Electrochemical Reoxidation Enables Continuous Methane-to-Methanol Catalysis with Aqueous Pt Salts

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ABSTRACT: The direct conversion of methane to methanol would enable better utilization of abundant natural gas resources. In the presence of stoichiometric PtIV oxidants, PtII ions are capable of catalyzing this reaction in aqueous solutions at modest temperatures. Practical implementation of this chemistry requires a viable strategy for replacing or regenerating the expensive PtIV oxidant. Herein, we establish an electrochemical strategy for continuous regeneration of the PtIV oxidant to furnish overall electrochemical methane oxidation. We show that Cl-adsorbed Pt electrodes catalyze facile oxidation of PtII to PtIV at low overpotential without concomitant methanol oxidation. Exploiting this facile electrochemistry, we maintain the PtII/IV ratio during PtII-catalyzed methane oxidation via in situ monitoring of the solution potential coupled with dynamic modulation of the electric current. This approach leads to sustained methane oxidation catalysis with 70% selectivity for methanol.

INTRODUCTION

Methane is an abundant hydrocarbon resource that is often underutilized because of its low boiling point and chemical inertness. Thus, technologies for converting methane to high-demand liquid chemicals such as methanol would enable better utilization of this low-carbon resource.1–3 Current methane valorization technologies rely on an indirect process involving initial steam reforming to H2 and CO. The reforming step requires capital-intensive facilities that are not amenable to remote deployment.4 Consequently, spontaneously released natural gas at oil wells is being flared at massive scales.5,6 The development of mild, direct methane-to-methanol processes (eq 1) that can operate portably is expected to stem flaring as well as expand the versatility of natural gas.7,8

\[
\text{CH}_4 + 0.5 \text{O}_2 \rightarrow \text{CH}_3\text{OH} \quad (1)
\]

While many homogeneous and heterogeneous systems have been investigated for methane-to-methanol conversion,1,8 simple PtII chloride salts in water, PtII\text{Cl}(\text{H}_2\text{O})_{(2\text{-}x)} \text{Cl}^{-x} (denoted collectively as PtII), offer unique advantages. The catalytic cycle (Scheme 1) is initiated by PtII ions, which carry out reversible C–H activation of CH4 to yield a PtII–CH3 intermediate. This intermediate is then oxidized by PtIV\text{Cl}(\text{H}_2\text{O})_{(6\text{-}x)} \text{Cl}^{(4\text{-}x)} (denoted collectively as PtIV) to generate a PtIV–CH3 species that undergoes rapid reductive elimination to produce CH3OH or CH3Cl, which can be hydrolyzed to CH3OH. This system has the following advantages: First, the organometallic activation of methane offers superior selectivity for mono-oxidation compared to catalysts that operate via radical intermediates.9,10–12 Second, while most homogeneous catalysts that do organometallic activation require impractical8,13 concentrated acid media for boosting the catalytic rate and selectivity14,15 PtII operates in dilute aqueous acids. Along with the relatively low reaction temperature (>100 °C), these advantages position PtII chloride salts, often referred to as “Shilov’s catalyst,” as privileged agents for methane-to-methanol conversion under mild conditions.

The key to developing an alternative oxidation strategy for this catalytic system is to...
achieve precise control over the driving force (thermodynamics) and/or rate (kinetics) of the oxidation reaction. In view of the catalytic cycle, there are two distinct approaches to the problem. First, PtIV may be directly replaced by an alternative oxidant that can oxidize the PtIV-CH3 intermediate (Scheme 1, Strategy A). Success of this strategy requires an oxidant that (i) rapidly oxidizes the fleeting PtIII-CH3 intermediate before it can undergo protonation back to PtII + CH4 and (ii) possesses a low enough redox potential to avoid oxidizing the PtIII catalyst to PtIV, which is unreactive toward CH4. The conflicting requirement for fast rates and low driving force places an inherent constraint on the oxidants that are viable. Second, one may employ PtIV itself, which is an efficient oxidant for PtIII-CH4, as a redox mediator for the overall reaction (Scheme 1, Strategy B). Success of this strategy hinges on carefully matching the rate of PtIV regeneration by PtII oxidation to the rate of PtIV consumption by methane functionalization. Rapid PtIV oxidation will progressively deplete the pool of PtII, retarding catalysis, whereas slow oxidation will deplete PtIV and induce irreversible decomposition of the PtIII to metallic Pt0 via, inter alia, disproportionation of PtII.\(^9,16\) Thus, a viable alternate oxidant must achieve good control over the oxidation driving force and/or rate.

