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

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Abstract

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

Keywords:

Methane activation, Membranes, Catalytic chemistry, Gas to liquids, Process intensification

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1. Introduction

The growing availability of low-cost and domestically sourced natural gas leads to increased interest in its conversion to more-valuable fuels and chemicals. Although natural gas is a mixture of small hydrocarbons and other components such as sulfur compounds, the dominant component is methane. This review focuses on the conversion of methane alone, where numerous research and development challenges remain to be met and overcome. To narrow the scope even further, the review is particularly concerned with the direct conversion of methane to hydrocarbons, not to oxygenated products such as alcohols or intermediates such as synthesis gas (i.e., CO and H₂). The term direct conversion here refers to the processes that do not involve the intermediate production of synthesis gas. In other words, “direct” means that reforming agents (i.e., H₂O and/or CO₂) are not added, or are added in very low levels that are not intended as reforming agents. Such low-level reforming agents can also be produced as reaction intermediates within the process, and can participate in some reforming chemistry within a so-called “direct” process. Previous authors have used a similar definition [1, 2].

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

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

A wide range of chemicals could be produced from methane. This paper focuses on the processes to form small hydrocarbons with aliphatic, olefinic, or aromatic content. The processes considered all involve ethylene formation, which may be an intermediate compo-

nent to produce compounds with higher olefin, paraffin, and aromatic (e.g., benzene) content. Oligomerization of ethylene can produce higher olefins that could be used in gasoline (C₅–C₁₀) or in diesel fuel (C₁₀–C₂₀). The higher olefins can also be converted to paraffins via catalytic hydrogenation processes [10, 11], leading to constituents needed for energy-dense fuels. Of course, ethylene itself is already a valuable chemical feedstock for numerous downstream processes. Oxygenates (e.g., methanol, ethanol) are not within this paper’s scope.

Processes such as Fischer–Tropsch (F–T) have been practiced commercially for decades. In this case, the methane is first catalytically reformed or partially oxidized to produce synthesis gas (primarily a mixture of H₂ and CO). The synthesis gas is then further processed to deliver a wide range of hydrocarbon or oxygenated products. However, assuming that a hydrocarbon product is desired, the sequence of first oxidizing to syngas and then reducing to the product has inherent inefficiencies. Nevertheless, despite any such inefficiencies, these processes are practical and industrially viable [12].

Direct conversion of methane to ethylene, as well as further oligomerization and hydrogenation, are all proven concepts. Ethylene oligomerization is an industrial-scale process, first developed by Shell in 1977 [10]. In that process, the ethylene is produced via a F–T process. However, despite substantial efforts in the last three decades, direct conversion of methane to ethylene requires improvements to be commercially successful.

In recent years, several patented technologies have been developed with the objective of commercializing gas-to-liquids (GTL) processes. Siluria Technologies [13] is apparently in the process of upscaling a pilot plant to produce ethylene as a precursor for logistic fuels. A large European Union framework program (2009–2014) focused on developing fully integrated processes for oxidative coupling of methane, where ethylene also served as a precursor for liquid logistic fuels. A number of alternative catalysts, processes, and reactors were investigated to demonstrate a proof of concept for ethylene to liquid fuels [14]. Nevertheless, despite significant efforts, these processes have not yet achieved commercial viability.

Direct methane conversion faces a number of significant challenges, including:

- Thermodynamically limited conversion,
- Catalyst selectivity to desired products,
- Catalyst deactivation via carbon deposits.

Membranes and membrane reactors can play important roles in mitigating the obstacles associated with direct conversion.

Consider, for example, methane dehydroaromatization (MDA) to produce benzene, which may be represented globally as

Another example is direct ethylene production, represented globally as

In both cases, the extent of methane conversion is thermodynamically limited by hydrogen accumulation within the reactor. In other words, the reaction can equilibrate with only a fraction of the methane being converted. Ideally, a hydrogen-permeable membrane that selectively removes H_2 can promote increased conversion and product yield.

Although reactions 1 and 2 represent desired global results, no actual processes can achieve such ideal outcomes. Catalysts must be designed and fabricated to be as selective as possible. However, even with the best catalysts, numerous side products are inevitably produced. Although membranes can usually increase conversion, they can also affect (both favorably and unfavorably) the selectivity to the desired products and a wide range of undesired side products. Undesired side products often include catalyst-fouling coke precursors and polyaromatic hydrocarbon (PAH) deposits. Membranes can play important roles in limiting or controlling the production of these unwanted and damaging products.

1.1. Catalysts

Today, more than 90% of all transportation fuels at some point during their production have passed over at least one catalyst. Some 80% of all chemical products are manufactured with the aid of catalysis and more than 20% of all industrial products rely on catalytic reaction technology [15].

Catalysts decrease activation barriers by altering reaction pathways, including the production of alternative species that may not be formed via gas-phase chemistry. Catalyst performance is usually governed by active sites on the catalyst surface. For example, noble metals (Rh, Pt, Ru, Pd) are effective reforming catalysts. Iron- and chromium-oxides are effective for F-T synthesis. Some processes require catalytic bi-functionality, meaning two different catalytic groups fractionalize sequential reactions. For example, Mo/zeolite catalysts are effective for methane dehydroaromatization (MDA). In this case, methane is activated on Mo_2C sites, primarily

forming C_2H_4 and H_2 . The C_2H_4 is further oligomerized and cyclized at Brønsted acid sites on the zeolite, forming benzene, toluene, and naphthalene.

Effective catalysts must enable desired reactions to proceed at suitable rates under conditions that are technologically desirable (e.g., at low temperature and pressure). Low temperature and pressure usually decrease design and operational complexity, thus decreasing the production cost and promoting safe operating environments. Achieving catalyst selectivity to desired product mixtures is a major objective. Undesired products (e.g., solid carbon and PAH) not only decrease the product yield but can also cause catalyst degradation and deactivation. Separating desired products from undesired side products can involve significant technical complexities and production costs, usually as downstream processes.

Effective catalysts should have structural integrity and chemical stability. Structural and mechanical integrity is important because catalysts can fracture under harsh operating conditions (e.g., acidic environments, high pressures). Chemical stability is important to prevent deleterious transformation of catalytically active surface sites. Impurities in reactant streams can poison the catalyst surfaces by strong adsorption on active sites, thus preventing desired adsorption of the reactants. For example, sulfur compounds are known to poison platinum and palladium catalysts. It is often possible to regenerate degraded or deactivated catalysts. However, doing so requires additional non-productive processes and time, increasing operational and production costs.

High-performance catalysts need to present readily accessible high surface areas to the reactant gases. Typical catalyst structures are formed as particles or pellets that are housed in packed-bed or washcoat configurations. In packed beds, gases flow around relatively large catalyst particles or pellets, which also have micro- and nano-scale pore structures that further increase active surface area. Washcoat structures are usually formed as thin layers (order of tens of microns) on the walls of millimeter-scale channels in **monolithic** structures or microchannel reactors [16, 17]. Especially with expensive noble-metal catalysts, it is important to design porous microstructures such that the active sites are readily accessible to the reactants.

1.2. Temperature and pressure tradeoffs

Essentially all processes that involve methane activation require elevated temperature (i.e., $\geq 700^\circ\text{C}$). However, operating pressure can vary, depending on the particular process and its integration with upstream

and downstream processing requirements. For example, industrial-scale methane reformers often operate at elevated pressure ($20 \leq p \leq 40$ bar), primarily to avoid the post-reforming compression of high temperature gases to be supplied to downstream processes that require high pressure (Fisher–Tropsch synthesis). High pressure actually compromises the performance of the reformation process. The design of particular chemical processes often depends on the integration with related processes, seeking overall optimal performance.

Similar to the methane reforming processes, the MDA process requires high temperatures and favors low pressure due to Le Châtelier’s principle. MDA process is thermodynamically limited. Even at 700°C and 1 bar, methane conversion is limited around 12% and the benzene yield is limited to approximately 8% [18]. Increasing pressure to 4 bar decreases methane conversion to 7%, and by 10 bar methane conversion is reduced to approximately 5.5%. Increasing temperature to 900°C increases the methane conversion to approximately 40%. However, the higher temperature favors the undesired formation of naphthalene over the desired benzene. Additionally, higher temperatures promote carbon deposits and accelerated catalyst fouling. Unlike reforming processes, MDA processes operate do not require reforming agents (H_2O , CO and CO_2) that tend to suppress carbon deposits. However, introducing low levels of H_2O ($\leq 2\%$), CO and CO_2 ($\leq 10\%$) can be beneficial but not fully eliminate catalyst-fouling carbon deposits. In isolation, an MDA reactor should operate at temperatures and pressures as low as possible.

The OCM process is significantly different from MDA. Methane conversion is limited by oxygen availability, with the process being oxygen mass-transport limited. Although increasing oxygen in the feed stream increases methane conversion, it also favors undesired total oxidation rather than the desired C_2 formation. The global rate OCM reaction ($2\text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$) is mole-neutral. Thus, at comparable residence times, increasing pressure has a negligible effect on the methane conversion. However, because the OCM process competes with total oxidation, increasing pressure increases methane conversion rate toward to total oxidation products and significantly decrease the C_2 yield. Although increasing temperature can increase the C_2 selectivity, catalyst stability is a major concern.

1.3. Membranes

A variety of membranes can play potentially beneficial roles in methane-conversion technology. In dehydrogenation processes, hydrogen-permeable membranes such as palladium or palladium-alloy membranes

Figure 1: Illustration of a shell-and-tube membrane reactors. a) The left-hand reactor uses a hydrogen-permeable such as for an MDA process. b) The right-hand reactor uses an oxygen-permeable membrane as for an ethylene-production process.

may be relevant. A variety of dense-ceramic ion-conducting membranes are also relevant. The proton-conducting ceramics are typically doped pervoskites (e.g., $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$, BZY10), which are usually mixed ionic-electronic conductors (MIEC). Depending on the particular membrane material, these ceramics may also have significant oxide-ion conductivity. In some cases, the material may also have significant electronic conductivity. Because of the required high temperatures for methane activation, polymer-based membranes are usually not relevant and not considered here.

Depending on the conversion process, the membranes may be hydrogen permeable, oxygen permeable, or a combination of both. Figure 1 illustrates two possible membrane-reactor configurations. In both cases, a packed-bed catalyst fills the annular space outside of a central sweep tube. The sweep tube is configured as a porous support, with a thin (order of tens of microns) membrane applied to the outer surface. The left-hand reactor illustrates a hydrogen-permeable membrane, such as might be used for an MDA process. In this case, hydrogen is transported from the catalyst bed, through the membrane, and into the sweep tube. Ideally, by reducing the hydrogen concentration within the catalyst bed, the thermodynamic equilibrium shifts in favor of increasing methane conversion and benzene yield (cf., Eq. 1). However, as discussed subsequently, the benzene yield may not always increase because of competition with the production of undesired side products such as naphthalene, toluene, or higher aromatics.

As illustrated in Fig. 1a, the membrane transports only hydrogen. A palladium membrane would deliver such performance. However, a ceramic mixed-conducting membrane can perform differently. Materials such yttrium- and cerium-doped barium zirconates (BCZY) can simultaneously transport both protons and oxide ions [19]. Depending on the sweep-gas and catalyst-bed composition, the net effect can be hydrogen leaving the catalyst bed and steam entering the catalyst bed. Because steam can react with deleterious side products such as naphthalene, ceramic MIEC membranes can offer potentially significant advantages compared to pure hydrogen-permeable membranes.

Figure 1b illustrates an oxygen-permeable membrane. Even in non-oxidative processes, low levels of oxygen onto the catalyst can be beneficial, including promotion of methane activation and preferential mitigation of carbon deposits. However, it should be emphasized that only low oxygen fluxes are relevant. If too much oxygen enters the catalyst bed, then undesired reforming or complete oxidation can dominate. In dehydrogenation processes, H_2 is readily available within the catalyst bed. Thus, under most circumstances, the oxygen (or oxide ions in the case of ion-transport membranes) emerging from the membrane reacts rapidly to produce H_2O .

Stated globally the oxidative coupling of methane (OCM) can be represented as

Typically, the oxygen and methane are premixed before entering the catalyst bed. However, there are potential benefits associated with oxygen-permeable membranes that deliver oxygen along the length of the bed (e.g., Fig. 1b). One approach is to use porous-alumina tubular structures. Another approach uses dense ceramic oxide-ion-conducting membranes such as $La_{1-x}Ca_xFeO_{3-\delta}$ (LCF).

Certain dense-ceramic ion-conducting membranes offer the possibility of control via electrical polarization. Ceramic membranes with low electronic conductivity compared to ionic conductivity can be polarized in the sense of using an external circuit to impose an electrostatic potential across the membrane. Yttria-stabilized zirconia (YSZ) is such a material, with good oxide-ion mobility but very little electronic conductivity. Such membranes are widely used in solid-oxide fuel cells (SOFC) and electrolyzers (SOEC). Doped barium cerates and zirconates have proton mobility, but relatively low electronic conductivity [20]. An applied electrostatic potential serves to mediate (accelerate or retard)

the electronically charged ion fluxes through the membrane. Electrodes that are spatially segmented along the length of the reactor provide an opportunity to locally control the fluxes through the membrane. However, because the ion conductivity of the ceramic membranes is relatively low, there can be substantial electrical costs associated with the polarization control.

Sections 6 and 7 discuss membrane materials and membrane reactor technologies in more detail.

1.4. Processes

This review concentrates on catalytic processes involving the initial conversion of methane to ethylene, and subsequently to gas mixtures with aliphatic and aromatic content. Broadly speaking, the processes may be oxidative or non-oxidative. However, in the oxidative case, this review is not concerned with reforming or partial oxidation to synthesis gas or the production of oxygenated compounds such as alcohols. The first sections of the paper are primarily concerned with reviewing and discussing alternative catalysts and catalytic processes. The following sections are concerned primarily with reactor design and performance. An important aspect of the paper is the consideration of membranes and membrane reactors.

1.5. Prior reviews on methane conversion

Direct conversion of methane to valuable chemical products has been the subject of several previous review articles. Because the topic involves a wide range of processes (oxidative, non-oxidative), products (aliphatic, aromatic, oxygenates), reactor concepts (flow reactors, membrane coupled flow reactors) and catalysts, some of the reviews are specific to subtopics.

A 2003 review by Choudhary et al. [21] considered the direct conversion of methane under non-oxidative conditions. They addressed some the main challenges associated with direct conversion, such as thermodynamic limitations and catalyst deactivation resulting in low yield. A 2014 review by Tang et al. [7] focused on methane activation either by high temperature or via oxygenates. Their review concluded that among the oxidative and non-oxidative conversion routes, non-oxidative processes such as methane to ethylene and aromatics are promising future technologies.

In 2013, Majhi et al. [22] reviewed the methane dehydroaromatization (MDA) process with a specific focus on Mo/zeolite catalysts, catalyst preparation methods, operating conditions (i.e., temperature and pressure), and reaction pathways. Their review discussed catalyst deactivation as a major technological impediment. They also discussed the effects of doping 2-3%

noble metals into Mo/zeolite catalysts, increasing benzene yield and catalyst stability. Also in 2013, Ma et al. [6] reviewed MDA processes. That review discussed key technologies for process up-scaling, including catalyst development and hydrogen-permeable membranes.

Mamonov et al. [23] published another 2013 review on methane dehydroaromatization, concentrating on Mo/ZSM-5 catalysts. This review concentrated on physical and chemical properties of the catalyst, including the structure of active sites, chemical mechanisms, and deactivation processes. The paper suggested approaches for improving catalytic activity, such as a second-metal doping.

