enhance the production of CH_3OH .

Our discovery that mildly reduced PTA can convert CH_4 to methanol at room temperature in an aerobic environment led us to develop an electrothermal process that combines PTA electroreduction with CH_4 thermal oxidation. Due to the low solubility of CH_4 in aqueous electrolytes, we employed a commercially available high-pressure electrochemical cell with compartments separated by a proton exchange membrane (Nafion-117) (Figure 4a). A carbon cloth or glassy carbon was used as working electrode (see details in Supporting Information) and experiments were run on potentiostatically. Parameters such as O_2 pressure, PTA concentration and applied potential were optimized using this electrochemical cell (Figures S26–29). The products were analyzed by UV/Vis, NMR and GC after a certain amount of charge was passed between the two electrodes

(consistent with the amount of achieving PTA_{1e} state). No H₂ was detected in any experiment. The system's reaction kinetics and PTA's reduction degree were revealed by the current value and open circuit potential (OCP, see details in Supporting Information, Figure S30), respectively.

The relatively stable currents for various O₂ pressures (except for 1 bar) and PTA concentrations (2.5–10 mM) at –0.2 V versus Ag/AgCl (approximately 0.1 V versus RHE) suggested the establishment of a rapid reaction equilibrium between electroreduction of PTA and thermal oxidation of PTA_{red} by O₂ (Figures S26a and S27a). The decay of current value for 1 bar O₂ condition indicated the reaction kinetics was partially restricted by the reoxidation rate of PTA_{red}, consistent with a higher reduction degree (around 0.85, Figure S30b) at the reaction equilibrium state. However, the relatively close current values (Figure S26a) for distinct O₂ pressures implied that O₂ was saturated inside the reactor when the pressure was higher than 1 bar. As the O₂ pressure increased, the yield of H₂O₂ rose dramatically, while the selectivity for CH₃O_xH first increased and then decreased (due to transformation to HCHO, Figures S26b–S26c). This observation demonstrates that while increased O₂ pressure promotes the formation of H₂O₂, it also accelerates the overoxidation of CH₃O_xH. The differing effect of O₂ pressure in high-pressure electrochemical cell versus batch reactor may stem from diffusion limitations, with the smaller batch reactor exhibiting more pronounced localized pressure effects due to its higher diffusion rates. The highest electron yield was achieved at ~12.5 % with a reaction rate of 21.20 $\mu\text{mol}_{\text{CH}_3\text{O}_x\text{H}}\text{g}_{\text{PTA}}^{-1}\text{h}^{-1}$ at 3 bar O₂ (Figures S26c, d). In contrast, the changes in current values for different PTA concentrations (Figure S27a) may be related to a higher concentration of PTA species near the electrode surface and O₂, enhancing the electron shuttle effect between the electrode and the reactant (O₂). Meanwhile, relatively linear relationships between the current value and PTA concentration were observed, supporting our previously detected first-order kinetics. The concentration of PTA had little effect on the selectivity and reaction rate of CH₃O_xH but it did reduce the selectivity of H₂O₂ (Figures S27b–d), aligning with the findings for the non-continuous process.

We also studied the effect of applied potential (Figures S28–S29). The current value increased with the negative potential indicating that the oxygen activation was limited by the rate of electron transfer from the electrode to PTA_{ox}. Compared with the one-electron reduced experiment, a one-hour experiment with different charge transfer number at various applied potentials (Figure S29) showed an increase in CH₃O_xH generation rate (Figures S28d and S29d) which could be related to a faster accumulation of ROS with reaction duration, suggesting a certain amount of ROS should be maintained to promote the activation of CH₄, despite a high chance of overoxidation (Figure S34). The highest reaction rate reached 10.71 $\mu\text{mol}_{\text{CH}_3\text{O}_x\text{H}}\text{h}^{-1}$, equivalent to 572.9 $\mu\text{A cm}^{-2}$ (1.0 cm² electrode geometry), almost 40-fold current density enhancement compared to direct electrochemical processes (Table S1). Surprisingly, the electron yield was increased dramatically to 36.6 % at 0 V versus Ag/AgCl, consistent with the observation in

separated process that milder reduction degree is more selective to oxidized methane species (Figure S30e) although the reaction kinetics was limited.

