Strategies toward the sustainable electrochemical oxidation of methane to methanol

Arminio Ravelo, José Alejandro; Escudero Escribano, Maria

Published in:
Current Opinion in Green and Sustainable Chemistry

DOI:
10.1016/j.cogsc.2021.100489

Publication date:
2021

Document version
Publisher's PDF, also known as Version of record

Document license:
CC BY

Citation for published version (APA):
Arminio Ravelo, J. A., & Escudero Escribano, M. (2021). Strategies toward the sustainable electrochemical oxidation of methane to methanol. Current Opinion in Green and Sustainable Chemistry, 30, [100489]. https://doi.org/10.1016/j.cogsc.2021.100489
Strategies toward the sustainable electrochemical oxidation of methane to methanol
José Alejandro Arminio-Ravelo and María Escudero-Escribano

The direct conversion of methane to methanol is very promising to achieve a decarbonized future but remains a great challenge. The electrochemical activation and partial oxidation of methane to methanol are highly attractive to enable the direct conversion in a sustainable and decentralized way. In this review, we present an overview of the main strategies that have allowed to gain mechanistic insight into the electrochemical activation of methane. We discuss the developments of the direct and indirect electrochemical methane activation strategies as well as the opportunities and challenges toward the electrocatalytic conversion of methane to methanol.

Addresses
Department of Chemistry, University of Copenhagen, Universitetsparken 5, Copenhagen, DK-2100, Denmark

Corresponding author: Escudero-Escribano, María (maria.escudero@chem.ku.dk)

Introduction
The direct conversion of greenhouse gases into green fuels and valuable chemicals is of paramount interest to achieve a decarbonized future [1,2]. Methane emissions are the second largest cause of global warming (IEA; URL: https://www.iea.org/articles/global-methane-emissions-from-oil-and-gas). Nowadays, the energy sector is one of the principal sources of methane in the atmosphere. Typically, methane surplus is destined to gas flaring, contributing to 1% of CO₂ annual emissions (The World Bank, https://www.worldbank.org/en/programs/gasflaringreduction). It is crucial to find more sustainable solutions for the use and conversion of methane to fulfill the energy demand with a negligible carbon footprint.

Direct conversion of methane to methanol is one of the most appealing alternatives to gas flaring. Currently, methanol is commercially produced via a two-step process involving the oxidation of methane to synthesis gas (syngas), a mixture of CO and H₂ [3], followed by its catalytic reduction to methanol. This process is high energy consuming and expensive [3]. At present, methane to methanol plants are economically justified only at large-scale productions of methanol when generating at least 2500 metric tons per day [4]. The possibility to convert directly methane to methanol would open the opportunity to reduce the energy consumption and costs of production [4]. However, this process remains a great challenge because of the inertness of methane’s C–H bonds and the difficulty to selectively oxidize it to methanol [4,5].

In the field of catalysis, methane to methanol conversion strategies can be divided into five areas: biocatalysis, homogeneous catalysis, thermal heterogeneous catalysis, photocatalysis, and electrocatalysis, summarized in Figures 1 and 2. In biocatalysis, methane monooxygenase (MMO) enzyme stands out for its ability to selectively convert methane to methanol [6,7]. In homogeneous catalysis, a great part of the work is based on the use of platinum (Pt) complexes [8,9]. These catalysts are capable to activate the C–H bond in methane and convert it selectively to methanol or methanol derivatives at mild conditions (~100°C–200°C) [9]. Inspired by the active centers of the MMO enzyme, heterogeneous catalysis has traditionally used catalyst materials based on Cu and Fe [10,11]. These catalysts can activate methane at mild to high temperature and pressure conditions. In photocatalysis, the driving force is the ultraviolet light. Typically, semiconductor materials are combined with metal or metal oxides that allow efficient electron transfers and enhance the formation of radicals [12,13]. Thus, methane is activated by radical chain reactions [14].
Electrocatalytic approaches for methane to methanol oxidation are inspired by biological, heterogeneous, and homogeneous catalytic systems [4]. Here, the driving force is an electrical potential difference. Electrochemical strategies are particularly appealing, as they can operate at low to mild temperatures. Yet, the reaction is extremely challenging. Methane is highly stable and less reactive than methanol. The Gibbs free energy ($\Delta G$) and the electrode potential ($E_{\text{red}}$) versus the reversible hydrogen electrode (RHE) in reactions 1 and 2 show that the oxidation of methane to methanol is less favorable than the full oxidation to CO$_2$. However, it is possible to oxidize selectively methane by tuning the reaction mechanism.

