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Advances in methane conversion processes

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ABSTRACT

In this short review, we highlight the recent advances in methane conversion processes at high and low temperatures. Methane conversion processes are of great importance in achieving a crude-oil independent supply of energy, fuels and chemicals for the future. Direct conversion of methane into chemicals and fuels has been often considered as the “holy grail” of current catalysis research due to the unreactive nature of methane, which makes targeted chemical transformations to fuels and chemicals very challenging. We discuss the progress in developing heterogeneous catalytic and electrocatalytic systems to overcome this challenge. We conclude by providing a perspective on the future of this area of research.

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1. Introduction

Development of efficient and selective methane conversion processes to electricity, fuels and chemicals has become critical in the recent years due to the emerging number of untapped, unconventional natural gas reserves (e.g., shale gas) and the need to reduced our dependence from limited crude oil resources [1–5]. Recent advancements in hydraulic fracturing have led to access of shale gas reserves that are rich in methane (>70% of the carbon) [3,5]. Currently, methane is mostly combusted for generation of electrical power and heat [5]. To date, industrial routes for one-step conversion of methane to fuels and chemicals are limited. The most technologically advanced routes involve the indirect conversion of methane (i.e., methane steam reforming [6]) to fuels and chemicals. For example, steam reforming generates H₂ and CO mixtures from methane at high temperatures (700 °C–1000 °C) and pressures (15–40 atm) [5], which are then used in the production of methanol and Fischer-Tropsch synthesis. The challenges associated with the one-step conversion of methane to chemicals and fuels arise from the fact that methane is a very stable molecule, comprised of C–H bonds that are weakly polarized. Hence, very aggressive reactants and operating conditions (e.g., temperature

and pressures) are required to activate the methane C–H bond, consequently favoring undesired reactions (e.g., complete combustion to CO₂) which lead to loss in activity, selectivity, and yield of desired products.

The schematic in Fig. 1 illustrates some of the main high- and low-temperature methane conversion processes. As indicated in Fig. 1, high-temperature processes mainly involve the partial or total oxidation of methane to CO, H₂, and CO₂ with the exception of oxidative coupling and non-oxidative conversion of methane that lead to the formation of C₂₊ hydrocarbons [6–12]. While, some of the high temperature processes are technologically advanced, they are energy intensive and high cost [13]. Hence, development of one-step processes for conversion of methane to useful intermediates or fuels and chemicals at low-temperatures would alleviate some of these challenges. To date, low-temperature processes (Fig. 1) have largely focused on partial/total oxidation of methane to valuable intermediates for synthesis of fuels and chemicals, such as methanol and dimethyl ether. However, most of these processes suffer from limited selectivity to targeted products, since under operating conditions most of the products or intermediates are more reactive than methane and undergo further transformation or decomposition. In this short review, we provide an overview of the latest advancements in methane conversion at high- and low-temperatures to fuels, chemicals, and electricity. In addition, we conclude with a perspective on the promises and drawbacks associated with each of these processes.

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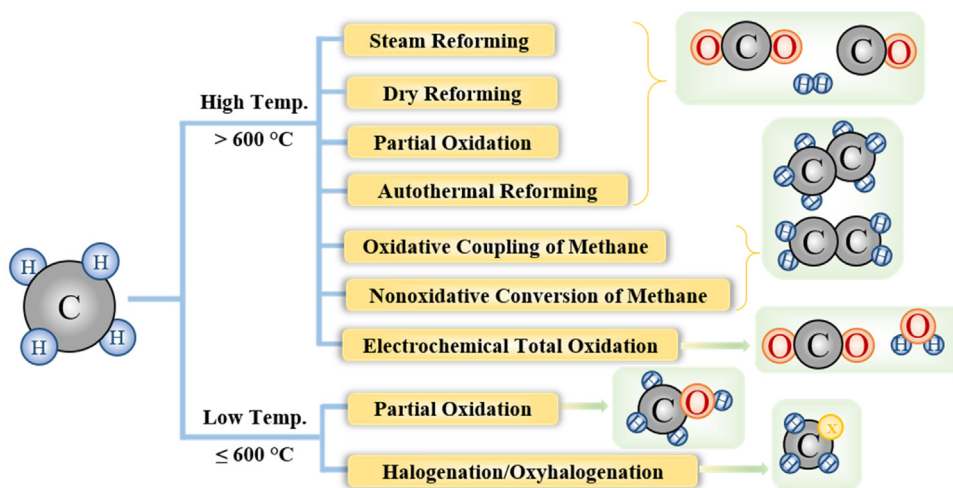


Fig. 1. Schematic of selected methane conversion processes at high- and low-temperatures.