The inherent difficulty of fine-tuning oxidation using chemical reagents has, presumably, contributed to the limited success in replacing stoichiometric PtIV. Notably, oxidants such as heteropoly acids, CuCl2, FeCl3, and Br2 were identified as kinetically competent toward the oxidation of PtIII-CH3 (Scheme 1, Strategy A).\(^{17-19}\) These oxidants have achieved PtIV-mediated oxidation of methane or other aliphatic substrates,\(^{18-21}\) and some of them, being air-regenerable, have been employed in concert with O2 to effect overall aerobic methane functionalization. However, none of these studies established long-term stability. For example, the combination of CuCl2 and O2 ultimately resulted in complete oxidation of PtIII to PtIV,\(^21\) highlighting the difficulty of controlling the oxidation driving force. Studies aimed at mediating turnover via the PtIII/IV redox couple (Scheme 1, Strategy B) showed that Cl2\(^-\) and H2O2\(^-\) are viable oxidants. However, the PtIV oxidation rate was not actively modulated, and thus, continuous operation was not demonstrated. Furthermore, neither of these oxidants are air-regenerable or affordable for methanol production. In sum, there exists yet no suitable alternative to stoichiometric PtIV for sustained aqueous PtIV-catalyzed methane-to-methanol conversion.

We show that electrochemistry affords a unique solution to this problem. Unlike all stoichiometric chemical oxidations, electrochemical oxidation allows for unparalleled control over the rate and driving force for electron transfer. Furthermore, the rate and driving force can be toggled instantaneously for real-time, dynamic modulation. While direct electro-oxidation of the fleeting PtIII-CH3 intermediate is unfeasible due to the small fraction of reaction solution volume in contact with the electrode surface, electrochemistry is well-suited to regenerate PtIV via reoxidation of PtIII (Scheme 1, Strategy C). As noted above, the success of this approach relies on maintaining a constant PtIII/PtIV ratio; electrochemistry allows for simultaneous measurement and fine-tuning of this ratio in real-time. In addition, coupling the methane oxidation half-reaction with an oxygen reducing cathode would render the overall process aerobic (eq 1).

Despite its attractiveness, there exist a paucity of examples of this approach. One report applied electrochemical oxidation in the presence of PtIV, heteropoly acids, and O2 to achieve 1.4 turnovers for methanol production, but no information about the mechanism or stability of the system was provided.\(^23\) Earlier, a similar scheme was employed to oxidize a test substrate, p-toluensulfonic acid; while 11 turnovers of the PtII catalyst were attained, deposition of Pt0 was observed with increasing reaction times.\(^24\) A particular impediment to electrochemical turnover of the aqueous PtIV catalyst is the general sluggishness of two-electron PtIV oxidation at an electrode.\(^25\) Previously, we used electrochemical oxidation of PtIV salts to generate a highly electrophilic PdIV,\(^26\) species that effects methane conversion to methanol precursors.\(^27\) While this system showed exceptional rates and high selectivity, it required concentrated acid media that restrict practical utility. Herein, we combine Pt electrodes that catalyze facile electrochemical oxidation of PtII to PtIV ions,\(^28\) with in situ modulation of electric current to achieve continuous, steady-state methane oxidation over the course of 30 h. We observe the generation of methanol and methyl chloride as the principal products with >80% combined selectivity, demonstrating continuous PtIV-catalyzed electrochemical methane oxidation.

