



When Electrochemistry Met Methane: Rapid Catalyst Oxidation Fuels Hydrocarbon Functionalization

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An electrochemical strategy for rapid generation of the highly reactive species necessary for C–H bond functionalization may enable improved technology for methane conversion.

Modern energy challenges have motivated the development of electrochemical transformations of abundant feedstocks into valuable fuels and commodity chemicals.¹ Now, reporting in *ACS Central Science*, Surendranath and co-workers introduce an electrochemical strategy that enables an organic transformation long-considered a grand challenge: selective methane activation.²

Methane, the primary component of natural gas, is globally abundant and inexpensive, making it an increasingly important part of the global energy portfolio. However, the dearth of efficient methods for converting this gaseous carbon feedstock into liquid fuels and commodity chemicals has limited our ability to take full advantage of this hydrocarbon, fueling decades of research into ways to overcome methane's chemical inertness. This endeavor is made even more challenging by methane's propensity for overoxidation and low selectivity.³

While the majority of industrial processes in the petrochemical industry utilize reactor beds with metal oxide or supported metal catalysts, the heterogeneous approach commercialized for the conversion of methane to methanol entails an indirect two-step route that operates at high temperatures, rendering it cost-prohibitive for more widespread use.³ Molecular catalysts are an attractive alternative to heterogeneous systems for the selective C–H functionalization of methane because they promise to operate at low temperatures and with high selectivity.³ To get past the chemical inertness of methane, these catalysts must be electrophilic, and most exploit high-valent transition metals, such as Pt(IV).⁴ C–H bond activation and functionalization by these electrophilic intermediates reduce the catalyst to a low-valent species that

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must be reoxidized in a two-electron process to regenerate the reactive, high-valent complex and turn over the catalyst. Building on the seminal work of Shilov, who demonstrated in the early 1970s that K₂PtCl₄ catalyzes the oxidation of methane to methanol and chloromethane with stoichiometric K₂PtCl₆, molecular catalysts have been developed for methane oxidation using stoichiometric oxidants.⁵ These include the system reported by Periana and co-workers in which (2,2'-bipyrimidyl)platinum(II) dichloride catalyzes the selective oxidation of methane to methyl bisulfate in concentrated sulfuric acid—with sulfuric acid acting as both solvent and oxidizing reagent.⁶ While this system boasts high conversion and selectivity, it still crawls along at rates of around 10 h⁻¹. Recent work by Schüth and co-workers demonstrated that both (2,2'-bipyrimidyl)platinum(II) dichloride and K₂PtCl₄ can carry out similar chemistry in 20% oleum (a H₂SO₄/SO₃ mixture) with turnover frequencies that are orders of magnitude higher than the original Periana system.⁷

The ideal terminal oxidant for a large scale commercial processes is O₂, but the sluggish kinetics associated with direct oxidation by O₂ renders it too impractical to be used directly. Many reported systems thus attempt to exploit intermediate chemical oxidants that can be directly regenerated by O₂, such

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as the SO_3/SO_2 couple.³ However, even with catalyst turnover mediated by these O_2 -regenerable oxidants, catalyst reoxidation is often still rate-limiting and continues to almost universally hinder the practicality of reported systems. Indeed, despite decades of research devoted to the discovery of catalytic systems for methane functionalization, the kinetics of catalyst reoxidation with O_2 -regenerable stoichiometric oxidants has stymied molecular catalysts, preventing them from meeting the performance metrics necessary for industrial applications.

Recognizing the limitations imposed by chemical oxidants, Surendranath and co-workers sought to employ an alternative approach to catalyst reoxidation. They posited they could generate and maintain the electrophilic high-valent catalytic intermediates necessary to activate C–H bonds with electrical polarization. Hypothetically, this method would effectively decouple catalyst oxidation from the O_2 reduction half reaction, thus circumventing the kinetic limitations imposed by stoichiometric chemical oxidants. This strategy had been previously employed to electrocatalytically functionalize alkane C–H bonds using Pt-based molecular catalysts; however the slow interfacial electron transfer kinetics typical of Pt ions made these systems ill-suited for methane functionalization.⁸ In this current report, the authors turned to Pd ions as a way to overcome the kinetic challenges that had hampered previous work.