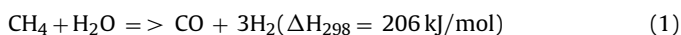
2. High temperature methane conversion processes

2.1. Thermochemical methane oxidation to CO and H₂

High temperature thermochemical processes for conversion of methane to synthesis gas (a mixture of CO and H₂) are the most developed technologies for the production of valuable intermediates. These processes include methane steam reforming, dry reforming, partial oxidation and autothermal reforming. Below, we discuss the advances and challenges associated with steam and dry reforming of methane. In the case of the partial oxidation and autothermal reforming, we refer to the cited reviews [3,14–16].

2.1.1. Methane steam reforming

Steam reforming of methane is the most developed industrial process for generation of H₂ from methane. This process involves the conversion of methane and water (steam) into H₂ and CO (rxn (1)), and is accompanied by the slightly exothermic water gas shift reaction (WGS) (rxn (2)), which converts CO and steam into CO₂ and hydrogen.



It is mainly catalyzed by transition metals, with Ni being the most commonly used industrially due to its high activity toward C–H bond activation in methane and low cost [6,9]. It has been well-established using both experiments and theory that at high operating temperatures of greater than 550 °C, the rate limiting step in methane steam reforming on Ni is C–H bond activation [17–20]. C–H bond activation in methane is surface structure sensitive with Ni under-coordinated edge sites exhibiting a lower energy barrier for this step when compared to the well-coordinated Ni terrace sites. Density functional theory (DFT) studies have also suggested that at lower temperatures (~500 °C) the formation of adsorbed CO* from adsorbed C* and O* atoms (C* + O* ⇒ CO*) becomes rate limiting for the process [21].

The major challenges with steam reforming of methane using Ni-based catalysts include: (i) catalyst deactivation due to carbon formation, (ii) catalyst deactivation due to impurities in the methane feed, such as sulfur, and (iii) sintering of the Ni particles at high operating temperatures that leads to a decrease in the active surface area, thus lower catalytic activity over time [22,23]. The carbon-induced deactivation of Ni has been studied extensively [6,9,22,24–34]. For example, it has been demonstrated using in-situ

transition electron microscopy (TEM) and DFT studies that carbon deposits are formed by the diffusion of carbon atoms on the surface of the Ni particles and their subsequent binding to carbon nucleation centers [27,29]. These studies also showed that carbon nucleation originated on under-coordinated, edge surface sites of Ni, which as we discussed above are also the most active for C–H bond activation [27,29]. An increase in the concentration of steam in the feed can alleviate this problem by enhancing the rate of carbon oxidation, however, this approach introduces a number of operational challenges, including an increase in the operational cost [6,9]. Improving the carbon-tolerance of Ni catalysts via promotion with alkaline metals or alloying with other metals have been explored as potential solutions to this challenge [30,35–42]. A number of efforts that utilize a combined experimental/theoretical approach have been instrumental in determining the mechanism that leads to carbon poisoning, and in proving insights on developing carbon-tolerant catalysts for this process [6,31,34,43]. For example, Nikolla and co-workers have shown that alloying Ni with a small amount of Sn (forming a Sn/Ni surface alloy) can lead to changes in the energetics associated with C–O bond formation versus C–C bond formation on the surface, consequently effecting the C-induced deactivation of the Ni catalyst [31]. Fig. 2a shows the reaction energies associated with methane steam reforming on Ni(111) obtained using DFT calculations [31]. This plot suggests that there are two thermodynamically stable sinks for the adsorbed C* atoms formed on the Ni surface from C–H bond activation in methane: (i) formation of adsorbed CO* and then CO₂ from the reaction with adsorbed O* atoms, or (ii) the reaction with other adsorbed C* atoms on the surface to form extended carbon structures that deactivate the catalyst. Fig. 2b and c shows that while the paths for formation of C–C and C–O bond on monometallic Ni are energetically comparable; this behavior changes when the Ni surface is modified with Sn atoms. In the case of Ni/Sn surface alloy, the C–C bond formation path becomes less energetically favorable than C–O bond formation leading to preferential removal of the C atoms from the surface forming CO or CO₂ instead of extended carbon structures. Nikolla and co-workers demonstrated experimentally that the Sn/Ni surface alloy led to a more carbon-tolerant catalyst than monometallic Ni during steam reforming of methane [31,34]. They also showed using energy loss near edge spectroscopy (ELNES), Auger electron spectroscopy (AES) studies along with DFT calculations that the changes in the C and O chemistry on Sn/Ni alloy surface as compared to monometallic Ni were due to Sn-induced electronic changes on the surface Ni atoms, in addition to the Sn-induced geometric effects (breaking the surface ensembles

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