### RESULTS AND DISCUSSIONS

#### Identification of a Suitable Electrode for the PtIV-Catalyzed Electrochemical Methane Oxidation Reaction (EMOR)

The electrochemical mediation scheme put forward above (Scheme 1, Strategy C) requires an electrode capable of oxidizing PtII to PtIV. In view of the high PtIV oxidation potential (\(E^\circ = 0.68\) V versus SHE for PtIICl4\(^2-\)/PtIVCl3\(^-\)) and the acidic environment required for stability of the Pt ions,\(^30\) we focused our investigations on carbon, fluorine-doped tin oxide (FTO), and Pt electrodes as possible candidates. Whereas carbon and FTO electrodes displayed progressive deactivation and/or sluggish PtIV oxidation kinetics (see the SI, Section S2), Pt electrodes showed facile oxidation of PtIV at modest potentials. In 0.5 M H2SO4, the Pt electrode displays the typical voltammetric features associated with hydrogen underpotential deposition (H UPD) and oxide formation at low and high potentials, respectively (Figure 1a, black; also Figure S1).\(^31,32\)

Upon addition of 1 mM PtIICl4\(^2-\), a reversible wave appears at \(E_{pa} = 1.1\) V and \(E_{pc} = 0.8\) V (Figure 1a, blue). The appearance of this wave is accompanied by a suppression in the background Pt oxo wave, which we ascribe to inhibition by surface-adsorbed Cl\(^-\) that has dissociated from the PtIICl4\(^2-\) ions (Figure S14).\(^33\) As sustained methanol production requires Cl\(^-\) ions (see below), we also examined the voltammetric response of PtIV in the presence of 10 mM Cl\(^-\) (Figure 1a, red). Whereas the PtIV oxidation wave is largely unaffected by the additional Cl\(^-\), the cathodic wave associated with PtIV back-reduction is significantly suppressed. These observations are in line with the previous literature on PtIV oxidation at Pt electrodes that invokes an inner-sphere electron transfer mechanism involving transfer of a surface-adsorbed Cl\(^-\) to PtII during the oxidation reaction.\(^28\) Indeed, the reported Cl-adsorption isotherm at 2 mM Cl\(^-\) stretches from 0 to 0.8 V versus SHE (Figure S15),\(^34\) showing near-saturation at the potential for PtIV reduction. These observations suggest that Cl\(^-\) surface coverage at this potential may be incomplete at low [Cl\(^-\)] but complete at 10 mM Cl\(^-\). Thus, higher surface...
coverage of Cl\(^-\) induced by higher [Cl\(^-\)] has a negligible impact on PtII oxidation, but the back-reduction of PtIV, which requires Cl\(^-\) transfer back to the electrode surface, is inhibited (see the SI, Section S2, for additional explanation). This inner-sphere mechanism explains why Pt electrodes display superior PtII electro-oxidation kinetics compared to carbon or FTO.

Having identified a suitable electrode material, we then investigated PtII/IV electro-oxidation at the elevated temperatures required for methane activation by Pt II. These experiments were conducted above the boiling point of water and were, therefore, carried out in a home-built high-pressure electrochemical cell (see the SI and below). As shown in Figure 1b, red, high PtII oxidation current flowed at 130 °C; the 5-fold enhancement in current and approximately 100 mV negative shift in E\(_{\text{p,a}}\) compared to room temperature (Figure 1b, blue) reflect faster mass transport and electrode kinetics. The decrease in current at E\(_{\text{p,a}}\) > 1.1 V is attributed to the formation of surface oxides that inhibit the inner-sphere PtII oxidation. This inhibition is particularly pronounced at high [PtII] and high temperatures (see the SI, Section S2, for details). We also examined the dependence of PtII oxidation current on electrochemical driving force (Figure 1c). Keeping the potential below Pt oxide formation, <1.1 V, the steady-state current increased 10-fold per 104 mV of additional overpotential (\(\eta = E - E_{\text{eq}}\)). This Tafel slope at 130 °C corresponds to a rate-limiting one-electron transfer with a transfer coefficient of 0.77, in agreement with the aforementioned mechanism.35 These results show that Pt electrodes are capable of facile oxidation of PtIV at elevated temperatures.

