Process intensification in the catalytic conversion of natural gas to fuels and chemicals

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Abstract

This paper explores alternative technologies for the conversion of natural gas to higher-value products. Because of methane's chemical stability, all practical processes require elevated temperature (e.g., $T > 700$ °C) and catalysts to activate the methane. Some approaches are mature and widely practiced at the commercial scale (e.g., steam reforming and Fischer–Tropsch synthesis). Others are emerging, based on laboratory-scale experimentation (e.g., oxidative coupling of methane). In all cases, the present paper is concerned with aspects of process intensification, seeking chemical methods and reactor implementations that can improve overall performance. Performance metrics include reactor size, energy efficiency, conversion rates, and product selectivity. Process intensification approaches include integrated microchannel reactors and heat exchangers as well as a range of permselective membranes.

Keywords:

Gas-to-liquids, Catalysis, Methane reforming, Fischer–Tropsch, Oxidative coupling of methane, Process intensification, Membrane reactors, Microchannel reactors

1. Introduction

In today's energy marketplace, natural gas is, and is projected to be, plentiful and inexpensive. Because of its relatively low carbon footprint, gas will surely play increasingly prominent roles in combustion. Ongoing research will likely lead to more efficient and environmentally friendly combustion processes. At the same time, natural gas is likely to be an increasingly important feedstock for the production of logistics fuels and commodity chemicals. The primary objective of this paper is to consider processes that can effectively transform natural gas into other higher-value hydrocarbons. This topic is the subject of much current interest and research [1–10].

Converting natural gas to liquids (GTL) is certainly not new. Broadly speaking, two routes have been scaled to commercial levels. One is Fischer–Tropsch [11] the other is methanol synthesis [12]. In both cases, the methane is first reformed to synthesis gas (i.e., H_2 and CO). However, if a hydrocarbon product is desired, the

initial oxidation to syngas represents an inherent inefficiency. Thus, there is at least the potential to develop more efficient and direct dehydrogenation processes. Processes such as oxidative coupling of methane (OCM) show promise, but have yet to achieve commercial viability.

All practical GTL processes require elevated temperature (e.g., $T > 700$ °C) and product-selective catalysts. Innovative research is leading to new catalyst materials and microstructures (e.g., nanorods or nanofibers) that improve performance. There is general agreement that “process intensification” concepts will contribute to the development of new processing approaches and reactor technologies. This paper is concerned mostly with opportunities for novel process and reactor concepts, especially considering the beneficial close coupling of chemical and thermal interactions.

1.1. Economic considerations

Natural gas will surely continue to have major impacts on the production of energy and chemicals. However, because of highly volatile markets and prices for natural gas and oil, planning the best uses for the gas is difficult. Figure 1 shows the history of gas and oil prices for the past ten years. There are periods where

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Figure 1: Comparison of oil and gas prices from 2005 through 2015. The historical data was downloaded from the U.S. Energy Information Agency (<http://www.eia.gov>).

the prices appear to be correlated, rising and falling together. There are periods where the gas price is relatively high while the oil price is low, and there are periods with just the opposite relationship. As of the present writing (early 2016), both oil and gas prices are at historic lows, but gas prices appear to be rising while oil prices are not.

Maitlis and de Klerk describe the impact of market volatility in terms of the “haitus effect” [13, 14]. Developing new, clean, sustainable processes requires long-term (order of 20 years or more) research and development. However, investment decisions, and thus research support, are often made on much shorter timescales. A consequence, for example, is that in periods of relatively low oil prices, interest in converting gas to fuels wanes and investment is low. During such periods, research loses momentum and knowledgeable people follow other pursuits. As periods of relatively high oil prices return, restarting the research and development can be slow and inefficient. In the long term, it is reasonably clear that natural gas will continue to play a central role in the production of logistics fuels and commodity chemicals. Thus, finding ways to sustain long-range research and development is likely to deliver societal, environmental, and economic benefits.

1.2. Combustion perspective

This paper is written in the context of a plenary lecture for the 36th International Symposium on Combustion (Seoul, Korea, July 2016). Of course, the Com-

bustion Community is concerned primarily with the efficient and complete oxidation of fuels, not the synthesis or transformation of fuels. Nevertheless, with sustained research in hydrocarbon chemistry over the past half century, this community has developed core capabilities that can play valuable roles in the alternative uses of fossil fuels, especially natural gas. Thus, there are interesting opportunities to build on the strong foundation of combustion research.

A quick electronic search of the program for the 35th International Symposium on Combustion reveals 471 occurrences of “methane,” 155 occurrences of “syngas,” and 166 occurrences of “catalysis.” At the 26th Symposium (1996), a colloquium was introduced on “Materials Synthesis and Catalytic Combustion.” A new colloquium on “New Concepts in Combustion Technology” was introduced at the 29th Symposium (2002). Beginning at the 30th Symposium (2004), there began to be discussion of solid-oxide fuel cells (SOFC) with hydrocarbon fuels [15]. Although fuel cells consume fuels to produce electricity and heat, they also involve new concepts in electrochemistry, ion-transport membranes, in-situ catalytic reforming, and small-channel reactive flow. All of these topics are relevant for advanced processes to transform natural gas and synthesize fuels and chemicals. At the same time, understanding and appreciating aspects of the process-intensification concepts that are proving to be valuable in the chemical processing context may be adaptable to advanced combustion technologies.

1.3. Natural gas and methane

Although methane is its dominant component, it is well known that natural gas is a mixture of small hydrocarbons and usually impurities such as sulfur compounds. In combustion processes, these non-methane components are often negligible for many purposes. However, in catalytic processes, the non-methane components can play much larger roles. The present paper does focus on methane, especially in the context of discussing process chemistry. Also, as is evident from the cited literature, much laboratory-scale research does focus on methane as a natural-gas surrogate. Nevertheless, practical technology development needs to be cognizant of the variable composition and added complexities associated with natural gas.

2. Methane reforming

Alternative forms of synthesis gas (i.e., mixtures of H_2 and CO) play foundational roles in the production of

chemicals (e.g., olefins, ethers, ammonia, alcohols) and synthetic logistics fuels (e.g., via Fischer–Tropsch processes). As measured in the megawatt thermal equivalent, the current annual syngas production exceeds 100,000 MWth and is estimated to double in the next five years.

Reforming to produce synthesis gas plays a central role in large-scale hydrogen production for a variety of purposes, including the upgrading of petroleum-derived fuels. As documented by Rostrup-Nielsen and colleagues [16, 5], catalytic steam reforming has been the subject of research since the early 1900s. However, it was not until the 1960s that large-scale, high-pressure, tubular steam reformers were used industrially. Prior to the development of methane reforming processes, hydrogen was produced by cracking petroleum-derived naphtha.¹

As is well known and widely practiced, catalytic methane reforming can be accomplished by one of three processes, or a combination of processes. Stated globally, endothermic steam reforming (SMR) can be expressed as

Dry reforming (DRM) can be expressed as

Both SRM and DRM are strongly endothermic. Catalytic partial oxidation (CPOX), which is exothermic, can be represented globally as

A thermally neutral combination of the three processes is known as autothermal reforming (ATR). All these processes operate at elevated temperature ($T > 700^\circ\text{C}$) and catalysts are needed. Ni-based catalysts are typical for SMR and precious-metal catalysts (e.g., Rh) are typical for CPOX. Especially in the case of SMR, a large excesses of H_2O is used to mitigate catalyst-fouling carbon deposits.

2.1. CO-H_2 ratio

Although the alternative methane reforming routes can all achieve high CH_4 conversion and syngas yield,

¹Heavy naphtha is a mixture of petroleum distillates composed of paraffins, aromatics, and naphthenes in the range of C_6 to C_{12} . Light naphthas (C_5 and C_6) were used directly for blending into gasoline and related products.

the resulting syngas compositions are different. Depending on the intended use for the syngas, the H_2/CO ratio is very important.

Steam reforming (Eq. 1) produces a H_2 -rich gas stream together with relatively low levels of CO. Because steam reformation is often intended to produce high-purity H_2 , the reformer itself is typically followed by downstream water-gas-shift ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$, WGS) reactors to convert CO to CO_2 and H_2 . The H_2 is usually purified further, such as with pressure-swing-adsorption (PSA). Pure H_2 is a valuable commodity that can be used for ammonia synthesis, petroleum refining, or in fuel-cell applications. Worldwide, approximately 50 metric tonnes of H_2 are produced and consumed annually.

Dry reforming (Eq. 2) yields a H_2/CO ratio of unity, which is an ideal stoichiometry for applications such as the production of acetic acid, which may be represented globally as

Partial oxidation (Eq. 3) yields a H_2/CO ratio of two, which is the ideal ratio for methanol synthesis or Fischer–Tropsch processes. Methanol synthesis can be represented globally as

The Fischer–Tropsch process can be written globally as

where $(-\text{CH}_2-)_n$ indicates a large alkane.

The syngas composition (i.e., H_2/CO ratio) can be adjusted by combining steam reforming and dry reforming. Written globally, the combined processes may be represented as

where x represents the amounts of H_2O and CO_2 in the feed stream. Dry reforming and combined dry and steam reforming have some appeal in the context of capturing and reusing the carbon in CO_2 . Although this may offer some environmental benefits, the production of CO_2 from fossil-fuel power plants massively exceeds the need for CO_2 in reforming processes. Thus, the primary reason to use CO_2 in reformation processes is to control the CO-H_2 content in the syngas. Nevertheless, there are certainly benefits to designing and locating reformers that can take advantage of available CO_2 .

Because both steam and dry reforming processes operate at high temperature, a great deal of energy is required to support the reforming endotherm. The needed

energy is typically generated by burning a substantial fraction of the natural gas, representing a significant process inefficiency. Thus, attention to overall thermal management in the design and operation of reformers is very important. One approach is to develop recuperators that use hot post-combustion flue gases as efficiently as possible. Another approach is to combine or closely couple exothermic partial-oxidation processes with endothermic reforming. The combination of steam reforming and partial oxidation can be represented globally as

Although autothermal reforming can assist with thermal balances, there are other important, and often competing, considerations. One is the resulting syngas composition, which is influenced by the intended downstream use of the syngas. Another is the need for pure oxygen. Air separation, which is usually accomplished upstream of the reformer, is also energy intensive. As discussed subsequently, there are significant opportunities for *process intensification* in the combination of reforming and partial-oxidation processes.

2.2. Process tradeoffs

Reformer operational parameters include feed composition, temperature, and pressure. In consideration of high-pressure downstream processes (e.g., Fischer-Tropsch synthesis), industrial-scale reformers typically operate at elevated pressure ($20 \leq p \leq 40$ bar). Post-reformer syngas compression is expensive [17]. The high-temperature durability of stainless steel reactor materials typically limits the operating pressure to around 40 bar [18].

From the chemistry perspective (i.e., Le Châtelier's principle), neither H_2O nor CO_2 reforming or partial oxidation processes are favored at high pressure. Figure 2a shows that increasing pressure from 1 bar to 25 bar decreases the CH_4 conversion significantly. The figure also shows that increasing temperature always increases conversion. However, at elevated pressure the temperature needs to be in the range of $900 \leq T \leq 1000$ °C to achieve significant CH_4 conversion. As shown in Figure 2b, another way to increase the CH_4 conversion at high pressure is to operate with excess H_2O . With excess H_2O , water-gas-shift processes act to convert CO to H_2 . As a result, H_2 selectivity increases while CO selectivity decreases. However, the excess H_2O reduces the methane concentration, thus reducing the syngas production rates.

Figure 2: Influence of temperature, pressure, and feed composition on the equilibrium methane conversion in steam reforming processes. a) Effect of pressure with $\text{CH}_4/\text{H}_2\text{O} = 1$. b) Effect of $\text{CH}_4/\text{H}_2\text{O}$ ratio at $p = 25$ bar.

With respect to pressure and temperature dependencies, partial oxidation behaves similarly to the steam reforming chemistry. That is, increasing pressure decreases both methane conversion and H_2 and CO selectivity. Increasing O_2 in the feed increases methane conversion toward the unwanted total oxidation products [19].

2.3. Reforming catalysts

Catalyst performance (i.e., reaction rates, methane conversion, product selectivity and yield) greatly influences reactor design and operating conditions. A number of transition metals, including Rh, Ni, Ir, Ru, Pt and Co, are known to be active as methane reforming catalysts [3]. The active metals are usually dispersed as small (nanoscale) particles that are supported on porous-ceramic supports, such as Al_2O_3 . Among these transition metals, Rh and Ru are known to be the most active and stable. However, at the industrial scale, Ni is usually preferred because of its lower cost. Unfortunately, Ni also has the highest potential to form catalyst-deactivating coke and carbon deposits [5]. The coking propensity is greatest for Ni, with the coking propensity of the other metals being ordered as $\text{Ni} \geq \text{Pd} \gg \text{Ir} \geq \text{Pt} \geq \text{Ru} \approx \text{Rh}$.

Transition metals and mixtures (e.g., Rh-Pd, Rh-Pt) on oxide supports are also used for methane partial oxidation. Although Ni can be used for CPOX, its rela-

Table 1: Heterogeneous reaction mechanism for CH₄ reforming on a Ni-based catalyst [24, 25, 32]. The phases are noted in parentheses, with (g) representing the gas and (Ni) representing the nickel surface.

1.	$\text{H}_2(\text{g}) + 2(\text{Ni}) \rightleftharpoons \text{H}(\text{Ni}) + \text{H}(\text{Ni})$
2.	$\text{O}_2(\text{g}) + (\text{Ni}) + (\text{Ni}) \rightleftharpoons \text{O}(\text{Ni}) + \text{O}(\text{Ni})$
3.	$\text{CH}_4(\text{g}) + (\text{Ni}) \rightleftharpoons \text{CH}_4(\text{Ni})$
4.	$\text{H}_2\text{O}(\text{g}) + (\text{Ni}) \rightleftharpoons \text{H}_2\text{O}(\text{Ni})$
5.	$\text{CO}_2(\text{g}) + (\text{Ni}) \rightleftharpoons \text{CO}_2(\text{Ni})$
6.	$\text{CO}(\text{g}) + (\text{Ni}) \rightleftharpoons \text{CO}(\text{Ni})$
7.	$\text{O}(\text{Ni}) + \text{H}(\text{Ni}) \rightleftharpoons \text{OH}(\text{Ni}) + (\text{Ni})$
8.	$\text{OH}(\text{Ni}) + \text{H}(\text{Ni}) \rightleftharpoons \text{H}_2\text{O}(\text{Ni}) + (\text{Ni})$
9.	$\text{OH}(\text{Ni}) + \text{OH}(\text{Ni}) \rightleftharpoons \text{O}(\text{Ni}) + \text{H}_2\text{O}(\text{Ni})$
10.	$\text{O}(\text{Ni}) + \text{C}(\text{Ni}) \rightleftharpoons \text{CO}(\text{Ni}) + (\text{Ni})$
11.	$\text{O}(\text{Ni}) + \text{CO}(\text{Ni}) \rightleftharpoons \text{CO}_2(\text{Ni}) + (\text{Ni})$
12.	$\text{HCO}(\text{Ni}) + (\text{Ni}) \rightleftharpoons \text{CO}(\text{Ni}) + \text{H}(\text{Ni})$
13.	$\text{HCO}(\text{Ni}) + (\text{Ni}) \rightleftharpoons \text{O}(\text{Ni}) + \text{CH}(\text{Ni})$
14.	$\text{CH}_4(\text{Ni}) + (\text{Ni}) \rightleftharpoons \text{CH}_3(\text{Ni}) + \text{H}(\text{Ni})$
15.	$\text{CH}_3(\text{Ni}) + (\text{Ni}) \rightleftharpoons \text{CH}_2(\text{Ni}) + \text{H}(\text{Ni})$
16.	$\text{CH}_2(\text{Ni}) + (\text{Ni}) \rightleftharpoons \text{CH}(\text{Ni}) + \text{H}(\text{Ni})$
17.	$\text{CH}(\text{Ni}) + (\text{Ni}) \rightleftharpoons \text{C}(\text{Ni}) + \text{H}(\text{Ni})$
18.	$\text{O}(\text{Ni}) + \text{CH}_4(\text{Ni}) \rightleftharpoons \text{CH}_3(\text{Ni}) + \text{OH}(\text{Ni})$
19.	$\text{O}(\text{Ni}) + \text{CH}_3(\text{Ni}) \rightleftharpoons \text{CH}_2(\text{Ni}) + \text{OH}(\text{Ni})$
20.	$\text{O}(\text{Ni}) + \text{CH}_2(\text{Ni}) \rightleftharpoons \text{CH}(\text{Ni}) + \text{OH}(\text{Ni})$
21.	$\text{O}(\text{Ni}) + \text{CH}(\text{Ni}) \rightleftharpoons \text{C}(\text{Ni}) + \text{OH}(\text{Ni})$

tively lower activity requires temperatures in excess of 750 °C. Unfortunately, at these temperatures Ni reacts with Al₂O₃ to form NiAl₂O₄, leading to rapid deactivation. Fresh catalysts can deliver high partial-oxidation activity that is close to equilibrium limits. However, similar to steam and dry reforming, coke formation can be a significant problem for CPOX processes. The coke propensity is ordered as Ni > Pd > Rh > Ru > Pt ≈ Ir [19, 20].

