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Review

Selective electrocatalytic conversion of methane to fuels and chemicals

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ABSTRACT

The increase in natural gas reserves makes methane a significant hydrocarbon feedstock. However, the direct catalytic conversion of methane into liquid fuels and useful chemicals remains a great challenge, and many studies have been devoted to this field in the past decades. Electrocatalysis is considered as an important alternative approach for the direct conversion of methane into value-added chemicals, although many other innovative methods have been developed. This review highlights recent advances in electrocatalytic conversion of methane to ethylene and methanol, two important chemicals. The electrocatalytic systems efficient for methane conversions are summarized with an emphasis on catalysts and electrolytes. The effects of reaction conditions such as the temperature and the acid–base property of the reaction medium are also discussed.

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1. Introduction

Methane is the principal component of natural gas. The discovery of increasingly abundant resources of unconventional natural gas, in particular shale gas, has stimulated a revolution in raw hydrocarbon feedstock supply [1,2]. Presently, more than 90% of the natural gas exploited is used for heating, cooking, transportation purposes and electricity generation. Despite its vast availability, the use of methane as chemical raw material is still insufficient [1–9].

The inherent chemical properties of methane, including low electron and proton affinity, low polarizability, weak acidity, high C–H bond energy (439 kJ mol⁻¹) as well as high ionization energy [4], make it very inert. The chemical utilization of methane is thus highly challenging [1–9]. In the current chemical industry, methane is first converted to syngas (CO/H₂) by steam reforming or partial oxidation, and syngas is transformed into methanol or liquid hydrocarbons via methanol synthesis or Fischer–Tropsch synthesis [10]. However, this indirect route by breaking all the C–H bonds of methane molecule is high energy consuming and expensive [11].

The direct transformation of methane into chemicals and liquid fuels is more cost- and energy efficient. Numerous studies have been devoted to this field for decades [1–9]. The transformation of methane into methyl halides has recently seen significant progress and methyl halides can be applied to the

synthesis of lower olefins or hydrocarbon fuels [12,13]. The non-oxidative coupling of methane to olefins and aromatics with high yields has been reported as a promising route [14], but technical difficulties caused by the high temperature (~1273 K) still need to solve. In spite of many significant advances, the direct transformation of methane via conventional heterogeneous and homogeneous catalysis remains highly difficult. New methodology is needed to challenge this “holy grail” in chemistry [15]. The activation of methane often requires severe conditions, under which the target product (such as methanol or ethylene) is typically far more reactive than methane and may undergo consecutive oxidations to CO and CO₂ under oxidative conditions (Fig. 1).

The electrocatalytic approach for oxidizing methane under mild conditions may stabilize the products from further oxidation. The rapid generation of the highly reactive species necessary for C–H bond functionalization under electrolytic conditions may overcome the mentioned difficulty of chemical inertness of methane, which may enable improved technology for methane conversions [16]. Using the sustainable electricity from solar energy or wind power to achieve direct electrocatalytic conversion of methane to chemicals and liquid fuels is an ideal process (Fig. 2). Moreover, the unique characteristics of electrocatalytic devices, such as miniaturization, integration, and easy scaling-up, can satisfy all sizes of methane conversion devices.

Many studies have been devoted to the development of electrocatalysts and relevant reaction systems for selective oxidation and/or oxidative functionalization of methane into value-added chemicals [17–22]. However, a review article systematically summarizing the research advances in the very field is still lacking.

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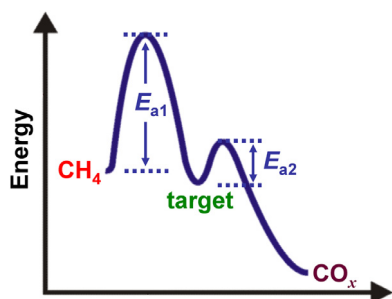


Fig. 1. Schematic plot illustrating the difficulty in obtaining a target product with high selectivity during the oxidative conversion of methane.

53 The present review aims to highlight recent advances in the direct
54 electrocatalytic conversion of methane to value-added chemicals.

55 2. Fundamental aspects for electrocatalytic oxidation of 56 methane

57 A typical electrocatalytic cell consists of anode, cathode, ion-
58 exchange membrane and external electric circuit (Fig. 3). The ion-
59 exchange membrane separates the anode from the cathode and
60 only allows transport of protons or oxide ions. Typically, the ox-
61 idative half reaction occurs on the anode surface, while the reduc-
62 tive half reaction takes place on the cathode surface. The external
63 electric circuit is used to control the applied potential or current.

64 Table 1 shows some possible reactions related to electrocat-
65 alytic conversions of methane in aqueous solution and the related
66 redox potentials versus normal hydrogen electrode at 25 °C. The
67 generation of CO₂ is the easiest reaction from thermodynamic con-
68 sideration because the redox potential required for the generation
69 of CO₂ is the lowest (Table 1). The formations of partial oxida-
70 tion products, including CH₃OH, HCHO, HCOOH and CO, and oxida-
71 tive coupling products, i.e., C₂H₆ and C₂H₄, have more positive redox
72 potentials in comparison to that of CO₂. These make the electro-
73 catalytic partial oxidation of CH₄ and the oxidative coupling of CH₄
74 difficult to realize.