Pt electrodes were also capable of sustained and efficient PtII/IV oxidation. We carried out bulk electrolyses of a stirred solution at 130 °C by applying a constant potential below 1.1 V. After chronoamperometry at 0.874, 0.924, and 0.974 V for 77, 40, and 17 min, respectively, half of the PtII ions in the initial solution were converted to PtIV ions as determined by UV−Vis analysis. At all three potentials examined, PtIV was generated with 100% Faradaic efficiency (Table S1).

Sustained methane oxidation catalysis will lead to a progressive rise in methanol concentration in the reactor over time. Thus, in addition to supporting facile PtII/IV oxidation, the electrode must be inert toward further oxidation of the CH\(_3\)OH product. This is a particular concern for Pt, which is the standard electrocatalyst for oxidation of CH\(_3\)OH to CO\(_2\).36 Indeed, in 0.5 M H\(_2\)SO\(_4\) at 130 °C, addition of 30 mM CH\(_3\)OH gives rise to the well-known anodic features associated with CH\(_3\)OH electro-oxidation (Figure 1d, blue).37 Remarkably, upon addition of 10 mM Cl\(^-\), this CH\(_3\)OH oxidation feature is almost completely suppressed (Figure 1d, red) over the entire potential range examined. This suppression is ascribed to surface adsorption of Cl\(^-\) ions.38 An additional control experiment confirmed that the non-electrochemical oxidation of CH\(_3\)OH catalyzed on metallic Pt39 is also negligible under our conditions (see the SI, Section S2). These data indicate that, fortuitously, the presence of Cl\(^-\) serves to simultaneously promote Pt II/IV oxidation and suppress surface-catalyzed oxidation of the methanol product. Together, these studies establish that Pt electrodes are suitable for EMOR.

Sustained Methane Oxidation Catalysis via Dynamic Electrochemical Control of the PtII/PtIV Ratio. The above studies provide the basis for carrying out continuous methane-to-methanol oxidation catalysis via electrochemical regeneration of PtIV (Scheme 1, Strategy C). The EMOR was carried out in a home-built high-pressure cell which consisted of a...
modified Parr reactor with electrical feedthroughs (Figure 2; see the SI, Section S1, for full details). The working compartment was charged with 3 mM PtII and 7 mM PtIV in 10 mM NaCl, 0.5 M H2SO4 (see the SI, Section S4, for details of electrolyte optimization). The counter compartment, separated by a H+-conducting membrane stack, contained 3 M vanadyl sulfate ((VIVO)(SO4)) as a sacrificial electron acceptor. The counter reaction prevented H2 evolution, fairly inert vanadyl ions enabled examination of long-term electrolysis. To maintain a constant PtII:PtIV ratio over the course of catalysis to maintain a steady ratio of PtII:PtIV. To achieve this, we employed the open-circuit potential (OCP) of the working compartment as an in situ probe of the instantaneous PtII:PtIV ratio in solution and adjusted the current (i) accordingly. In our reactor, the PtII and PtIV ions exist in various ligated states (PtIICl(H2O)(4−x)), each pair of which has different redox potentials. Assuming that [Cl−] is constant, the following modified form of the Nernst equation may be derived:

\[
E = E^\circ + \frac{RT}{2F} \ln \frac{[Pt^{IV}]}{[Pt^{II}]} \\
E = E^\circ + \frac{RT}{2F} \ln \frac{1}{[Cl^{-}]}^n
\]

where \(E^\circ\) and \(n\) represent the weighted average of the redox potentials and Cl− stoichiometries, respectively. Thus, using eq 2, we can estimate the instantaneous PtII:PtIV ratios potentiometrically. \(E^c\) can be determined from the initial OCP reading and the known initial PtII:PtIV ratio.