2.4. Reforming kinetics

The discussion to this point in the paper has considered only global reactions. Of course, the actual processes are far more complex, with quantitative predictive understanding depending on detailed mechanisms composed of elementary reaction steps [21–31]. As an example, Table 1 lists a 21-step mechanism that represents catalytic interactions of CH₄, H₂, O₂, H₂O, CO, and CO₂ on Ni surfaces [24, 25, 32].

Unlike global reactions that consider only gas-phase species (e.g., global steam-reforming, Eq. 1), the detailed mechanisms consider both gas-phase and surface-adsorbed species. Detailed reaction mechanisms provide a much richer description of the chemistry than the global reactions can, which has practical benefits. Note that global steam-reforming, dry reforming, partial oxidation, and water-gas-shift reactions, per se, do not appear as individual reactions in the detailed mechanisms. The detailed mechanisms capture wide process ranges, whereas a few global steps usually can not. In other words, mechanisms such as the one in Table 1 represent

the entire range of behaviors that span steam reforming, dry reforming, partial oxidation, and autothermal reforming. Although developing the elementary reaction pathways and rate expressions can be challenging, a validated elementary mechanism has very great value.

Despite the generality and practical success of detailed reaction mechanisms, there are important fundamental and practical challenges for future research. Available detailed reaction mechanisms for heterogeneous catalysis are generally restricted to applications such as methane reforming or oxidation. Even in these cases, extensions are needed. For example, although catalyst-fouling carbon deposition is a major practical issue, there is relatively little research devoted to incorporating carbon deposition into the detailed mechanisms. Feedstocks often contain sulfur compounds and sulfur can play a major role in catalyst performance. Thus, there are opportunities to extend detailed reaction mechanisms to account for sulfur [29]. Yet other examples include a wide range of process and chemical feedstocks. Detailed reaction mechanisms have not yet been developed for many industrially practiced processes. These include a range of traditional processes such as olefin production. The reaction pathways for processes such as Fischer–Tropsch synthesis or the oxidative coupling of methane (OCM) are understood qualitatively. However, detailed quantitative and predictive reaction mechanisms are generally not available.

Essentially all current reaction mechanisms are based on a mean-field approximation. That is, the surface-adsorbate activities are assumed to be represented in terms of a average coverage fractions. In fact, it is known that adsorbates can cluster into islands on catalyst surfaces. To some extent this behavior can be approximated by using rate expressions with coverage-dependent activation energies [33]. Relaxing the mean-field approximation in favor of better physical representations is difficult, but research in this direction would be highly valuable.

Although Table 1 represents the reactions as being microscopically reversible, most available reaction mechanisms represent the reactions as irreversible pairs. In this case, the microscopic reversibility is only approximately satisfied. Because most of the reactions involve surface-adsorbed species, the thermodynamic properties of those species are needed to establish equilibrium constants, and hence microscopic reversibility. The needed properties are difficult, or even impossible, to measure. In principle, ab-initio theory can be used to determine the needed thermodynamic properties [34–36]. However, such properties are certainly not generally available. There is active research devoted to esti-

mating the thermodynamic properties needed to assure microscopic reversibility [37, 38, 33, 39].

To date, research on detailed reaction mechanisms has focused on transition-metal catalysts (primarily, Pt, Pd, Rh, and Ni). However, a much wider variety of catalysts are used in industrial practice. For example, the chemistry of zeolite-based catalysts is quite different from the chemistry in precious-metal catalysts. Thus, there are important opportunities to develop detailed reaction mechanisms for other catalysts and catalyst classes. An important topic in gas-to-liquids chemistry (e.g., methane dehydroaromatization, MDA) is the development and use of bi-functional catalysts. In the case of MDA, Mo/zeolite catalysts are prominent. Methane is first activated on molybdenum-carbide sites, with subsequent oligomerization and cyclization proceeding on zeolite Brønsted-acid sites [40, 41].

To be practical, using the detailed reaction mechanisms requires a richer software infrastructure than is needed to model a few global reactions. At present there are several alternative and available software implementations. In most cases, the reaction-description taxonomy generally follows the one proposed by Coltrin, et al. [42, 43] and implemented in the CHEMKIN software [44]. Other implementations include DETCHEM² and DARS³. Most high-level computational fluid dynamics (CFD) software (e.g., ANSYS FLUENT⁴ and CD-adapco STAR-CCM+⁵) has capabilities to implement detailed reaction mechanisms that can describe heterogeneous catalysis. The CANTERA software⁶ that was developed by Prof. David Goodwin (Caltech) is different from the foregoing implementations. The CANTERA software, which is object-oriented and implemented in C++, is freely available and community supported.

The development and validation of detailed reaction mechanisms are difficult and time consuming processes. Fortunately, a variety of reaction mechanisms have been made freely available from the group of Prof. Olaf Deutschmann (Karlsruhe Institute of Technology)⁷. Reaction mechanisms can be downloaded electronically in commonly used formats. Even in cases where one of the Deutschmann mechanisms may not be entirely suitable for a particular application, it may well provide a good starting point for further extension or development.

²<http://www.detchem.com>

³<http://www.cd-adapco.com/products/star-ccm/dars>

⁴<http://www.ansys.com>

⁵<http://www.cd-adapco.com>

⁶<http://www.cantera.org>

⁷<http://www.detchem.com/mechanisms.html>

Figure 3: Carbon formation limits for graphitic carbon and surface whisker carbon on a 250 nm Ni catalyst as functions of the feed composition at 25.5 bar and 950 °C. The operating conditions span between fully dry reforming (O/C=2, H₂O/CH₄=0), fully steam reforming (H/C=4, CO₂/CH₄=0) or steam and dry reforming combined regimes. This chart is reproduced from Rostrup-Nielsen and Christiansen [5, 45].

2.5. Carbon deposits

Catalyst fouling carbon deposition is often problematic in hydrocarbon processing, including reforming. The deposits may be graphitic carbon (coke) that grows as a film on the active catalyst. The deposits may also be polyaromatic hydrocarbons (PAH), which are formed in the gas phase and deposit on the catalyst or they may be formed directly on the catalyst. Stated globally, the formation of solid carbon C(s) can follow several routes. The Boudouard reaction,

describes CO disproportionation. Other pathways include CO reduction,

and CH₄ dehydrogenation,

Nickel-based catalysts are especially prone to carbon formation. The carbon formation begins on Ni particles, followed by carbon nanotube growth with Ni at the tip of the growing nanotube. These nanotube structure are

Figure 4: Ternary chart showing the equilibrium coke limit and the H_2/CO ratio for mixtures of species containing hydrogen, carbon, and oxygen.

called “whisker” carbon [46, 47]. The whisker carbon is mechanically strong. The whiskers not only deactivate the catalyst, but can also cause catalyst pellets to fracture and break apart. Whisker growth and particle fracture lead to increasing pressure drop within the catalyst bed, eventually requiring process shutdown. After sufficiently severe degradation, catalyst regeneration may no longer be possible and the catalyst bed must be replaced.

The carbon formation can be reasonably and easily estimated from equilibrium thermodynamics. Figure 3 shows an interesting representation of the CH_4 - H_2O - CO_2 reforming operating space [5]. The primary abscissa and ordinate represent the O/C and H/C atomic ratios, respectively. The nonlinear axes on the 45° bias represent the H_2O/CH_4 and CO_2/CH_4 feed ratios. The dashed lines represent the equilibrium H_2/CO ratios of the resulting syngas at $T = 950^\circ C$ and $p = 25.5$ bar. The thick red curved lines represent different equilibrium coke limits, with the region to the left of the lines being in coking regime. The right-most line represents graphite and the left-most line represents whisker carbon. Although equilibrium estimates are useful, at least qualitatively, caution must be exercised in using a chart such as that in Fig. 3. The actual syngas composition and the coke limits depend on the particular catalyst as well as the operating temperature and pressure. Also, this chart is not designed to accommodate CPOX or ATR conditions.

Sasaki and Teraoka explored the regimes in which graphitic carbon can be formed under equilibrium conditions [48]. They represented the results in the form of ternary charts, such as the one shown in Fig. 4. The feed composition is represented in terms of its elemental composition, and the equilibrium composition is computed in the usual way by minimizing the Gibbs free energy. In the C-H-O ternary diagram (i.e., Fig. 4), the coordinates of a feed mixture having the species mole fractions X_k can be represented using the element fractions X_e of carbon ($e = C$), hydrogen ($e = H$), and oxygen ($e = O$). Because the ternary chart considers hydrogen, oxygen, and carbon, a very wide range of feed mixtures are accommodated. The element fractions are easily evaluated as

$$X_e = \frac{\sum_k X_k n_{k,e}}{\sum_{e \in \{C,H,O\}} \sum_k X_k n_{k,e}}, \quad (12)$$

where $n_{k,e}$ is number of the e th element in the k th species. The three values of X_e form the particular coordinates of the ternary chart. To be more specific, the individual X_e can be evaluated as

$$X_C = \frac{\sum_k X_k n_{k,C}}{\sum_k X_k (n_{k,C} + n_{k,H} + n_{k,O})} \quad (13)$$

$$X_H = \frac{\sum_k X_k n_{k,H}}{\sum_k X_k (n_{k,C} + n_{k,H} + n_{k,O})} \quad (14)$$

$$X_O = \frac{\sum_k X_k n_{k,O}}{\sum_k X_k (n_{k,C} + n_{k,H} + n_{k,O})} \quad (15)$$

From the definitions, it must be the case $X_C + X_H + X_O = 1$. Only two of the three X_e values are needed to enter the chart. One of the values is redundant.

Figure 4 shows contours of the equilibrium H_2/CO ratio that results from particular feed mixtures (at $T = 900^\circ C$, $p = 25$ bar). The thick red line indicates the equilibrium graphite deposition boundary. Below the line, no solid carbon is formed at equilibrium. Above the line, equilibrium carbon is stable. As an example, the “star” symbol is for an equimolar mixture of CH_4 and H_2O (i.e., the stoichiometry of Eq. 1). As can be anticipated from Eq. 1, the equilibrium H_2/CO ratio is approximately three. It is not exactly three because the equilibrium computation involves many more species than are in the single global reaction. The star symbol resides essentially on the carbon-deposition boundary, indicating a poor operating point. However, it should be noted that the equilibrium graphite line is not necessarily a conservative estimate for coke formation. That is, considering kinetic behavior on actual catalysts carbon deposits may be observed in regions below the equilibrium graphite boundary.

The syngas composition is a very important consideration, depending on the intended downstream process. For example, the H_2/CO ratio should ideally be close to two if the syngas is being fed to a Fischer–Tropsch process (Eq. 6) or is being used for methanol synthesis (Eq. 5). Figure 4 can be used to estimate the effects of alternative inlet feed mixtures on the equilibrium H_2/CO ratio.

It is important to run a reformer in a regime that effectively converts the methane and avoids coking, but also yields the desired CO/H_2 ratio. Using Ni catalysts at high pressure and temperature, coke formation is inevitable with the stoichiometric feed compositions for either steam- ($H_2O/CH_4=1$) or dry-reforming ($CO_2/CH_4=1$) processes. Thus, practical reactors are operated with excess H_2O and CO_2 . In these cases, additional heating is required for steam generation and CO_2 preheating. Also, additional downstream separation costs are required to remove H_2O and CO_2 .

2.6. Other catalyst degradation mechanisms

In addition to coke formation, there are numerous other mechanisms that act to diminish catalytic activity [49]. Degradation is usually the result of coupled chemical, thermal, and mechanical phenomena. In some cases catalyst degradation can be reversed and in other cases the degradation is irreversible. The consideration of catalyst degradation, and possible regeneration, is usually an important aspect of process design and reactor development.

Catalyst poisoning is caused by the strong adsorption of reactants, products, or the impurities on active catalytic active sites, thus blocking the desired catalytic function. In addition to physically blocking adsorption sites, adsorbed poisons may also induce deleterious changes in the electronic or geometric structure of the surface [50, 51]. For example, CO has a very high adsorption probability on Rh and Ni catalysts at low temperatures ($T \leq 500^\circ C$) [31, 33]. However, such adsorption is reversible. As temperature increases the equilibrium shifts toward lower CO adsorption and desorption rates increase.

Unlike CO, some poisoning effects can be irreversible. For example, sulfur compounds can interact unfavorably with transition-metal catalysts. In addition to strong adsorption, the sulfur can react to form metal sulfides. Such behavior is particularly active with Ni and Co catalysts. Sulfur reactivity with other metal catalysts is generally ordered as $Ni > Co > Rh > Ru > Re > Pt > Pd$ [52]. Sulfur poisoning can be severe, meaning very low levels (e.g., ≤ 1 ppm) can severely reduce the catalytic activity [53–55]. Because

sulfur is prevalent in petroleum- and bio-derived fuels, understanding and controlling sulfur-catalyst interactions is important.

There is current research on designing sulfur tolerant catalysts by modifying metal catalysts. Modifications include changing the electron deficiency of noble metals via interaction with an acidic support or introducing a secondary metal [52, 56]. Doping Ni catalysts with a second sulfur-tolerant metal such as Rh, Ru, La and B is known to increase the sulfur resistance [57–59]. Although sulfur usually decreases catalytic activity, there may also be some benefits. For example, Holdør-Topsoe has developed a process in which sulfur (H_2S) is used beneficially to reduce carbon deposits [60, 17].

Ideally, the catalysts themselves do not react. In fact, catalysts can and do undergo chemical transformations. At high temperature and in the presence of excess oxygen metal catalysts can be oxidized (e.g., Ni to NiO [61, 62], or Rh to RhO_x [63, 64]). In high-temperature H_2 -rich reducing environments, a metal-oxide catalyst can be reduced to its comparatively inactive metallic form (e.g., PdO to Pd [65]). Such relatively straightforward redox processes can often be reversed. However, catalyst regeneration requires changing operating conditions and non-productive reactor time.

Some chemical transformations are largely irreversible. Metal catalyst particles may react with the underlying ceramic (e.g., Al_2O_3 , CeO_2) support structure. A typical example is the interaction of an alumina support with Rh or Ni, forming $Rh(AlO_2)_y$ and $NiAl_2O_4$. Reactions between steam and zeolite-based catalysts can remove Al from the zeolite framework (dealuminization), causing irreversible loss of zeolite crystallinity and catalytic activity.

Especially at high temperatures active catalysts can sinter together, causing a loss of active surface area that manifests itself as effective deactivation [66–68]. High temperatures can also cause changes the support structure, decreasing the accessible surface and hence the activity [69].

Catalyst particles or pellets can be damaged mechanically as they interact physically, especially in reactors operating at high space velocities. As particles fracture, catalytic activity can decrease irreversibly. Another mechanical degradation can occur on metal reactor walls. The reaction of deposited carbon on steel reactor walls can cause a damaging effect called “metal dusting.” Although not affecting the catalyst directly, reactor damage of any sort is problematic.

Broadly speaking, most degradation processes are exacerbated at higher temperatures. Thus, an important aspect of process and reactor design is the control of

temperature and temperature variations. As discussed subsequently, novel reactor-design approaches that include microchannel reactors and permselective membranes can assist in achieving thermal control.

3. Reformer reactor technology

3.1. Industrial-scale reformers

Figure 5 illustrates a large-scale combustion-fired steam reformer. The catalysts are housed in long narrow tubes, which are typically around 10-20 cm in diameter and 10-12 m long. Such reformers may have several hundred catalyst tubes. In this configuration, the heat is provided by down-fired natural-gas flames. The combustion exhaust gases are captured in large rectangular ducts called “coffins.” The hot exhaust gases are used in recuperating heat exchangers to preheat the methane-steam feed stream.

The feed mixture enters the catalyst tubes at the top and flows downward through the packed-bed catalysts. The methane-steam flow rate (and hence the magnitude of the endotherm) and the combustion heat must be balanced such as to maintain the catalyst bed above 800 °C. As illustrated in the inset, the bed is typically configured as catalyst-impregnated ceramic pellets. The pellet design and the catalyst packing depends on operational tradeoffs, such as between effective catalyst area and flow pressure drop.