Next, –0.2 V (versus Ag/AgCl) was employed to test the system durability. The electrothermal CH₄ partial oxidation system was operated continuously for more than 10 h without obvious deactivation (Figure 4b). The main organic product was CH₃OOH under the optimum working condition (Figure 4c) and the generation rate of primary oxygenates (CH₃O_xH) was as high as 19.90 $\mu\text{mol}_{\text{CH}_3\text{O}_x\text{H}}\text{g}_{\text{PTA}}^{-1}\text{h}^{-1}$ with 12.3 % electron yield and over 74.3 % selectivity (Figure 4d). Overoxidation products, HCHO and HCOOH, were detected after 1 h (Figure S31) and 7 h reaction, respectively. The concentration of H₂O₂ accumulated to around 20 mM after 10 h reaction which could potentially be utilized by design of new redox cycle like Fe²⁺/Fe³⁺ (Figure S32). However, the direct addition of 50 μM of Fe²⁺, Cu²⁺, or Mn²⁺ to the solution resulted in a change of selectivity (Figures S32 and S33). Thus, a more designable strategy should be developed to maintain the selectivity and increase the reaction rate. Compared with pure H₂SO₄ electrolyte system which mainly generates H₂O₂ from traditional 2e-ORR process through carbon electrode, the current and yield of C₁ oxygenates of PTA electrolyte system has a dramatic increase (Figure S34). Thus, high electron yield, selectivity towards primary oxygenates and acceptable durability for CH₄ partial oxidation under mild reaction condition were successfully achieved without using noble metals and highly corrosive acids. The applied potential limits both CH₃OH electrooxidation and HER, as the electrode of carbon cloth is rather inert in the CH₃OH electrooxidation and H₂ evolution compared with noble-metal based electrocatalysts, as shown in Figure S35.

This electrothermal catalysis process exhibits notable scalability advantages over thermal, electrochemical and photocatalytic processes (Supplementary Note V and Table S3). The reaction rate can be enhanced up to 10 times by adjusting PTA concentration, O₂ pressure and applied potential (Figure S36), though this may come at the cost of selectivity. Operating under mild conditions, this method reduces hazards associated with corrosive strong acid, and avoids the use of expensive or toxic materials (e.g., H₂O₂, transition metal cations). It also integrates well with renewable energy sources, offering both flexibility and sustainability. Additionally, this method is compatible with existing industrial electrolyzer infrastructure, facilitating a smoother transition to full-scale production. Nonetheless, challenges such as product separation, low conversion, and overoxidation (Figure S37) need to be addressed before large-scale implementation.

Conclusion

In summary, we report an electrothermal process for the aerobic oxidation of methane to methanol by reduced phosphotungstic acid at room temperature. Under the optimum conditions the system possesses a primary oxygenates productivity of 29.45 or 19.90 $\mu\text{mol}_{\text{CH}_3\text{O}_x\text{H}}\text{g}_{\text{PTA}}^{-1}\text{h}^{-1}$,

electron yields of 20.3 % and 12.3 % and almost 100 % and 74.3 % selectivity for separate and continuous operation, respectively. The applied potential does not coincide with other reaction potentials such as methanol electrooxidation and hydrogen evolution, minimizing the notorious over-reaction in methane conversion. The electrochemical and thermochemical reaction steps occur separately and are coupled through PTA as redox mediator. This setup allows for the conversion of intermittent renewable energy with readily obtainable oxidants like air or pure oxygen. In addition, the system is free from the utilization of noble metals, hazardous combustible reaction mixtures and corrosive acids, and operates at ambient temperature. From a mechanistic perspective, the selective oxidation of CH₄ is mainly promoted by the intermediate hydroxyl radicals produced via the reaction between reduced polyoxotungstate and oxygen. Those findings speak broadly to the utility of POMs to unify electrochemical and thermochemical catalysis and perhaps even photocatalysis.^[20a,b]

Supporting Information

The Supporting Information is available free of charge on the website.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Methane Partial Oxidation • Electrocatalysis • Polyoxometalates • Phosphotungstic Acid

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