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Direct methane conversion routes to chemicals and fuels

M.C. Alvarez-Galvan, N. Mota, M. Ojeda, S. Rojas, R.M. Navarro, J.L.G. Fierro*

Instituto de Catálisis y Petroleoquímica (CSIC), C/Marie Curie 2, Cantoblanco, 28049 Madrid, Spain

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ABSTRACT

This paper addresses the options developed over the past two decades for the conversion of methane into valuable chemicals and fuels while avoiding the high energy requirements of the steam reforming process for producing H_2/CO mixtures. Several aspects of the approaches undertaken accordingly are briefly examined here. Each option has its own set of limitations. Nonetheless, the cost-effective separation of useful products is a common denominator across the board in these processes, with the other most important issue being the separation of oxygen from air, requiring C–H bond activation by oxygen. The widespread use of methane for producing fuels and chemicals appears to be within reach, but current economic uncertainties limit both the amount of research activity and the implementation of emerging technologies, although the extensive use of methane for the production of fuels and chemicals is expected to become a reality very soon.

1. Introduction

Methane is the main component of natural gas (NG), landfill gas and a by-product from oil refining and chemical processing. It has an enormous potential value as a source of clean fossil energy or as a raw material provided it can be brought to the point of use economically. NG reservoirs are large and widespread throughout the world, mainly in the Middle East and Russia, although other areas also have their fair share. The estimated reserves at the end of 2006 amounted approximately to 6300 trillion cubic feet [1], but the technology for the conversion of these reserves into chemicals and liquid fuels remains as yet elusive due to the extremely high stability of the C–H bonds in the CH_4 molecule. The mastery of methane chemistry would provide chemicals and liquid fuels, presenting an alternative to petroleum in these applications and enabling the use of a plentiful, though often remote, natural gas that is currently uneconomical to transport to target markets. In addition, it could also reduce the severe greenhouse effect of CH_4 [2] (21 times higher than the equivalent volume of CO_2) or the gas flaring associated with petroleum production, and it might even provide a way of upgrading landfill gas.

Many concepts have been developed for improving the industrial processes that convert methane into olefins, higher hydrocarbons and gasoline via indirect and direct conversion processes. However, these industrial technologies involve expensive separation steps and/or require high temperatures, usually above 600 °C, with the corresponding high energy consumption. On the one hand, direct methane conversion removes this requirement and consequently improves the economy of the process; on the other hand, since methane is a very stable molecule, its reactions have generally recorded high activation energy values, and once activated it is difficult to keep the reaction within pre-determined limits [3–5]. The unfavourable thermodynamics for methane self-interaction reactions has led us to conclude that without strong oxidants it would be difficult to convert methane into higher hydrocarbons at moderate temperatures using conventional catalytic approaches.

Currently, two viable large-scale approaches for converting methane to liquid hydrocarbons are being used: the methanol-to-gasoline (MTG) route and Fischer–Tropsch (FT) synthesis. Both processes begin with the production of synthesis gas (H_2/CO mixtures) from methane, which is a high-temperature, endothermic and costly operation [6]. Generally speaking, the steam reforming process involves two reactions, namely, the splitting of hydrocarbons with steam (Eq. (1)) and water gas shift (WGS) (Eq. (2)):

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H^\circ_{298K} = +206.2\,\text{kJ/mol} \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H^\circ_{298K} = -41.2\,\text{kJ/mol} \tag{2}$$

Direct methods for the conversion of methane to useful chemicals and fuels circumvent the extremely expensive intermediate syngas step [7]. Conceptually, direct methods should have a distinct economic advantage over indirect methods, but to date no direct processes have reached a commercial stage. Product yields are generally smaller [8] when operating in a single-pass mode, which makes separations difficult and costly.

Here, we offer an overview of recent developments relevant to the low- and high-temperature activation of methane, in either the

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* Corresponding author. Tel.: +34 91 585 4769; fax: +34 91 585 4760.
E-mail address: jlgfierro@icp.csic.es (J.L.G. Fierro).

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presence or absence of oxygen, with the aim being to explore their implications for the future. The widespread use of methane for the production of fuels and chemicals appears to be near, but current economic uncertainties limit both the amount of research activity and the implementation of emerging technologies, although the extensive use of methane for the production of fuels and chemicals is expected to become a reality very soon.

2. Oxidative processes for methane conversion

2.1. Oxidative coupling of methane to higher hydrocarbons

The oxidative coupling of methane (OCM) involves the reaction of CH_4 and O_2 over a catalyst at high temperatures to form C_2H_6 as a primary product and C_2H_4 as a secondary product. Unfortunately, both the CH_4 and the C_2H_4 may be converted to CO_2, and the single-pass combined yield of C_2H_4 and C_2H_6 (C_2 products) is limited to about 25%. In the OCM process at around 800 °C, the following selective (Eqs. (3)–(5)) and non-selective (Eq. (6)) reactions occur simultaneously:

$$2CH_4 + 1/2O_2 \rightarrow C_2H_6 + H_2O \quad (\Delta H^\circ = -174.2\,\mathrm{kJ/mol}) \tag{3}$$

$$C_2H_6 + 1/2O_2 \rightarrow C_2H_4 + H_2O \quad (\Delta H^\circ = -103.9\,\mathrm{kJ/mol}) \tag{4}$$

$$C_2H_6 \rightarrow C_2H_4 + H_2 \quad (\Delta H^\circ = +114.6\,\mathrm{kJ/mol}) \tag{5}$$

$$C_xH_y + O_2 \rightarrow CO_2 + H_2O + \text{large amount of heat} \tag{6}$$

Since the pioneering work of Keller and Bhasin [9], a large body of work has been developed over the past twenty years as a potentially interesting process for upgrading natural gas. Many metal oxide catalysts have therefore been tested for this reaction. The catalysts can be grouped as: (i) oxides of groups 4 and 5 metals; (ii) oxides of group 3 metals; (iii) oxides of group 2 metals; (iv) oxides of group 1 metals; (v) lanthanide-based oxides; and (vi) transition metal oxides. The work already done in OCM reaction with the (i)–(vi) categories of catalysts up to 1993 has been reviewed and discussed in some detail [8,10].