Reformers can be designed with alternative burner configurations, including top fire, bottom fire, terrace fire, and side fire [5, 70]. An important consideration is to establish high heat flux while maintaining temperature uniformity throughout the catalyst bed. Yet another consideration is concerned with interactions between the flame and the tube materials. Because the metal tubes are directly exposed to the flame, the high-temperature oxidizing environment can irreversibly corrode and damage the reformer tubes. Nonuniform temperature profiles and local hot spots can also cause performance and materials degradation, including catalyst activity loss and particle fracture.

3.2. Process intensification in reformers

Process intensification is broadly defined in terms of finding novel approaches that significantly improve performance [71]. One avenue is to combine unit processes in ways that greatly increase energy efficiency or reduce plant size. For example, consider two unit processes, one of which is exothermic and the other is endothermic. An intensified process seeks to closely couple the two processes such that the excess heat from

the exothermic process can be used directly to support the endothermic process. Microchannel heat exchangers and reactors offer a route to process intensification. Other opportunities are associated with membranes reactors that integrate separation processes.

Figure 6 illustrates a microchannel reactor that combines an exothermic process (say methane combustion) with an endothermic process (say steam reforming) [75]. Another alternative is to flow waste heat from one process through one layer of channels to support endothermic catalysis in the adjoining layer of channels [76–79]. The “microchannel” height is typically on the order of a fraction of a millimeter. Microchannel reactors have two significant benefits. One is the high heat and mass transfer associated with the small channel dimensions. The Nusselt (dimensionless heat transfer coefficient) and Sherwood (dimensionless mass transfer coefficient) numbers are constants for laminar flow in small channels. The Nusselt and Sherwood number values depend on the channel aspect ratio, but are independent of the channel dimensions [80]. Thus, as the channel dimensions decrease, the heat and mass transfer coefficients increase. A second benefit of the microchannel design is the closely coupled heat transfer between layers. Such microchannel designs can deliver very good performance in a compact reactor [81, 82].

Although microchannel reactors such as illustrated in Fig. 6 can be effective, there can also be some problematic aspects. The reactors often need to be fabricated from high-temperature metals [83, 84], which can be expensive and limited in temperature ranges. The reactors can be fabricated from ceramics [85], which expands operating ranges but could suffer from reduced mechanical strength. Especially in counter-flow arrangements, design and fabrication of the flow manifolding can be

Figure 6: Illustration of a microchannel reactor with alternating layers of endothermic and exothermic catalysts. As illustrated here the catalysts are washcoated onto the channel walls.

Figure 5: Methane steam reformer in a top-fired configuration. The stick figure provides some sense of the scale.

Figure 7: Planar membrane-assisted partial-oxidation syngas reactor developed by Air Products [72–74].

difficult. Once a microchannel reactor is fabricated and sealed, incorporating the catalyst layer can be difficult. Removing and replacing deactivated catalysts can be even more difficult. There are practical operational benefits associated with designs that facilitate disassembly and catalyst replacement [86]. The channels shown in Fig. 6 are in a counter-flow arrangement and configured as individual layers that can be mechanically compressed together. Although this layout may facilitate catalyst maintenance, sealing and manifolding is diffi-

cult.

Figure 7 illustrates a process-intensified reactor for a partial-oxidation process that has been developed and demonstrated by Air Products⁸ and Ceramtec⁹ [72–74]. The reactor is configured as multi-functional planar blades. Natural gas flows over the external surfaces of the blades, which house partial-oxidation catalysts within a porous-ceramic support structure. Air

⁸www.airproducts.com

⁹www.ceramtec.com

Table 2: Global reactions in Fischer-Tropsch synthesis.

1.	$(2n+1)\text{H}_2 + \text{nCO} \rightleftharpoons \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$
2.	$2n\text{H}_2 + \text{nCO} \rightleftharpoons \text{C}_n\text{H}_{2n} + n\text{H}_2\text{O}$
3.	$2n\text{H}_2 + \text{nCO} \rightleftharpoons \text{C}_n\text{H}_{2n+2}\text{O} + (n-1)\text{H}_2\text{O}$
4.	$(2n-1)\text{H}_2 + \text{nCO} \rightleftharpoons \text{C}_n\text{H}_{2n}\text{O} + (n-1)\text{H}_2\text{O}$
5.	$(2n-2)\text{H}_2 + \text{nCO} \rightleftharpoons \text{C}_n\text{H}_{2n}\text{O}_2 + (n-2)\text{H}_2\text{O}$

flows through microchannels that are housed within the blades. The air flow and the catalyst structures are separated by a thin ion-transport membrane (ITM). Membrane materials such as calcium-doped lanthanum ferrites ($\text{La}_x\text{Ca}_{1-x}\text{FeO}_{3-\delta}$, LCF) are perovskite mixed ionic-electronic conductors (MIEC) that conduct oxide ions. The membrane serves to separate oxygen from air and deliver pure oxygen to the catalyst structure where it reacts with the natural gas. The partial-oxidation process produces syngas according to Eq. 3.

Figure 8 illustrates a process-intensified approach that has been developed and demonstrated by Praxair, Inc.¹⁰ [87–89]. In this case, intensification is achieved by in-situ air separation and a combination of endothermic and exothermic processes. Figure 8 shows one panel of a multi-panel reactor. Each panel is composed of multiple U-shaped reformer tubes and partial-oxidation tubes. A mixture of steam and methane enters the endothermic steam-reformer tubes, which are packed with catalyst pellets. The flow rates are set such that the methane is only partially reformed, with some methane remaining in the exit stream.

The partially reformed mixture from the steam-reformer tubes is directed into the partial-oxidation tubes. These tubes feature a mixed-conducting ion-transport membrane that separates oxygen from an external air flow. As illustrated in the upper-right balloon of Fig. 8, the partial-oxidation tubes have a relatively complex architecture. The structural support is a chemically inert porous ceramic tube. The first exterior layer is a porous partial-oxidation catalyst. The next layer is the ceramic oxygen transport membrane. The final outer layer is an oxygen-reduction catalyst that facilitates the incorporation of oxygen into the membrane. Because only oxide-ions are transported through the membrane, the oxygen is separated from air. The partial-oxidation tubes are hot as a result of exothermic reactions. The high-temperature tubes radiate to the relatively cooler steam-reforming tubes, thus supplying the heat needed to the support the endothermic steam reforming.

¹⁰www.praxair.com

Figure 9: Mass-based distribution of product species as functions of carbon number.

4. Fischer-Tropsch synthesis

Fischer-Tropsch synthesis is an intermediate step between syngas and the subsequent refining to fuels or chemicals. The chemistry and the technology are well known and extensively documented [6, 11, 90]. Thus, the present paper provides only a superficial discussion, concentrating primarily on alternative reactor technologies and opportunities for process intensification.

Although the actual chemistry is complex and involves a great many elementary steps, Table 2 summarizes the processes in terms of five global reactions [90, 91]. The reactants are H_2 and CO with the ratio of H_2 to CO being approximately two. The products include alkanes ($\text{C}_n\text{H}_{2n+2}$), alkenes (C_nH_{2n}), alcohols and ethers ($\text{C}_n\text{H}_{2n}\text{O}$), aldehydes and ketones ($\text{C}_n\text{H}_{2n}\text{O}$), and carboxylic acids and esters ($\text{C}_n\text{H}_{2n+2}\text{O}_2$). In all cases, H_2O is a reaction product. The specific product distribution depends on operating conditions and the catalyst.

In broad terms, the Fischer-Tropsch process can be categorized in terms of operating temperature and choice of catalyst, with both considerations affecting the product distributions. High temperature (HTFT) is generally understood as $T > 320^\circ\text{C}$ with low temperature (LTFT) being $T < 250^\circ\text{C}$. The catalysts are usually either iron-based or cobalt-based. The operating pressure is usually in the range of 10 to 30 bar.

The product distribution can be estimated using the Anderson-Schultz-Flory equation [92, 93],

$$Y_n = n(1 - \alpha)^2 \alpha^{(n-1)}, \quad (16)$$

where Y_n is the mass fraction of species with carbon number n ($n > 2$). The parameter α depends on the rates of chain propagation r_p and chain termination r_t on the catalysts,

$$\alpha = \frac{r_p}{r_p + r_t}. \quad (17)$$

Figure 8: Illustration of an integrated air-separation and autothermal reforming reactor developed by Praxair [87–89].

As temperature increases, the desorption rates increase, which diminishes the chain-propagation rates and hence decreases α . High-temperature Fischer–Tropsch processes are characterized by $0.65 \leq \alpha \leq 0.7$ and low-temperature Fischer–Tropsch processes are characterized by $0.85 \leq \alpha \leq 0.95$.

Figure 9 shows the distribution of product species with carbon number n as a function of carbon number. As the temperature increases the product species shift toward lower carbon numbers. Low-temperature Fischer–Tropsch processes deliver carbon-number product distributions with peaks in the mid carbon-number ranges. It is at least interesting to note that LTFT processes with $\alpha \approx 0.9$ delivers a carbon-number distribution that is similar to light crude oil.

Because the reactions are exothermic (around 160 kJ mol^{-1}), the process itself produces substantial heat. If the heat is not removed, the relatively low operating temperature for the Fischer–Tropsch process cannot be maintained. Moreover, depending on how the heat is removed, maintaining temperature uniformity through the catalyst bed can be difficult. The heat-removal from Fischer–Tropsch processes is typically accomplished with pressurized boiling water. By controlling pressure, the saturation temperature can be controlled. By controlling the water flow rate, the requisite heat can be removed.

4.1. Large-scale Fischer–Tropsch

At the refinery scale (thousands of barrels per day), Fischer–Tropsch processes have been implemented in

Figure 10: Illustration of large-scale packed-bed Low-Temperature Fischer–Tropsch (LTFT) reactor.

a variety of large-scale pressurized catalytic reactors. These include fixed-bed, fluidized-bed, and slurry-bubble reactors [94]. Figure 10 illustrates some aspects

Figure 11: Illustration of large-scale slurry-bubble Low-Temperature Fischer-Tropsch (LTFT) reactor. The heat-exchanger tubes as shown are stylized and not intended to represent any particular reactor.

of a fixed-bed LTFT reactor. Syngas enters at the top and flows downward through an array of long packed-bed catalyst tubes. The product exits through the lower section of the reactor, with the large paraffins (waxes) being separated from the more volatile products. A large LTFT reactor could have several hundred catalyst tubes. Pressurized water circulates in the space outside the catalyst tubes, with steam exiting at the top of the tube array. Maintaining radial and axial temperature uniformity is an important design and operational challenge [95]. The relatively narrow and long tubes tend to promote radially uniform plug-flow through the catalyst beds. Although the chemistry and the catalysts are quite different, there is at least a superficial similarity with the tubes in large-scale reformers such as illustrated in Fig. 5.

Although the designs are more complex, fluidized-bed reactors offer one approach to maintaining better temperature control. Fluidizing and circulating the catalyst particles promotes mixing and enhances heat transfer to internal cooling media. As in the fixed-bed reactors, high-pressure water is typically used for cooling. In the case of fluidized-bed reactors, the coolant is circulated through internal heat exchangers. Although

Figure 12: Illustration of segment of a microchannel Fischer-Tropsch reactor, generally modeled after the Velocys approach. The individual microchannels have characteristic dimensions on the order of one millimeter or less.

the reactor manufacturers do not disclose details of the coolant circuits, one expects that they are implemented as arrays of tubes throughout the fluidized beds.

Figure 11 illustrates features of a slurry-bubble Fischer-Tropsch reactor [96]. In such reactors the catalysts are carried in an oil-based slurry that is intended to be chemically inert. Syngas enters from below, forming bubbles within the slurry. High pressure water circulates within heat-exchanger tubes. The reaction chemistry proceeds on the distributed catalyst surfaces, with gas-phase reaction products contributing to the bubbles. The gas flow and the bubbles agitate the slurry, promoting good heat-transfer coupling between the slurry and the heat exchanger tubes. The fluid motion also promotes mixing that tends to limit temperature variations within the system.

4.2. Microchannel reactors

Although the large-scale Fischer-Tropsch reactors are being operated with commercial success, there is great interest in applying process-intensification approaches to reduce the reactor size and improve performance [78, 7, 97–99, 76, 100]. Figure 12 illustrates a small section of a microchannel design that is modeled after the approach taken by Velocys¹¹. In this design

¹¹www.velocys.com

Figure 13: Three microchannel Fischer-Tropsch reactors within a pressure vessel, generally modeled after the Velocys approach. Each of the three microchannel reactors have overall characteristic dimensions of around one meter.

the catalyst is housed within wave-like fin structures that promote heat transfer from the catalyst bed. Syn-gas enters from the top and flows downward through the catalyst bed, with Fischer-Tropsch products exiting at the bottom. The reaction heat is removed by the pressurized-water coolant within cross-flow microchannels. The fin spacing and coolant channels are on the order of a millimeter. The highly efficient heat transfer associated with microchannels delivers a compact, high-performance reactor.

Figure 13 illustrates the packaging of three microchannel Fischer-Tropsch reactors within a pressure vessel. Each of the reactors, which have overall dimensions on the order of a meter, are composed of microscale features as illustrated in Fig. 12. Syngas enters the reactors' catalyst sections from above via a gas-distribution manifold. The Fischer-Tropsch products are collected through manifolds at the bottom of the reactors. Pressurized cooling water enters through manifolds that feed the microchannel arrays, with the water-steam exhaust mixture leaving the reactors into the outer pressure-vessel housing. Water vapor exhausts at the top of the pressure vessel and condensed water drains through the bottom.

Microchannel-based Fischer-Tropsch reactors are now mature to the point that they are being offered commercially by Velocys¹². The reactor illustrated in cartoon form by Fig. 13 is demonstrated to deliver approx-

imately 175 barrels of Fischer-Tropsch products per day. Thus, this technology is particularly well suited for small-scale GTL production with remote or stranded gas sources.

5. Oxidative coupling of methane

Although the Fischer-Tropsch technology is mature and practiced commercially, direct conversion of natural gas offers some potential benefits. In this context, "direct conversion" means processing that is not based on first producing synthesis gas [101]. One of the possible direct-conversion routes is Oxidative Coupling of Methane (OCM), which is intended to produce ethylene as the primary product.

The OCM process, which first proposed by Keller and Bhasin in 1982 [102], can be represented globally as

This process usually operates at temperatures around 700 °C and requires a selective catalyst. The elevated temperature is needed to activate the methane and the catalyst promotes selectivity toward ethylene. Because of the elevated temperature and the presence of oxygen, there is general agreement that gas-phase chemistry plays a significant role in the overall process.

In addition to using different catalysts, the CH_4/O_2 feed ratio affects the process selectivity. According to Eq. 18 the process requires a stoichiometric CH_4/O_2 ratio of 2. However, at high temperatures and in an oxidizing environment the partial and total oxidation of methane and the C_2 species compete with the desired OCM process. In practice OCM processes operate with large excesses of CH_4 (typically, $5 \leq \text{CH}_4/\text{O}_2 \leq 10$). Under CH_4 -rich conditions, the methane conversion is limited by the deficient O_2 concentration. The desired C_2 products are more stable at low O_2 levels, resulting in higher C_2 selectivity at low O_2 partial pressures where methane conversion is low. In other words there is a trade-off between the C_2 selectivity and yield. High C_2 selectivity (e.g., 70%) is possible when methane conversion is low (e.g., $\leq 20\%$). In any case, there is always a significant competition between desired and undesired outcomes, with actual performance being a combination of multiple competing pathways.

The OCM process has been the subject of extensive research since its discovery in 1982 [103–114] and several reviews have been published [115–118]. Economic analyses suggest that commercial viability demands single-pass C_2H_4 yields that exceed 25% [119, 1]. To

¹²www.velocys.com

date, with one possible recent exception (Siluria Technologies, Inc.¹³), OCM has not yet achieved practical viability. Continued development of the OCM technology depends on improved catalysts as well as the innovative concepts for reactor design. The following sections are concerned primarily with opportunities for process intensification and reactor development.

5.1. OCM catalysts

The OCM process depends on C₂-selective catalysts that are stable at elevated temperature. Broadly speaking, two classes of catalysts are found to deliver reasonable performance. One class is based on La₂O₃ that is doped with alkaline-earth metals (Sr, Mg, Ca) [120–124]. The other class is broadly represented as Mn/Na₂WO₄/SiO₂ [125–129]. There is also considerable literature on Li/MgO as an OCM catalyst, but these materials are not practically viable because they are unstable under OCM operating conditions [130–136]. The La₂O₃ and Li/MgO catalysts deliver moderate C₂ yield (≤ 20%), but suffer significant stability problems. Doping the La₂O₃ with Sr, CaO, or CeO₂ can improve the catalyst performance. The maximum C₂ yield reported over Sr-La₂O₃ at 800 °C is 17% [137].

