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Progress in the direct catalytic conversion of methane to fuels and chemicals

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ABSTRACT

This paper reviews the state-of-the-art in catalytic processes to convert methane (a major component of natural gas) to more valuable hydrocarbons as fuels or chemicals. The scope is restricted to "direct" conversion, meaning that processes involving synthesis gas as an intermediate are not considered. Oxygenated products (e.g., alcohols) are also not considered. In all cases, the processes are concerned with catalytic dehydrogenation. The two most widely studied processes are oxidative coupling of methane (OCM) and methane dehydroaromatization (MDA). After reviewing the relevant catalysis literature, the paper goes on to review reactor implementations. Hydrogen- and/or oxygen-permeable membranes can potentially play valuable roles in improving methane conversion and product yields. Despite over 30 years of research, there are still no direct-conversion processes that can compete commercially with methane reforming followed by processes such as Fischer–Tropsch synthesis. Thus, the future practical development and deployment of OCM and MDA will rely on the research and development of advanced catalysts and innovative processes. The present review helps to document the foundation on which the needed development can build.

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1. Introduction

The growing availability of low-cost and domestically sourced natural gas leads to increased interest in its conversion to more-valuable fuels and chemicals. Although natural gas is a mixture of small hydrocarbons and other components such as sulfur compounds, the dominant component is methane. This review focuses on the conversion of methane alone, where numerous research and development challenges remain to be met and overcome. To narrow the scope even further, the review is particularly concerned with the direct conversion of methane to hydrocarbons, not to oxygenated products such as alcohols or intermediates such as synthesis gas (i.e., CO and H_2). The term direct conversion here refers to the processes that do not involve the intermediate production of synthesis gas. In other words, “direct” means that reforming agents (i.e., H_2O and/or CO_2) are not added, or are added in very low levels that are not intended as reforming agents. Such low-level reforming agents can also be produced as reaction intermediates within the process, and can participate in some reforming chemistry within a so-called “direct” process. Previous authors have used a similar definition [1,2].

Essentially all such direct methane conversions require dehydrogenation, with details depending on the desired products. Because its regular tetrahedron structure forms a perfectly symmetric zero dipole moment, methane is a very stable molecule. Without any functional groups to facilitate the chemical attacks, methane activation requires breaking a strong C—H bond (approximately 439 kJ mol^{-1}). Thus, elevated temperatures are necessary. Although still considered to be high-temperature processes, catalysts can decrease reaction temperatures to approximately 800 °C and lower. Despite the potential value of direct dehydrogenation processes and despite considerable fundamental research, practical, commercially viable, technology remains elusive.

This review is concerned primarily with aspects of oxidative coupling of methane (OCM) and methane dehydroaromatization (MDA) [3–9]. Particular topics range from catalyst performance to innovative reactor design and development. The development and integration of permselective membranes can be important aspects of process intensification and reactor development.

A wide range of chemicals could be produced from methane. This paper focuses on the processes to form small hydrocarbons with aliphatic, olefinic, or aromatic content. The processes considered all involve ethylene formation, which may be an intermediate component to produce compounds with higher olefin, paraffin, and aromatic (e.g., benzene) content. Oligomerization of ethylene can produce higher olefins that could be used in gasoline (C_5—C_{10}) or in diesel fuel (C_{10}—C_{20}). The higher olefins can also be converted to paraffins via catalytic hydrogenation processes [10,11], leading to constituents needed for energy-dense fuels. Of course, ethylene itself is already a valuable chemical feedstock from numerous downstream processes. Oxygenates (e.g., methanol, ethanol) are not within this paper’s scope.

Processes such as Fischer–Tropsch (F–T) have been practiced commercially for decades. In this case, the methane is first catalytically reformed or partially oxidized to produce synthesis gas (primarily a mixture of H_2 and CO). The synthesis gas is then further processed to deliver a wide range of hydrocarbon or oxygenated products. However, assuming that a hydrocarbon product is desired, the sequence of first oxidizing to syngas and then reducing to the product has inherent inefficiencies. Nevertheless, despite any such inefficiencies, these processes are practical and industrially viable [12].