75 3. Solid–gas reaction system

76 The solid–gas electrocatalytic reactions are usually carried out
77 in a fuel cell type reactor [20,21,23]. The reaction temperature
78 determines the types of solid–electrolyte materials and influences
79 the reaction products thermodynamically. Generally, there are two

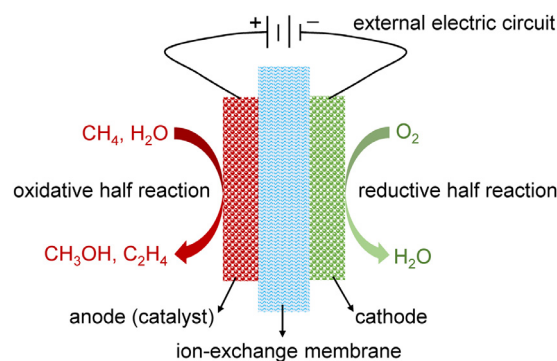


Fig. 3. Schematic illustration of typical electrocatalytic cell for methane conversions.

Table 1. Some possible reactions related to electrocatalytic conversion of CH₄.

Reaction	<i>E</i> (V) versus NHE (pH=0, 298 K)
CH ₄ (g) + H ₂ O(l) → CH ₃ OH(a) + 2H ⁺ (a) + 2e ⁻	0.58
CH ₄ (g) + H ₂ O(l) → HCHO(a) + 4H ⁺ (a) + 4e ⁻	0.46
CH ₄ (g) + 2H ₂ O(l) → HCOOH(a) + 6H ⁺ (a) + 6e ⁻	0.26
CH ₄ (g) + H ₂ O(l) → CO(g) + 6H ⁺ (a) + 6e ⁻	0.26
CH ₄ (g) + 2H ₂ O(l) → CO ₂ (g) + 8H ⁺ (a) + 8e ⁻	0.17
2CH ₄ (g) → C ₂ H ₆ (g) + 2H ⁺ (a) + 2e ⁻	0.35
2CH ₄ (g) → C ₂ H ₄ (g) + 4H ⁺ (a) + 4e ⁻	0.44

The redox potentials are obtained from the thermochemical software "HSC Chemistry".

80 types of solid–gas electrocatalytic reactions for CH₄ conversions
81 based on reaction temperatures, i.e., low-temperature (<300 °C)
82 and high-temperature (>300 °C, mostly >600 °C) reactions.

83 3.1. High-temperature reaction

84 At high temperatures (>300 °C, mostly >600 °C), the oxida-
85 tion of CH₄ is often carried out in a solid oxide fuel cell (SOFC)
86 reactor [21,24–30]. The reactor mainly consists of two porous elec-
87 trodes (i.e., anode and cathode) and a dense solid oxide electrolyte.
88 A schematic illustration of solid oxide-based cell using oxide ion-
89 conducting electrolytes for CH₄ conversions is displayed in Fig. 4.
90 Briefly speaking, the catalyst is coated on the surface of solid ox-
91 ide electrolyte and is used as the anode to catalyze the oxidation
92 of CH₄. The oxide ion is transferred to anode from cathode to par-
93 ticipate in the oxidation of CH₄. It has been found that when the
94 reaction temperature is higher than 600 °C, a solid oxide elec-

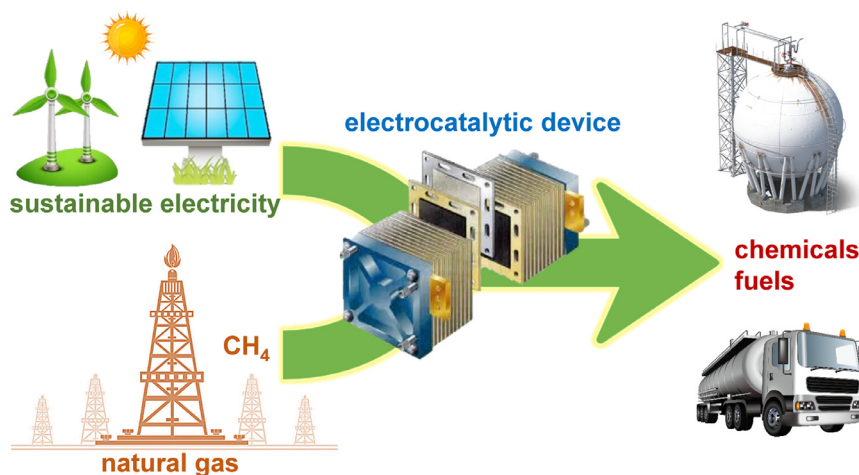


Fig. 2. Illustration of selective electrocatalytic conversion of methane to liquid fuels and chemicals.

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