**Figure 1**

Simplified schematic representation of different catalytic systems for the methane to methanol reaction. (a) Biocatalysis by a methanotroph bacterium. (b) Homogeneous catalysis. The green and the red spheres represent the reduced and oxidized versions of the catalyst, respectively. (c) Heterogeneous catalysis. (d) Photocatalysis.

**Figure 2**

Methane to methanol direct conversion strategies. (a) Direct methane activation. (b) Indirect methane activation: by using catalytic species capable to regenerate on the electrode surface (pink arrows) or by the electrogeneration of radical species (red arrows).
and enhancing the formation of intermediates that lead to the formation of methanol rather than CO2 \[15, 16\]**. Therefore, electrocatalytic approaches focus on the selection of electrode materials that activate methane and generate adequate intermediates to enhance the production of methanol.

The electrochemical oxidation of methane takes place by direct or indirect electrochemical methane activation (Figure 2). On the one hand, direct methane activation is focused on its direct adsorption on the electrode active sites (Figure 2a); on the other hand, the indirect methane activation involves the electrochemical generation of highly reactive species capable to activate methane in the interface neighborhoods or/and the bulk of the solution (Figure 2b) \[5\]. Herein, we present a brief overview of the developments of the electrocatalytic conversion of methane to methanol at mild to low temperatures and discuss the strategies toward both the direct and indirect electrochemical methane activation.

**Direct electrochemical methane activation**

Direct electrochemical methane to methanol strategies focus on tuning the electrode surface structure and composition \[15,16**,**17\]. The materials selected need to (1) activate methane and (2) stabilize the intermediates involved in the formation of methanol to avoid the formation of CO2 \[4,18\]. These strategies offer the opportunity to integrate methane to methanol conversion in electrochemical devices such as fuel cells \[16]**. This would not only allow the production of methanol but also the generation of electricity (Figure 3a). Here, we discuss the advances on the three main materials used as electrodes for direct methane to methanol conversion: metallic surfaces, metal oxides/promoted oxygenated surfaces, and ZrO2 composites.

**Metallic surfaces**

The use of metallic surfaces for direct methane activation has emerged as a collateral result of the studies on the electro-oxidation of hydrocarbons for fuel cell applications \[19,20\]. These studies were the base for understanding the potential dependence of methane adsorption and activation. Studies on Pt electrodes have shown that methane adsorption is a slow process and potential dependent \[15,19\]. Methane adsorbs at potentials higher than 0.2 V versus RHE and oxidizes to CO2 around 0.6–0.8 V versus RHE (Figure 3b) \[15,19\]. Both adsorption and activation potentials are sensitive to the temperature and electrolyte used \[15,19,21\]. Kinetic studies show that methane oxidation has an initial electron transfer step to form adsorbed CH3* (Reaction 3, the rate-determining step) \[15,20\], followed by the formation of CO* and/or COH* (Reaction 4) before its oxidation to CO2 (Reactions 5–7) \[15,21,22\].

\[
\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \quad (\Delta G = -131.2 \text{ kJ mol}^{-1}; \quad E_{\text{rev}} = 0.17 \text{ V vs RHE})
\] (1)

\[
\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{OH} + 2\text{H}^+ + 2\text{e}^- \quad (\Delta G = -125.4 \text{ kJ mol}^{-1}; \quad E_{\text{rev}} = 0.65 \text{ V vs RHE})
\] (2)