Spivey and Hutchings [9] reviewed the status of MDA chemistry as of 2014. The primary focus of that review was on catalysts and catalytic reactor designs. Thermodynamic limitations, coke formation, and rapid catalyst deactivation were identified as significant problems. The review suggested that computational modeling would likely play a major role in understanding the catalytic chemistry and mitigating the deactivation problems.

Numerous studies have been published on the direct conversion of methane via oxidative processes, especially concentrating on catalyst research [24, 4, 5, 25, 8]. Zavyalova et al. [4] published an extensive review of the OCM catalysts, including the effects of metals and metal doping. A 2012 review by Takanabe [5] that reported the status of OCM processes, emphasizing the importance of developing alternative catalysts that improve ethylene selectivity.

Usachev et al. [3] published a 2009 review that focused on oxidative processes for small alkanes, including the oxidative coupling of methane. That review identified the primary challenges as being low selectivity, low C_2 yield, catalyst stability, coke formation, and temperature control. Integration with oxygen-permeable membranes was discussed in the context of improving thermal control and C_2 yield.

Liu et al. [26] published a 2001 review that concentrated on membrane-coupled methane-conversion processes, with a specific focus on protonic and mixed-conducting membrane reactors. Low hydrogen or oxygen fluxes through the membranes were identified as important drawbacks for the membrane technology. The paper suggested that the successful development of ultra-thin inorganic hollow-fiber perovskite membranes would play important roles in increasing the ion fluxes. Other reviews generally come to similar conclusions [27–31]. There are certainly opportunities for developing new high-performance membranes, seeking to increase and control fluxes and to improve chemical

and mechanical stability.

Compared with membrane-coupled oxidative processes, MDA processes coupled with hydrogen-permeable membranes are much less mature. Although removing hydrogen from the product stream increases methane conversion, it also tends to increase carbon deposits and catalyst deactivation rates. Hydrogen removal can also promote selectivity toward unwanted polyaromatic hydrocarbons, thus competing with the desired benzene yield. Although limited to only a few studies, there is growing interest in oxygen membrane coupled MDA processes [32, 33]. However, to date there are no published reviews in this area.

2. Oxidative conversion of methane

In the early 1980s, Keller and Bhasin [34] first introduced the concept of direct conversion of methane to ethylene, written globally as Eq. 3. Methane was first activated by oxygen in the absence of a catalyst at temperatures above 800 °C. The process was later called Oxidative Coupling of Methane (OCM).

Assuming that the OCM process behaves as shown by Eq. 3, the downstream H_2O separation is straightforward by condensation. However, together with the desired C_2H_4 , the process also yields considerable levels of C_2H_6 and low levels of higher hydrocarbons (e.g., C_3H_6 , C_3H_8). Unfortunately, significant levels of undesired oxidation products CO , CO_2 , and H_2O are also formed, thus decreasing the desired C_{2+} selectivity. Moreover, the CO and CO_2 separations can be difficult.

All practically viable OCM processes depend on a catalyst. High reaction temperatures (i.e., $T \geq 700$ °C) are generally necessary to activate methane. However, with recent advances in catalyst technologies, significant conversion and yield can be obtained at somewhat lower reaction temperatures as well. The methane conversion is controlled by the oxygen concentration in the mixture. The formation of side products is associated with the high reaction temperature because the total oxidation of CH_4 and C_2 (C_2H_4 and C_2H_6) are favored at high temperatures. The formation of side products not only decreases the product yield, but also introduces additional downstream gas-separation costs.

To date, despite considerable research, no particular catalyst has emerged that fully meets practical industrial and economic requirements. Two important challenges remain to be overcome. The first is the catalyst selectivity and the second is catalyst deactivation as a function of time-on-stream. Several reviews of OCM catalysts and processes have been published [35, 24, 36]. The 2015 review by Kondratenko et al. [37] explores OCM

catalyst and process design. Economic analyses suggest commercial viability demands single-pass C_2H_4 yields that exceed 25% [38, 39].

Broadly speaking, OCM catalysts and processes can be categorized as being either high- and low-temperature processes. Most of the literature considers high-temperature catalysis ($T \geq 700$ °C). The low-temperature processes appear to hold promise, but are relatively new and undeveloped. High temperature catalysts include Li/MgO, Mn/Na₂WO₄/SiO₂, and Sr/La₂O₃.

2.1. Li/MgO catalyst

Li/MgO catalysts were first developed by Ito et al. in 1985 [40]. Although the ethylene yield was considered to be good ($\approx 12\%$ C₂), it did not meet the economic expectations of 25% C₂₊ single-pass yield [41]. Another problem was catalyst stability, with significant Li loss after long time-on-stream [42]. An electron microscopy study by Myrach et al. [43] revealed that Li/MgO undergoes morphological changes under OCM operating conditions. Above 427 °C, Li segregates and above 777 °C Li desorbs from the MgO. Because there is a strong relationship between the Li loss and the catalyst deactivation, early findings by Lunsford and colleagues [40, 44] and Peng et al. [45] concluded that the catalytically active center was Li⁺O⁻. Both research groups supported their findings with the experimental surface characterization techniques, including Electron Paramagnetic Resonance (EPR) [40, 44] and X-ray Photoelectron Spectroscopy (XPS) [45]. Recently, Kwapien et al. [46] published a density functional theory (DFT) model that supported the idea of morphological change. However, unlike the early conclusions, more recent studies find no indication of Li⁺O⁻ formation, suggesting that the active center is not Li⁺O⁻ but rather oxygen-centered radicals on metal oxides (e.g., Mg²⁺O²⁻) [46].

Despite substantial research efforts, the exact structure of the Li/MgO and its relationship to the catalytic activity remain unclear [25]. There continues to be considerable experimental and theoretical research focused on Li/MgO [47–49]. Compared to other mixed oxides, Li/MgO has a relatively simple microstructure. With only one active center, catalyst preparation and theoretical studies are more easily accomplished than they are with other more complex alternatives. However, the poor stability limits the practical use of Li/MgO as an OCM catalyst.

2.2. Mn/Na₂WO₄/SiO₂ catalyst

Two reviews on the family of Mn/Na₂WO₄/SiO₂ catalysts were published in 2012 by Takanabe [5] and Arndt et al. [50]. This class of catalyst is expected to deliver practical OCM performance.

In 1992 Fang et al. [51] first reported a mixed-oxide catalyst in the form of Mn/Na₂WO₄/SiO₂. They reported 23.9% C₂ yield at 800 °C in a packed-bed reactor. The active metals in Mn/Na₂WO₄/SiO₂ catalysts are Mn, Na, and W. There are also synergic effects with the SiO₂ supports. Mn/Na₂WO₄/SiO₂ catalysts can produce higher C₂ yield compared to Li/MgO and they are more stable at high temperature. However, they are much complicated to understand in terms of structural and chemical complexity and active centers. Elemental composition and relative loadings, as well as the catalyst preparation techniques, play critical roles in the catalytic activity [52–57]. The final chemical composition is a mixed oxide, that contains MnO₂, Mn₂O₃, MnWO₄ and Na₂WO₄ and SiO₂ [55]. The synthesis process leads to the formation of bulk oxides. However, the catalyst undergoes further chemical and physical changes under OCM conditions. Amorphous silica undergoes a phase transformation to α -cristobalite. Amorphous silica behaves as a total oxidation catalyst whereas α -cristobalite is essentially inert. Surface reconstruction also occurs among the metal oxides and the silica [58]. All these dynamic changes make fundamental understanding and catalyst optimization difficult [59–65].

Numerous theories have been proposed about the catalytic active center for Mn/Na₂WO₄/SiO₂. Broadly speaking, two distinct theories arise. The theory proposed by Lunsford and colleagues suggested that the active site contains Na-O-Mn species. The Mn was expected to be responsible for activation of gas-phase oxygen, the Na was essential for preventing the total oxidation of methane, and W was claimed to be controlling the stability of the catalyst [59]. Using XPS, laser Raman spectroscopy, and XRD diffraction, this theory was later supported by Green and coworkers [63, 64].

An alternative theory, based on the XRD and Raman spectra analysis, suggested that the catalyst undergoes a surface reconstruction. Surface clusters including W=O and W-O-Si species are expected to be the active centers that control methane activation as well as C₂ selectivity. The Mn was suggested to increase the mobility of surface lattice oxygen [66, 60, 63]. Bulk metal oxides (MnO₂, Na₂WO₄) are expected to be physically unstable because their melting points are below 700 °C. Thus, it is more reasonable to believe that the a MnWO₄ related bulk oxide is responsible for the active center formation.

Processes based Mn/Na₂WO₄/SiO₂ catalysts require operating temperatures around 800 °C and higher. Although recent advances show that the economical goal of 25% single pass yield can be achieved with Mn/Na₂WO₄/SiO₂, the long-term catalyst stability remains a concern at these elevated temperatures.

Hiyoshi and Ikeda considered increasing OCM activity by mixing Mn/Na₂WO₄/SiO₂ catalysts with alkali chlorides (LiCl, NaCl, KCl, CsCl) [56]. Doping the catalyst with an equimolar mixture of NaCl and KCl increased the ethylene yield up to 31% at 750 °C. The catalytic performance was measured in a packed-bed reactor at atmospheric pressure. Although the paper noted that alkali chlorides are volatile at OCM reaction temperatures, stability data was not reported.

Mahmodi et al. [67] prepared M/Na/Mn/SiO₂-based nanocatalysts, where “M” represents a metal. By incorporating different metals (M = W > Mo > Nb > Cr > V) into the structure, a maximum C₂ yield of 31.6% was reported at 775 °C and 1 bar in a packed-bed reactor. The gas phase species were measured by online gas chromatography. However, the catalysts were unstable after 9 h on stream, with the deactivation being apparently due to the loss of catalytic surface area by sintering. In a related approach, Ha et al. [68] patented a composition of NaW/MnO₂/SiO₂ with 3.5 wt.% NaW, 1.3 wt.% MnO₂ (remainder SiO₂) catalyst and showed 18.4% C₂ yield at 800 °C. This catalyst was found to be durable even after 40 h of operation. Catalyst screening experiments were carried out in a packed-bed reactor, and the effects of gas-hourly space velocity and fuel/oxygen ratio were tested.

A 2011 patent by Zarrinpashne et al. [69] reported significant increases in C₂ yield. The catalyst, which was prepared by either co-precipitation or impregnation techniques, contained 1.9 wt.% Nb, 2 wt.% Mn, 1.8 wt.% Na, 2.8 wt.% W, with a SiO₂ support. An ethylene yield of 27.24% was reported at 850 °C in a packed-bed reactor. Substitution of Nb into the Mn/Na₂WO₄/SiO₂ structure was shown to have a promotional effect on the C₂ yield.

2.3. La₂O₃ catalyst

Another potentially viable OCM catalyst is La₂O₃. The catalytic activity can be increased by doping with alkaline-earth metals (Sr, Mg, Ca), which produces strong basic sites [70–72]. Early studies indicated that Sr doping showed the most promising OCM activity [73–75]. Choudhary et al. [72] reported 17% C₂ yield over Sr/La₂O₃ at 800 °C in a continuous-flow packed-bed reactor.

Although not as active and selective as Sr/La₂O₃, the catalytic performance of CaO doped La₂O₃ has been investigated. Becker and Baerns [76] reported 76% C₂₊ selectivity and 9% C₂₊ yield at 740 °C, with the optimum La₂O₃/CaO ratio being in the range of 60–80%. Stansch et al. [71] studied the kinetics of La₂O₃/CaO in a packed-bed reactor and developed a ten-step reaction mechanism among eight gas-phase species. The reaction mechanism was validated using measurements in packed-bed reactors. A 2010 study by Rane et al. [77] showed that the catalyst preparation method (i.e., physical mixing of La₂O₃ and CaO or co-precipitation method) and source of precursors (i.e., acetates, carbonates, nitrates, and hydroxides) strongly influence the catalytic activity. Rane et al. demonstrated 15.2% C₂ yield at 800 °C in a packed-bed reactor using catalysts prepared by co-precipitation with carbonates as precursors. Unfortunately, the La₂O₃/CaO shows low stability and activity in OCM processes. Nevertheless, the synthesis is relatively straightforward and the catalytic activity can be controlled by the ratio between La₂O₃ and CaO. In part, because validated reaction mechanisms are available, a number of groups use La₂O₃/CaO as a basis for model-based reactor development and parameter studies [78–83].

Unlike the Li/MgO and Mn/Na₂WO₄/SiO₂, the La₂O₃ catalysts produce significant yields of C₂H₆. The doping metal and the support structure can significantly affect the C₂H₄ to C₂H₆ ratio. Operating at 730 °C, Baidya et al. [84] reported a C₂H₄/C₂H₆ ratio of 0.4, with the overall C₂₊ yield at approximately 16%. Baidya et al. found that by changing the support to Al₂O₃, the C₂₊ yield can be varied. By tuning the Sr/Al ratio in the catalyst mixture, they were able to increase the C₂H₄/C₂H₆ ratio to 1.7, with 18% overall C₂₊ yield at 810 °C. The catalyst was durable for 48 h on stream, showing stable methane conversion and C₂₊ selectivity.

Stability is a major concern with La₂O₃ catalysts, especially when CO₂ is present at temperatures above 650 °C. Under these conditions, La₂O₃ reacts to form a dioxy monocarbonate structure [85, 86],

which is unstable at high temperature (850–900°C) [86]

2.4. Fe₂O₃ catalyst

Another potentially viable OCM catalyst group is based on iron oxides [87, 88]. Although methane conversion can be as high as 55–60% at temperatures above 700°C and the catalyst is stable, the C₂ yield is below

5% [88]. The low C_2 yield is caused by complete oxidation of methane at high temperatures. Iron forms the active $\alpha\text{-Fe}_2\text{O}_3$ phase and the oxygen in the lattice promotes the complete oxidation of methane. Van Der Vaart [89] patented a process using a 100-150 μm layer of Fe_2O_3 catalyst supported on a low-surface-area non-porous 150-215 μm layer of SiO_2 . By mixing steam into the CH_4/O_2 mixture, the C_2 selectivity was increased with yields up to 7% at 850 °C in a fluidized bed reactor. Van Der Vaart proposed that water preferentially poisoned the catalyst surface by occupying the catalytic sites that would otherwise serve to oxidize the methyl radicals prior to the desired desorption. Although Fe-containing catalysts may not be sufficiently selective for OCM, they may be promising catalysts under non-oxidative conditions [90, 91].

2.5. Low temperature catalysts

The inherent nature of methane activation generally requires high-temperature processes. Thermal management, including temperature uniformity, catalyst deactivation, and coke formation, presents potential problems in the design and operation of high-temperature reactors. Thus, there is ongoing interest in finding OCM catalysts that are effective at relatively low operating temperatures.

Early catalyst screening studies focused on decreasing reaction temperatures by considering different metals and metal oxides. Using alkali- and alkaline-doped metal oxides, Roos et al. [92] showed that reaction temperatures could be decreased to around 530 °C with approximately 12% C_{2+} yield over a Li/MgO catalyst (5.3 wt.% Li) in a packed-bed reactor. Alternatively, Fe-P-O catalysts, which belong to the transition-metal group, also showed promising low-temperature activity [93, 94]. Using mass spectrometry and gas chromatography, Annapragada and Gulari reported approximately 6.5% C_{2+} yield at 575°C over a Fe-O-P catalyst in U-shaped and straight packed-bed reactors [93].