Despite the low C₂ yield and durability problems, there is considerable experimental and theoretical research focusing on the Li/MgO catalysts. The relatively simpler catalyst structure makes a fundamental understanding of the OCM chemistry more accessible than in more complex catalysts [134–136].

The Mn/Na₂WO₄/SiO₂ materials were first identified as OCM catalysts by Fang, et al. [125]. The high-temperature stability enables operating the OCM reactors at sufficiently high temperatures to achieve good C₂ yield. Experiments in laboratory-scale packed-bed reactors deliver 16–25% C₂ yield at 800 °C [125, 138]. A 2011 patent by Zarrinpashne et al. [139] reported 27% C₂ yield at 850 °C. The increased yield was attributed to the catalyst elemental composition and the catalyst-synthesis technique. Further improvements are associated with doping the Mn/Na₂WO₄/SiO₂ catalysts with alkali chlorides (LiCl, NaCl, KCl, CsCl), increasing ethylene yield up to 31% at 750 °C [129].

Recent research is focused on OCM catalysts that enable low-temperature ($T \leq 600$ °C) performance. The catalyst activity is found to depend not only on the catalyst's metal composition, but also on particle size and morphology [140–143]. Nano-structured catalysts activate the methane at lower temperatures [111,

140]. Nano-structured (nanowire, nanorods, nanofibers) La₂O₃, Sr-La₂O₃ and La₂O₃-CeO₂ catalysts delivered superior OCM performance compared to the same catalysts in powder form [111, 141, 143, 142]. Song et al. [142] developed a stable Sr-La₂O₃ nanofiber catalyst that delivered approximately 16% C₂ yield at 500 °C, with the catalyst being stable up to 800 °C. The catalytic activity of nanorods and nanofibers is attributed to high surface areas, well defined crystalline structures, and the ability to form surface oxides [141].

Achieving economic viability depends on improving catalyst selectivity and/or reducing process temperature. The recent development of nano-structured catalysts has beneficially influenced the course of OCM technology. Recently, Siluria Technologies announced a commercial OCM process. However, their patent application reveals that their process does not achieve 25% C₂ single-pass yield [144]. Two different nanowire catalysts are considered. One that is composed of 20 wt.% Mg, 5 wt.% Na, and 75 wt.% La₂O₃ delivers yields of approximately 12% C₂₊ at 600 °C [145]. The other is Ln₁Ln₂Ln₃O₆ (Ln₁ and Ln₂ are rare-earth metals), which delivers 22.6% C₂₊ yield.

5.2. Reaction kinetics

Although the details of OCM depend on the particular catalyst and specific operating conditions, there is general agreement that the reaction pathways are similar on all catalysts. The rate-limiting step is methane activation on the catalyst surface and in the gas phase to form methyl radicals. Possible surface reactions for methane activation include thermal cracking as

or surface-oxygen attack as

The gas-phase reaction and rate are known from combustion literature as [104, 119, 146–148].

Experimental studies show that the C₂ formation rates depend strongly on methyl-radical concentrations [131, 123, 149, 150]. There is general agreement that the methyl radicals recombine in the gas-phase to form C₂H₆. Subsequent dehydrogenation of C₂H₆ produces C₂H₄. In high-temperature oxidative environments, the methane and C₂ species can be easily oxidized to produce CO_x and H₂O, which is problematic

¹³www.siluria.com

Table 3: Global reactions in Oxidative Coupling of Methane as proposed by Staunich, et al. [108].

1.	$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$
2.	$2\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O}$
3.	$\text{CH}_4 + \text{O}_2 \rightarrow \text{CO} + \text{H}_2\text{O} + \text{H}_2$
4.	$\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$
5.	$\text{C}_2\text{H}_6 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$
6.	$\text{C}_2\text{H}_4 + 2\text{O}_2 \rightarrow 2\text{CO} + 2\text{H}_2\text{O}$
7.	$\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$
8.	$\text{C}_2\text{H}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{CO} + 4\text{H}_2$
9.	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$
10.	$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2\text{O}$

and needs to be avoided. The unwanted full oxidation proceeds on the catalyst with significant contributions from gas-phase reactions [105, 151, 107, 109].

Considering $\text{La}_2\text{O}_3/\text{CaO}$ catalysts, Stansch et al. developed a global 10-step reaction mechanism (Table 3) [108]. Although the chemistry concerns heterogeneous catalysis, the reaction mechanism involves only gas-phase species. The paper reported empirical rate expressions for each of the reactions. Up to the present day, the Stansch et al. reaction mechanism is used widely in modeling studies of OCM processes [152–154, 114].

Considering $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts, Ahari et al. [155] developed a microkinetic reaction mechanism that involves gas-phase and surface reactions. The surface reactions are represented as 11 irreversible steps. The gas-phase reactions are represented as 39 reversible steps among 13 species. The product gas-phase species include CO , CO_2 , H_2 , H_2O , C_2H_4 , and C_2H_6 , but not higher hydrocarbons and aromatics. This reaction mechanism extends earlier studies by Marin and colleagues [105, 151].

There is clearly a need to develop and validate new reaction mechanisms that are catalyst specific and represent elementary reaction steps. Especially when surface-reaction steps are included, there is a need to evaluate thermodynamic properties of the surface-adsorbed species. Although estimating or measuring such thermodynamic properties may be difficult, they play a central role in ensuring microscopic reversibility.

6. OCM reactors

Most laboratory-scale OCM reactors are implemented as catalytic packed beds within small-diameter tubes, such as illustrated in Fig. 14. Because the OCM process is highly exothermic, thermal control is important. Small-diameter tubes limit the radial temperature variations, but axial temperature variations can be significant. To avoid large axial temperature excursions,

Figure 14: Laboratory-scale packed-bed reactor configuration modeled after Zohour et al. [113]. This experiment is configured with two separated catalyst beds and a central capillary tube for measuring gas-phase species profiles. The catalysts are held in place by chemically inert glass-fiber packing.

Figure 15: Measured temperature and species profiles from a packed-bed experiment [156]. The feed mixture had a ratio of $\text{CH}_4/\text{O}_2 = 7$ and an inlet temperature of 600 °C. The catalyst was $\text{La}_2\text{O}_3\text{-CeO}_2$ in a nanofiber fabric configuration.

experiments are often run in dilute mixtures with low methane conversions. However, while useful in the laboratory setting, practical processes cannot be operated

in dilute atmospheres. Typical experiments measure only the product species that leave the catalyst bed. An important aspect of the configuration shown in Fig. 14 is that species and temperature profiles can be resolved within the catalyst bed [157–159, 156, 113].

Figure 15 shows temperature and species profiles measured by Zohour et al. [156]. A mixture of methane and oxygen ($\text{CH}_4/\text{O}_2=7$) enters the reactor at 600 °C. Several very interesting observations emerge from these measurements. The reaction chemistry is essentially completed within about 5 mm of the gases first encountering the active catalyst material. The reaction heat associated with the rapid O_2 consumption produces a rapid temperature rise of approximately 225 °C. The O_2 is mostly consumed, with exhaust mole fraction being below 1%. The major gas-phase products (C_2H_4 , C_2H_6 , H_2O , CO , CO_2) are formed within the first 5 mm of the 19 mm catalyst bed. Minor C_3 products (C_3H_8 and C_3H_6) were detected, but with mole fractions well below 1%. Following the initial reaction zone, the species concentrations remain essentially unchanged until they exit the reactor. Although H_2 measurements are usually not reported in the OCM literature, Fig. 15 shows significant H_2 . Zohour et al. suggest that the significant levels of H_2 may be due to surface reactions, such as are typical in catalytic partial oxidation (CPOX) over Rh and Pt catalysts.

As is evident from the Zohour et al. measurements, OCM processes are characterized by a sharp local temperature rise (i.e., local hot spots). These measurements are consistent with other reported results [160–162]. However, the locally high temperatures apparently play no beneficial role on the process. Actually, the high temperature plays a detrimental role in the sense that it contributes to the production of unwanted total-oxidation products (i.e., H_2O and CO_2). The appearance of total-oxidation products diminishes the yield of the desired C_2 products. Moreover, the downstream separation of CO and CO_2 from the C_2 products is inefficient and costly. The locally high temperatures contribute to other undesired, or unsafe, conditions. Thermal runaway can result from the gas-phase ignition of CH_4 and the desired C_2 product stream. High temperatures also contribute to catalyst degradation and deactivation. Maintaining spatially uniform and relatively low temperature beneficially affects OCM processes. Thus, as is also true for other GTL processes, thermal control is important in the design and development of high-performance reactor technology.

In broad terms, thermal control in OCM reactors may follow three approaches. These include microchannel reactors, membrane reactors, and staged reactors. Inno-

Figure 16: Illustration of an OCM reactor in a shell-and-tube configuration with an oxygen-permeable membrane.

vative designs may use combinations of the approaches.

6.1. Microchannel reactors

Microchannel reactors and integrated heat exchangers are known to be effective in controlling reaction temperature. Figure 12 illustrates a catalytic microchannel-reactor design that is effective for Fischer–Tropsch synthesis. In this case the coolant is pressurized water, which is feasible for processes that require temperatures of around 300 °C and lower. For processes such as OCM that operate at temperatures around 600 °C and higher, pressurized water is not an option. Finding a suitable non-reactive high-capacity heat-transfer fluid is challenging, if possible. At these temperatures, the coolant must be a gas.

Chemically inert channels with flowing gases can help to control temperature on the adjacent catalyst beds. However, gases have limited capacity to accept high heat loads and maintain small temperature increases. An alternative is to develop a reactor such as the one shown in Fig. 6, where both sets of microchannels are catalytically active. In this case, the exothermic heat from the OCM process is accepted by an endothermic process within the mating channels.

High-performance catalytic microchannel reactors must accommodate some practical considerations. The thermal demands of the endothermic and exothermic processes must be roughly balanced. Assuming that OCM is the target process, to be economic the endothermic process must also deliver some valuable product in addition to simply controlling temperature for the OCM process. An endothermic steam or dry reforming process would represent one potentially viable option.

In addition to balancing the overall exothermicity and endothermicity, designing a high-performance catalytic microchannel reactor must consider the spatial locations

of the exothermic and endothermic chemistry. As may be noted from Fig. 15, the OCM exothermic heat release can be highly localized. It may be difficult to find a mating endothermic process that is also localized and occurs at the appropriate location within the reactor.

6.2. Membrane reactors

In reactors such as the one illustrated by Fig. 14, premixed methane and oxygen enter the catalyst bed together. One of the reasons for the localized heat release is that all of the available O_2 can be consumed rapidly (Fig. 15). If the oxygen were added in a distributed manner along the length of the reactor, the local temperature spikes could be significantly diminished.

Figure 16 illustrates a permselective oxygen membrane reactor [163]. The membranes may take alternative forms. Oxide-ion conducting membranes are typically dense ceramics that are mixed ionic-electronic conductors (MIEC). A doped perovskite, particularly $La_xCa_{1-x}FeO_{3-\delta}$ (LCF), is a good candidate because it is stable in both oxidizing and reducing environments and has reasonably good oxide-ion conductivity [164–169]. Because the ion conductivity of these materials is activated (in the range of 75 kJ mol^{-1}), elevated temperature is needed to achieve good oxygen fluxes. Practical operating temperatures around 600°C and above are compatible with OCM processes.

To avoid costly downstream separations, practical OCM processes need pure oxygen, not air. Materials such as LCF conduct only oxide ions (and electronic charge carriers). Thus, in a reactor such as illustrated in Fig. 16, the outer shell can be fed with air. The membrane accomplishes in-situ air separation, avoiding the need for an upstream air-separation process. Such process intensification (i.e., combining two otherwise separate unit processes) can be beneficial.

Although the MIEC ceramics are oxide-ion conductors, the ion conductivity is not high. To achieve practical oxygen fluxes, the membranes must be thin (order tens of microns). Such thin membranes must be supported on compatible porous-ceramic supports.

Another membrane approach is based on so-called hollow-fiber tubes [170–175]. These tubes, which are fabricated from mixed-conducting ceramics using a phase-inversion technique, have a very interesting architecture [171, 176]. Conically shaped “microchannels” emanate radially from the inside of the tube toward the exterior surface. The diameters of the radial microchannels are relatively large at the tube’s inner surface and decrease radially, with the tube’s exterior surface being a dense membrane. In some cases, a catalyst coating can be deposited within the radial channels.

Figure 17: Possible configuration of a swirling tubular membrane reactor.

Yet another membrane approach depends on nanoporous ceramic (e.g., Al_2O_3) structures [177–181]. The oxygen fluxes can be much higher than those in the dense-ceramic MIEC materials. Porous ceramics are much less costly than dense ceramic ion-transport membranes. However, upstream air separation is needed to produce the pure oxygen. Also, porous membranes can permit diffusion of hydrocarbons from the catalyst bed to the oxygen shell gas. Such reactors are usually operated with high oxygen pressure on the shell side (e.g., 6 bar) to prevent the deleterious back diffusion.

6.3. Tubular-swirl reactors

Even with a membrane reactor such as illustrated in Fig. 16, axial variation in temperature and composition must be expected. Introducing the oxygen in a spatially distributed manner via the membrane diminishes the axial variations, but does not eliminate them [112]. As illustrated in Fig. 17, a swirling tubular membrane configuration forms the basis for a potentially interesting reactor design.

In 1985, Ishizuka first introduced the concept of swirling tubular flames and demonstrated the axial independence of the flow field [182]. Shortly thereafter, Takeno and Ishizuka then developed the similarity analysis showing the axial independence in a mathematical setting [183]. Since that time, a significant body of literature documents the flow behavior in both premixed and non-premixed settings. Ishizuka wrote an extensive review in 1993 [184]. The recent book edited by Ishizuka and Dunn-Rankin documents the fundamental and practical state of the art up to 2013 [185].

The swirling tubular flow is analogous to the similarity behavior of the much-better-known stagnation flows that are widely used in fundamental flame studies [43]. In an ideal axisymmetric stagnation flow (e.g., Fig. 18), the temperature and concentration fields are functions

Figure 18: Cartoon image of an axisymmetric planar stagnation flow, illustrating radial independence of the temperature and concentration fields.

of the axial position and independent of the radial position. In an ideal swirling tubular flow, the temperature and concentration fields are functions of the radial position and independent of the axial position. Thus, in a configuration such as the one shown in Fig. 17 the chemistry performance will be essentially independent of the axial position within the reactor.

As illustrated in Fig. 17, an oxygen-permeable membrane is supported on the exterior surface of an inner porous tube. A porous OCM catalyst layer is deposited onto the exterior surface of the membrane. The methane feed is introduced into the annular reaction volume via swirl vanes [186]. The reaction products exit axially. Based on the tubular similarity, and neglecting some inevitable end effects, the temperature and composition profiles within the annular reaction zone should be essentially independent of the axial position. Thus, unlike a typical membrane reactor (e.g., Fig. 16) the oxygen flux and the reaction chemistry should be uniform through the reactor.

Based on numerous tubular flame studies, there is good reason to expect that a tubular swirl reactor should perform well. However, the present paper is the first to suggest such an approach. Reactors of this type have not yet been designed or tested.

6.4. Segmented reactors

Figure 19 illustrates a process and reactor configuration that integrates two unit processes. As illustrated, the system combines an exothermic OCM process with an endothermic steam-reforming process. However, the approach is significantly different from the approach as represented by the microchannel reactor illustrated in Fig. 6. In Fig. 19 two processes are running in parallel, with the catalytic processes confined to relatively small, insulated, reaction chambers. The exothermic OCM process heats the reactive gases and the catalyst bed. The endothermic SRM process cools the reactive gases and the catalyst bed. The heated gases from the

OCM reactors and the cooled gases from the SRM reactors enter a counter-flow microchannel heat exchanger. The role of the heat exchanger is to heat the cool gases and cool the hot gases. The partially reacted output streams from the heat exchangers are directed to the next set of reactors. Oxygen (or steam) can be added between the reactor stages. The two gas streams remain separated throughout the process in the sense that the OCM stream never mixes with the SRM stream. After a series of reactor-heat-exchanger sets, two final product streams emerge.

This segmented-reactor approach is motivated by Mleczko and colleagues [187, 86], who introduced such a novel multi-bed reactor that integrates OCM and methane dry reforming (DRM). The approach enables good oxygen control and thermal control, and hence process performance. In this sense, despite the separated catalytic reactors and heat exchangers, the overall process is “intensified.”