Recent theoretical calculations suggest that methane is thermochromically activated on Pt surfaces (Reaction 3) \[15\]. This means that the rate of methane activation is independent of the potential applied but dependent on the temperature. Methane activation is also sensitive to the electrode surface structure and composition. It has been reported that Pt terraces can activate the C–H bonds, but only on Pt (100) single-crystalline surfaces, CH4* intermediates can combine with oxygen species with a low energy barrier \[23]**. This shows that direct electrochemical methane activation presents a strong structure sensitivity, similar to other electrocatalytic reactions such as CO2 electroreduction \[24\]. Moreover, the electric field on the interface can modify importantly the efficiency of methane activation, being
Electrochemical approaches for direct methane activation. (a) Polymer electrolyte membrane fuel cell model for direct methane to methanol conversion using direct methane activation approaches. (b) Methane activation on metallic (Pt) surface. Adapted with permission from Ref. [15]. Copyright 2019 American Chemical Society. (c) Top: Free energies of various metal oxides for the third step in the OER (Reaction 10) and methane activation step (Reaction 12). Adapted with permission from Ref. [36]. Copyright 2020 American Chemical Society. Bottom: Scheme of reaction pathway on RhO₂ for methane oxidation. Adapted with permission from Ref. [16]**. (d) Left: Polymer electrolyte membrane fuel cell for direct methane to methanol conversion using ZrO₂ composites and CO₃²⁻ exchange membrane. Right: Mechanism suggested for methane to methanol conversion using CO₃²⁻ as oxidizing agent. Adapted with permission from Ref. [17]. Further permissions related to the material excerpted should be directed to the ACS.
Electrochemical oxidation of methane to methanol: Metal oxides and oxygen-promoted surfaces

The use of metal oxides or oxygen-promoted surfaces to convert methane to methanol is a promising approach. The use of metal oxides was inspired by the electro-oxidation of light alkenes to oxygenated species at potentials close to the oxygen reduction reaction (ORR)/oxygen evolution reaction (OER). Here, the discharge of water forms oxygenated active species responsible for the oxidation of methane to methanol [26,27].

The initial studies on oxygen-promoted surfaces focused on the production of oxygenated active species through the ORR mechanism. Pt, Rh, and Pd were supported on carbon and tested as electrodes in a fuel cell configuration. Only Pt and Pd supported on carbon worked as electrocatalysts for converting methane to methanol, but with poor selectivity [26]. Better results were attained through the OER mechanism [28]. A recent study showed the OER mechanism [29].

Materials composed of V2O5 and/or RuO2 reported the best selectivity toward methanol [27–29]. Interestingly, NiO–V2O5/Rh nanocomposites showed high selectivity toward methanol production at current efficiencies of 91% at 100 °C [30]. According to different studies on these nanocomposites, methane is activated through the oxygenated active species generated during the OER [16–19]. Alternative mechanisms suggest the formation of redox pairs on the catalyst surface; however, there is not enough experimental evidence to confirm this. Recently, Armarson et al. created a model to identify the ideal metal oxides for the electrochemical methane to methanol conversion based on their oxygen binding energy [16**].

Notwithstanding, the challenge is higher for methane to methanol to occur via the OER, giving a narrow range of potential to convert methane to methanol without competing with the OER [16**]. Thus, in theory, it is necessary to work in potentials close to 1.23 V versus RHE, but not higher to evolve O2.

ZrO2-based composites

Composites based on ZrO2 have been recently used for the direct methane activation. The composites are made of a ZrO2 matrix with metal oxide nanoparticles. The...
first composite reported was made of ZrO₂ and NiO [17]. This approach was inspired by the idea of using carbonate (CO₃²⁻) to activate methane through oxygen insertion. NiO was selected because of its ability to activate methane in heterogeneous catalysis and its use for organic oxidation in alkaline media. The results showed that the composite was capable to activate and partially oxidize methane. Interestingly, the catalyst produced methanol, isopropanol, acetate, acetic acid, acetone, ethanol, and formic acid. However, all products were further oxidized in fuel cell experiments (Figure 3d) [17]. Similar experiments have been reported with ZrO₂ composites using Co₃O₄ [32], NiCo₂O₄ [33], and CuO₂ [34]*, showing higher catalytic activity toward partial methane oxidation compared with the composite with NiO. Still, the results showed the generation of methanol only as an intermediate to produce higher alcohols and/or carboxylic acids. In general, it seems that methanol is efficiently produced in the fuel cell configurations but rapidly oxidized [17,32,34]*.