A number of recent studies have shown that the catalyst activity depends not only on the catalyst's metal composition, but also on particle size and morphology [95–98]. Nano-structured catalysts were found to activate the methane at lower temperatures [99, 98]. The superior catalytic activity of nanorods and nanofibers was attributed to high surface areas, well defined crystalline structures, and their ability to form surface oxide species [95].

Noon et al. [99] showed that $\text{La}_2\text{O}_3\text{-CeO}_2$ nanofibers delivered superior OCM performance compared to the same catalysts in powder form. Earlier studies by Dedov et al. [100] measured catalytic activity of $\text{La}_2\text{O}_3\text{-}$

CeO_2 in powder form and they reported optimum reaction temperatures in the range of 715-830 °C. The Noon et al. study also showed that the methane activation temperatures can be as low as 470 °C using the same catalyst composition as the earlier findings of Dedov et al. Noon et al. reported a maximum of 18% C_{2+} yield at 520 °C [99] in a packed-bed reactor.

Hou et al. [97] studied $\text{La}_2\text{O}_2\text{CO}_3$ catalysts with different nanoscale plate and rod morphologies, particle sizes, and calcination temperatures. Catalytic performance was measured in a packed-bed reactor at atmospheric pressure. The process delivered 30% CH_4 conversion and 50% C_{2+} selectivity at 420 °C. The catalyst was found to be stable for over 50 h on stream.

Huang et al. [95] studied shape effects for nano-structured La_2O_3 catalysts under OCM conditions. The catalytic performance was measured in a packed-bed reactor where the catalyst was diluted with the quartz sand. They reported that La_2O_3 nanorods were more active than nano-particles. Approximately 10% C_2 yield was reported at 450 °C, with reaction being initiated at 400 °C. However, elevated-temperature stability was a problem with the $\text{La}_2\text{O}_3\text{-CeO}_2$ material. Above 550 °C, the C_2 selectivity decreased greatly. A recent study by Song et al. [96] developed a stable Sr/ La_2O_3 nano-fiber catalyst. They reported approximately 16% C_2 yield at 500 °C, with the catalyst being stable up to 800 °C.

Siluria Technologies filed patent applications for a series of nanowire catalysts that operate at reaction temperatures below 600 °C [101]. One group of the nanowire lanthanum oxides catalysts were composed of $\text{Ln}_{14-x}\text{Ln}_{2-x}\text{O}_6$, where Ln1 and Ln2 are two different lanthanide-group metals (i.e., Y-La, Zr-La, Pr-La and Ce-La). The C_{2+} yield was reported to exceed 22.5%. Another catalyst composition recently patented by Siluria Technologies was a nanowire catalyst composed of 20 wt.% Mg, 5 wt.% Na, and 75 wt.% La_2O_3 . The reported C_{2+} yield was approximately 12% at 600 °C [102]. Using these catalysts, Siluria Technologies has apparently commercialized an ethylene production process. Although the reported single-pass C_{2+} yields do not meet the nominal target of 25%, the process temperature is below 600 °C and the catalyst is durable over a long operating periods. The low reaction temperature reduces overall heating costs and decreases catalyst-deactivation rates. The up-scaled reactor was composed of multiple OCM packed-bed reactors. Thermal management systems were designed to achieve either adiabatic or isothermal conditions.

Fina Technology Inc. patented a composition using MgO as a second support for the Sr/La catalyst on a low-temperature process ($T = 500$ °C) [103]. Although

the C_2 yield was relatively low at approximately 10%, the low reaction temperature offered other potential benefits. At low temperature, deactivation from sintering is greatly diminished.

2.6. OCM Reaction kinetics

Although OCM is generally understood to be a catalytic process, it does depend on homogeneous chemistry as well. Especially above 600 °C the homogeneous chemistry can produce ethylene and ethane without a catalyst. The relative importance of gas-phase chemistry depends on residence time and pressure, as well as the CH_4/O_2 ratio in the feed stream [104–106].

Experimental studies show that C_2 formation rates depend strongly on gas-phase methyl-radical concentrations [70, 107, 44, 108, 74, 75, 109]. Increasing the temperature and pressure increases the formation rate of methyl radicals almost independently of the catalyst. However, in low-pressure regimes, the methyl-radical formation rate depends weakly on temperature, but varies significantly depending upon the particular catalyst. Because the catalyst increases the methyl-radical formation rate, the C_2 formation rate also increases.

Despite differences in the active catalytic sites on particular catalysts, there is general consensus that at high temperature the methane needs to be activated to form CH_3 radicals, with the CH_3 formation step being the rate determining step. The activation may be via C-H bond breaking,

or by surface-oxygen attack,

A study by Takanabe and Iglesia [110] proposed an alternative reaction pathway for methane activation. In addition to the thermal cracking and surface oxygen attacks, Takanabe and Iglesia's study suggested that the reaction product H_2O has a promotional effect on methane conversion and C_{2+} yield. Their study introduced an additional CH_3 formation pathway via OH radicals. According to the reaction steps 8 and 9, OH radicals are generated either via surface-adsorbed oxygen $O(s)$ or in the gas-phase via O_2 and H_2O reactions.

Between these reactions it is more likely that the Reaction 8 is the dominant pathway to form OH radicals.

Figure 2: Reaction pathways for the oxidative coupling of methane proposed by Lunsford [111] and Sun et al. [112]. Yellow highlighted reaction paths indicate the catalytic routes where as blue highlighted reaction paths indicate the gas-phase reactions.

H_2O is a very stable molecule and O-H bonds in H_2O (497 kJ mol^{-1}) are stronger than C-H bond in CH_4 (439 kJ mol^{-1}). The OH can react with CH_4 in the gas phase to form CH_3 radicals as

Takanabe and Iglesia [110] conducted a series of OCM experiments in a recirculating batch reactor to support the proposed reactions. They studied the effects of contact time and H_2O addition or removal on CH_4 conversion and C_{2+} yield. Their results showed that adding approximately 4% H_2O into the CH_4/O_2 mixtures at 800 °C significantly improved the CH_4 conversion and C_{2+} yield. However, when H_2 was removed the CH_4 conversion was significantly suppressed.

Lunsford and colleagues studied OCM reaction kinetics for a wide range of catalysts, including Li/MgO, Sr/CaO, Sr/La₂O₃, Mn/Na₂WO₄/SiO₂ and Mn/Na₂WO₄/MgO [70, 107, 108, 74, 111]. Using matrix isolation electron spin resonance (MIESR), they identified active sites as well as methyl-radical formation pathways. The results showed that C_2H_6 is formed in the gas phase via CH_3 -radical recombination as

where M represents a gas-phase third body. Further C_2H_6 dehydrogenation produces C_2H_4 (cf., Fig. 2). The surface oxygen further increases the ethyl radical (C_2H_5) formation rate. Lunsford argued that CO is formed via a gas-phase reaction, whereas H_2O and CO_2 are formed on the surface and then desorb [111]. Sun et al. [112], proposed that the CO, CO_2 , and H_2O are formed both via homogeneous and heterogeneous pathways. Consistent with these studies, Fig. 2 illustrates methane activation and formation of CO, CO_2 , and H_2O via both homogeneous and heterogeneous pathways.

Reyes et al. [38] developed an OCM reaction mechanism involving both homogeneous and heterogeneous

reaction pathways. The homogeneous reaction pathways and rates were taken from earlier studies [113–116]. Methane-oxygen reactions can proceed in the gas phase as

or on the surface as Eq. 7. The surface-reaction model included global representations of the CH_3 (Eq. 13) and C_2H_5 (Eq. 14) radical production,

Although Reactions 13 and 14 involve only gas-phase species, they are understood to be surface reactions. Homogeneous recombination of CH_3 radicals produces gas-phase C_2H_6 according to Eq. 11.

In addition to the reaction pathways, individual reaction rates need to be established. There is literature that reports global and partially elementary OCM reaction mechanisms for several different catalysts. Global representations of the OCM catalytic kinetics use reactions that involve only gas-phase species (e.g., Table 1). The rate expressions are empirical, with details of the catalysts (e.g., specific surface area, bed porosity and tortuosity, etc.) subsumed implicitly into the rate expressions. The reaction pathways and functional forms of the rate expressions are presumed to be general. However, because the rate expressions are fit to particular experiments, and for specific temperature and pressure ranges, the kinetic parameters need to be fine-tuned before applying in other circumstances. Nevertheless, with appropriate tuning for particular catalysts and operating conditions, the mechanisms can be used to predict reactor behavior and assist reactor design. Because the gas-phase thermodynamic properties are well established, the global kinetics can predict exothermic behavior and hence temperature variations within reactor catalyst beds.

As an alternative to global mechanisms, there are potential benefits to developing elementary-step reaction mechanisms. Because the elementary-step mechanisms involve surface adsorbates, establishing the thermodynamics, and hence microscopic reversibility, is difficult. Although there is very little literature on elementary-step OCM catalysis, there are certainly benefits to such development. Because they are based on fundamentals, validated elementary-step mechanisms have better predictive capability than do global reaction mechanisms with empirical rate expressions.

Table 1: Global reactions in Oxidative Coupling of Methane, OCM [71].

	Reaction	$\approx \Delta H_{298}^\circ (\text{kJ})$
1.	$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	-802
2.	$2\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O}$	-177
3.	$\text{CH}_4 + \text{O}_2 \rightarrow \text{CO} + \text{H}_2\text{O} + \text{H}_2$	-277
4.	$\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$	-283
5.	$\text{C}_2\text{H}_6 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$	-105
6.	$\text{C}_2\text{H}_4 + 2\text{O}_2 \rightarrow 2\text{CO} + 2\text{H}_2\text{O}$	-757
7.	$\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$	+137
8.	$\text{C}_2\text{H}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{CO} + 4\text{H}_2$	+210
9.	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	-41
10.	$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2\text{O}$	+41

Although OCM catalysts based on Li/MgO have relatively simple atomic structure and are the easiest to understand, elementary reaction mechanisms have yet to be fully developed. Practical catalysts such as Mn/ $\text{Na}_2\text{WO}_4/\text{SiO}_2$ structures are far more complex. In addition to establishing reaction-pathway details, surface thermodynamics need to be established such that thermal balances can be accurately represented. Synergistic combinations of theory and experiment are needed to develop and validate general-purpose reaction mechanisms.

Stansch et al. [71] developed an OCM reaction mechanism for $\text{La}_2\text{O}_3/\text{CaO}$ catalysts (Table 1). The global reactions represent total and partial oxidation as well as water-gas-shift chemistry. Stansch et al. validated their kinetic parameters in the temperature range $700 \leq T \leq 955^\circ\text{C}$. In subsequent research Daneshpayeh et al. [117] modified the kinetic parameters in Stansch’s mechanism to represent Mn/ $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts. Daneshpayeh et al. used the same reaction network as Stansch’s model, but modified activation barriers and the reaction-rate orders to fit experimental measurements over a range of temperatures ($750 \leq T \leq 875^\circ\text{C}$).

Ahari et al. [118] developed an OCM microkinetic reaction mechanism with gas-phase and surface reactions. The nominal values of the pre-exponential factors were derived from collision theory. The activation barriers were estimated according to the Bell–Evans–Polanyi relationship. The rate parameters were fine-tuned based on packed-bed reactor experiments, where the effects of temperature, feed composition (fuel/oxygen) and gas-hourly space velocity were investigated. An isothermal, one-dimensional, packed-bed reactor model was developed to assist interpreting the measurements and assigning rate parameters. The surface reactions were represented as 11 irreversible steps. The surface adsorbates that were considered are O(s), OH(s), CO(s), CHO(s), CH_2O (s) and CH_3O (s). The reaction mechanism considers gas-phase adsorption on the catalytic

active sites, adsorbate-adsorbate reactions, and the reaction of gas-phase radicals with surface adsorbates. The detailed gas-phase reactions were represented with 39 reversible steps among 13 species. This reaction mechanism was adapted from the earlier studies of Marin and colleagues [119, 120]. The product gas-phase species included CO, CO₂, H₂, H₂O, C₂H₄, and C₂H₆, C₃H₆ and C₃H₈.

Sun et al. [112] proposed a detailed OCM reaction mechanism to represent gas-phase and surface reactions over Li/MgO and Sn/Li/MgO catalysts. This mechanism consists of 14 surface reactions and 39 gas-phase reactions. As with the Mn/Na₂WO₄/SiO₂ catalysts, the methane activation proceeds via methyl-radical formation in the gas-phase as well as on the catalyst surface. Methyl radicals recombine to form C₂H₆. The desired gas-phase products are C₂H₄ and C₂H₆, with the undesired oxidation products being CO, CO₂, and H₂O. The surface species include O(s), OH(s), H₂O(s), CH₃O(s), CH₂O(s), CHO(s), CO(s), CO₂(s). The reaction mechanism includes the adsorption of gas-phase species, reaction of gas-phase species (either radical or stable molecules) with surface adsorbates (Eley-Rideal steps), or the surface-surface reactions. The model is validated under isothermal reactor conditions.

To date, there are no published reaction mechanisms for the low-temperature OCM catalysts (i.e., $T < 700$ °C). However, there is general agreement that the methane activation on La₂O₃ catalysts relies on CH₃-radical formation mechanisms. The high-temperature reaction pathway is thought to be different from the low-temperature pathways. Although the surface can create sufficient methyl radicals, the CH₃ recombination and C₂H₆ dehydrogenation steps must occur in gas-phase. Thus, even for low-temperature processes, it should be expected that the temperature plays an important role.

3. Non-oxidative conversion of methane

There are two broad approaches to achieve the non-oxidative conversion of methane. Both are catalytic dehydrogenation processes, but seek different products. The first seeks to produce primarily ethylene, which is a valuable feedstock for further downstream processing. The second, which is usually called methane dehydroaromatization (MDA) seeks to produce benzene. In principle, both approaches are feasible at high temperatures with sufficiently selective catalysts.

3.1. Methane to ethylene and ethane

Figure 3: Equilibrium thermodynamics of direct conversion of CH₄ under non-oxidative conditions.

The desired production of C₂H₄ from CH₄ can be represented globally as in Eq. 2 and the C₂H₆ formation from methane can be represented as

Unlike OCM, where some H₂ is converted to H₂O, the non-oxidative conversion retains H₂ as reaction product. Because the chemistry does not involve oxygen or oxygen-containing species, it is theoretically possible to increase the carbon selectivity toward C₂H₄ and C₂H₆. However, even assuming a perfect catalyst, Fig. 3 shows that equilibrium direct conversion of C₂H₄ or C₂H₆ is thermodynamically limited and only favored at high temperatures. Figure 3 also shows that graphitic carbon (C) is much more favorable than the reactions to form C₂ and benzene. At 500 °C, the equilibrium conversions of CH₄ to C₂H₆ and C₂H₄ are only about 0.6% and 1%, respectively. The direct conversion of CH₄ to C₂ is practical only above about 800 °C, with the C₂H₄ being significantly greater than C₂H₆.

Although the formation of both C₂H₄ and C₂H₆ occur via methane dehydrogenation pathways, Fig. 4 shows the nature of these two reactions to be quite different. Based on the Gibbs free energy change associated with the global reactions, direct C₂H₄ formation (i.e., $2\text{CH}_4 \rightleftharpoons \text{C}_2\text{H}_4 + 2\text{H}_2$) is favorable only at high temperatures. The direct C₂H₆ formation (i.e., $2\text{CH}_4 \rightleftharpoons \text{C}_2\text{H}_6 + \text{H}_2$) is always significantly endothermic, with very little temperature dependence. Even at the high temperature of 900 °C the direct conversion of CH₄ to C₂H₆ is only around 4.8%. This suggests that C₂ formation may not be direct at practical reactor temperatures.