The segmented OCM process behaves as a discrete implementation of a membrane reactor (e.g., Fig. 16). In the membrane reactor the oxygen is transferred through the membrane along the entire length of the reactor. In the segmented approach, the oxygen is added between stages. The membrane is passive in the sense that the local oxygen flux depends on the local oxygen partial pressures across the membrane. In the segmented approach, the oxygen addition can be actively controlled at each injection point. A number of studies have addressed the beneficial role of multi-stage O_2 feed in OCM [119, 113, 188–190].

Zohour et al. [113] reported interesting OCM experiments in a reactor such as the one illustrated Fig. 14. In these experiments the catalyst bed was separated into two sections. Although not illustrated in Fig. 14, the experiments introduced oxygen separately just upstream of both catalyst sections. Compared to an experiment that introduced all the oxygen together with the methane at the entrance of the catalyst bed, the two-point injection produced better results. With all the oxygen introduced with the methane, Fig. 15 shows a significant and rapid temperature increase. With only a portion of the oxygen introduced in the first bed, Zohour et al. reported a significantly lower temperature rise. Upon introduction of oxygen into the second catalyst bed, the temperature again increases, but less than it did in the first bed. Because the process using two catalyst beds and segmented oxygen addition reduced the temperature excursions, the process was overall more efficient than the single-bed process.

The segmented approach represented by Fig. 19 shares some similarities with compressor intercooling

Figure 19: Illustration of a staged segmented process, combining an exothermic OCM process with an endothermic SRM process.

and segmented combustion in gas-turbine engines [191, 192]. As shown by Ramakrishnan and Edwards [191], dividing an overall process into smaller segments can improve thermodynamic efficiency by limiting temperature excursions. Sirignano, et al. [193] explored similar interturbine-burner (ITB) concepts to distribute the combustion between gas-turbine stages and improve overall efficiency. Of course, there are also prices to be paid for adding complexity and increasing parasitic losses such as pressure drop.

Although certainly not proven, there are reasons to expect that novel designs such as in Fig. 19 might prove beneficial. In addition to the consideration of chemical and thermodynamic performance and parasitic losses, practical reactor development must also be concerned with operational and maintenance costs. Essentially all high-temperature hydrocarbon-processing catalysts suffer degradation and deactivation over time. Thus, the regeneration and/or replacement of deactivated catalysts could be easier and less costly if the catalysts were housed on small detachable vessels such as illustrated in Fig. 19.

7. Methane dehydroaromatization

Methane Dehydroaromatization (MDA) is a process that is intended to produce benzene from methane [194–197, 8]. In gross global terms, MDA may be represented as

The MDA chemistry is quite different from the OCM chemistry. The MDA process is usually implemented with a bi-functional catalyst such as Mo/ZSM and operated at temperatures around 800 °C [40, 41]. The methane is activated on the Mo sites, primarily producing ethylene and hydrogen. The ethylene can subsequently react at the zeolite Brønsted-acid sites which initiate a series of hydrogenation, dehydrogenation, oligomerization, β -scission, and cyclization reactions, producing cyclohexane and ultimately the desired benzene.

Unfortunately, the process does not automatically terminate at benzene, but continues to produce naphthalene and higher aromatics. For example, the competing naphthalene (C_{10}H_8) production,

decreases the desired benzene yield. Additionally, naphthalene contributes to carbon deposits and catalyst deactivation via the subsequent formation of higher polycyclic aromatic hydrocarbons (PAH). Equation 23 is qualitatively instructive, but much too simplified to predict actual MDA performance that includes significant production of unwanted side products. Karakaya et al. [41] have developed a 50-step reaction mechanism to describe the MDA process up through naphthalene formation.

As is evident from the global reaction, a great deal of H_2 is produced, which causes a significant equilibrium limitation on the methane conversion and benzene yield. Based on the thermodynamics of Reaction 23, the

Figure 20: Illustration of a shell-and-tube MDA reactor with a polarized proton-conducting membrane.

equilibrium methane conversion is typically around 10–12% at 700 °C. As with the methane reforming or OCM, MDA processes may also be able to benefit from novel reactor design and process intensification. For example, a hydrogen-permeable membrane that removes H_2 from the catalyst bed would increase methane conversion and may improve benzene yield [198, 199].

Figure 20 illustrates aspects of a possible MDA reactor in a shell-and-tube configuration with a polarized proton-conducting membrane. Methane is introduced on the shell side where it reacts on a catalyst washcoat, producing hydrogen, benzene, and a range of other side products. The role of the membrane is to remove H_2 , enabling further conversion of the CH_4 . Assuming a pure hydrogen-permeable membrane, the separated hydrogen is itself a valuable product.

As discussed in the following section, there are two types of high-temperature hydrogen-permeable membranes. One is based on palladium or palladium alloys [200]. The other is based on dense ceramic perovskites such as doped barium zirconates (e.g., $BaZr_{0.9}Y_{0.1}O_{3-\delta}$, BZY10), which are mixed ionic-electronic conductors [201–204].

The proton flux generally follows a Nernst–Planck relationship, which depends on gradients of defect concentration and electrostatic potential [204]. Although these ceramic membranes are proton conductors, the ion conductivity is relatively low. Because the electronic conductivity is also very low, it is possible to establish an electrostatic potential across the membrane, which can increase the proton flux by increasing the protonic migration. Although the electrode fabrication and attachment can be challenging, it is possible to control the hydrogen flux via electrical polarization [201].

The removal of hydrogen (e.g., via a membrane) tends to favor naphthalene production over benzene production. Thus, although H_2 membranes promote in-

creased methane conversion, benzene yield may not be improved. Interventions, such as low-level steam addition, may assist in depressing the carbon deposition [205, 206]. However, the MDA process must overcome significant challenges to become practically viable.

8. Membrane technology

Membranes for gas-to-liquids applications must be stable at high temperature, which effectively eliminates polymer materials. Hydrogen-permeable membranes can be fabricated from palladium and palladium alloys [207, 200]. Some dense perovskite ceramics, such as doped barium zirconates, are proton conductors that enable hydrogen permselectivity [208–211]. Practical oxygen-permeable membranes are all fabricated from ceramics, but can take alternative forms that include porous structures, mixed ionic-electronic conductors (MIEC), and nearly pure oxide-ion conductors. The ceramic ion conductors are based on heterovalently doped polycrystalline materials [2].

8.1. Oxygen-transport membranes

Mixed-conducting oxygen-transport membranes are typically doped perovskites such as $La_{1-x}Ca_xFeO_{3-\delta}$ (LCF). These materials conduct oxide ions with internal charge compensation relying on the formation and transport of small-polaron electronic defects [167, 212]. In addition to oxide-ion conductivity, these materials also have relatively high electronic conductivity. For applications such as reformers or OCM, one side of the membrane is exposed to air (i.e., oxidizing) but the other side is exposed to hydrocarbons (i.e., reducing). The LCF material is particularly appropriate because it is stable in both oxidizing and reducing environments [164, 213, 167, 169, 214]. Many of the otherwise good MIEC oxide-ion conductors, such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF), are stable only in oxidizing environments.

Oxygen transport through the membrane depends on the reaction of molecular oxygen on one membrane surface to fill an oxygen vacancy within the membrane crystal lattice, and the reverse reaction at the opposite surface to release O_2 into the gas phase. Written in Kröger-Vink notation, the “incorporation” and “disproportionation” reactions at the membrane surfaces may be represented as

Reactions 25 and 26 involve three mobile charged defects. They are the oxygen-ion vacancies $\text{V}_{\text{O}}^{\bullet\bullet}$, the reduced iron small polaron Fe_{Fe}' , and the oxidized iron small polaron $\text{Fe}_{\text{Fe}}^{\bullet}$. In the Kröger-Vink notation the superscript “•” indicates a defect with a positive charge, the “’” indicates a defect with negative charge, and the “×” indicates charge neutrality. The subscripts indicate the “site” where the defect is localized. The disproportionation reaction is the result of the possibility that Fe^{2+} , Fe^{3+} , and Fe^{4+} can all be present simultaneously [167].

The defect concentrations are governed by conservation equations as

$$\frac{\partial [X_k]}{\partial t} + \nabla \cdot \mathbf{J}_k = 0, \quad (27)$$

where $[X_k]$ are defect concentrations and $\mathbf{J}_k$ are the Nernst–Planck defect fluxes. Assuming dilute transport, the Nernst–Planck relationship may be written as

$$\mathbf{J}_k = -D_k \left(\nabla [X_k] + \frac{z_k F}{RT} [X_k] \nabla \Phi_e \right), \quad (28)$$

where D_k are defect diffusion coefficients, z_k are the defect charges, R is the gas constant, F is the Faraday constant, and Φ_e is the electrostatic potential. The electrostatic potential must be established to effectively maintain electroneutrality, which can be represented in terms of the Gauss law as

$$\nabla \cdot (\epsilon \nabla \Phi) = -\rho_e = -\sum_{k=1}^K F z_k [X_k], \quad (29)$$

where ϵ is the dielectric constant and the local charge density is represented as ρ_e . Additionally, the reaction chemistry and transport must respect site constraints. The defect transport within the ceramic MIEC materials is activated, with activation energies usually in the range of 75 kJ mol^{-1} . Thus, the net oxygen flux depends greatly on the operating temperature. Details for modeling the incorporation chemistry and the defect transport within the membrane may be found in previous publications [201–204].

Although materials such as LCF are certainly viable, oxide-ion conductors such as doped ceria or doped zirconia are oxide-ion conductors and are usually more stable than the perovskite oxide-ion membranes. The ceria and zirconia materials have good oxide-ion conduction but very low electronic conduction. Because of the low electronic conductivity, the membrane can be polarized

Figure 21: Illustration of dual-phase oxygen-ion conducting membrane.

in the sense that an electric potential can be maintained across the membrane. This property enables electrochemical membrane applications such as in solid-oxide fuel cells. As can be seen from Eq. 28 the defect flux depends on the electrostatic-potential gradient. Thus, there may be benefits to polarizing the membrane in the sense that an applied electric field can be used to control the oxide-ion fluxes.

Without imposed polarization, oxide-ion flux through the ceria and zirconia materials is greatly limited by the electronic conduction. Dual phase membranes provide a means to incorporate highly stable ceramics and also deliver good oxygen fluxes [215–219]. As illustrated in Fig. 21, a dual-phase membrane is typically a ceramic-ceramic composite that is composed of one phase that is dominantly an electron conductor (e.g., strontium-doped lanthanum chromate LSCr) and the other phase that is dominantly an oxide-ion conductor (e.g., yttria-doped zirconia, YSZ) [218].

8.2. Hydrogen-transport membranes

Materials such as doped barium zirconates (e.g., $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$, BZY10) are MIECs that are proton conductors, and hence can operate as permselective hydrogen membranes. The incorporation reactions may be written as

The mobile charged defects are protons ($\text{OH}_{\text{O}}^{\bullet}$), oxygen vacancies ($\text{V}_{\text{O}}^{\bullet\bullet}$), O-site polarons ($\text{O}_{\text{O}}^{\bullet}$) [203]. The

protonic ceramics do not behave as pure hydrogen-transport membranes. These materials also conduct oxide ions as well as small polarons. Thus, depending on the gas-phase conditions across the membranes, the materials enable the defacto simultaneous transport of H_2 , O_2 , and H_2O . Depending on the application, such membrane behavior may be beneficial, or not.

8.3. Palladium membranes

Palladium is a well known and well studied hydrogen membrane material [207, 200]. The hydrogen molar flux through the Pd membrane generally follow Sieverts law as

$$J_{H_2}^M = k_{Pd} \frac{p_{H_2,I}^n - p_{H_2,II}^n}{L_{Pd}}, \quad (33)$$

where L_{Pd} is the membrane thickness and the local hydrogen partial pressures across the membrane are represented as $p_{H_2,I}$ and $p_{H_2,II}$, respectively. The exponent $n \approx 0.5$ can depend on the hydrogen incorporation chemistry. The hydrogen permeability can be expressed in the Arrhenius form as

$$k_{Pd} = k_{Pd}^0 \exp\left(-\frac{E_a}{RT}\right), \quad (34)$$

where E_a is an activation energy.

9. Summary and conclusions

As a clean-burning fuel, natural-gas combustion will surely continue to play a major role in the energy landscape. One can expect continuing progress in the development of advanced combustion technology, further increasing combustion efficiency and reducing environmental impact. At the same time, natural gas is poised to play increasingly important roles in the production of logistics fuels and commodity chemicals.

The large-scale reforming of natural gas is the primary route for hydrogen production, which is central to a wide variety of products that include petroleum refining, ammonia synthesis, and polymer processing. The annual production of H_2 exceeds 50 million metric tons. In the future, many predict a “hydrogen economy,” which could include fuel cells and hydrogen combustion. Although reforming processes are technologically mature and commercially practiced on a very large scale, there are significant opportunities for improvement. For example, process intensification via integrated microchannel reactors and heat exchangers is maturing rapidly, reducing capital cost and improving process efficiency. New hydrogen permselective membranes are likely to play important roles in improving the reforming and separation processes.

Fischer–Tropsch synthesis provides a commercially viable means to transform synthesis gas to refinery feedstocks. The synthesis gas is mostly produced via natural-gas reforming. Substantial research and development efforts are focused on innovative approaches for improving these processes. For example, microchannel reactor technology is likely to replace large-scale fixed-bed and slurry-bubble reactors.

Remote or stranded gas is a potentially valuable resource and also a source of environmentally harmful greenhouse-gas emissions. The development of practical, cost-effective, small-scale gas-to-liquids technology is necessary for the beneficial exploitation of these resources. Compared to refinery-scale processes, novel reactor technology based on process intensification concepts will surely be needed.

Processes such as oxidative coupling of methane (OCM) have been known for years and laboratory-scale research continues to be active. Such direct routes are potentially more efficient than first producing syngas and subsequently transforming to desired product streams. However, the eventual success of such processes will almost certainly depend on advanced catalysts and novel reactor technologies.

Based on new and innovative concepts that are being developed and demonstrated at the laboratory and pilot scales, there is ample reason to expect the growth and maturation of new commercially viable gas-to-chemicals technology. Process intensified approaches, including the combination of nanostructured catalysts, microchannel reactors, permselective membranes, closely coupled processes, and thermal control, will surely contribute to significant advances in critically needed technologies.