Through the electrochemical generation of a high-valent Pd species, Surendranath and co-workers now demonstrate the rapid and selective catalytic functionalization of methane to the methanol precursors methyl bisulfate and methanesulfonic acid (Figure 1).² This simple system, based on PdSO_4 in

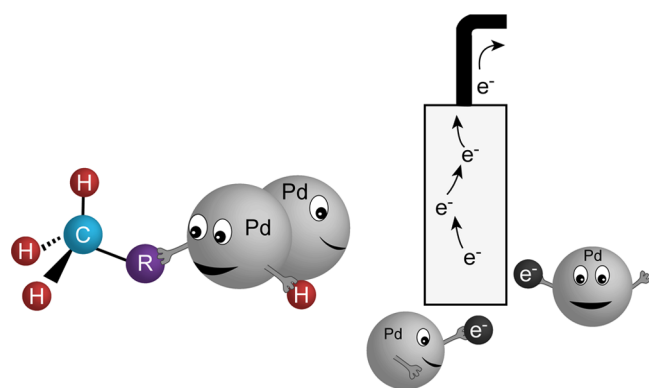


Figure 1. An electrochemically generated binuclear $\text{Pd}^{\text{III}}\text{--Pd}^{\text{III}}$ species catalyzes the rapid monofunctionalization of methane to methanol precursors, demonstrating a new strategy for C–H bond activation.

concentrated sulfuric acid, catalyzes methane functionalization at high rates without necessitating high reaction temperatures—reaching turnover frequencies of 2300 h^{-1} at only $140\text{ }^\circ\text{C}$. Comparatively, the current state-of-the-art non-

electrochemical catalysts functionalize methane at rates that are over 20-fold slower under these conditions. The rate enhancement illustrates the power of the electrochemical approach to develop efficient catalytic systems while still maintaining mild reaction temperatures. Further, the work highlights a key advantage of electrochemical methods, namely, the ability to extract kinetic and mechanistic information with relative ease; information much more difficult to obtain for conventional stoichiometric systems. The authors applied these electroanalytical techniques to establish that an electrophilic high-valent binuclear $\text{Pd}^{\text{III}}\text{--Pd}^{\text{III}}$ species is the intermediate responsible for methane functionalization. The mechanistic aspects of this discovery have far-reaching parallels in chemical oxidant-based C–H functionalization, where the groups of Ritter and Sanford have led a wave of interest in binuclear Pd catalysts for activation of aryl compounds with chelating nitrogen donors.^{9,10} This sort of chemical oxidant-based reactivity was subsequently translated to an electrocatalytic system for chlorination of benzo[*h*]quinoline by Gray and co-workers, who demonstrated that the two-electron oxidation of a binuclear $\text{Pd}^{\text{II}}\text{--Pd}^{\text{II}}$ species can be driven electrochemically.¹¹ The similarity between this reactive, electrochemically accessed $\text{Pd}^{\text{III}}\text{--Pd}^{\text{III}}$ intermediate and the motif identified by Surendranath is intriguing. As research moves forward, electrochemical methods could prove essential to identifying and characterizing important structural motifs of catalysts for C–H functionalization.

The authors' general approach of using electrochemical methods to generate and maintain highly reactive high-valent metal species could prove invaluable for accessing catalytic intermediates for the functionalization of other chemically inert substrates, thus providing a strategy to accelerate a variety of kinetically challenging reactions.

Prior to this work, the use of electrochemical methods to enable rapid and selective methane functionalization had proved an elusive goal despite success in developing electrocatalysts for a variety of other reactions. This newly reported electrochemical approach has potentially powerful implications. The authors' general approach of using electrochemical methods to generate and maintain highly reactive high-valent metal species could prove invaluable for accessing catalytic intermediates for the functionalization of other chemically inert substrates, thus providing a strategy to

accelerate a variety of kinetically challenging reactions. Moving away from chemical oxidants for these transformations could ultimately lead to the development of electrochemical cells where electrons extracted to maintain reactive populations of catalytic intermediates drive O₂ reduction at a separate electrode, allowing for continuous generation of a variety of C–H bond functionalization products. More extensive application of this methodology may thus prove central in advancing catalysis research for a wide range of important chemical reactions.

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