Despite the satisfactory performance of this type of composites, there is a need for further mechanistic understanding. The reaction pathways suggested are based on possible oxidation reactions reported in the literature (Figure 3d) without theoretical nor experimental studies that support them. Recent theoretical calculations on this type of materials suggest that methane activation barrier is decreased, thanks to the high-speed electronic network formed between the oxygen atoms between ZrO₂ and the metal oxide [34]*. It seems that the use of CO₃²⁻ as the oxidizing agent is responsible to produce higher alcohols. Interestingly, some of the faradaic efficiencies for some of the products reported are above 100% [32,33,34]*. This suggests that more than one step of the mechanism or reaction does not occur by electron transfers at the electrode—electrolyte interface but by redox reactions between species in solution. In general, the results also evidence the competition between methane oxidation and the OER [34*,35]. Yet, it is not clear if they are involved in the same mechanism pathway or as parallel reactions.

### Indirect electrochemical activation of methane

Strategies on the indirect electrochemical activation of methane focus on the generation of species capable to break or activate the C—H bond [37,38]. In contrast to direct methane activation strategies, methane is not activated on the electrode surface. Besides, the electrodes do not act as electrocatalysts but as a source of electrons for the main active species. This allows to efficiently decouple methane conversion and methanol selectivity, as they do not share the same active sites [39]. Here, we discuss the two main approaches for the indirect methane to methanol conversion: electrochemical generation of active species and electrochemical-assisted homogeneous catalysis.

### Electrochemical generation of highly active species

In this approach, methane is activated by homogeneous reactions with highly reactive species, such as radicals. In electrochemistry, the focus is on the electrolysis of the new natures of these species, which are typically oxygenated species that can react to methane forming methanol or to derivatives that can be easily converted to methanol.

The research on this approach traces back to the end of the 80s and the beginning of the 90s. These works involve the study of complex systems based on the formation of Cl₃⁺ radicals by photochemical reactions [40], generation of HO⁺ radicals through the Fenton reaction [37] and formation of superoxide radicals, O₂⁺, in highly alkaline media to activate methane [41] (Table 1). It is important to mention that the mechanisms are based on radical chain reactions, and therefore, more than one product was generated. The experiments succeeded to produce methanol at ambient temperatures. However, the current efficiency and selectivity toward methanol were not high enough for scalable applications. It also seems relevant to limit the content of O₂ in the electrolyte to reduce the formation of side products such as formaldehyde [37,41]. Nonetheless, further understanding of how methane is activated through these oxygenated radicals is essential to improve selectivity.

### Electrochemical-assisted homogeneous catalysis

This approach was inspired by previous research in homogeneous catalysis [38]. The idea is to make use of electrochemistry to overcome some of the common
Electrochemical-assisted homogeneous catalysis for methane to methanol conversion strategies. (a) Proposed mechanism for electrochemical methane functionalization by a putative Pd$^{II,III}$ intermediate. Green and blue arrows indicate faradaic and nonfaradaic reaction pathways, respectively. Reproduced with permission from Ref. [38]. Copyright 2017 American Chemical Society. (b) Simplified catalytic cycle for electrochemical methane functionalization by Rh-based catalyst in nonaqueous media and Si nanowires as electrodes. Reproduced with permission from Ref. [45]. Copyright 2019 American Chemical Society. Further permissions related to the material excerpted should be directed to the ACS.

One of the main advantages of using electrochemical-assisted homogeneous catalysis is the number of possibilities to activate methane with high selectivity to methanol. Coupling electrochemistry with homogeneous catalysis offers the possibility to avoid competition with the OER or ORR. This approach allows the production of methanol without its further oxidation. Notwithstanding, the use of homogeneous catalysis has
other limitations. Methane to methanol conversion depends on how fast the catalyst diffuses to the electrode to be regenerated [42]. Besides, it is important to select adequate catalysts that contain metallic centers that allow fast electron transfers to avoid high overpotentials for the regeneration of the catalyst [38].

Declaration of competing interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements
The authors gratefully acknowledge the Villum Foundation for the award of a Villum Young Investigator grant (Project number 19142).