The practical conversion of CH₄ to C₂ may be feasible at moderate temperatures via indirect routes. According to Fig. 4, the direct conversion of methane to

Figure 4: Gibbs free energy change as a function of temperature at atmospheric pressure for the relevant reactions of methane non-oxidative coupling. This graph was adapted from Garnier et al. [121].

carbon (i.e., $\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$) is exothermic at temperatures above about 500 °C. Thus, the methane could be first converted to graphitic carbon, subsequently reacting with H_2 to form either C_2H_4 , C_2H_6 , or CH_4 . Such a two-step process is called a methane-homologation process [121–127]. Figure 4 shows that the indirect C_2H_6 formation ($2\text{C} + 3\text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6$) is exothermic below about 200 °C. However, the reaction must compete with methanation ($\text{C} + 2\text{H}_2 \rightleftharpoons \text{CH}_4$), which is more exothermic at low temperatures. The indirect C_2H_4 formation is always endothermic, but at high temperatures (≥ 800 °C) it is more favorable than the indirect route to form ethane.

Even if direct or indirect C_2 formation is possible, equilibrium thermodynamics severely limits conversion and yield (cf., Fig. 3). Even at the 800 °C, equilibrium methane conversion to C_2 reaches only about 8.5%. Thus, as discussed subsequently, hydrogen-permeable membranes offer the possibility to significantly increase the CH_4 conversion.

3.2. Methane to ethylene and aromatics

Under non-oxidative conditions ethylene formation is usually followed by the further growth of aromatics. With a selective catalyst, potentially valuable aromatic yields (e.g., benzene) can be further increased. The overall methane dehydroaromatization (MDA) process can be represented globally as shown by Reaction 1. Of

course, such a simplified global representation provides very little insight into the complexities of the process.

As is typical of dehydrogenation processes, the direct conversion of methane to both ethylene and aromatics is thermodynamically limited. Figure 3 shows that even at 700 °C, the equilibrium thermodynamics limits the methane conversion to below 10% for either ethylene or benzene; the dominant reaction produces carbon. Figure 3 shows that the benzene formation is more favorable than ethylene. Although not shown in Fig. 3, higher aromatic compounds such as naphthalene (C_{10}H_8) are thermodynamically more favorable than benzene. Moreover, a wide range of usually undesired aromatic side compounds (e.g., indene, anthracene and higher polyaromatic hydrocarbons) are inevitably produced.

4. Methane dehydroaromatization (MDA)

The MDA process was first discovered in 1993 by Wang et al. [128]. The most relevant catalysts are metal-loaded (e.g., Mo, W, Cu, Re, V, Ga) bi-functional zeolites [129–132]. Methane is first activated on the metal sites to form small C_2 species (typically ethylene) and H_2 . Aromatization then follows at zeolite acid sites. Among the metal possibilities, Mo is the most active for methane conversion. Benzene selectivity depends on the zeolite cage dimensions, and hence on the zeolite type. Depending on the particular zeolite, the cage dimensions typically range between 0.35 and 0.85 nm. Zeolites with small cage dimensions, close to the atomic diameter of benzene, are most selective for benzene formation [133, 134]. The particular zeolites that are most effective for benzene production include HZSM-5 [135–142], HMCM-22 [143–146], HMCM-36 [147], and HMCM-49 [148, 149].

Figure 5 is a three-dimensional representation of the atomic positions within a HZSM-5 zeolite crystal. The hydrogen atoms on the periphery of the large zeolite cage form the Brønsted-acid sites. Catalytic performance and selectivity depends on the cage dimension relative to the characteristic dimensions of reactant or product molecules.

The Mo/zeolite catalysts can be fabricated using alternative preparation methods. In most cases, a wet impregnation is followed by calcination. That is, a Mo precursor (e.g., ammonium molybdate) is first introduced into zeolite powders. Upon calcination, the Mo precursor forms an oxide, MoO_x . Another approach is to physically mix MoO_x and zeolite powders. In either case, the catalyst is initially in the form of a MoO_x /zeolite mixture. However, the MoO_x is not stable in reducing envi-

Figure 5: Illustration of a portion of a zeolite crystal (HZSM-5) with a silicon-to-aluminum ratio of 11. The primary cage is at the upper left of the image. The Brønsted-acid sites are formed by the atomic hydrogens on the periphery of the zeolite cage.

Figure 6: Illustration of a zeolite Brønsted-acid site and a molybdenum-carbide complex at the acid site.

ronments. In MDA processes, the MoO_x is transformed to a molybdenum-carbide structure.

4.1. Catalyst and active sites

Although it is generally established that CH_4 is first activated on Mo_2C sites, their specific configuration, oxidation state, interactions with zeolite Brønsted acid sites, and dimerization kinetics are not yet fully understood. It is well accepted that the molybdenum undergoes transformation from Molybdenum oxide to a complex carbide when it is exposed to methane. Beginning with freshly synthesized Mo/zeolite catalysts the Mo is initially in the Mo^{6+} state. Exposing calcined Mo/HZSM-5 to CH_4 at 700°C causes the reduction of 60 to 80% of the Mo^{6+} to a molybdenum-carbide structure. During the carburization process the molybdenum incorporation is associated with the Brønsted acid sites. Thus, as molybdenum is incorporated, the Brønsted acid sites are replaced by molycarbide structures.

The transition between the oxide and carbide phases can be represented notionally as [150, 151]

The carburization process may be accomplished in-situ within an MDA reactor or it may be prepared beforehand. When the carburization is accomplished in-situ, the MDA process starts with an induction period that may require several hours. During this transient process the Mo_2C concentration increases, which also

serves to increase the benzene formation rate. During the induction period, the reaction of methane with MoO_x forms CO , CO_2 and H_2O as products. The carburization time depends on the gas-hourly space velocity and temperature. Under typical MDA reaction conditions ($700\text{--}800^\circ\text{C}$ and $750\text{--}4500\text{ ml gc}^{-1}\text{ h}^{-1}$) the process is typically completed in one to two hours. In the context of MDA, “completing” the carburization process means that a quasi-steady state is reached in terms of methane conversion and benzene yield. However, not all the molybdenum oxide phases are transformed to the molybdenum carbide, with some MoO_3 , MoO_xC and Mo_2C co-existing.

The distribution between the MoO_3 , MoO_xC and Mo_2C depends strongly on the zeolite Si/Al ratios. At low Si/Al ratios the MoO_x phase is stabilized inside the zeolite structure whereas at high Si/Al ratios (typically in the range of 25–140), the MoO_x is stabilized outside of the zeolite cages [152]. The surface MoO_3 is easily converted to Mo_2C in a reducing atmosphere (i.e., during carburization). However, the MoO_x that is stabilized within the zeolite cages is less accessible by virtue of mass-transport limitations within small cage channels. Thus, the interior molybdenum-oxides are more difficult to reduce and can remain partially oxidized under MDA reaction conditions [151].

The relative catalytic activities of alternative molybdenum structures for methane activation are not yet established. A number of studies show that Mo_2C is the active center for methane activation [137, 153–156]. Experimental studies also indicate that molybdenum oxides co-exist with the carbides, but their catalytic role is de-

bated [153, 157–159].

Although the notation Mo_2C is compact and widely used, the chemical structures of molybdenum carbides are considerably more complex. The exact carbide structure, possibly including oxycarbides (MoO_xC), remains uncertain, and likely depends on the particular zeolite and the processing conditions. The Mo within the zeolite framework is found to be in the form of a dimer $(\text{Mo}_2\text{O}_5)^{2+}$, associating with two Brønsted acid sites [153, 160, 161]. Monomeric bidendate $(\text{MoO}_2)^{2+}$ with a single Mo atom is anchored into the cage structure through oxygen bridges [144]. According to DFT simulations [162, 163], the particular Mo structure in monomer or dimer form within the zeolite framework is determined by the zeolite Si/Al ratios. A DFT study by Zhou et al. [164] identified three alternative molybdenum carbide structures with different coordination at the zeolite acid sites. For low Si/Al ratios, the linearly bonded Mo is either in Mo^{5+} or Mo^{6+} states and it is in dimer form. The monomeric Mo^{6+} is less stable in the $\text{Mo}(\text{CH}_2)_2(\text{CH}_3)^+$ structure that is formed when Si/Al ratios are high. The dimeric forms of the molybdenum carbide, which can be represented as $\text{Mo}_2(\text{CH}_2)_5^{2+}$ or $\text{Mo}_2(\text{CH}_2)_4^{2+}$, are more stable than the monomeric forms at low silicon-to-aluminum ratios [164].

The upper image in Fig. 6 schematically illustrates a zeolite Brønsted acid site before the molybdenum introduction. The lower image illustrates the molybdenum-carbide complex in the form of $\text{Mo}_2(\text{CH}_2)_5^{2+}$ [164].

It is generally established that the Mo structure and its catalytic activity depend on the synthesis method and the molybdenum loading [165, 160, 161]. The Mo content in the zeolite can vary between 1 wt.% and 20 wt.% [157, 166–168, 151], with the optimum Mo loading depending on the preparation method, carburization temperature, and reaction conditions [139, 160, 161, 166, 153]. Typically, Mo loading in the range of 4–6 wt.% delivers best MDA performance.

Lu et al. [168] studied Mo loading effects on HZSM-5 zeolites. The catalyst was prepared by wet impregnation and the Mo loading was varied between 1 and 10 wt.%. They identified three different molybdenum structures: molybdenum carbide (Mo_2C), molybdenum-oxide carbide (MoO_xC), and molybdenum oxide (MoO_3). The best Mo loadings were found to be between 4 and 6 wt.%. Increasing the Mo content further did not increase the benzene selectivity.

Li et al. [167] prepared a 6 wt.% Mo/HZSM-5 catalyst. They identified $[\text{Mo}_5\text{O}_{12}]^{6+}$ in the zeolite channel, which is incorporated into the zeolite structure by the replacement of an acid site that is coordinated through Al. They also reported that $\alpha\text{-MoO}_3$ and amorphous

MoO_3 are distributed on exterior zeolite surfaces. Furthermore, at very high Mo loadings entrance to the zeolite cages could be blocked by Mo particles.

Chen et al. [157] studied the effects of Mo loadings between 1 and 20 wt.% on HZSM-5 catalysts in a packed-bed reactor. By measuring the methane conversion and aromatic yield, they showed that increasing Mo content above 10 wt.% decreased the aromatic yield. The best Mo loading was found to be between 2 and 3 wt.%. The study suggested that both the molybdenum sites and zeolite acid sites were active for methane aromatization. Although Mo_2C structures were formed within zeolite channels, it was suggested that small crystallites of MoO_3 were the active sites for methane dimerization.

Using Density Functional Theory (DFT), Fadeeva et al. [151] studied alternative molybdenum structures in HZSM-5 zeolites. At high Mo loadings, (e.g., 15 wt.%) Al was predicted to be extracted from the zeolite framework to form $\text{Al}_2(\text{MoO}_4)_3$.

4.2. Catalyst deactivation

In addition to thermodynamic limitations, rapid or gradual catalyst deactivation represents a significant practical challenge. Even with highly selective catalysts, undesired hydrocarbon products (e.g., C_{10}H_8 , C_{10+}) are formed, thus limiting the C_6H_6 and C_2H_4 yield. Furthermore, condensed carbon or polyaromatic hydrocarbons, which are thermodynamically the most stable products of the direct dehydrogenation process, cause severe catalyst deactivation during the MDA process [39, 169]. Broadly speaking, catalyst-deactivating carbon can take the form of solid carbon (coke) and polyaromatic hydrocarbons (PAH) [170, 171].

Ichikawa and co-workers studied deposit formation in isothermal packed-bed reactors with Mo/zeolite catalysts [170, 172, 173]. After measuring activity as a function of time-on-stream they characterized the deposits using ex-situ Temperature Programmed Oxidation (TPO). At low temperatures the deposits were found to be in the form of graphitic carbon on, or near to, the Mo_2C . The high temperature deposits were in the form of PAH within, or near the entrance of, the zeolite channels. The PAHs diminish the methane aromatization chemistry because they block access to the zeolite channels. As discussed subsequently, the surface deposits can be removed by reaction with oxygenated species. The PAH deposits, especially those within zeolite channels, are more difficult to remove because of transport limitations within the channels. These PAHs are suggested to be the major hydrocarbons that are responsible for catalyst fouling [174, 175].

Figure 7: Carbon formation pathways based on the mechanisms proposed by Zhang and coworkers [176, 177] and Liu et al. [178].

Zhang and co-workers [176, 177] published studies investigating deposit formation pathways and chemical composition on Mo/HZSM-5 catalysts at 800 °C. They used thermogravimetric analysis (TGA), X-ray Photoelectron Spectroscopy (XPS), and TPO techniques to characterize the catalyst-deactivating deposits and identify deposit-forming pathways. Figure 7 graphically summarizes alternative carbon-deposit pathways. Graphitic coke was attributed to CH_4 dehydrogenation or C_2H_4 cracking. The PAH deposits were the result of molecular-weight growth and condensation.

By dividing the reactor into three zones, the Zhang group was able to identify different deposit characteristics along the length of a packed-bed reactor. The deposit types along a packed-bed reactor were non-uniform and depended greatly on the local hydrogen concentration. In the upstream regions, graphite-like coke was dominant and it was mainly formed by dehydrogenation of CH_4 . In the second and third zones (downstream), the main carbon-formation path was via C_2H_4 cracking on the zeolite. The PAHs were formed primarily in the third zone of the reactor. The study showed that the overall dominant deposit-formation pathway was via C_2H_4 cracking.

4.3. Catalyst regeneration

Because catalyst deactivation is practically inevitable under MDA reaction conditions, some catalyst regeneration strategy is necessary. In-situ catalyst regeneration can be accomplished by switching the feed-stream gas to an oxidant such as O_2 or NO [172] or a reducing gas such as H_2 [179–184]. Ex-situ regeneration is also possible, but often less desirable because the reactors must be shut down and the catalysts removed.

Oxygen is an effective regeneration gas in the sense that the carbon deposits can be removed via oxidation to gas-phase species. However, oxygen regeneration

is often accompanied by other deleterious processes. The O_2 not only removes the deposited carbon, but can also oxidize the active Mo_2C to inactive or less active MoO_x . The molybdenum carburization process is reversible, but a non-productive induction period is required. Additionally, the exothermic carbon oxidation could cause catalyst degradation associated with temperature excursions and local hot spots. Nitric oxide reacts more aggressively with carbon deposits than does oxygen. Thus, alternative oxidants, such as NO or O_2 - NO mixtures, can reduce the oxidation temperatures in the range $330 \leq T \leq 450$ °C.

Regeneration based on periodic switching of feed gases is inherently inefficient because of non-productive reactor time. Thus, there are benefits associated with alternative operating conditions that can extend the interval between regeneration cycles. Introducing very low levels of oxidizers (e.g., O_2 , NO , CO , CO_2 , H_2O) with the methane feed gas can be effective [185, 186]. Although hydrogen is a product of dehydrogenation, mixing low levels of H_2 with the methane feed can also have beneficial effects on long-time catalyst stability [158, 173].

It is interesting to note that in-situ catalyst-regeneration approaches, such as co-feeding of CO , CO_2 , H_2O and H_2 are patented technologies. As recently as 2015, Shell Oil patented an MDA application where mixtures of CO , CO_2 , and H_2 are premixed with the methane feed to improve the catalyst stability [187]. Exxon Mobil also patented an MDA application where different levels of CO , CO_2 , H_2O , and H_2 are co-fed in a fluidized-bed reactor [188–190]. Improved catalytic stability was one of the claims.