Figure 3 shows the electrochemical data recorded during a typical EMOR trial with periodic OCP monitoring and adjustment of the current. To aid the interpretation, the PtII:PtIV ratio was converted to the percentage of PtII ions (PtII%), defined as \([Pt^{II}] / ([Pt^{II}] + [Pt^{IV}])\). In a representative reaction, after 1.0 mA of current was passed for 1 h, the PtII% decreased from 30% to 25%. This led us to adjust the current to 0.9 mA, and after another 1 h, the PtII% rose to 29%. This process of quantifying the PtII% in the solution and adjusting the current to maintain a roughly constant PtII% was repeated periodically until the reaction was terminated. Incidentally, while our test reactor was too congested to conveniently add a fourth electrode, incorporation of a separate sensing electrode

**Figure 2.** High-pressure, three-electrode, two-compartment electrochemical cell for the EMOR. WE, Pt foil working electrode; RE, Ag/AgCl reference electrode; CE, Pt mesh counter electrode. 1, glass cell; 2, working solution containing the Pt ions; 3, fritted tube for housing the RE; 4, PTFE stir bar; 5, H+-conducting membrane separating the counter compartment; 6, PTFE body holding the membrane stack; 7, counter compartment solution containing (VIVO)(SO4) as the sacrificial electron acceptor.

**Figure 3.** Representative electrochemical data recorded during an EMOR trial (the 10.5 h long trial in Table 1). The open-circuit potential (EOC) reading at approximately 1 h time intervals (bottom, black triangles) was used to calculate the PtII% in the solution (top, red line), and the electrode potential during the electrolysis (ECP) was recorded (bottom, blue line).
could allow, in principle, for real-time feedback modulation of i.

The potential required for electrolysis (E_{CP}, CP = chronopotentiometry) equals the equilibrium electrode potential (E_{OCP}) plus the magnitude of overpotential (ξ) applied. By definition, ξ is the difference between the applied potential (E_{CP}) and E_{OCP}, as marked with green arrows in Figure 3. Over multiple trials, we consistently observed a steady decrease in ξ during the initial 2–3 h of each electrolysis, which we attribute to a slow initial electrode activation process. After stabilization of the electrode activity, ξ was ca. 20–40 mV, at an average current of around 0.9 mA. Normalizing by the electrode surface area, we estimate an average current density of 0.09 mA cm⁻².

Figure 4. (a) Amounts of methane oxidation products generated in the EMOR reactor versus reaction time. Each point represents a different trial in Table 1, and the product concentrations were normalized by i_ave of each trial (see the SI, Section S6, for explanation). The lines represent fitting with the (b) set of putative reactions.

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**Table 1. Results of EMOR Trials at T = 130 °C and P_{CH₄} = 675 psi**

| Time (h) | i_ave (mA) | ΔOCP (mV) | Final PtII% | Product (μmol, relative fraction) | TON | TOP (h⁻¹) |
|---------|------------|-----------|-------------|-------------------------------|-----|-----------|
| 4.9     | 1.19       | 7.9       | 22%         | CH₃OH: 60.5 (72%), CH₂Cl: 20.1 (24%), CH₂(OH)₂: 2.2 (3%), CH₂(OH): 0.1 (0%) | 1.4 | 1.6       |
| 10.5    | 0.88       | 5.7       | 19%         | CH₃OH: 93.7 (71%), CH₂Cl: 27.9 (21%), CH₂(OH)₂: 5.1 (4%), CH₂(OH): 1.2 (1%) | 2.3 | 2.9       |
| 18.4    | 1.00       | -2.8      | 22%         | CH₃OH: 205.4 (72%), CH₂Cl: 44.8 (16%), CH₂(OH)₂: 21.9 (8%), CH₂(OH): 2.9 (1%) | 4.5 | 6.3       |
| 29.3    | 0.91       | -6.0      | 23%         | CH₃OH: 268.0 (69%), CH₂Cl: 52.0 (13%), CH₂(OH)₂: 36.4 (9%), CH₂(OH): 7.2 (2%) | 5.8 | 9.3       |