References
Papers of particular interest, published within the period of review, have been highlighted as:
* of special interest
** of outstanding interest

1. De Luna P, Hahn C, Higgins D, Jaffer SA, Jaramillo TF, Sargent EH: What would it take for renewably powered electrolysis to displace petrochemical processes? Science 2018, 364. https://doi.org/10.1126/science.aav3506.
2. Schiffer ZJ, Manthiram K: Metallophilics: a critical assessment of the catalytic domains. ACS Catal 2018, 8:11854–11862. https://doi.org/10.1021/acscatal.8b04101.
3. Gunsalus NJ, Koppaka A, Park SH, Bischof SM, Hashiguchi BG, Periana RA: Homogeneous functionalization of methane. Chem Rev 2017, 117:8521–8573. https://doi.org/10.1021/acs.chemrev.6b00739.
4. Cui X, Li H, Wang Y, Hu Y, Hua L, Li H, Han X, Liu Q, Yang F, He L, Chen X, Li Q, Xiao J, Deng D, Bao X: Room-temperature methane conversion by graphene-confined single iron atoms. Inside Chem 2018, 4:1092–1110. https://doi:10.1016/j.ijchemr.2018.05.006.
5. Ravi M, Ranocchiari M, van Bokhoven JA: The direct catalytic oxidation of methane to methanol—a critical assessment.

Angew Chemie - Int Ed 2017, 56:16464–16483. https://doi.org/10.1002/anie.201702550.
12. Xie J, Jin R, Li A, Bi Y, Ruan Q, Deng Y, Zhang Y, Yao S, Sankar G, Ma D, Tang J: Highly selective oxidation of methane to methanol at ambient conditions by titanium dioxide-supported iron species. Nat Catal 2018, 1:889–896. https://doi.org/10.1038/s41929-018-0170-x.
13. Song H, Meng X, Wang S, Zhou W, Wang X, Kako T, Ye J: Direct and selective photocatalytic oxidation of CH4 to oxygenates with O2 on cocatalysts/ZnO at room temperature in water. J Am Chem Soc 2019, 141:20507–20515. https://doi.org/10.1021/jacs.9b11440.
14. Sher Shah MSA, Oh C, Park H, Hwang YJ, Ma M, Park JH: Catalytic oxidation of methane to oxygenated products: recent advancements and prospects for electrocatalytic and photocatalytic conversion at low temperatures. Adv Sci 2020, 7:2001946. https://doi.org/10.1002/advs.202001946.
15. Boyd MJ, Latimer AA, Dickens CF, Nielander AC, Hahn C, Norskov JK, Higgins DC, Jaramillo TF: Electro-oxidation of methane on platinum under ambient conditions. ACS Catal 2019, 9:7578–7587. https://doi.org/10.1021/acscatal.9b01207.
16. Arnason L, Schmidt PS, Pandey M, Bagger A, Thygesen KS, Stephens IEL, Rossmel J: Fundamental limitation of electrocatalytic methane conversion to methanol. Phys Chem Chem Phys 2018, 20:111152–11159. https://doi.org/10.1039/C8CP10476K.

This article reports the first kinetic model for the direct electrochemical activation of methane through OER intermediates. The authors identify the main limitations for methane oxidation and suggest rutile oxides and two-dimensional transition metal nitrides and carbides (MXenes) as promising electrode materials for this reaction.

17. Spinner N, Mustain WE: Electrochemical methane activation and conversion to oxygenates at room temperature. J Electrochem Soc 2013, 160:F1275–F1281. https://doi.org/10.1149/2.07131jes.
18. Bagherzadeh Mostaghimi AH, Al-Attas TA, Kibria MG, Siahrostami S: A review on electrocatalytic oxidation of methane to oxygenates. J Mater Chem A 2020, 8:15575–15590. https://doi.org/10.1039/d0ta03758c.
19. Niedrach LW, Tochner M: Studies of hydrocarbon fuel cell anodes by the multipulse potentiodynamic method. J Electrochem Soc 1987, 114:233. https://doi.org/10.1149/1.2446554.
20. Heihe SY: Anodic oxidation of methane. J Electrochem Soc 1977, 124:1171. https://doi.org/10.1149/1.2135522.
21. Sustersic MG: The electrosorption of methane and its potentiodynamic electrooxidation on platinized platinum. J Electrochem Soc 1980, 127:1242. https://doi.org/10.1149/1.1219863.
22. Hahn F, Melendres CA: Anodic oxidation of methane at noble metal electrodes: an “in situ” surface enhanced infrared spectroelectrochemical study. Electrochim Acta 2001, 46:3525–3534. https://doi.org/10.1016/S0013-4686(01)00645-1.
23. Bin Ma H, Sheng T, Yu WS, Ya JY, Wan LY, Tu N, Sunn Z, Zhou ZY: High catalytic activity of Pt(100) for CH4 electrochemical conversion. ACS Catal 2019, 9:10159–10165. https://doi.org/10.1021/acscatal.9b02738.