4.3.1. Co-feeding O_2 , CO and CO_2

Tan et al. [158] studied the effects of co-feeding O_2 , CO_2 , and H_2 on MDA performance in a packed-bed reactor at 770 °C over a 2 wt.% Mo/HZSM-5 catalyst. The results showed that premixing up to 5.3% O_2 and 12.8% CO_2 reduced the catalyst deactivation rate. The catalyst was stable up to 6 h, producing 4% aromatic yield at 770 °C. However, after the first 6 h, the catalyst deactivated rapidly over the next 4 h and the process no longer produced aromatic species. Based on XPS analysis, the deactivation was attributed to excess O_2 or CO_2 that promoted a phase change of molybdenum carbide to less-active molybdenum oxide.

Although high levels of CO_2 are detrimental, low levels can play beneficial roles. Rodrigues et al. [191] studied the effect of co-feeding CO_2 in a packed-bed reactor over a Mo/HMCM-22 catalyst. The CO_2 feed concentration varied between 5.7 and 6.7%. They measured

the gas-phase H_2 , CH_4 , C_2H_4 , C_2H_6 , benzene, toluene and naphthalene as functions of time-on-stream using online gas chromatography coupled with thermal conductivity (TCD) and flame ionization detectors (FID). The results showed that CO_2 beneficially extended the catalyst lifetime. Apparently, the CO_2 reacts with surface carbon [C], cleaning the catalyst surface (s), and producing CO. It is likely that the CO_2 reacts with any deposited coke according to the Boudouard process as

Yao et al. [149] studied the promotional role of CO in MDA over a Mo/HMCM-49 catalyst. Using isotopically labeled carbon in CO as ^{13}C , they showed that CO participates in oxidizing the carbonaceous surface species. By measuring the isotopically tagged benzene $^{13}C_xC_{6-x}H_6$ ($x=0-3$) as a function of time-on-stream, the results revealed complexities associated with the influence of CO in MDA. In addition to reaction with surface-adsorbed carbon, CO also participates in the benzene formation. The added CO did not affect the methane conversion, but improved the catalyst stability. This result is consistent with the earlier studies of Liu et al. [192] that also used isotopically labeled CO. A subsequent study by Liu et al. [178] explained the beneficial role of CO by the reaction of surface-deposited carbon [C] with the surface oxygen O(s) as in Eq. 19. Liu et al. [178] also reported that co-feeding CO increases the benzene and naphthalene formation rates, increases methane conversion, and extends the catalyst lifetime.

Liu et al. [192] also studied the effects of co-feeding CO_2 (10% or higher) in MDA over a Mo/HZSM-5 catalyst. Perhaps surprisingly, the process was reported to be more sensitive to CO_2 in the feed than it was to CO in the feed. Co-feeding only 1.6% CO_2 decreased the benzene formation rate, but increased the methane conversion. Increasing the feed CO_2 concentration above 10% greatly suppressed the aromatic yield. Apparently, the CO_2 participated in methane dry reforming as

With high CO_2 levels, the reforming reaction path was thermodynamically favored over the desired MDA path.

4.3.2. H_2O co-feeding

Co-feeding H_2O in the MDA reactive gas mixture is experimentally demonstrated to improve the catalyst stability and several research groups have explored the behavior [192–199]. The beneficial role of steam is generally explained by the removal of surface carbon [C] by H_2O to form CO and H_2 , via either the change in zeolite acid site density or by the steam reforming of naphthalene.

Ichikawa and co-workers published a series of papers studying the beneficial role of steam in MDA [192, 193, 173]. According to their studies, the H_2O can play several, possibly competitive, roles. Steam may promote methane reforming, react with surface carbon, or modify the Mo_2C structure. Ma et al. [173] studied the co-feeding effects of H_2 and/or H_2O in MDA over Mo/HZSM-5 catalysts at 750 °C and 3 bar. They reported the principal methane reactions and their Gibbs free energies (evaluated at 750 °C and 3 bar) as

Based on the Gibbs free energy change ($\Delta G = -33$ kJ), the steam-reforming path was expected to dominate. Adding less than 1.8% H_2O was beneficial in suppressing catalyst deactivation. However, increasing the H_2O concentration also caused rapid catalyst deactivation, which is likely associated with Mo_2C oxidation and dealumination of the zeolite. This study also reported synergistic effects of co-feeding H_2 and H_2O . The H_2 inhibited the degradation of the Mo_2C complex which can be oxidized by reaction with H_2O [200]. Using low-level H_2O co-feed, Ma et al. [173] reported durable catalyst performance in a packed-bed reactor for over 1000 minutes time-on-stream. Improved MDA stability was explained by the suppression of PAH at the zeolite acid sites. Figure 8 reproduces the Ma et al. [173] benzene formation rates, with different co-feed streams.

Yao et al. [194] also studied the effect of premixing H_2O in the MDA feed over a Mo/HMCM-49 catalyst in a packed-bed reactor. By introducing 2.9% H_2O into the 87.4% CH_4 and 9.7% N_2 feed stream, they claimed to synergistically combine methane steam reforming and MDA chemistry. Stable catalyst performance was reported for up to 60 h time-on-stream. These results were explained by the beneficial participation of H_2O in reforming chemistry, producing CO and H_2 . The CO, which is a product of Eq. 25, can further react with the surface deposited carbon [C] according to Eqs. 17–19.

Figure 8: Co-feeding effect of H₂ and/or H₂O in MDA at 750 °C, 3 atm over Mo/HZSM-5 [173].

Liu et al. [195] studied MDA chemistry over a 3 wt.% Mo/HZSM-5 catalyst at 730 °C. They reported that up to 2% H₂O can improve the catalyst activity and stability. According to their TPO, XPS, and high-resolution transmission electron microscopy (HRTEM) measurements, the improvement of catalytic activity was related to the removal of weakly bound surface carbon prior to its transformation to the graphitic or aromatic carbon that causes catalyst deactivation. They found molybdenum in the form of Mo₂C and Mo₂O_xC_y after carburization. However, with greater than 2% H₂O the carbide structures reacted to form oxides, Mo₂O-MoO₃.

Skutil and Taniewski [196] studied the effects of pre-mixing H₂O, CO, and CO₂ in methane feed for an MDA process using Mo/HZSM-5 catalysts at 725 °C. They showed that up to 2% H₂O and 2.5% CO₂ increased the catalytic activity, benzene yield, and improved the catalyst stability. However, further increases in H₂O (9.5%) and CO₂ (5 and 11%) caused rapid catalyst deactivation. Premixing 8.5% CO enhanced the catalytic activity and catalyst stability, but slightly decreased the benzene selectivity.

Several groups studied the role of H₂O in the context of changing the Brønsted-acid site density [197, 141, 198, 199]. According to Ding et al. [197] zeolite deactivation is caused by the PAH formation. The Brønsted acid sites promote cyclization and aromatization. Any excess of acid sites tends to promote further aromatization from benzene to naphthalene and higher condensable PAHs. Steam reduces the Brønsted acidity, leading to significant improvement in benzene selectivity and catalyst stability.

4.3.3. Reaction of steam with naphthalene

Steam can play a significant role in cracking naphthalene, which is the primary precursor leading to deleteri-

Figure 9: Schematic illustrating possible pathways for the interactions of steam with naphthalene.

ous condensed PAHs. Naphthalene is a gas-phase compound under the MDA reaction conditions, but can react rapidly to form higher polyaromatics (e.g., anthracene, phenanthrene, fluoranthene, pyrene,...), which condense to form solid deposits on the catalyst. These species can block zeolite cage openings, inhibiting transport into and out of the small channels. The result appears as catalyst deactivation.

Low levels of H₂O can react beneficially with naphthalene, interrupting the pathway to higher PAH. The reaction products (including hydrogen, carbon monoxide, ethylene, benzene,...) also beneficially affect the MDA process. Figure 9 shows two possible reaction pathways for subsequent reaction with naphthalene. Without an oxidant in the reactive stream, molecular weight growth processes pyrolyze naphthalene toward higher aromatics and PAH deposits (left-hand pathway). However with low-level steam addition (right-hand pathway) naphthalene steam-cracking chemistry can impede molecular weight growth and form small aromatics as well as CO and H₂ [201]. Moreover, as discussed previously, steam can react with deposited carbon to assist surface regeneration. Thus, low levels of steam are expected to reduce the catalyst deactivation rate.

Buchireddy et al. [202] studied naphthalene steam cracking in a packed-bed reactor with a mixture of synthesis gas (20% CO, 9% CO₂, 20% H₂, 3% CH₄),

C₁₀H₈, and H₂O at 750 °C and a steam-to-carbon ratio of 5. They proposed that cracking reactions take place within the zeolite cage structure at Brønsted acid sites. Therefore, higher acidity tends to increase naphthalene cracking activity. Because naphthalene must be transported inside the zeolite cages, the cage size strongly influences the cracking rate. Zeolites with larger cages produce higher cracking activity. For example, H-ZSM5, which has a characteristic cage dimension of 55 nm, delivered 19% naphthalene conversion. The ZY-30, which has a characteristic cage dimension of 80 nm, increased the naphthalene conversion to 33%. Buchireddy et al. suggested that the naphthalene cracking produces graphitic carbon C(s) as well as volatile CO, CO₂, and smaller hydrocarbons. The surface carbon reacts further with CO₂ (Eq. 22) and H₂O (Eq. 25) to form CO.

Incorporating Ni into zeolites can significantly increase the naphthalene conversion up to 98%. Buchireddy et al. [202] explained the high conversion by the effect of Ni in promoting steam and dry reforming as

Buchireddy et al. measured naphthalene conversion, but did not report the product composition. Thus, the chemical pathways governing steam-naphthalene interaction remain unclear. Nevertheless, based on thermodynamics considerations, steam reforming of naphthalene should be fast above 700 °C. The Gibbs free energy change of the naphthalene-steam-reforming reaction (Eq. 27) is $\Delta G = -66 \text{ kJ}$ at 750 °C.

Naphthalene steam cracking is certainly not limited to zeolite catalysts. Devi et al. [201] studied naphthalene steam cracking over olivine (Mg-Fe silicate) catalysts and proposed a detailed reaction pathway, producing gas-phase benzene, toluene, ethylene, indene and acetylene. The reaction mechanism also involved PAH species, including fluoranthene, anthracene, phenanthracene, crysene, and pyrene. These higher PAH are also responsible for deactivation under MDA conditions [175, 174]. Thus, it is at least possible that similar molecular-weight-growth pathways are active on the Mo/Zeolite catalysts.

Wang et al. [203] proposed a reaction pathway for naphthalene steam cracking over Rh₂O₃/HY zeolite and Mo-Ni oxide catalysts. In this reaction pathway, naphthalene ring opening favors the formation of smaller alkanes and aromatics. However hydrogenation reac-

tions proceed in parallel with steam cracking, producing very large polyaromatic hydrocarbons (e.g., teralin and decalin) through condensation reactions.

In addition to dominantly catalytic chemistry, gas-phase reactions may also play important roles, especially at high temperature. Jess [204] studied homogeneous gas-phase reaction of naphthalene and steam at temperatures between 700 and 1400 °C. Although naphthalene is difficult to activate homogeneously at temperatures below 800 °C, at higher temperatures numerous gas-phase products were measured (CO, CO₂, C₂H₂, C₂H₄, C₂H₆, C₆H₆ and C₇H₈, C₉H₈ and C₉H₁₀). These gas-phase species are also products of catalytic naphthalene steam cracking processes [201, 203]. Although gas-phase chemistry may be active, the catalyst certainly affects reaction pathways and the product distribution.

Although low-level steam addition surely has a beneficial influence for MDA processes, there is very limited fundamental understanding of naphthalene-steam chemistry on zeolite-based catalysts. Improved understanding the interaction of naphthalene-steam reactions and the catalyst deactivation mechanisms will likely contribute to improved MDA process technology. Synergistic theoretical and experimental research is certainly needed.

4.4. Incorporating a second metal into Mo/Zeolite

Catalyst stability and performance can be varied by incorporating another metal in addition to Mo. Noble metals (i.e., Pt, Pd, Rh, Ru, Ir, Re) [205–207], transition metals (i.e., Fe, Cr, Co, Ga, Ni, Zn, Ti, W) [91, 208–211] and their combinations [212, 213] have been evaluated for MDA applications. Among the noble metals, Pt- and Re-doped Mo/zeolite catalysts showed increased catalytic activity and stability.

Burns et al. [208] studied incorporating transition metals (Ga, Co, Al, Fe) into Mo/Zeolite catalysts using an impregnation technique. Using a packed-bed reactor, measurements were reported for methane conversion as well as hydrogen and benzene formation rates. Catalyst screening revealed that Ga, Fe, and Al can all help to improve the catalyst stability. The second metal can change the zeolite catalyst structure via reaction with aluminum to form a secondary metal-aluminum-oxide phase. The second metal also has the effect of modifying the Brønsted acidity. Yet another potential role of the secondary metal is to form mixed molybdenum-containing phases. The second metal can also affect the initial molybdenum-oxide dispersion.

Although only indirectly related to MDA, Yeh et al. [214] compared Ga- and Pt-incorporated

metal/ZSM-5 structures in endothermic hexane reforming. The Ga was shown to enhance both the aromatization rates and catalyst stability.

Aboul-Gheit et al. [211] studied bimetallic Mo-Fe, Mo-Co and M-Ni/HZSM-5 catalysts (equal weights, 3% each) in a packed-bed reactor at 700 °C. The metals were incorporated into the catalyst by mechanical mixing. They measured the catalytic activity in terms of methane conversion and aromatic yield as functions of time-on-stream. Based on ex-situ TPO measurements they determined the cumulative coke formation rate. Unlike Burns et al. [208], Aboul-Gheit et al. [211] reported that second-metal incorporation increased the coke and hydrogen formation rates, with the effects being greatest for Fe, followed by Co and then Ni. Aboul-Gheit et al. interpreted the low catalytic activity of Mo mixed with group-VIII metals (Fe, Co, Ni) in terms of electronic structure and unfilled d-orbitals. The mixed-metal structures influenced the chemisorption behavior, strengthening the CH₄ adsorption and leading to coke formation.

In addition to the second-metal identity, the loading also affects the activity. However, there appear to be no general rules for determining the optimal ratios between Mo and the second metal. Masiero et al. [215] studied effects of the Mo/Fe ratio in HZSM-5 catalysts. X-ray diffraction (XRD) was used to characterize the catalyst phases. The catalytic activity at 700 °C was reported in terms of methane conversion and benzene selectivity. Catalyst deactivating deposits were analyzed using thermogravimetric analysis (TGA), differential thermal analysis (DTA), and temperature-programmed oxidation (TPO). The study showed that increasing Fe content decreased the acid strength and hence decreased aromatization. A Mo/Fe ratio of 4 increased the catalytic activity as well as the stability. In addition to improved activity, the Fe formed a second bimetallic Fe₂(MoO₄)₃ structure that enhanced the catalytic stability.

A 2015 study by Abdelsayed et al. [91] confirmed that Fe incorporation increased methane conversion and catalyst stability. Unlike, Masiero et al. [215], Abdelsayed et al. did not observe any secondary Mo phases. However, they found that carbon nanotubes were formed on the spent catalysts. The carbon nanostructures apparently enhanced reactant and product diffusion and coke resistance.