“Initial [PtII] and [PtIV] in the working solution were 3 mM and 7 mM, respectively, and the solution volume was 23 mL. The electrochemically active surface area of the Pt working electrode was 10.3 cm². The TONs were determined from dividing the moles of product by the average of the initial and final moles of Pt⁰ for each reaction. The TOPs were obtained by dividing the TON by the time duration of each reaction. The total number of turnovers was calculated by assuming that all oxidation reactions were catalyzed by PtV: (μmolCH₃OH + μmolCH₂Cl + 2 × μmolCH₂(OH)₂ + 3 × μmolHCOOH + 4 × μmolCO₂) was divided by the average μmol⁰. The reaction time is the length of time the reactor was at the designated temperature, which spanned from ~80 min after the start of heating to the time at which the reactor was removed from the oil bath. i_ave was calculated by dividing the total charge passed by the reaction time. ΔOCP is the difference between the first and last OCP readings (= OCP_{last} - OCP_{first}). The hydrated form of formaldehyde, which is the predominant form of formaldehyde in the acidic pH employed.

The TONs were determined from dividing the moles of product by the average of the first and last OCP readings (= OCP_{last} - OCP_{first}). The hydrated form of formaldehyde, which is the predominant form of formaldehyde in the acidic pH employed.

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composition is thermodynamically inclined to deposit Pt^0 (Figure S19), our results demonstrate that, under sufficiently high [Pt^IV], nucleation of Pt^0 may be inhibited (see the SI, Section S5 and Table S3). Although an extensive discussion of Pt^0 deposition mechanisms is beyond the scope of the current work, these considerations highlight the importance of maintaining a stable Pt^II:Pt^IV ratio.

Analysis of Methane Oxidation Products from the EMOR Reactor. Operation of the EMOR reactor using the feedback modulation procedure described above allowed for continuous functionalization of methane (Table 1 and Figure 4). In all cases, we observe CH_3OH as the majority product in 69−72% yield (Table 1). We also observe appreciable quantities of CH_3Cl with a yield that decreases from 24% to 13% as the reaction time increases. Small amounts of overoxidized products (CH_2(OH)_2, HCOOH, and CO_2) were observed in less than 20% combined yield. Taking these overoxidized products to represent Pt^II-catalyzed oxidation of CH_3OH by 1, 2, and 3 equivalents of Pt^IV, respectively, the overall Faradaic efficiencies were in excess of 90% in all cases (Table S2). The per-Pt turnover numbers (TON) could not be rigorously determined due to minor fluctuations in [Pt^II] over the course of the reaction (see above), but approximate values were calculated from the known initial and final Pt^II amounts. For the longest trial, TON values of 6 and 9 for monofunctionalized products (CH_3X = CH_3OH and CH_3Cl) and total oxidation events were obtained, respectively (Table 1). The TOF for CH_3X, estimated to be 0.2−0.3 h^−1, showed a decreasing trend with increasing reaction time due to the overoxidation of CH_3OH. In contrast, the TOF for total oxidation events was relatively constant at ca. 0.3 h^−1 for different reaction times. Together, these observations demonstrate that electrochemical reoxidation effectively sustains Pt^II-based methane functionalization catalysis.