Unfortunately, both CH_4 and C_2H_4 can be converted to CO_2, and the single-pass combined yield of C_2H_4 and C_2H_6 (C_2+ products) appears to be limited. In fact, an upper theoretical limit has been reported of about 30% yield to C_2 at 1 bar and O_2/CH_4 molar ratio of 0.5 [11,12]. Over the better catalysts, which include SrO/La_2O_3 and $Mn/Na_2WO_4/SiO_2$, a C_2 selectivity of about 80% can be achieved at a CH_4 conversion of 20% [13]. About half of the C_2 is C_2H_4 and half is C_2H_6, although the C_2H_4/C_2H_6 ratio can be enhanced by using a second catalyst. Still better performances have been recently reported for the Mn/Na_2WO_4 catalyst, with a C_2+ yield being achieved when using a CH_4/O_2 ratio of 5 and steam as diluent in the feed stream [14]. This catalyst records good stability for periods on stream up to 100 h (66–61% selectivity to C_2+ and C_2+ yield of 24.2–25.4%). The high C_2 selectivity is almost always achieved under oxygen limiting conditions; thus, the specific activity of the catalyst is not a factor. As the overall reaction is exothermic, a zone within the catalyst bed may be 150–300 °C hotter than the external temperature. Heat management, therefore, is a serious engineering problem. This is complicated by the fact that the metals normally used for the construction of reactors catalyze the total combustion of methane.

The reaction network is interesting from a fundamental perspective because it is an example of a heterogeneous–homogeneous system [15]. Methyl radicals formed at the surface of the catalyst enter the gas phase where they combine to form ethane. At atmospheric pressure, this coupling occurs mainly in the void space between catalyst particles. In addition to coupling, the gas phase radicals may enter the chain reactions that result in the formation of CO and subsequently CO_2. A simplified reaction scheme is presented in Fig. 1. Isotopic labelling experiments have shown that at small conversion levels most of the CO_2 is derived from CH_4, but at commercially significant conversion levels C_2H_4 would be the dominant source of CO_2. Additional experiments have shown that this occurs mainly via a heterogeneous reaction. One of the challenges in catalyst development is to modify a material so that the secondary reaction of C_2H_4 will be inhibited while the activation of CH_4 will still occur. There is no inherent reason for these two reactions to take place on the same types of sites.

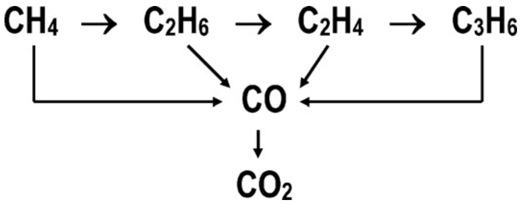

Fig. 1. Simplified reaction mechanism for the oxidative coupling of metane.

Both porous ceramic and dense ionic membranes and mixed-conducting ones have been applied for the OCM reaction [16]. Porous membranes such as alumina, zirconia, or Vycor glass have high stability for the reactions but low oxygen selectivity. By contrast, the oxygen selectivity for dense ionic or mixed-conducting oxide membranes is theoretically infinite and, therefore, air can be used as an oxygen source without contaminating the products with nitrogen and nitrogen oxides. A novel kind of hollow-fibre ceramic membranes, consisting of a dense, thin separating layer integrated with a porous substrate of the same material, record much higher oxygen permeation rates than the disc-shaped membranes [17], and hence appear particularly suited to commercializing mixed-conducting membrane reactors for OCM. Although the membrane concept is particularly suited to increasing CH_4 conversion, the major problem to be solved is the increase in the permeation rate.

In spite of the work existing on OCM, this technology has not yet been commercialized because there are important hurdles to be overcome in this process: (i) since C_2 hydrocarbons are much more reactive than methane, high selectivity in the process can be obtained only at low methane conversion; (ii) as the reaction is conducted at high temperatures (ca. 800 °C), a catalyst with high thermal and hydrothermal stability is required; (iii) using a low O_2/CH_4 molar ratio in the feed, the selectivity to C_2 hydrocarbons is high, but CH_4 conversion is rather low; and (iv) due to the low concentration of ethylene in the exit stream the cost of its separation is high, thereby rendering its separation uneconomical.

2.2. Partial oxidation of methane to oxygenates

The direct conversion of methane into C_1 oxygenates (CH_3OH and HCHO) involves partial oxidation under specific reaction conditions. This reaction operates at 350–500 °C under fuel-rich mixtures with the oxidant to minimize the extent of combustion reactions. Under these conditions, the gas-phase oxidation reactions of methane operate at high temperatures, which are detrimental to the control of selectivity to C_1 oxygenates.

$$CH_4 + 1/2O_2 \rightarrow CH_3OH(HCHO) \tag{7}$$

Accordingly, considerable efforts have been made to develop active and selective catalysts for the partial oxidation of methane. High selectivities to methanol have already been obtained by working under non-catalytic reaction conditions [18]. The Huels process uses cold-flame burners operating at 60 bar, with a selectivity of 71% to methanol and 14% to formaldehyde, and a recycle ratio of 200 to 1 [19]. The adiabatic temperature rise under these condi-