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References

References

- [1] J.H. Lunsford. Catalytic conversion of methane to more useful chemicals and fuels: A challenge for the 21st century. *Catal.*

- Today, 63:165–174, 2000.
- [2] K. Li. *Ceramic Membranes for Separation and Reaction*. Wiley, Hoboken, NJ, 2007.
- [3] K. Aasberg-Petersen, I. Dybkjaer, C.V. Ovesen, N.C. Schjødt, J. Sehested, and S.G. Thomsen. Natural gas to synthesis gas: Catalysts and catalytic processes. *J. Nat. Gas Sci. Eng.*, 3:423–459, 2011.
- [4] A. de Klerk and D.L. King, editors. *Synthetic Liquids Production and Refining*. ACS Symposium Series. American Chemical Society, Washington, DC, 2011.
- [5] J.R. Rostrup-Nielsen and L.J. Christiansen. *Concepts in Syngas Manufacture*, volume 10 of *Catalytic Science Series*. Imperial College Press, London, 2011.
- [6] P.M. Maitlis and A. de Klerk, editors. *Greener Fischer-Tropsch Processes for Fuels and Feedstocks*. Wiley-VCH, Weinheim, Germany, 2013.
- [7] D.A. Wood, C. Nwaoha, and B.F. Towler. Gas-to-liquids (GTL): A review of an industry offering several routes for monetizing natural gas. *J. Nat. Gas Sci. and Eng.*, 9:196–208, 2012.
- [8] J.J. Spivey and G. Hutchings. Catalytic aromatization of methane. *Chem. Soc. Rev.*, 43:792–803, 2014.
- [9] D.A. Wood. Catalytic conversion of natural gas and methane to synthesis gas and beyond: A collection of published research (2009–2015). *J. Nat. Gas Sci. Eng.*, 26:737–745, 2015.
- [10] F. Gallucci and M. van Sint Annaland, editors. *Process Intensification for Sustainable Energy Conversion*. Wiley, West Sussex, UK, 2015.
- [11] A. de Klerk. *Fischer-Tropsch refining*. Wiley-VCH, Weinheim, Germany, 2011.
- [12] G.A. Olah, A. Goepfert, and G.K.S. Prakash. *Beyond Oil and Gas: The Methanol Economy*. Wiley-VCH, Weinheim, Germany, 2006.
- [13] P.M. Maitlis and A. de Klerk. New directions, challenges, and opportunities. In P.M. Maitlis and A. de Klerk, editors, *Greener Fischer-Tropsch Processes for Fuels and Feedstocks*. Wiley-VCH, Weinheim, Germany, 2013.
- [14] M. Crow, B. Bozeman, W. Meyer, and Jr. R. Shangraw. *Synthetic Fuel Technology Development in the United States: A Retrospective Assessment*. Praeger, New York, 1988.
- [15] R.J. Kee, H. Zhu, and D.G. Goodwin. Solid-oxide fuel cells with hydrocarbon fuels. *Proc. Combust. Inst.*, 30:2379–2404, 2005.
- [16] J.R. Rostrup-Nielsen. Steam reforming of hydrocarbons. A historical perspective. *Stud. Surf. Sci. Catal.*, 147:121–126, 2004.
- [17] J.R. Rostrup-Nielsen, J. Sehested, and J.K. Nørskov. Hydrogen and synthesis gas by steam and CO₂ reforming. *Adv. Catal.*, 47:65–139, 2002.
- [18] H. Gunardson. *Industrial Gases in Petrochemical Processing: Chemical Industries*. Marcel Dekker, Inc, New York, NY, 1998.
- [19] B.C. Enger, R. Lødeng, and A. Holmen. A review of catalytic partial oxidation of methane to synthesis gas with emphasis on reaction mechanisms over transition metal catalysts. *Appl. Catal. A*, 346:1–27, 2008.
- [20] J.B. Claridge, M.L.H. Green, S.C. Tsang, A. York, A.T. Ashcroft, and P.D. Battle. A study of carbon deposition on catalysis during the partial oxidation of methane to synthesis gas. *Catal. Lett.*, 22:299–305, 1993.
- [21] J. Warnatz, M. D. Allendorf, R. J. Kee, and M. E. Coltrin. A model of elementary chemistry and fluid mechanics in the combustion of hydrogen on platinum surfaces. *Combust. Flame*, 96:393–406, 1994.
- [22] L.D. Schmidt, O. Deutschmann, and Jr. C.T. Goralski. Modeling the partial oxidation of methane to syngas at millisecond contact times. *Stud. Surf. Sci. Catal.*, 119:685–692, 1998.
- [23] A.B. Mhadeshwar and D.G. Vlachos. Hierarchical, multiscale surface reaction mechanism development: CO and H₂ oxidation, water-gas shift, and preferential oxidation of CO on Rh. *J. Catal.*, 234:48–63, 2005.
- [24] E.S. Hecht, G.K. Gupta, H. Zhu, A.M. Dean, R.J. Kee, L. Maier, and O. Deutschmann. Methane reforming kinetics within a Ni-YSZ SOFC anode. *Appl. Catal. A*, 295:40–51, 2005.
- [25] V.M. Janardhanan and O. Deutschmann. CFD analysis of a solid oxide fuel cell with internal reforming: Coupled interactions of transport, heterogeneous catalysis and electrochemical processes. *J. Power Sources*, 162:1192–1202, 2006.
- [26] M. Maestri, D.G. Vlachos, A. Beretta, G. Groppi, and E. Tronconi. Steam and dry reforming of methane on Rh: Microkinetic analysis and hierarchy of kinetic models. *J. Catal.*, 259:211–222, 2008.
- [27] L. Maier, B. Schaedel, K. Herrera Delgado, S. Tischer, and O. Deutschmann. Steam reforming of methane over nickel: Development of a multi-step surface reaction mechanism. *Top. Catal.*, 54:845–858, 2011.
- [28] O. Deutschmann. *Modeling and Simulation of Heterogeneous Catalytic Reactions: From the Molecular Process to the Technical System*. Wiley-VCH, Weinheim, Germany, 2012.
- [29] S. Appari, V.M. Janardhanan, R. Bauri, S. Jayanti, and O. Deutschmann. A detailed kinetic model for biogas steam reforming on Ni and catalyst deactivation due to sulfur poisoning. *Appl. Catal. A*, 471:118–125, 2014.
- [30] K. Herrera Delgado, L. Maier, S. Tischer, A. Zellner, H. Stotz, and O. Deutschmann. Surface reaction kinetics of steam and CO₂-Reforming as well as oxidation of methane over nickel-based catalysts. *Catalysts*, 5:871–904, 2015.
- [31] C. Karakaya, L. Maier, and O. Deutschmann. Surface reaction kinetics of the oxidation and reforming of CH₄ over Rh/Al₂O₃ catalysts. *Int. J. Chem. Kinet.*, in press, 2016. DOI:10.1002/kin.20980.
- [32] H. Zhu, R.J. Kee, V.M. Janardhanan, O. Deutschmann, and D.G. Goodwin. Modeling elementary heterogeneous chemistry and electrochemistry in solid-oxide fuel cells. *J. Electrochem. Soc.*, 152:A2427–A2440, 2005.
- [33] L. Maier, N. Schaedel, K.H. Delgado, S. Tisher, and O. Deutschmann. Steam reforming of methane over nickel: Development of a multi-step surface reaction mechanism. *Top. Catal.*, 54:845–858, 2011.
- [34] Y.-A. Zhu, D. Chen, X.-G. Zhou, and W.-K. Yuan. DFT studies of dry reforming of methane on Ni catalyst. *Catal. Today*, 148:260–267, 2009.
- [35] J.M. Bray and W.F. Schneider. First-principles thermodynamic models in heterogeneous catalysis. In A. Asthagiri and M.J. Janik, editors, *Computational Catalysis*. The Royal Society of Chemistry, Cambridge, UK, 2012.
- [36] P. Sautet F. Göltl. Density functional theory as a key approach in surface chemistry and heterogeneous catalysts. In J. Reedijk and K. Poeppelemeier, editors, *Comprehensive Inorganic Chemistry II*, volume 7, pages 405–420. Elsevier, Oxford, UK, 2 edition, 2013.
- [37] A.B. Mhadeshwar and D.G. Vlachos. Hierarchical multiscale mechanism development for methane partial oxidation and reforming and for thermal decomposition of oxygenates on Rh. *J. Phys. Chem. B*, 109:16819–16835, 2005.
- [38] R.S. Vincent, R.P. Lindstedt, N.A. Malik, I.A.B. Reid, and B.E. Messenger. The chemistry of ethane dehydrogenation over a supported platinum catalyst. *J. Catal.*, 260:37–64, 2008.
- [39] C.F. Goldsmith. Estimating the thermochemistry of adsorbates based upon gas-phase properties. *Topics in Catalysis*, 55:366–

- 375, 2012.
- [40] K.S. Wong, J.W. Thybaut, E. Tangstad, M.W. Stocker, and G.B. Marin. Methane aromatization based upon elementary steps: Kinetic and catalyst descriptors. *Micropor. Mesopor. Mat.*, 164:302–312, 2012.
- [41] C. Karakaya, H. Zhu, and R.J. Kee. Kinetic modeling of methane dehydroaromatization chemistry on Mo/Zelite catalysts in packed-bed reactors. *Chem. Eng. Sci.*, 123:474–486, 2015.
- [42] M.E. Coltrin, R.J. Kee, and F.M. Rupley. Surface Chemkin: A generalized formalism and interface for analyzing heterogeneous chemical kinetics at a gas-surface interface. *Int. J. Chem. Kinet.*, 23:1111–1128, 1991.
- [43] R.J. Kee, M.E. Coltrin, and P. Glarborg. *Chemically Reacting Flow*. Wiley, Hoboken, NJ, 2003.
- [44] M.E. Coltrin, R.J. Kee, F.M. Rupley, and E. Meeks. Surface Chemkin-III: A fortran package for analyzing heterogeneous chemical kinetics at a solid-surface – gas-phase interface. Technical Report SAND96-8217, Sandia National Laboratories, 1996.
- [45] J.R. Rostrup-Nielsen and J. Sehested. Whisker carbon revisited. *Stud. Surf. Sci. Catal.*, 139:1–12, 2001.
- [46] S. Helveg, J. Sehested, and J.R. Rostrup-Nielsen. Whisker carbon in perspective. *Catal. Today*, 178:42–46, 2011.
- [47] S. Helveg and P.L. Hansen. Atomic-scale studies of metallic nanocluster catalyst by in situ high-resolution transmission electron microscopy. *Catal. Today*, 111:68–73, 2006.
- [48] K. Sasaki and Y. Teraoka. Equilibria in fuel cell gases. *J. Electrochem. Soc.*, 150:A878–A888, 2003.
- [49] M.D. Argyle and C.H. Bartholomew. Heterogeneous catalyst deactivation and regeneration: A review. *Catalysts*, 5:145–269, 2015.
- [50] L.L. Hegedus and R. W. McCabe. Catalyst poisoning. *Stud. Surf. Sci. Catal.*, 6:481–505, 1980.
- [51] C.H. Bartholomew. Mechanisms of nickel catalyst poisoning. *Stud. Surf. Sci. Catal.*, 34:81–104, 1987.
- [52] C. Hultberg. Sulphur-tolerant catalysts in small-scale hydrogen production, a review. *Int. J. Hydrogen Energ.*, 37:3978–3992, 2012.
- [53] Y. Matsuzaki and I. Yasuda. The poisoning effect of sulfur-containing impurity gas on a SOFC anode: Part I. Dependence on temperature, time, and impurity concentration. *Solid State Ionics*, 132:261–269, 2000.
- [54] G. Mancino, S. Cimino, and I. Lisi. Sulphur poisoning of alumina supported Rh catalyst during dry reforming of methane. *Catal. Today*, in press, 2015. DOI:10.1016/j.cattod.2015.10.035.
- [55] W.S. Jablonski, S.M. Villano, and A.M. Dean. A comparison of H₂S, SO₂, and COS poisoning on Ni/YSZ and Ni/K₂O-CaAl₂O₄ during methane steam and dry reforming. *Appl. Catal. A*, 502:399–409, 2015.
- [56] C. Xie, Y. Chen, Y. Li, X. Wang, and C. Song. Sulfur poisoning of CeO₂-Al₂O₃-supported mono- and bi-metallic Ni and Rh catalysts in steam reforming of liquid hydrocarbons at low and high temperatures. *Appl. Catal. A*, 390:210–218, 2010.
- [57] D.A.J.M. Ligthart, J.A.Z. Pieterse, and E.J.M. Hensen. The role of promoters for Ni catalysts in low temperature (membrane) steam methane reforming. *Appl. Catal. A*, 405:108–119, 2011.
- [58] S.L. Lakhapatri and M.A. Abraham. Sulfur poisoning of Rh-Ni catalysts during steam reforming of sulfur-containing liquid fuels. *Cata. Sci. Technol.*, 3:2755–2760, 2013.
- [59] C. Yuan, N. Yao, X. Wang, J. Wang, D. Lv, and X. Li. The SiO₂ supported bimetallic Ni-Ru particles: A good sulfur-tolerant catalyst for methanation reaction. *Chem. Eng. J.*, 260:1–10, 2015.
- [60] J.R. Rostrup-Nielsen. Sulfur-passivated nickel catalysts for carbon-free steam reforming of methane. *J. Catal.*, 85:31–43, 1984.
- [61] H-S. Roh, K.-W. Jun, and S.-E. Park. Methane-reforming reactions over Ni/Ce-ZrO₂/θ-Al₂O₃. *Appl. Catal. A*, 251:275–283, 2003.
- [62] S. Chenna, R. Banerjee, and P.A. Crozier. Atomic-scale observation of Ni activation process for partial oxidation of methane using in situ environmental TEM. *ChemCatChem*, 3:1051–1059, 2011.
- [63] E.P.J. Mallens, J.H.B.J. Hoebink, and G.B. Marin. The reaction mechanism of the partial oxidation of methane to synthesis gas: A transient kinetic study over rhodium and a comparison with platinum. *J. Catal.*, 167:43–56, 1997.
- [64] T. Montini, A.M. Condó, N. Hickey, F.C. Lovey, L. De Rogatis, P. Fornasiero, and M. Graziani. Embedded Rh (1 wt.%)@Al₂O₃: Effects of high temperature and prolonged aging under methane partial oxidation conditions. *Appl. Catal. B*, 73:84–97, 2007.
- [65] T. Mony, J. Barbier Jr., and D. Duprez. Reactivity of steam in exhaust gas catalysts III. steam and oxygen/steam conversions of propane on a Pd/Al₂O₃ catalyst. *Appl. Catal. B*, 9:251–266, 1996.
- [66] S.E. Wanke and P.C. Flynn. The sintering of supported metal catalysts. *Catal. Rev.*, 12:93–135, 1975.
- [67] E. Ruckenstein and D.B. Dadyburjor. Sintering and redispersion in supported metal catalysts. *Rev. Chem. Eng.*, 1983:251–356, 1.
- [68] C.H. Bartholomew. Sintering kinetics of supported metals: New perspectives from a unifying GPLe treatment. *Appl. Catal. A*, 107:1–57, 1993.
- [69] C. H. Bartholomew and R.J. Farrauto. *Fundamentals of Industrial Catalytic Processes*. Wiley, Hoboken, NJ, 2006.
- [70] H.I. de Lasa, G. Dogu, and A. Ravella. *Chemical reactor technology for environmentally safe reactors and products*. Springer, New York, 1992.
- [71] A.I. Stankiewicz and J.A. Moulijn. Process intensification: Transforming chemical engineering. *Chem. Eng. Prog.*, 96:22–34, 2000.
- [72] M.F. Carolan, P.N. Dyer, M.A. Wilson, T.R. Ohn, K.E. Kneidel, D. Peterson, C.M. Chen, and K.G. Rackets. Planar ceramic membrane assembly and oxidation reactor system. U.S. Patent 7,513,932, 2009.
- [73] C.F. Miller, J. Chen, M.F. Carolan, and E.P. Foster. Advances in ion transport membrane technology for syngas production. *Catal. Today*, 228:152–157, 2014.
- [74] L.L. Anderson, P.A. Armstrong, R.R. Broekhuis, M.F. Carolan, J. Chen, M.D. Hutcheon, C.A. Lewinsohn, C.F. Miller, J.M. Repasky, D.M. Taylor, and C.M. Woods. Advances in ion transport membrane technology for oxygen and syngas production. *Solid State Ionics*, in press, 2015. DOI: <http://dx.doi.org/10.1016/j.ssi.2015.11.010>.
- [75] R.C. Pattison and M. Baldea. Robust autothermal microchannel reactors. *Comput. Chem. Eng.*, 81:171179, 2015.
- [76] M. Ostadi, K. Dalane, E. Rytter, and M. Hillestad. Conceptual design of an autonomous once-through gas-to-liquid process – Comparison between fixed bed and microchannel reactors. *Fuel Process. Technol.*, 139:186–195, 2015.
- [77] D.M. Murphy, A. Manerino, M. Parker, J. Blasi, R.J. Kee, and N.P. Sullivan. Methane steam reforming in a novel ceramic microchannel reactor. *Int. J. Hydrogen Energy*, 38:8741–8750, 2013.
- [78] J.J. Lerou, A.L. Tonkovich, L. Silva, S. Perry, and J. McDaniel. Microchannel reactor architecture enables greener processes.