4.5. Alternative catalysts

Although zeolite catalysts with a range of cage sizes and metal loadings are used, there may be viable alternatives with non-zeolite catalysts. A 2014 discovery by Guo et al. [90] suggested that Fe with SiO₂ sup-

ports is an excellent catalyst for the non-oxidative conversion of methane to ethylene. They reported a 30% C₂H₄ yield at 950 °C in a packed-bed reactor. The process also yielded significant amounts of aromatics (approximately 23%), primarily benzene and naphthalene. The catalyst showed excellent durability over long periods up to 60 h, without the appearance of carbon deposits. The reported very high process temperatures, 1000 ≤ T ≤ 1200 °C. Typical processes for methane dehydrogenation to ethylene operate in the range of 800 ≤ T ≤ 900 °C. At 1020 °C, Guo et al. reported methane conversion to be 32%, with steady product selectivities of 52.7% ethylene, 21.5% benzene, and 25.8% naphthalene for 60 h on stream. Operating in the temperature range 950 ≤ T ≤ 1090 °C, the product distribution remained almost constant. Although high operating temperature represents a practical technological disadvantage, the performance of Fe/SiO₂ catalysts for C₂H₄ or aromatics production merits further investigation.

4.6. MDA reaction kinetics

There is relatively little literature on the detailed reaction pathways and associated rates for MDA kinetics on bi-functional Mo/zeolites catalysts. It is reasonably well established that molybdenum-carbide complex is the active center for methane activation. The Mo₂C is believed to be responsible for activating methane to form small C₂ olefins (mainly C₂H₄) and hydrogen. Describing the methane-activation chemistry on the Mo₂C probably requires fewer reaction steps than does the subsequent chemistry on the zeolite acid sites. Nevertheless, because of the relatively complex Mo₂C structure (cf., Fig. 6), establishing the elementary reaction steps is challenging.

Iglesia and co-workers [216, 18] proposed a global reaction for the methane activation as

The rate expression for this reaction was assumed to be first-order, being expressed empirically as

$$r = k p_{\text{CH}_4} (1 - \gamma), \quad (30)$$

where γ is evaluated as

$$\gamma = \frac{p_{\text{C}_2\text{H}_4} p_{\text{H}_2}^2}{p_{\text{CH}_4} K}, \quad (31)$$

with k being a rate constant, p_i being partial pressures, and K being the equilibrium constant.

As illustrated in Fig. 10, Xing et al. [163, 164] were the first to propose elementary reaction steps to form

Figure 10: Illustration of a proposed catalytic cycle for methane activation on the Mo_2C sites (adapted from Zhou et al. [164]).

C_2H_4 on Mo_2C structures. The cycle begins by methane adsorption, followed by a transition state leading to hydrogen desorption. Methane is again adsorbed, followed by hydrogen and ethylene desorption restoring the catalyst to its original Mo_2C structure.

Following the methane dimerization on the Mo_2C , aromatization takes place on the zeolite Brønsted acid sites. The aromatization chemistry is complex, involving numerous reaction steps. As is typical of Brønsted acid sites, chemistry proceeds according to chemisorption, desorption, hydride transfer, pyrolytic dehydrogenation/hydrogenation, protolysis, oligomerization, and β -scission processes.

Iglesia and co-workers [216, 18] proposed a three-step lumped kinetics model for MDA on $\text{Mo}/\text{HZSM-5}$ catalysts. Following the methane dimerization reaction (Eq. 29) the global aromatization reactions include

Based on the gas-phase chemistry of methane pyrolysis as originally developed by Dean [217], the Iglesia studies also discuss the effects of gas-phase reactions in MDA. Under the packed-bed conditions studied, the gas-phase contributions were found to be negligible [216].

As illustrated in Fig. 11, Wong et al. reported heterogeneous reaction pathways for aromatization chemistry on HZSM-5 and HMCM-22 zeolites [218]. The methane dimerization kinetics on molybdenum was explained in a global step following the reaction pathway proposed by Li et al. [216]. In the Wong et al. study, the formation of ethylene is followed by aromatization on zeolites Brønsted acid sites. Chemisorption, oligomerization, pyrolysis, hydride transfer and alkylation are

the major reaction paths leading to gas-phase products C_2H_4 , C_2H_6 , C_6H_6 , C_7H_8 and C_{10}H_8 . The reaction pathway also includes gas-phase reaction intermediates (e.g., hexane, cyclohexane) and surface species (e.g., C_2H_5^+ , C_4H_9^+). Although they did not report reaction-rate expressions, Wong et al. reported activation barriers for each of the reaction families. They also provided the nominal values of pre-exponential factors as evaluated by transition-state theory.

Based on the pathways suggested by Wong et al [218], Karakaya et al. [134] proposed an elementary reaction mechanism for bi-functional $\text{Mo}/\text{HZSM-5}$ catalysts. The C_2H_4 formation pathway on the Mo_2C sites was developed according to a DFT study by Zhou et al. [164]. The Karakaya et al. reaction mechanism, which involved 50 elementary reactions, was implemented into a one-dimensional packed-bed computational model. In this reaction mechanism, C_2H_4 production over Mo_2C is close to its equilibrium limit. Using previously published data from packed-bed experiments [219–221], Karakaya et al. fine-tuned and validated the reaction model. However, the model did not include deposit formation and catalyst deactivation behavior.

Despite considerable research on MDA processes, predictive models have yet to be developed to describe the inherently unsteady behavior (i.e., carburization, benzene production, catalyst deactivation, regeneration). Even for more traditional processes (e.g., steam reforming), state-of-the-art surface-reaction models do not include the catalyst deactivation behavior. Yet another problem with most elementary-step surface-kinetics reaction mechanisms is the imposition thermodynamic consistency and microscopic reversibility. Because the thermochemistry of adsorbed species is generally unknown (or at least uncertain), the detailed surface-reaction models usually fail to satisfy the enthalpic and entropic consistency. Although estimating or measuring such thermodynamic properties may be difficult, the properties play a central role in ensuring microscopic reversibility. There is active research devoted to estimating the thermodynamic properties needed to assure microscopic reversibility [222–224]. To date, most modeling research on detailed reaction mechanisms has focused on transition-metal catalysts (primarily, Pt, Pd, Rh, and Ni). Clearly, developing and validating predictive models for the bi-functional catalysts used in MDA represent much larger challenges.

Figure 11: MDA reaction pathway proposed by Wong et al. [218] for a bi-functional Mo/zeolite catalyst.

5. Reactor technologies

Although catalysts are central to both oxidative and non-oxidative processes, the catalyst is only one factor in controlling the overall process. Considerations such as catalyst packing, thermal management, reactor operating conditions, and downstream gas separations also play critical roles. Turnover rates (e.g., ethylene or benzene produced per unit catalyst area per unit time) contribute greatly to the process efficiency and cost. An analysis by Hall [225] showed that separating ethylene from the other effluent gases (CH_4 , CO , C_2H_6) is a major cost-driver. Thus, developing systems with higher product selectivity increases product yield and also contributes to decreasing overall process cost.

Reactor and process design involves numerous, often competing, considerations. Generally speaking, catalysts may be deployed in packed beds, washcoat layers, or in fluidized beds. The catalysts themselves may take a variety of shapes and sizes, ranging from small particles to larger pellets. The reactors can take a variety of forms, including shell-and-tube, monolith, or planar microchannels. A variety of membranes can be used, including micro- or nano-porous structures, thin-film metals (e.g., Pd or Pd alloys), or dense-ceramic ion-transport materials. The general reactor configuration (e.g., tubular or planar) is an important design consid-

eration. The following subsections discuss reactor considerations for OCM, MDA, and membrane-assisted reactor design and operation.

5.1. OCM reactors

Because OCM processes are highly exothermic ($\Delta H_{298}^\circ = -281 \text{ kJ}$), careful attention to thermal management can avoid deleterious local hot spots and unsafe operating conditions. Limiting temperature excursions and limiting high-temperature residence time are important considerations in process and reactor design. The CH_4/O_2 stoichiometry, especially at the catalyst surfaces, greatly affects the product composition. Operating conditions (e.g., flow rates, operating pressure and temperature) should be established to achieve certain temperature distributions, residence times, and space velocities. Usually, operating conditions that avoid mass-transport limitations at the catalyst surfaces are desirable.

Most laboratory-scale OCM studies are carried out in small packed-bed reactors where catalyst particles (or pellets) are packed within **small-diameter** (i.e., $\leq 20 \text{ mm}$) tubes [226]. The temperature is typically controlled by an external furnace. Small tube diameters help to maintain radially uniform temperatures within the bed. As illustrated in Fig. 12, the catalyst particles are held in place by a chemically inert packing material

Figure 12: Illustration of a typical laboratory-scale catalytic packed-bed reactor in a tube furnace.

such as silica wool. Reacting mixtures flow through the bed, with product species being measured at the outlet.

Ras and Gomes-Quero [227] developed small-scale packed-bed OCM reactors operating at temperatures between 755 and 875 °C. They showed that the small-diameter tubular configuration enabled good temperature control. Alternatively, high-performance heat exchangers can be integrated into packed-bed reactors. A recent patent application from Siluria Technologies disclosed a packed-bed OCM reactor with integrated heat-exchangers that maintain precise temperature control [228].

Although the small-diameter tubes reduce radial temperature gradients, understanding axial temperature gradients and local hot spots is important. Consider a premixed CH_4/O_2 feed entering into a reactor such as illustrated in Fig. 12. The O_2 is consumed rapidly, causing high local heat-release rates. Senkan and coworkers have measured local temperature increases on the order of 200 °C over axial distances of less than 10 mm [99, 229]. The reaction heat is controlled by the limiting reactant O_2 . Thus, the methane conversion, reaction heat, and C_2 selectivity depend strongly on the local CH_4/O_2 mixtures.

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 prod-

ucts are more stable at low O_2 levels, meaning the C_2 selectivity is higher 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., $\leq 20\%$). Of course, processes seek to achieve high methane conversion and high C_2 yield.

Tye et al. [230] published a model-based study of an OCM packed-bed reactor with a $\text{La}_2\text{O}_3/\text{CaO}$ catalyst. The results included the effects of feed composition and isothermal operating conditions on conversion, yield, and selectivity. The reaction chemistry was based on the Stansch mechanism [71]. Figure 13 shows a summary of the results. The methane conversion depends strongly on the CH_4/O_2 ratio. The C_2 selectivity is high when CH_4/O_2 ratio is high (e.g., greater than ten). However, due to relatively low CH_4 conversion at high CH_4/O_2 ratios, the overall C_2 yield is low. The C_2 selectivity is highest at 875 °C. Due to the increased methyl-radical formation rates and the contributions of gas-phase chemistry at high temperature, increasing temperature from 700 °C to 875 °C increases the C_2 yield and selectivity. However, further increasing temperature above 875 °C causes deep oxidation of C_2 , decreasing the C_2 selectivity. The optimum C_2 yield is predicted at 875 °C and CH_4/O_2 ratios around five.

The Tye et al. study also considers the influence of isothermal or adiabatic (non-isothermal) operation. The results show that heat generation and temperature variations have significant influence on C_2 yield. The study suggests that feed dilution (e.g., up to 50% at 750 °C, $\text{CH}_4/\text{O}_2=4$) can be beneficial. The diluents can smooth the temperature distributions and avoid the local hot spots.

A possible way to control the reaction heat and improve the C_2 yield is to distribute the O_2 feed axially rather than premixing. One approach is to introduce the O_2 via a membrane, such as illustrated in Fig. 1b. Another approach is via discrete O_2 injection points with segmented reactors or catalyst beds [229]. When the oxygen is introduced in a distributed manner along the length of the reactor, the local exotherms can be significantly diminished.

Stunkel et al. [230] published a case study considering several alternative OCM reactor designs and processes. These included packed-bed, fluidized-bed, and membrane reactors. In all cases, a Na-W-Mn/SiO_2 catalyst was used. Process performance was evaluated in terms of ethylene yield. The study included the effects of operating conditions, including temperature, pressure, reactant stoichiometry, and feed rates. The experiments demonstrated that membrane-coupled

Figure 13: Model-predicted influence of the CH_4/O_2 ratio and temperature on OCM methane conversion (a), C_2 selectivity (b) and yield (c). The figure is reproduced from Tye, et al. [78].

susceptible to local hot spots than were packed-bed reactors. Fluidized-bed reactors had the most uniform temperature distributions. The Stunkel et al. [230] economic analysis showed that gas-separation (especially CO_2 removal) has a major impact on the overall cost. They concluded that membrane-coupled packed-bed reactors offered the best potential for the industrial scale OCM plants.

Fluidized-bed reactors may offer potentially better thermal management compared to packed-bed reactors. The OCM process depends on both homogeneous and heterogeneous chemistry. Methyl radicals are mostly generated on the catalyst surface, with exothermic recombination reactions taking place in the gas-phase. Hence, much of the heat is released in the gas-phase, potentially creating large temperature differences between the gas and the solid catalyst. The formation rates of undesired oxidation products (e.g., CO , CO_2 , and H_2O) are increased at high gas-phase temperature. The particle motion in fluidized beds tends to diminish temperature variations [231, 89, 232–234]. However, capital and operating costs are usually higher for fluidized-bed reactors, compared to fixed-bed reactors [234].

5.1.1. Modeling packed-bed OCM reactors

Models of OCM processes must be concerned with thermal behavior and the closely coupled interactions between temperature and catalytic chemistry. The selectivity between desired C_2 products and undesired total-oxidation products depends strongly on temperature. The temperature distribution depends on catalyst activity, flow rates, and feed composition. Local temperature maldistribution or local hot spots can be problematic for a variety of reasons. Reactor and process design can benefit greatly from model-based predictive capabilities that couple thermal and chemical interactions.

The accuracy of the model predictions relies on understanding the catalytic chemistry and the physical transport within catalyst beds. The exothermic nature of the OCM chemistry requires coupling heat and mass transfer effects to predict the overall reactor performance. Models must at least predict the gas-phase composition and temperature profiles as well as the local catalyst temperature. Although small-diameter tubes tend to limit radial temperature variations, axial variation are usually significant. An experimental study by Senkan and colleagues [99, 229] measured the axial temperature and gas-phase concentration profiles in a small-diameter OCM packed-bed reactor. Their results revealed very high axial temperature and composition gradients.

packed-bed reactors can improve C_2 yield compared to fluidized-bed reactors. Membrane reactors were less

The most straightforward modeling studies are based on assuming one-dimensional plug-flow behavior within packed catalyst beds [78, 235, 236]. In such configurations radial heat and mass transports are neglected. Especially for catalysts beds that are packed in narrow tubes, one-dimensional models are appropriate. However, as the beds become larger, radial temperature and composition variations become important. Thus, two- and three-dimensional models are needed to accurately represent the packed-bed performance [237–239]. Membranes that deliver radial fluxes into the packed beds tend to increase radial gradients, and thus increase the need for multi-dimensional models.