This article presents a detailed study on methane activation and oxidation using well-defined Pt surfaces. The combination of cyclic voltammetry, in situ infrared spectroscopy, and theoretical calculations on Pt single-crystalline and stepped surfaces highlights the structure sensitivity of this reaction, with Pt(100) being the only active surface for the electrochemical activation of methane.

24. Sebastián-Pasqual P, Mezzavilla S, Stephens IEL, Escudero-Escirba M: Structure-sensitivity and electrolyte effects in CO2 electroreduction: from model studies to applications. ChemCatChem 2019, 11:3626–3645. https://doi.org/10.1002/cctc.201900552.
25. Panaritis C, Hajar YM, Treps L, Michel C, Baranova EA, Steinmann SN: Demystifying the atomic origin of the electrochemical effect on methane oxidation. J Phys Chem Lett 2020, 11:6976–6981. https://doi.org/10.1021/acs.jpclett.0c01485.
This article shows the electrochemical oxidation of methane to methanol from methane. 

27. Rocha RS, Camargo LM, Lanza MRV, Bertazzoli R: A feasibility study of the electro-recycling of greenhouse gases: design and characterization of a (TiO2/RuO2)/PTFE gas diffusion electrode for the electro-synthesis of methanol from methane. 

28. Rocha RS, Reis RM, Lanza MRV, Bertazzoli R: Electrochemistry of methanol from methane: the role of V2O5 in the reaction selectivity for methanol of a TiO2/RuO2/V2O5 gas diffusion electrode. 

29. Sarno M, Ponticorvo E, Funicello N, De Pasquale S: Methane electrochemical oxidation at low temperature on Rh single atom/NiO/V2O5 nanocomposite. 

30. Man I, Su HY, Calle-Vallejo F, Hansen HA, Martinez JL, Inoglu NG, Kitchin J, Jaramillo TF, Norskov JK, Rosseinsky J: Universality in oxygen evolution electrocatalysis on oxide surfaces. 

31. Ma M, Jin BJ, Li P, Jung MS, Il Kim J, Moon JH, Park JH: Ultrahigh electrocatalytic conversion of methane at room temperature. 

32. Xu N, Coco CA, Wang Y, Su T, Wang Y, Peng L, Zhang Y, Liu Y, Qiao J, Zhou X: Applied Catalysis B: environmental electroconversion of methane to alcohols on “capsule-like” binary metal oxide catalysts. 

33. Omasta TJ, Rigdon WA, Lewis CA, Stanis RJ, Liu R, Fan CQ, Mustain WE: Two pathways for near room temperature electrochemical conversion of methane to methanol. 

34. Omasta TJ, Rigdon WA, Lewis CA, Stanis RJ, Liu R, Fan CQ, Mustain WE: Two pathways for near room temperature electrochemical conversion of methane to methanol. 

35. O'Reilly ME, Kim RS, Oh S, Surendranath Y: Catalytic methane monofunctionalization by an electrogenerated high-valent Pd intermediate. 

36. Fornaciari JC, Princ D, Kawashima K, Wygant BR, Verma S, Spanu L, Mullins CB, Bell AT, Weber AZ: A perspective on the electrochemical oxidation of methane to methanol in membrane electrode assemblies. 

37. Cook RL: Ambient temperature methane activation to condensed species under cathodic conditions. 

38. El-Aasser MS, Arminio-Ravelo and Escudero-Escribano: Arminio-Ravelo and Escudero-Escribano.