- Chem. Eng. Sci.*, 65:380–385, 2010. 1943
- [79] B. Blakeley and N.P. Sullivan. Fuel processing in a ceramic microchannel reactor: Expanding operating windows. *Int. J. Hydrogen Energy*, 41:3794–3802, 2016. 1944
- [80] R.K. Shah and D.P. Sekulić. *Fundamentals of Heat Exchanger Design*. Wiley, Hoboken, NJ, 2003. 1945
- [81] V. Hessel, A. Renken, J.C. Schouten, and J. Yoshida. *Handbook of Microreactors*. Wiley VCH, Weinheim, Germany, 2009. 1946
- [82] G. Tekautz, B. Zechner, L.E. Wiesegeger, and D. Kirschneck. Principle and guidelines for selection of microstructured devices for mixing and reaction. In V. Hessel, A. Renken, J.C. Schouten, and J. Yoshida, editors, *Handbook of Microreactors*. Wiley VCH, Weinheim, Germany, 2009. 1947
- [83] I. Aartun, H.J. Venvik, A. Holmen, P. Pfeifer, O. Görke, and K. Schubert. Temperature profiles and residence time effects during catalytic partial oxidation and oxidative steam reforming of propane in metallic microchannel reactors. *Catal. Today*, 110:98–107, 2005. 1948
- [84] Z. Anxionnaz, M. Cabassud, C. Gourdon, and P. Tochon. Heat exchanger/reactors (HEX reactors): Concepts, technologies: State-of-the-art. *Chem. Eng. Process.*, 47:2029–2050, 2008. 1949
- [85] R.J. Kee, B.B. Almand, J.M. Blasi, B.L. Rosen, M. Hartmann, N.P. Sullivan, H. Zhu, A.R. Manerbin, S. Menzer, W.G. Coors, and J.L. Martin. The design, fabrication, and evaluation of a ceramic counter-flow microchannel heat exchanger. *Appl. Therm. Eng.*, 31:2004–2012, 2011. 1950
- [86] J.W. Thybaut, G.B. Marin, C. Mirodatos, Y. Schuurman, A.C. van Veen, V.A. Sadykov, H. Pennemann, R. Bellinghausen, and L. Mleczko. A novel technology for natural gas conversion by means of integrated oxidative coupling and dry reforming of methane. *Chem. Ing. Tech.*, 86:1588–1870, 2014. 1951
- [87] J.W. Hemmings, L. Bonnell, and E.T. Robinson. Method and apparatus for producing synthesis gas. U.S. Patent 7686856 B2, 2010. 1952
- [88] S. Chakravarti, M.M. Shah, R.F. Drnevich, W.Y. Sarmiento-Darkin, B.r. Kromer, and S.M. Kelly. Method and system for producing methanol using oxygen transport membrane based reforming system. U.S. Patent 9115045 B2, 2015. 1953
- [89] S. Gupta, J.J. Adams, J.R. Wilson, E.G. Eddings, M.K. Mahapara, and P. Singh. Performance and post-test characterization of an OTM system in an experimental coal gasifier. *Appl. Energy*, 165:72–80, 2016. 1954
- [90] A. de Klerk and E. Furimsky. *Catalysis in the Refining of Fischer-Tropsch Syncrude*. Royal Society of Chemistry, Cambridge, England, 2010. 1955
- [91] S. Mousavi, A. Zamaniyan, M. Irani, and M. Rashidzadeh. Generalized kinetic model for iron and cobalt based Fischer-Tropsch synthesis catalysts: Review and model evaluation. *Appl. Catal., A*, 506:57–66, 2015. 1956
- [92] M.N. Yakubovich and P.E. Strizhak. Kinetic models of the molecular mass distribution of the products of the Fischer-Tropsch synthesis at cobalt catalysts. *Theor. Exp. Chem.*, 43:361–379, 2007. 1957
- [93] D. Fortsch, K. Pabst, and E. Groß-Hardt. The product distribution in Fischer-Tropsch synthesis: An extension of the ASF model to describe common deviations. *Chem. Eng. Sci.*, 138:333–346, 2015. 1958
- [94] S.T. Sie and R. Krishna. Fundamentals and selection of advanced Fischer-Tropsch reactors. *Appl. Catal., A*, 186:55–70, 1999. 1959
- [95] G. Chabot, R. Guilet, P. Cognet, and C. Gourdon. A mathematical modeling of catalytic milli-fixed bed reactor for Fischer-Tropsch synthesis: Influence of tube diameter on Fischer-Tropsch selectivity and thermal behavior. *Chem. Eng. Sci.*, 127:72–83, 2015. 1960
- [96] R. Krishna and S.T. Sie. Design and scale-up of the Fischer-Tropsch bubble column slurry reactor. *Fuel Process. Technol.*, 64:73–105, 2000. 1961
- [97] D.Y. Shin, K.S. Ha, M.J. Park, G. Kwak, Y.J. Lee, and K.W. Jun. CFD modeling of a modular reactor for the Fischer-Tropsch synthesis: Effectiveness of a micro-scale cross-current cooling channel. *Fuel*, 158:826–834, 2015. 1962
- [98] S. Saeidi, M.K. Nikoo, A. Mirvakili, S. Bahrani, N.A.S. Amin, and M.R. Rahimpour. Recent advances in reactors for low-temperature Fischer-Tropsch synthesis: Process intensification perspective. *Rev. Chem. Eng.*, 31:209–238, 2015. 1963
- [99] S. Park, I. Jung, U. Lee, J. Na, K.S. Kshetrimayum, Y. Lee, C.J. Lee, and C. Han. Design and modeling of large-scale cross-current multichannel Fischer-Tropsch reactor using channel decomposition and cell-coupling method. *Chem. Eng. Sci.*, 134:448–456, 2015. 1964
- [100] S. Park, I. Jung, Y. Lee, K.S. Kshetrimayum, J. Na, S. Park, S. Shin, D. Ha, Y. Lee, J. Chung, C. Lee, and C. Han. Design of microchannel Fischer-Tropsch reactor using cell-coupling method: Effect of flow configurations and distribution. *Chem. Eng. Sci.*, 143:63–75, 2016. 1965
- [101] C. Karakaya and R.J. Kee. Progress in the direct catalytic conversion of methane to fuels and chemicals. *Prog. Energy Combust. Sci.*, 55:60–97, 2016. 1966
- [102] G.E. Keller and M.M. Bhasin. Synthesis of ethylene via oxidative coupling of methane. *J. Catal.*, 73:9–19, 1982. 1967
- [103] J.A. Labinger and K.C. Ott. Mechanistic studies on the oxidative coupling of methane. *J. Phys. Chem.*, 91:2682–2684, 1987. 1968
- [104] H. Zanthoff and M. Baerns. Oxidative coupling of methane in the gas phase. Kinetic simulation and experimental verification. *Ind. Eng. Chem. Res.*, 29:2–10, 1990. 1969
- [105] Q. Chen, J.H.B.J. Hoebink, and G.B. Marin. Kinetics of the oxidative coupling of methane at atmospheric pressure in the absence of catalyst. *Ind. Eng. Chem. Res.*, 30:2088–2097, 1991. 1970
- [106] J.H.B.J. Hoebink, P.M. Couwenberg, and G.B. Marin. Fixed bed reactor design for gas-phase chain reactions catalyzed by solids: The oxidative coupling of methane. *Chem. Eng. Sci.*, 49:5453–5463, 1994. 1971
- [107] J.H. Lunsford. The catalytic oxidative coupling of methane. *Angew. Chem. Int. Ed.*, 34:970–980, 1995. 1972
- [108] Z. Stansch, L. Mleczko, and M. Baerns. Comprehensive kinetics of oxidative coupling of methane over the $\text{La}_2\text{O}_3/\text{CaO}$ catalyst. *Ind. Eng. Chem. Res.*, 36:2568–2579, 1997. 1973
- [109] J. Sun, J.W. Thybaut, and G.B. Marin. Microkinetics of methane oxidative coupling. *Catal. Today*, 137:90–102, 2008. 1974
- [110] K. Tanakabe and E. Iglesia. Mechanistic aspects and reaction pathways for oxidative coupling of methane on $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts. *J. Phys. Chem. C*, 113:10131–10145, 2009. 1975
- [111] D. Noon, A. Subai, and S. Senkan. Oxidative coupling of methane by nanofiber catalysts. *ChemCatChem*, 5:146–149, 2013. 1976
- [112] H.R. Godini, S. Xiao, M. Kim, N. Holst, S. Jaso, O. Gorke, J. Steinbach, and G. Wozny. Experimental and model-based analysis of membrane reactor performance for methane oxidative coupling: Effect of radial heat and mass transfer. *Ind. J. Eng. Chem.*, 20:1993–2002, 2014. 1977
- [113] B. Zohour, D. Noon, and S. Senkan. Spatial concentration and temperature profiles in dual-packed-bed catalytic reactors: Oxidative coupling of methane. *ChemCatChem*, 6:2815–2880, 2014. 1978
- [114] Z. Zhang, Z. Guo, and S. Ji. Numerical simulation of packed-bed reactor for oxidative coupling of methane. *J. Energy* 1979

- Chem.*, 24:23–30, 2015.
- [115] N.Y. Usachev, V.V. Kharlamov, E.P. Belanova, and T.S. Starostina. Oxidative processing of light alkanes: State-of-the-art and prospects. *Russ. J. Gen. Chem.*, 79:1252–1263, 2009.
- [116] U. Zavyalova, M. Holena, R. Schloegl, and M. Baerns. Statistical analysis of past catalytic data on oxidative methane coupling for new insights into the composition of high-performance catalysts. *ChemCatChem.*, 3:1935–1947, 2011.
- [117] C. Hammond, S. Conrad, and I. Hermans. Oxidative methane upgrading. *ChemSusChem*, 5:1668–1686, 2012.
- [118] Evgenii V. Kondratenko, Michael Schlter, Manfred Baerns, David Linke, and Martin Holena. Developing catalytic materials for the oxidative coupling of methane through statistical analysis of literature data. *Catal. Sci. Technol.*, 5:1668–1677, 2015.
- [119] S.C. Reyes, E. Iglesia, and C.P. Kelkar. Kinetic-transport models of bimodal reaction sequences-I. Homogeneous and heterogeneous pathways in oxidative coupling of methane. *Chem. Eng. Sci.*, 48:2643–2661, 1993.
- [120] J.M. DeBoy and R.F. Hicks. Kinetics of the oxidative coupling of methane over 1 wt. % Sr/La₂O₃. *J. Catal.*, 113:517–527, 1988.
- [121] R.P. Taylor and G.L. Schrader. Lanthanum catalysts for CH₄ oxidative coupling-A comparison of the reactivity of phases. *Ind. Eng. Chem. Res.*, 30:1016–1023, 1991.
- [122] Y. Feng, J. Niiranen, and D. Gutman. Kinetic studies of the catalytic oxidation of methane. I. Methyl radical production on 1% Sr/La₂O₃. *J. Phys. Chem.*, 95:6558–6563, 1991.
- [123] M.T. Xu and J.H. Lunsford. Effect of temperature on methyl radical generation over Sr/La₂O₃ catalysts. *Catal. Lett.*, 11:295–300, 1991.
- [124] T.L. Van, M. Che, J.M. Tatibouet, and M. Kermarec. Infrared study of formation and stability of La₂O₂CO₃ during the oxidative coupling of methane on La₂O₃. *J. Catal.*, 142:18–26, 1993.
- [125] X. Fang, S. Li, J. Lin, J. Gu, and D. Yang. Production of C₂H₄ through oxidative coupling of CH₄ over W-Mn catalysts. *J. Mol. Catal. (China)*, 6:427–433, 1992.
- [126] H. Liu, X. Wang, D. Yang, R. Gao, Z. Wang, and J. Yang. Scale up and stability test for oxidative coupling of methane over Na₂WO₄-Mn/SiO₂ catalyst in a 200 mL fixed-bed reactor. *J. Nat. Gas. Chem.*, 17:59–63, 2008.
- [127] R. Koirala, R. Bchel, S.E. Pratsinis, and A. Baiker. Oxidative coupling of methane on flame-made Mn-Na₂WO₄/SiO₂: Influence of catalyst composition and reaction conditions. *Appl. Catal. A*, 484:97–107, 2014.
- [128] T.W. Elkins and H.E. Hagelin-Weaver. Characterization of Mn/Na₂WO₄/SiO₂ and Mn/Na₂WO₄/MgO catalysts for the oxidative coupling of methane. *Appl. Catal. A*, 497:96–106, 2015.
- [129] N. Hiyoshi and T. Ikeda. Oxidative coupling of methane over alkali chloride MnNa₂WO₄/SiO₂ catalysts: Promoting effect of molten alkali chloride. *Fuel Process. Technol.*, 133:29–34, 2015.
- [130] T. Ito, J.-X. Wang, C.-H. Lin, and J.H. Lunsford. Oxidative dimerization of methane over a lithium-promoted magnesium oxide catalyst. *J. Am. Chem. Soc.*, 107:5062–5068, 1985.
- [131] D.J. Driscoll, W. Martir, J.X. Wang, and J.H. Lunsford. Formation of gas-phase methyl radicals over MgO. *J. Am. Chem. Soc.*, 107:58–63, 1985.
- [132] P. Myrach, N. Nilius, S.V. Levchenko, A. Gonchar, T. Risse, K.-P. Dinse, L.A. Boatner, W. Frandsen, R. Horn, H.-J. Freund, R. Schlogl, and M. Scheffer. Temperature-dependent morphology, magnetic and optical properties of Li-doped MgO. *ChemCatChem*, 2:854–862, 2010.
- [133] S. Arndt, U. Simon, S. Heitz, A. Berthold, B. Beck, O. Gorker, J. D. Epping, T. Otremba, Y. Aksu, E. Irran, G. Laugel, M. Driess, H. Schubert, and R. Schomaecker. Li-doped MgO from different preparative routes for the oxidative coupling of methane. *Top. Catal.*, 54:1266–1285, 2011.
- [134] L. Tang, D. Yamaguchi, L. Wong, N. Burke, and Ken Chiang. The promoting effect of ceria on Li/MgO catalysts for the oxidative coupling of methane. *Catal. Today*, 178:172–180, 2011.
- [135] U. Simona, S. Arndt, T. Otremba, T. Schlingmann, O. Görke, K.-P. Dinsec, R. Schomäcker, and H. Schubert. Li/MgO with spin sensors as catalyst for the oxidative coupling of methane. *Catal. Comm.*, 18:132–136, 2012.
- [136] A. Vatani, E. Jabbari, M. Askarieh, and M. A. Torangi. Kinetic modeling of oxidative coupling of methane over Li/MgO catalyst by genetic algorithm. *J. Nat. Gas Sci. Eng.*, 20:347–356, 2014.
- [137] V.R. Choudhary, S.A.R. Mulla, and V.H. Rane. Surface basicity and acidity of alkaline earth-promoted La₂O₃ catalysts and their performance in oxidative coupling of methane. *J. Chem. Technol. Biotechnol.*, 72:125–130, 1998.
- [138] S. Pak, P. Qui, and J.H. Lunsford. Elementary reactions in the oxidative coupling of methane over Mn/Na₂WO₄/SiO₂ and Mn/Na₂WO₄/MgO catalysts. *J. Catal.*, 179:222–230, 1998.
- [139] S. Zarrinpashne, R. Ahmedi, and S. M. Zekordi. Catalytic direct conversion of methane to ethane and ethylene. U.S. Patent 7902113B2, 2011.
- [140] B. Fallah and C. Falamaki. A new nano-(2Li₂O/MgO) catalyst/porous alpha-alumina composite for the oxidative coupling of methane reaction. *AIChE J.*, 56:717–728, 2010.
- [141] P. Huang, Y. Zhao, J. Zhang, Y. Zhu, and Y. Sun. Exploiting shape effects of La₂O₃ nanocatalysts for oxidative coupling of methane reaction. *Nanoscale*, 5:10844–10848, 2013.
- [142] J. Song, Y. Sun, R. Ba, S. Huang, Y. Zhao, J. Zhang, Y. Sun, and Y. Zhu. Monodisperse Sr/La₂O₃ hybrid nanofibers for oxidative coupling of methane to synthesize C₂ hydrocarbons. *Nanoscale*, 7:2260–2264, 2015.
- [143] Y.H. Hou, W.C. Han, W.S. Xia, and H.L. Wan. Structure sensitivity of La₂O₂CO₃ catalysts in the oxidative coupling of methane. *ACS Catal.*, 5:1663–1674, 2015.
- [144] W.P. Schammel, J. Wolfennarger, M. Ajinkya, J. McCarty, J.M. Cizeron, S. Weinberger, J.D. Edwards, D. Sheridan, E.C. Scher, and J. McCormick. Oxidative coupling of methane systems and methods. U.S. Patent 2014/0107385 A1, 2014.
- [145] A. Tkachenko, J. Gamoras, D. Karshtedt, G. Nyce, and F.R. Zurcher. Method for oxidative coupling of methane in the presence of nanowire catalyst. EP 2853521 A1, 2015.
- [146] G.B. Skinner, A. Lifshitz, K. Scheller, and A. Burcat. Kinetics of methane oxidation. *J. Chem. Phys.*, 56:3853–3861, 1972.
- [147] J. Warnatz. *Rate coefficients in the C/H/O system in combustion chemistry*. Springer, Berlin, 1984.
- [148] W. Tsang and R.F. Hampson. Chemical kinetic data base for combustion chemistry. Part I. Methane and related compounds. *J. Phys. Chem. Ref. Data*, 15:1087–1279, 1986.
- [149] K.D. Campbell, H. Zhang, and J.H. Lunsford. Methane activation by the lanthanide oxides. *J. Phys. Chem.*, 92:750–753, 1988.
- [150] L. Luo ad X. Tang, W. Wang an Y. Wang, S. Sun, F. Qui, and W. Huang. Methyl radicals in oxidative coupling of methane directly confirmed by synchrotron VUV photoionization mass spectroscopy. *Sci. Rep.*, 3:1625–1631, 2013.
- [151] Q. Chen, P.M. Couwenberg, and G.B. Marin. Effect of pressure on the oxidative coupling of methane in the absence of catalyst. *AIChE J.*, 40:521–535, 1994.
- [152] H.R. Godini, S. Jaso, S. Xiao, H. Arellano-Garcia, M. Omid-