5.1.2. One-dimensional packed-bed formulation

A system of governing equations to represent transport and chemistry within a one-dimensional packed-bed reactor may be summarized as:

Gas-phase species continuity

$$\frac{\partial(\phi_g \rho_g Y_k)}{\partial t} + \nabla \cdot \mathbf{j}_k = (A_s \dot{s}_k + \phi_g \dot{\omega}_k) W_k + \frac{P_B}{A_B} \mathbf{j}_k^M \quad (34)$$

Overall gas-phase continuity

$$\frac{\partial(\phi_g \rho_g)}{\partial t} + \sum_{k=1}^{K_g} \nabla \cdot \mathbf{j}_k = \sum_{k=1}^{K_g} A_s \dot{s}_k W_k + \frac{P_B}{A_B} \sum_{k=1}^{K_g} \mathbf{j}_k^M \quad (35)$$

Gas-phase energy

$$\frac{\partial \phi_g \rho_g e}{\partial t} + \nabla \cdot \mathbf{q}_g = -\dot{q}_{\text{conv}} - \dot{q}_{\text{surf}}, \quad (36)$$

Catalyst-phase energy

$$\frac{\partial}{\partial t} (\phi_s \rho_s c_{p,s} T_s) + \nabla \cdot \mathbf{q}_s = \dot{q}_{\text{conv}} + \dot{q}_{\text{surf}} - \dot{q}_{\text{env}}. \quad (37)$$

Catalyst surface coverage

$$\frac{\partial \theta_{k,m}}{\partial t} = \frac{\dot{s}_k}{\Gamma_m} \quad (38)$$

Gas-phase flux within catalyst bed

$$\mathbf{j}_k = -\rho_g Y_k \frac{B_g}{\mu} \nabla p - D_k^e W_k \nabla [X_k] \quad (39)$$

Effective diffusion coefficient

$$D_k^e = \phi_g^2 D_{k,m} + \frac{\phi_m^2 (1 + 3\phi_g)}{1 - \phi_g} D_{k,\text{Kn}}, \quad (40)$$

The independent variables in these equations are time t and the spatial coordinates. Dependent variables include gas-phase mass fractions Y_k , gas-phase density ρ_g ,

gas-phase internal energy e ($de = c_{v,g} dT_g$), gas-phase temperature T_g , solid-phase temperature T_s , and catalyst surface coverage $\theta_{k,m}$ (k is the species index and m is the phase index, with Γ_m being the phase site density). Axial gas-phase fluxes within the bed are $\mathbf{j}_k$, which include pressure-driven convection (superficial velocity is $U = B_g \nabla p / \mu$) and Fickian diffusion. The pressure is represented as p and the gas-phase concentrations as $[X_k]$. The effective diffusion coefficient D_k^e considers ordinary and Knudsen diffusion. The parameter ϕ_m represents the microscale porosity within catalyst particles.

Gas-phase fluxes through a membrane are represented as $\mathbf{j}_k^M$. As discussed in Section 6, the constitutive relationships governing the membrane fluxes depend on the type of membrane.

The species production rates via catalytic surface chemistry are represented as $\dot{s}_k$. Species production rates via gas-phase chemistry are represented as $\dot{\omega}_k$. Evaluation of these rates depends on particular reaction mechanisms.

Physical parameters include the gas-phase and solid-phase volume fractions ϕ_g and ϕ_s , respectively. The catalyst specific area (catalyst surface area per unit volume) is represented as A_s . The parameters P_B and A_B represent the bed perimeter and cross-sectional areas, respectively. The gas-phase dynamic viscosity is μ , the bed permeability is B_g , and W_k are the gas-phase molecular weights.

The gas internal energy is e ($de = c_{v,g} dT_g$). The solid-phase volume fraction is $\phi_s = 1 - \phi_g$, temperature is T_s , the density is ρ_s , and heat capacity is $c_{p,s}$. Heat fluxes within the gas and solid (catalyst) phases are represented as $\mathbf{q}_g$ and $\mathbf{q}_s$, respectively. Convective heat exchange between phases or the environment are represented as $\dot{q}_{\text{conv}}$ and $\dot{q}_{\text{env}}$. The variable $\dot{q}_{\text{surf}}$ represents the heat associated with adsorption and desorption between the catalyst and gas phases.

In a one-dimensional setting, these equations are usually solvable on typical personal computers. In high dimensions, more computational resources are usually appropriate.

5.1.3. Modeling OCM membrane reactors

Several computational studies have addressed the performance of membrane-coupled OCM reactors. Predictive models require knowledge of the chemical kinetics as well as the oxygen transport mechanisms [240, 79–82]. These studies have considered both one- or two-dimensional reactor models.

One-dimensional models, which necessarily assume radial uniformity, deliver qualitatively accurate predictions of the axial concentration and temperature profiles.

However, a study by Holst et al. [79] showed the possibility of significant differences between one- and two-dimensional models, with the two-dimensional models being able to more accurately represent measured experimental data. Incorporating radial variations in the oxygen composition played a major role in predicting the overall temperature and composition fields.

Koa and Lin [240] modeled a membrane coupled OCM reactor and compared the results with a packed-bed reactor without a membrane. The Li/MgO catalyst was housed within an inner tube, with oxygen flowing in an outer annular space. The membrane was fabricated from mesoporous alumina. A four-step global reaction mechanism for the catalytic chemistry was taken from Wang and Lin [60]. The oxygen flux through the porous membrane was modeled using a Knudsen-diffusion model. One-dimensional plug flow was assumed within the catalyst bed. The model predicted that the membrane-coupled OCM reactor, operating at atmospheric pressure and 750 °C, can deliver a maximum of 30% C₂ yield at 53% C₂ selectivity. The results also showed that a co-flow configuration was much better than a counter-flow configuration.

Patcharavorachot et al. [82] developed a one-dimensional packed-bed model to study OCM performance using a dense-ceramic oxide-ion-conducting membrane. The La₂O₃/CaO catalyst was housed in an interior tube, with air flowing in the exterior annulus. The perovskite membrane (Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}) served to separate oxygen from air as well as to deliver oxygen flux onto the catalyst bed. The ten-step catalytic chemistry was taken from Stansch et al. [71]. This reaction mechanism involved only gas-phase species, and used empirical rate expressions. The simulations predicted that the membrane could increase C₂₊ yield from 7.2% to 33% at 830 °C. Operating at 843 °C with CH₄/O₂ ratio of 0.83, the model also predicted a maximum C₂₊ yield of 36.5%.

Holst et al. [79] developed one- and two-dimensional models of packed-bed OCM reactors with oxygen-permeable membranes. The porous ceramic membranes were modeled using empirical expressions to represent the oxygen fluxes. In addition to the catalytic chemistry, these models represented axial and radial heat and mass transfer. Two catalysts were considered. Reaction kinetics for the La₂O₃/CaO catalyst were taken from Stansch et al. [71]. This reaction mechanism consisted of nine global surface reactions and one global gas-phase reaction. The four-step global heterogeneous reactions for the Li/MgO catalyst were taken from Wang and Lin [60], who also considered oxygen-ion transport membranes. Additionally, four global gas-phase reac-

Figure 14: Dual-membrane reactor concept for integrating dry reforming chemistry into an OCM process [241].

tions were taken from Lane and Wolf [104]. The Holst et al. study emphasized the importance of radial concentration gradients that resulted from oxygen flux through membranes.

Godini et al. [81] also studied membrane-coupled OCM in a packed-bed reactor, with a specific focus on comparing reactor performance with La₂O₃/CaO and Na₂/WO₄/Mn/SiO₂ catalysts. The reaction mechanisms for the La₂O₃/CaO were adopted from Stansch et al. [71]. The reaction mechanisms for the Na₂/WO₄/Mn/SiO₂ were adopted from Daneshpayeh et al. [117]. This mechanism considered ten reaction steps among eight gas-phase species. Similar to the Holst et al. [79] study, the Godini et al. model also emphasized the importance of two-dimensional models that incorporate the effects of radial heat and mass transfer.

5.1.4. Combined OCM processes

Godini et al. [241] introduced a reactor concept that integrated dry reforming of methane and OCM reactions. As illustrated in Fig. 14, the reactor was designed in a laboratory-scale co-annular configuration. A porous-alumina membrane is used to introduce air from an inner tube into the annular OCM catalyst bed. The reactant CH₄ was introduced into both inner and outer annular catalyst beds. The inner bed housed the OCM catalyst (Mn/Na₂WO₄/SiO₂ and La₂O₃/CaO) and the outer bed housed a dry-reforming catalyst (Ni/La/SiO₂). Carbon dioxide, produced by the OCM process, is separated via a CO₂-permeable membrane and used for dry reforming within the outer catalyst bed.

The OCM process is exothermic, while dry reforming is endothermic. Combining the processes offers opportunities for thermal balancing and control, with the

Figure 15: Illustration of a microchannel reactor with alternating layers of endothermic and exothermic catalysts.

endothermic dry reforming taking advantage of excess heat from the OCM process. Moreover, because CO_2 is consumed in dry reforming, there is very little CO_2 leaving the catalyst beds (nearly 90% CO_2 is consumed). Thus, downstream separation costs can be significantly decreased.

Controlling temperature is often important, especially for exothermic processes such as OCM. Catalytic microchannel reactors can be designed to tightly couple excess heat from an exothermic process to supply needed heat to a endothermic processes. Figure 15 illustrates an exploded view of a generic microchannel configuration [243]. Washcoated catalyst layers are in direct contact with microchannel networks. Depending on fabrication approach, the “microchannels” have characteristic heights of a fraction of a millimeter [244, 245]. The thin-layer sandwich construction transfers heat efficiently between the exothermic and endothermic layers. There has been considerable research on systems that use catalytic combustion in the exothermic channels to supply heat to a reforming process in the endothermic channels. In the present context, the exothermic channels could house an OCM process, with the endothermic channels housing a methane-reforming process [246, 242].

Although the heat- and mass-transfer within microchannel reactors is highly efficient, there are challenges in achieving high-performance results. For example, at high temperature, sealing between layers can

be difficult. The operation is passive in the sense that there is no direct control of the flow and temperature uniformity within the channels [247]. Once the microchannel reactor is fabricated and sealed, access to the catalysts is limited. Thus, catalyst replacement is difficult, which can be operationally problematic for processes that are susceptible to carbon deposition and other catalyst deactivation processes.

Thybaut et al. [242] introduced a novel multi-bed reactor concept, integrating OCM and methane dry reforming (DRM) chemistry. As illustrated in Fig. 16, the OCM and methane dry reforming (DRM) chemistry takes place in parallel, using small-scale staged catalytic packed-beds. The two gas streams remain separated, enabling the two processes to operate at different temperatures, pressures, and flow rates. Gas-phase heat exchangers transfer excess heat from the exothermic OCM reaction to the endothermic DRM process. Thybaut et al. designed the microchannel heat exchangers in a cross-flow configuration, but with baffel sections yielding partially counter-flow performance.

The small-scale reactors are insulated, seeking nominally adiabatic performance within individual reactors. Thus, the gas temperature within the exothermic reactors increases and the gas temperature within the endothermic reactors decreases. However, because the reactors are small, the temperature excursions are small. The heat exchangers between stages reduce the temperature of the exothermic stream and increase the temperature of the endothermic stream. Although the temperatures within the reactors vary in a step-wise manner, the temperature steps are small. Thus, staging the small-scale unit processes delivers an approximately continuous result. An advantage of staging is that the small-scale packed-bed reactors can be maintained or replaced as needed. Thybaut et al. suggested that five stages are sufficient to provide good performance (Fig. 16 shows three stages).

Using computational simulation, Tiemersma et al. [248] studied the possibility of designing dual-function catalysts within single catalyst particles. The inner core of the spherical catalyst particles was a steam-reforming catalyst (e.g., $\text{Pt}/\text{Al}_2\text{O}_3$). The outer shell was an OCM catalyst (e.g., $\text{La}_2\text{O}_3/\text{CaO}$). The two active catalyst regions were separated by a chemically inert annular region. Combining the two catalytic functions within individual particles enabled close thermal and chemical integration of the endothermic steam reforming and the exothermic OCM. Tiemersma et al. [249] went on to explore the possibility of integrating the dual-function catalysts into a co-annular, packed-bed, membrane reactor. Oxygen was introduced

Figure 16: A staged-reactor system that integrates oxidative coupling of methane (OCM) and dry reforming of methane (DRM) [242].

through the central porous-membrane tube and CH_4 and H_2O were introduced in the outer shell that housed the dual-function catalyst. The model-based results showed a 36% C_2 yield at 866 °C. These approaches suggest interesting advantages of innovative new catalyst and reactor concepts.

Figure 17 illustrates a multi-layer membrane-coupled reformer reactor [250, 251]. Using ceramic ion transport membranes, this system effectively integrates air separation with the supply of oxygen to partial-oxidation (CPOX) catalysts. Air flows within internal microchannels whose upper and lower walls are formed as thin oxide-ion membranes. Aspects of the fabrication technology lead to the relatively complex flow patterns within the microchannels. The perovskite membrane is $\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$ (LCF), which has the important advantage of being stable in both oxidizing and reducing environments. The thin membrane is supported on a porous ceramic structure, which is also loaded with the partial-oxidation catalyst. Natural-gas flows across the external porous catalyst structures. Although this system was designed for syngas (H_2 and CO) production by partial oxidation, the design approach is also applicable for OCM. Of course, the OCM catalysts would be different from the CPOX catalysts. The tight integration of air separation and catalysis enhances process intensification.

5.2. MDA reactors

Most laboratory-scale MDA experiments are carried out in packed-bed reactors [168, 218–221], which are

relatively straightforward to build and operate. Small amounts of catalyst (i.e., 0.5–2.0 g) are usually sufficient for catalyst screening experiments. Radially uniform temperature profiles can be achieved by packing the catalysts in small-diameter tubes within furnaces. Although axial temperature can vary, radial temperature variations are usually negligible with packed-bed diameters around 10 mm. Small-diameter packed beds lend themselves to one-dimensional approximations in computational modeling. The experimental-modeling synergy is important in understanding and establishing chemical pathways and evaluating reaction rates.

A few studies consider MDA in fluidized beds. Cook et al. [252] compared the MDA performance in packed-bed and fluidized-bed reactors. They used 4 wt.% Mo/HZSM-5 catalysts. Results showed that at the beginning of the process (up to 2 h) the fluidized-bed reactor improved the aromatic yield up to 15%. However, as explained by the increased residence time in fluidized-bed reactors, naphthalene selectivity was preferred over benzene. Also, at longer time-on-stream, deactivation was more severe in their fluidized-bed reactor compared to packed-bed reactor. The relatively rapid fluidized-bed deactivation was attributed to the particle-particle collisions and weak mechanical stability of the catalyst particles.

Gimeno et al. [253] presented a cylindrical catalytic two-zone fluidized-bed reactor. The fluidization was accomplished primarily via mechanical stirring. Methane was introduced axially downward from the top of the

Figure 17: Partial-oxidation reformer integrated with air-separation oxygen-transport membranes [250, 251].

reactor and combinations of O_2 , H_2O , and CO_2 were introduced axially upward from the bottom of the cylindrical reactor. Product gases were extracted radially outward near the top of the reactor. The catalyst particles recirculated between the upper and lower zones. The upper portion of the two-zone reactor was responsible for the MDA chemistry. The lower portion of the reactor was intended to promote continuous in-situ catalyst regeneration. The concept delivered good catalyst stability and aromatic yield, with the methane conversion being close to its thermodynamic limit in the temperature range $700 \leq T \leq 800$ °C. Benzene, toluene and xylenes accounted for 95% of the aromatic products.

5.2.1. Modeling MDA reactors

There are far fewer modeling studies for MDA processes than there are for OCM processes. At least in part, the lack of MDA reaction mechanisms impedes the development of MDA models. Because of factors such as relatively rapid deposit formation and catalyst deactivation, MDA processes do not achieve long-term steady-state operation. Thus, interpreting the experiments and establishing relatively simple global reaction pathways and rates is difficult. Moreover, because the catalyst continuously changes (carburization and deactivation), the MDA process is inherently transient, making modeling more complex than is the case for nominally steady-state processes.