Combining the four trials in Table 1, Figure 4a visualizes the temporal progression of EMOR. We fit these data to the set of reactions suggested earlier: oxidation of CH_4 to CH_3OH and CH_3Cl, hydrolysis of CH_3Cl to CH_3OH, and subsequent overoxidation of CH_3OH to CH_2(OH)_2, HCOOH, and CO_2 (Figure 4b). While the fitted apparent rate constants (Table S6) for CH_3(OH)_2 and HCOOH oxidation show deviation from values separately determined outside the reactor (Table S7), the fitted values for CH_4 and CH_3OH oxidation are in good agreement with those independent measurements (Table S8). Thus, this simple model provides a reasonable description of the methane oxidation processes taking place during the EMOR.

All of the EMOR experiments shown in Table 1 were performed with identical reaction solution compositions with a low (3 mM) catalyst concentration. When the concentrations of Pt^II, Pt^IV, and Cl^− were increased, CH_3OH and CH_3Cl output increased while the fraction of CO_2 decreased (see the SI, Section S6 and Table S5). These results suggest that there is ample room for optimization of the solution composition to maximize yield and selectivity.

Outlook for Practical Methane Oxidation. Our studies establish that electrochemical oxidation endows Shilov’s catalyst with a sustainable mechanism for turnover and an inherent stability against deactivation through either complete oxidation of Pt^II to Pt^IV or Pt^0 deposition. However, we acknowledge that the Pt^II catalyst displays a relatively low reaction rate and moderate selectivity. Our work does not directly address these inherent limitations of the catalyst; furthermore, our proof-of-concept reactor was not designed to demonstrate optimal TON, TOF, or selectivity for methanol. However, the EMOR approach developed here opens the door toward a broader exploration of reaction conditions and reactor configurations that may overcome these rate and selectivity limitations. For example, higher temperatures and catalyst concentrations could be employed to enhance the reaction rate, but these conditions would lower the kinetic barrier to deactivation by Pt^0 deposition. The EMOR can be used to maintain an optimal Pt^II:Pt^IV ratio that is matched to these conditions (e.g., Figure S19, red square) and thereby sustain catalysis at higher volumetric productivity. Additionally, since the Pt^IICl_4(H_2O)_8(4−x) catalyst displays modest selectivity for methane versus methanol oxidation (~1:1) (SI, Table S8), strategies for continuous product removal would be needed to minimize overoxidation. As opposed to a volatile chemical oxidant that may be released at a similar rate as the methanol product, electrochemical oxidation could allow for independent control of oxidant delivery and product release. While many challenges remain, EMOR offers new opportunities for developing practical Shilov-type systems for methane-to-methanol conversion.

Safety Statement. No unexpected or unusually high safety hazards were encountered.

**CONCLUSIONS**

We have established an electrochemical approach for continuous methane-to-methanol conversion using aqueous Pt^II catalysts. Cl-adsorbed Pt surfaces were shown to be competent for the inner-sphere two-electron oxidation of Pt^II to Pt^IV while inert toward parasitic oxidation of the methanol product. In situ potential measurements and current modulation allowed us to carry out continuous steady-state catalysis by maintaining the Pt^II:Pt^IV ratio. While our test reactors were run up to 30 h, further reactor engineering to automatically modulate the current in real-time, enhance solution mixing, and rigorously separate the anode and cathode compartments should allow for extended operation. Moreover, integration of an oxygen-consuming counter electrode will enable net aerobic methane-to-methanol conversion (eq 1). While many additional challenges remain to realize viable Pt^II-catalyzed methane conversion, we envision that the electrochemical approach developed here will stimulate continued progress toward practical technologies for aerobic methane valorization.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.9b00273.

Full experimental details, description of the high-temperature electrochemistry, additional electrochemical data, additional EMOR reactor data, electrolyte optimization, and substrate oxidation experiments (PDF)

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ABBREVIATIONS

EMOR, electrochemical methane oxidation reaction; FE, Faradic efficiency; OCF, open-circuit potential; SHE, standard hydrogen electrode; FTO, fluoride-doped tin oxide; TON, turnover numbers; TOF, turnover frequencies

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