- khah, and G. Wozny. Methane oxidative coupling: Synthesis of membrane reactor networks. *Ind. Eng. Chem. Res.*, 51:7747–7761, 2012.
- [153] N. Holst, S. Jaso, H.R. Godini, S. Gloser, H. Arellano-Garcia, G. Wozny, and J. Steinbach. Two-dimensional model for oxidative coupling of methane in a packed-bed membrane reactor. *Chem. Eng. Technol.*, 35:294–301, 2012.
- [154] H.R. Godini, S. Xiao, M. Kim, N. Holst, S. Jaso, O. Gorke, J. Steinbach, and G. Wozny. Experimental and model-based analysis of membrane reactor performance for methane oxidative coupling: Effect of radial heat and mass transfer. *Ind. J. Eng. Chem.*, 20:1993–2002, 2014.
- [155] J.S. Ahari, S. Zarrinpashne, and M.T. Sadeghi. Micro-kinetic modeling of ocm reactions over Mn/Na₂WO₄/SiO₂ catalyst. *Fuel Process. Technol.*, 115:79–87, 2013.
- [156] B. Zohour, D. Noon, and S. Senkan. New insights into the oxidative coupling of methane from spatially resolved concentration and temperature profiles. *ChemCatChem*, 5:2809–2812, 2013.
- [157] R. Horn, K.A. Williams, N.J. Degenstein, and L.D. Schmidt. Syngas by catalytic partial oxidation of methane on rhodium: Mechanistic conclusions from spatially resolved measurements and numerical simulations. *J. Catal.*, 242:92–102, 2006.
- [158] R. Horn, K.A. Williams, N.J. Degenstein, and L.D. Schmidt. Mechanism of H₂ and CO formation in the catalytic partial oxidation of CH₄ on Rh probed by steady-state spatial profiles and spatially resolved transients. *Chem. Eng. Sci.*, 62:1298–1307, 2007.
- [159] A. Donazzi, M. Maestri, B.C. Michael, A. Beretta, P. Forzatti, G. Groppi, E. Tronconi, L.D. Schmidt, and D.G. Vlachos. Microkinetic modeling of spatially resolved autothermal CH₄ catalytic partial oxidation experiments over Rh-coated foams. *J. Catal.*, 275:270–279, 2010.
- [160] D. Schweer, L. Mleczko, and M. Baerns. OCM in a fixed-bed reactor: Limits and perspectives. *Catal. Today*, 21:357–369, 1994.
- [161] J.Y. Lee, W. Jeon, J.-W. Choi, Y.-W. Suh, J.-M. Ha, D.J. Suh, and Y.-K. Park. Scaled-up production of C₂ hydrocarbons by the oxidative coupling of methane over pelletized Na₂WO₄/Mn/SiO₂ catalysts: Observing hot spots for selective process. *Fuel*, 106:851–887, 2013.
- [162] M.-S. Salehi, M. Askarishahi, H.R. Godini, O. Görke, and G. Wozny. Sustainable process design for oxidative coupling of methane (OCM): Comprehensive reactor engineering via computational fluid dynamics (CFD) analysis of OCM packed-bed membrane reactors. *Ind. Eng. Chem. Res.*, 2016. DOI:10.1021/acs.iecr.5b03292.
- [163] K. Otsuka, S. Yokoyama, and A. Morikawa. catalytic activity and selectivity control for oxidative coupling of methane by oxygen pumping through yttria stabilized zirconia. *Chem. Lett.*, pages 319–322, 1985.
- [164] S.J. Xu and W.J. Thomson. Oxygen permeation rates through ion-conducting perovskite membranes. *Chem. Eng. Sci.*, 54:3839–3850, 1999.
- [165] J. Hong, P. Kirchen, and A.F. Ghoniem. Numerical simulation of ion transport membrane reactors: Oxygen permeation and transport and fuel conversion. *J. Membr. Sci.*, 407-408:71–85, 2012.
- [166] S.H. Lee, V.R. Manga, M.F. Carolan, and Z.-K. Liu. Defect chemistry and phase equilibria of (La_{1-x}Ca_x)FeO_{3-δ} thermodynamic modeling. *J. Electrochem. Soc.*, 160:F1103–F1108, 2013.
- [167] T.C. Geary and S.B. Adler. Oxygen nonstoichiometry and defect chemistry of the mixed conductor La_{0.9}Ca_{0.1}FeO_{3-δ} at low oxygen partial pressure. *Solid State Ionics*, 253:88–93, 2013.
- [168] P. Kirchen, D.J. Apo, A. Hunt, and A.F. Ghoniem. A novel ion transport membrane reactor for fundamental investigations of the permeation and oxy-combustion under reactive flow conditions. *Proc. Combust. Inst.*, 34:3463–3470, 2013.
- [169] A. Hunt, G. Dimitrakopoulos, P. Kirchen, and A.F. Ghoniem. Measuring the oxygen profile and permeation flux across an ion transport La_{0.9}Ca_{0.1}FeO_{3-δ} membrane and the development and validation of a multistep surface exchange model. *J. Membr. Sci.*, 468:62–72, 2014.
- [170] T. Schiestel, M. Kilgus, S. Peter, K.J. Caspary, H. Wang, and J. Caro. Hollow fiber perovskite membranes for oxygen separation. *J. Membr. Sci.*, 258:1–4, 2005.
- [171] X. Tan, Y. Liu, and K. Li. Mixed conducting ceramic hollow-fiber membranes for air separation. *AIChE J.*, 51:1991–2000, 2005.
- [172] S. Liu and G.R. Gavalas. Oxygen selective ceramic hollow fiber membranes. *J. Membr. Sci.*, 246:103–108, 2005.
- [173] O. Czuprat, T. Schiestel, H. Voss, and J. Caro. Oxidative coupling of methane in a BCFZ perovskite hollow fiber membrane reactor. *Ind. Eng. Chem. Res.*, 49:10230–10236, 2010.
- [174] N.H. Othman, Z. Wu, and K. Li. A micro-structured La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} hollow fibre membrane reactor for oxidative coupling of methane. *J. Membr. Sci.*, 468:31–41, 2014.
- [175] N.H. Othman, Z. Wu, and K. Li. An oxygen permeable membrane microreactor with an in-situ deposited Bi_{1.5}Y_{0.3}Sm_{0.2}Fe_{0.8}O_{3-δ} catalyst for oxidative coupling of methane. *J. Membr. Sci.*, 488:182–193, 2015.
- [176] J. Zhu, S. Guo, Z. Zhang, X. Jiang, Z. Liu, and W. Jin. CO₂ tolerant mixed conducting multichannel hollow fiber membrane for efficient oxygen separation. *J. Membr. Sci.*, 485:79–86, 2015.
- [177] D. Lafarga, J. Santamaria, and M. Menendez. Methane oxidative coupling using porous ceramic membrane reactors-I. reactor development. *Chem. Eng. Sci.*, 49:2005–2013, 1993.
- [178] J. Coronas, J. Santamaria, and M. Menendez. Methane oxidative coupling using porous ceramic membrane reactors-II. reaction studies. *Chem. Eng. Sci.*, 49:2015–2025, 1993.
- [179] W. Kiatkittipong, T. Tagawa, S. Goto, S. Assabumrungra, K. Silpasup, and P. Praserttham. Comparative study of oxidative coupling of methane modeling in various types of reactor. *Chem. Eng. J.*, 115:63–71, 2005.
- [180] H.R. Godini, H. Trivedi, A. Gili de Villasante, O. Gorke, S. Jaso, U. Simon, A. Berthold, W. Witt, and G. Wozny. Design and demonstration of an experimental membrane reactor set-up for oxidative coupling of methane. *Chem. Eng. Res. Des.*, 91:2671–2681, 2013.
- [181] H. Shirasaka, T. Shimonosono, Y. Hirata, and S. Sameshima. Analysis of gas permeability of porous alumina powder compacts. *J. Asian Ceram. Soc.*, 1:368–373, 2013.
- [182] S. Ishizuka. On the behavior of premixed flames in a rotating flow field: Establishment of tubular flames. *Proc. Combust. Inst.*, 20:287–294, 1985.
- [183] T. Takeno and S. Ishizuka. A tubular flame theory. *Combust. Flame*, 64:83–98, 1986.
- [184] S. Ishizuka. Characteristics of tubular flames. *Prog. Energy Combust. Sci.*, 19:187–226, 1993.
- [185] S. Ishizuka, editor. *Tubular Combustion*. Momentum Press, New York, 2013.
- [186] R.J. Kee, A.M. Colclasure, H. Zhu, and Y. Zhang. Modeling tangential injection into ideal tubular flames. *Combust. Flame*, 152:114–124, 2008.
- [187] R. Schellen, L. Mleczko, E.H. Hoffmann, and S. Schubert. Method for oxidative coupling of methane and producing syngas. U.S. Patent 2011/0240926 A1, 2011.

- [188] J.M. Santamaria, E.E. Miro, and E.E. Wolf. Reactor simulation studies of methane oxidative coupling on a Na/NiTiO₃ catalyst. *Ind. Eng. Chem. Res.*, 30:1157–1165, 1991.
- [189] J. Santamaria, M. Menéndez, J.A. Peña, and J.I. Barahona. Methane oxidative coupling in fixed bed catalytic reactors with a distributed oxygen feed. A simulation study. *Catal. Today*, 13:353–360, 1992.
- [190] I.P. Androulakis and S.C. Reyes. Role of distributed oxygen addition and product removal in the oxidative coupling of methane. *AIChE J.*, 45:860–868, 1999.
- [191] S. Ramakrishnan and C.F. Edwards. Maximum-efficiency architectures for steady-flow combustion engines, II: Work-regenerative gas-turbine engines. *Energy*, 72:58–68, 2014.
- [192] T. Nada. Performance characterization of different configurations of gas turbine engines. *Propul. Power Res.*, 3:121–132, 2014.
- [193] W.A. Sirignano, D. Dunn-Rankin, F. Liu, B. Colcord, and S. Puranam. Turbine burners: Performance improvement and challenge of flameholding. *AIAA J.*, 50:1645–1669, 2012.
- [194] U. Zavyalova, M. Geske, R. Horn, G. Weinberg, W. Frandsen, M. Schuster, and R. Schlögl. Morphology and microstructure of Li/MgO catalysts for the oxidative coupling of methane. *ChemCatchem*, 3:949–959, 2011.
- [195] S. Ma, X. Guo, L. Zhao, S. Scott, and X. Bao. Recent progress in methane dehydroaromatization: From laboratory curiosities to promising technology. *J. Energy Chem.*, 22:1–20, 2013.
- [196] P. Tang, Q. Zhu, Z. Wu, and D. Ma. Methane activation: The past and future. *J. Energy Environ. Sci.*, 7:2580–2591, 2014.
- [197] R. Horn and R. Schlögl. Methane activation by heterogeneous catalysts. *Catal. Lett.*, 145:23–29, 2015.
- [198] L. Li, R. Borry, and E. Iglesia. Reaction-transport simulations of non-oxidative methane conversion with continuous hydrogen removal – homogeneous-heterogeneous reaction pathways. *Chem. Eng. Sci.*, 56:1869–1881, 2001.
- [199] W. Li, R.W. Borry, and E. Iglesia. Design and optimization of catalysts and membrane reactors for the non-oxidative conversion of methane. *Chem. Eng. Sci.*, 57:4595–4604, 2002.
- [200] Ø. Hatlevik, S.K. Gade, M.K. Keeling, P.M. Thoen, A.P. Davidson, and J.D. Way. Palladium and palladium alloy membranes for hydrogen separation and production: History, fabrication strategies, and current performance. *Sep. Purif. Technol.*, 73:59–64, 2010.
- [201] R.J. Kee, H. Zhu, B.W. Hildenbrand, E. Völlestad, M.D. Sanders, and R.P. O’Hayre. Modeling the steady-state and transient response of polarized and non-polarized proton-conducting doped-perovskite membranes. *J. Electrochem. Soc.*, 160:F290–F300, 2013.
- [202] E. Völlestad, H. Zhu, and R.J. Kee. Interpretation of defect and gas-phase fluxes through mixed-conducting ceramics using Nernst–Planck–Poisson and integral formulations. *J. Electrochem. Soc.*, 161:F114–F124, 2014.
- [203] H. Zhu, S. Ricote, W.G. Coors, and R.J. Kee. Interpreting equilibrium-conductivity and conductivity-relaxation measurements to establish thermodynamic and transport properties for multiple charged defect conducting ceramics. *Faraday Discuss.*, 182:49–74, 2015.
- [204] H. Zhu and R.J. Kee. Membrane polarization in mixed-conducting ceramic fuel cells and electrolyzers. *Intl. J. Hydrogen Energy*, 41:2931–2943, 2016.
- [205] L. Devi, K.J. Ptasinski, and F.J.J.G. Janssen. Decomposition of naphthalene as a biomass tar over pretreated olive: Effect of gas composition, kinetic approach, and reaction scheme. *Ind. Eng. Chem. Res.*, 44:9096–9104, 2005.
- [206] P. R. Buchireddy, R. M. Bricka, J. Rodriguez, and W. Holmes. Biomass gasification: Catalytic removal of tars over zeolites and nickel supported zeolites. *Energy Fuels*, 24:2707–2715, 2010.
- [207] S.N. Paglieri and J.D. Way. Innovations in palladium membrane research. *Sep. Purif. Method.*, 31:1–169, 2002.
- [208] K.D. Kreuer. Proton-conducting oxides. *Annu. Rev. Mater. Res.*, 33:333–359, 2003.
- [209] T. Norby and Y. Larring. Mixed hydrogen ion-electronic conductors for hydrogen permeable membranes. *Solid State Ionics*, 136-137:139–148, 2000.
- [210] Y. Liu, X. Tan, and K. Li. Mixed conducting ceramics for catalytic membrane processing. *Catal. Rev. Sci. Eng.*, 48:145198, 2006.
- [211] H. Matsumoto, T. Shimura, H. Iwahara, T. Higuchi, K. Yashiro, A. Kaimai, T. Kawada, and J. Mizusaki. Hydrogen separation using proton-conducting perovskites. *J. Alloys Compd.*, 408-412:456–462, 2006.
- [212] B. Euser, J.R. Berger, H. Zhu, and R.J. Kee. Defect-transport-induced stress in mixed ionic-electronic conducting (MIEC) ceramic membranes. *J. Electrochem. Soc.*, 163:F264–F271, 2016.
- [213] K.J. Yoon, P.A. Zink, S. Gopalan, U.B. Pal, and L.R. Pederson. Defect chemistry and electrical properties of (La_{0.8}Ca_{0.2})_{0.95}FeO_{3-δ}. *J. Electrochem. Soc.*, 156:B795–B800, 2009.
- [214] A. Hunt, G. Dimitrakopoulos, and A.F. Ghoniem. Surface oxygen vacancy and oxygen permeation flux limits of perovskite ion transport membranes. *J. Membr. Sci.*, 489:248–257, 2015.
- [215] S.K. Kim, M.J. Shin, J. Rufner, K. van Benthem, J.H. Yu, and S. Kim. Sr_{0.95}Fe_{0.5}Co_{0.5}O_{3-δ}–Ce_{0.9}Gd_{0.1}O_{2-δ} dual-phase membrane: Oxygen permeability, phase stability, and chemical compatibility. *J. Membr. Sci.*, 462:153–159, 2014.
- [216] T. Zhu, Z. Yang, and M. Han. Dual-phase material and its potential application in oxygen transport membrane. *J. Mater. Sci. Technol.*, 30:954–958, 2014.
- [217] H. Cheng, L. Luo, W. Yao, X. Lu, X. Zou, and Z. Zhou. Novel cobalt-free CO₂-tolerant dual-phase membranes of Ce_{0.8}Sm_{0.2}O_{2-δ}–Ba_{0.95}La_{0.05}Fe_{1-x}Zr_xO_{3-δ} for oxygen separation. *J. Membr. Sci.*, 492:220–229, 2015.
- [218] A.S. Yu, T.-S. Oh, R. Zhu, A. Gallegos, R.J. Gorte, and J.M. Vohs. Surface modification of La_{0.8}Sr_{0.2}CrO_{3-δ}-YSZ dual-phase membranes for syngas production. *Faraday Discuss.*, 182:213–225, 2015.
- [219] S.K. Kim, M.J. Shin, J. Rufner, K. van Benthem, J.H. Yu, and S. Kim. Highly stable dual-phase Y_{0.8}Ca_{0.2}Cr_{0.8}Co_{0.2}O₃–Sm_{0.2}Ce_{0.8}O_{1.9} ceramic composite membrane for oxygen separation. *J. Membr. Sci.*, 499:301–306, 2016.