Modeling studies have considered both global reaction kinetics developed by Lui et al. [254] and detailed reaction kinetics proposed by Wong et al. [218] and Karakaya et al [134]. The models assume nominally steady-state operating conditions, with catalyst

deactivation and PAHs formation chemistry not being included. The models are used to explore the effects of operating conditions (i.e., temperature, weight hourly space velocity) on product yield and selectivity [218, 134]. Results indicate a strong relationship between naphthalene formation rate, temperature, and residence times. Increasing temperature and residence times generally increase the methane conversion toward equilibrium. However as conversion increases, naphthalene formation is favored over benzene. Seeking to increase both methane conversion and benzene yield, a number of computational studies have investigated the effects of incorporating hydrogen-permeable membranes.

The Iglesia group considered membrane-assisted MDA in tubular reactors [216, 18]. A 4 wt.% Mo/H-ZSM-5 catalyst bed was housed within a tube, with the tube walls forming the hydrogen-permeable membrane. The models used a global three-step kinetic model to predict benzene and naphthalene formation rates. The modeling results revealed a strong interaction between the operating conditions, membrane hydrogen fluxes, and benzene formation rates. The results showed that methane conversion increases as a function of hydrogen removal rate. However, benzene selectivity follows a non-linear trend. At low hydrogen removal rate ($\leq 5\%$) the benzene yield increases slightly. As the methane conversion further increases by increasing the hydrogen removal rate, the process favors naphthalene. Experimental studies also confirm that increased hydrogen removal rate favors the coke formation and without a significant beneficial effect on benzene yield [254–258]. The value of the hydrogen-permeable membrane

integration relies on developing catalysts with improved benzene selective and controlling the catalyst deactivating coke formation.

5.2.2. Combined MDA processes

Because catalyst stability and thermodynamic limitations are major concerns in MDA, a number of studies focus on alternative technologies to improve the single-pass yield. One such approach is called “one-pot” synthesis, meaning that processes can be tightly integrated as sequential processes in single reactor. Such process intensification can improve performance and reduce downstream separation processes.

Samarth et al. [259] combined OCM and MDA chemistry in a sequential two-zone packed-bed reactor. The first zone contained an OCM catalyst (Si/Sn/MgO), followed by an MDA catalyst (5 wt.% Ga/HZSM-5). Combining these two processes increased both the OCM and MDA performance (i.e., conversion, yield, and catalyst stability). The undesired products of OCM reactions (i.e., CO₂, H₂O) can be beneficial for the MDA chemistry.

Xu and co-workers [260, 261] developed another two-zone reactor concept. In this case, the first-zone OCM catalyst was a mixture of 20 wt.% SrO and 20 wt.% La₂O₃/CaO. The second-zone MDA catalyst was 6 wt.% Mo/HZSM-5. The reactor was operated at atmospheric pressure and 730 °C. Under these conditions the process is primarily one of MDA. However, the low levels of CO₂ and H₂O produced in the upstream OCM section served to enhance catalyst stability and increase benzene yield over 16 h of time-on-stream [260]. Similar trends were observed with the MDA catalyst being 6 wt.% Mo/MCM-49. In this case, the study reported 5% aromatic yield for up to 72 h time-on-stream [261].

MDA chemistry has also been used to enhance the efficiency of coal pyrolysis. Jin et al. [262] designed and developed a two-zone packed-bed reactor. The first zone was supplied with methane over a 4 wt.% Mo/HZSM-5 catalyst. The coal to be pyrolyzed was introduced into a catalyst-free second zone. Results showed that combining MDA with coal pyrolysis beneficially improved the desired tar yield by around 40% at 700 °C and 1 atm. The increased tar yield from the combined process was attributed primarily to the participation of free radicals that were formed in the MDA zone.

Li et al. [263] demonstrated a two-zone reactor in which the flash pyrolysis of coal was followed by aromatization. The pyrolysis took place in an upstream reactor zone, followed by MDA chemistry in the second zone. Methane was a product of the coal pyrolysis. The

study reported that the downstream MDA promoted the aromatization of olefins and alkanes, and the dehydroxylation of phenolic compounds.

Huang et al. [264] demonstrated a combined bio-fuel pyrolysis and MDA process in a two-stage catalytic reactor. The pyrolysis produces a methane-rich gas stream. Methane-rich gas from the pyrolysis reaction was fed to a second-stage reactor, which housed a packed-bed MDA catalyst (HZSM-5 with 3 wt.% Mo and 3 wt.% Cu). The C₆-C₁₂ yield was improved compared to the bio-fuel pyrolysis alone. The approach showed the potential of improving the conversion of bio-derived fuels to bio-oils.

Although MDA processes generally require high temperature to activate methane, combining processes can assist in reducing overall process temperatures. For example, Majhi et al. [265] studied combined methanol and methane aromatization over Mo/HZSM-5 and Zn-Mo/ZSM-5 catalysts. Unlike the endothermic methane aromatization, methanol aromatization is exothermic. By mixing 1.6-2.5% methanol in the methane feed, the reaction temperature of MDA was decreased to 550 ≤ T ≤ 650 °C. Full methanol conversion was reported at temperatures above 500 °C. The Zn incorporation into the Mo/ZSM-5 catalyst increased methane conversion from 18% to 22% at 650 °C. The product composition was mainly C₆H₆, C₇H₈, and C₈ and C₉₊ aromatics. Benzene selectivity was around 20-30%, which is relatively low, compared to pure methane aromatization. Gradual catalyst deactivation was observed during 5 h on stream.

A number of investigations have shown that co-feeding higher hydrocarbons with methane offers the possibility of reducing MDA operating temperatures. Co-aromatization studies have included several hydrocarbons, including ethane [266, 267], propane [268–272], butane [273], pentane [274], hexane [275], light gasoline (C₅ and C₆ mixtures) [276], and alkenes (butene, iso-butene, propene) [268]. These studies have used a variety of zeolite catalysts with second-metal incorporation (Ga, Mo, Zn, Mo-Zn, La-Zn, Co-Zn). Although the co-aromatization of methane with higher hydrocarbons increases the methane conversion and aromatic yield, the catalyst deactivation is more rapid compared to MDA alone [267, 269, 277]. Thus, although several studies have been reported, the benefits of co-aromatization remain somewhat inconclusive.

Using isotopically labeled ¹³CH₄, Luzgin et al. [270, 272] studied the co-aromatization of methane with propane over Zn- and Mo-containing H-BEA zeolites at 550 ≤ T ≤ 600 °C. Figure 18 illustrates CH₄ reaction pathways with propane co-aromatization. Solid-

Figure 18: Possible reaction pathway for the co-aromatization of methane and propane. The ^{13}C -labeled methane facilitates understanding the role of methane [270].

state NMR and GC-MS analyses showed that in the presence of propane, aromatization proceeds primarily via propane conversion to benzene, toluene, or xylene. These reactions are highly favorable due to low Gibbs free energy changes. The methane consumption is mainly via methylation reactions.

Despite reports of the benefits associated with hydrocarbon co-aromatization processes, there is also dissenting literature. A recent study of Bijani et al. [277] questioned the effectiveness of propane co-aromatization. Using a thermodynamic analysis, they evaluated the effect of temperature ($400 \leq T \leq 600$ °C), pressure ($1 \leq p \leq 10$ bar), and methane-to-propane ratio ($0 \leq \text{CH}_4/\text{C}_3\text{H}_8 \leq 20$). The thermodynamic analysis supported the idea that equilibrium methane conversion could not exceed 1% when propane is co-fed at temperatures below 600 °C and atmospheric pressure. Bijani et al. supported their analysis by experimentally studying the effects of temperature, gas-hourly space velocity, and $\text{CH}_4/\text{C}_3\text{H}_8$ ratio over a Zn/HZSM-5 catalyst in a packed-bed reactor at atmospheric pressure. They measured the aromatic yield as well as the CH_4 and C_3H_8 conversion as functions of time-on-stream. Higher temperatures enhanced aromatic formation, but also increased coke formation by pyrolysis of the thermodynamically less-stable propane.

The Bijani et al. results are consistent with an earlier study of Naccache et al. [278] who studied co-aromatization of olefins (C_2H_4 and C_3H_6) over Ga doped MFI. By labeling the carbon in the methane, Naccache et al. showed that labeled carbon was

not incorporated into the reaction products. Apparently the methane is essentially unreactive during co-aromatization.

Another concept for a combined processes involves using H_2 from an MDA process in ammonia synthesis. A patent from BASF disclosed a combined MDA and ammonia-synthesis process within the same reactor [279]. The feed gas was a mixture of natural gas ($\text{C}_1\text{-C}_6$ aliphatic hydrocarbons) and nitrogen. The ratio of aliphatic hydrocarbons to nitrogen varied between 1:1 and 20:1. The hydrogen, which is a product of MDA chemistry, was used as a reactant in the ammonia synthesis. By removing the hydrogen in-situ via the ammonia synthesis, the reactor increased methane conversion and benzene yield. A further advantage of the process is that the combination of endothermic MDA and exothermic ammonia synthesis can assist thermal management. The MDA catalyst was an MFI-type zeolite with 0.5-20 wt.% Mo and 0.02-6 wt.% Ru. The reported operating temperatures were $400 \leq T \leq 1000$ °C at pressures in the range $0.5 \leq p \leq 100$ bar. The patent discussed implementation in either packed-bed or fluidized bed reactors.

As discussed in Section 1.2, increasing pressure significantly decreases methane conversion. However, increasing pressure increases benzene selectivity while decreasing naphthalene selectivity. In an MDA reactor with a H_2 -permeable membrane operating at elevated pressures, it is likely that the decreased methane conversion due to the increased pressure can be compensated by shifting the thermodynamic equilibrium via H_2 removal. In this case, benzene selectivity can increase and the catalyst is more stable due to the low naphthalene formation rates. Moreover, the benzene turnover rates can be higher due to the increased mass throughputs at increased inlet pressure. A membrane-coupled MDA reactor operating at high pressures offers a potentially valuable approach that merits further study.

6. Membrane materials and transport

Hydrogen- and/or oxygen-permeable membranes offer the possibility of improving methane conversion, product selectivity, and yield. Membranes can also contribute to reducing catalyst deactivation and extending productive time-on-stream. Thus, integrating membranes into catalytic reactors may play important roles in developing commercially viable gas-to-liquids technology.

Hydrogen-transport membranes can be used in dehydrogenation processes where the conversion reaction is equilibrium-limited. By removing the excess hydrogen,

the methane conversion and hence the product yield can be increased. Consider, for example, direct methane dehydroaromatization (Eq. 1) to produce benzene or direct conversion of methane to ethylene (Eq. 2); both reactions produce significant amounts of H₂.

Permselective membranes can take several physical forms, including polymers (e.g., Nafion), thin-film metals (e.g., palladium), micro- or nano-porous ceramics, and ceramic ion-transport membranes (ITM). Because of the high temperatures needed for methane activation, polymer membranes are not relevant, and are not considered here.

Palladium and palladium-alloy membranes have very good hydrogen permeability, and are frequently used in hydrogen-separation processes [280]. These membranes operate at elevated temperatures and can be valuable for increasing conversion in dehydrogenation processes.

Porous membranes can be effective in OCM membrane reactor concepts. However, air separation is not possible through porous structures. Thus, for applications needing oxygen transport, any air separation must be accomplished upstream of the membrane reactor. Very high selectivity can usually not be achieved. Consider an application in which the membrane is intended to deliver oxygen into a catalyst bed. The porous membrane may allow some undesired diffusion of reactants and product gases back to the oxygen supply side of the membrane. However, maintaining high pressure on the oxygen side helps to avoid the back diffusion.

A range of ceramic ion-transport membranes (ITM) are well suited to dehydrogenation chemistry and membrane reactors [27, 281]. Broadly speaking, ITM membranes fall into two categories – one promoting proton conduction and the other promoting oxide-ion conduction. In both cases, the membranes are based on heterovalently doped polycrystalline structures. The so-called protonic ceramics are typically represented by doped perovskites such as yttrium-doped barium zirconates (e.g., BaZr_{0.9}Y_{0.1}O_{3-δ}, BZY10). Although called protonic ceramics, these materials are mixed conductors that conduct protons, oxide ions, and small polarons.

Ceramic materials such as yttria-stabilized zirconia (YSZ) or gadolinia-doped ceria (GDC) are suitable as oxygen-transport membranes. These materials, which have a cubic fluorite crystal structure, are widely used as electrolyte membranes in solid-oxide fuel cells and electrolyzers. Because the electronic conductivity is low they can be polarized by applying an electrostatic potential across the membrane. The electrostatic field promotes the migration of oxide ions within the mem-

brane, delivering a de-facto oxygen flux.

6.1. Palladium membranes

The fact that hydrogen diffuses through Pd has been known since the mid 1800s. In more recent times, various Ag-Pd and Au-Pd alloys have been developed to improve hydrogen fluxes. Membranes, which are typically around one micrometer thick, are usually applied on the outside of porous support tubes. Depending on temperature and hydrogen partial pressure across the membrane, hydrogen fluxes are on the order of 1 mol m⁻² s⁻¹. Although research is still active, palladium-based membranes are now produced commercially. Reviews by Way and colleagues provide historical and technical perspectives [280, 282].

The effective H₂ fluxes may be expressed in the form of Sieverts law as

$$J_{H_2} = \frac{P}{L} (p_{H_2,1}^n - p_{H_2,2}^n), \quad (41)$$

where P represents the permeance (mol m⁻² s⁻¹ Pa⁻ⁿ), L represents the membrane thickness, $p_{H_2,1}$ and $p_{H_2,2}$ represent hydrogen partial pressures (Pa) at the membrane surfaces. The exponent n is ideally 1/2, but membrane defects such as pinholes or microcracks can increase n . Any such defects also decrease the hydrogen selectivity.

At the membrane surfaces, molecular hydrogen must react ($H_2 \rightleftharpoons 2H$) to form the atomic hydrogen that is transported through the dense Pd membrane. Thus, there is the possibility that the hydrogen transport is rate-limited by surface reaction. However, it is usually assumed that the transport is dominated by bulk-phase diffusion (i.e., Eq. 41).

6.2. Porous ceramic membranes

Because of the high temperature needed for OCM of MDA processes, porous membranes are often fabricated from chemically inert ceramic materials such as alumina. Membranes for MDA processes usually demand high selectivity for hydrogen, which is difficult to achieve via porous membranes. Membranes for OCM processes are usually used to distribute oxygen along the length of the catalyst bed. Oxygen selectivity is also a factor, but not as demanding as for hydrogen selectivity in MDA. With a porous membrane in OCM processes, oxygen is usually separated from air prior to entering the reactor. If oxygen is not separated beforehand, then there will be substantial nitrogen dilution in the catalyst bed. Because the porous structure is not selective (or only weakly selective), back diffusion of hydrocarbon species into the oxygen flow can be problematic. This problem is usually minimized or avoided

by maintaining a high oxygen pressure (e.g., up to 6 bar is typical) on the O₂ feed side [283–285].

The gas flux through porous media depends on the pore microstructure (porosity, pore dimensions, tortuosity) and membrane thickness. When the pore structure is relatively open, a pressure-driven Darcy flow representation is usually appropriate. When the characteristic pore dimensions are on the same order as the gas-phase mean-free-path length, multicomponent Knudsen diffusion becomes dominant. In the intermediate length scales, multicomponent Fickian and Knudsen diffusion are both active.

Alternative porous-media transport models have been developed in the context of representing gas-phase transport in porous-ceramic electrode structures for solid-oxide fuel cells [286–288]. The Dusty-Gas (DGM) formulation provides an effective model for bridging all the relevant length scales in a single model [289]. The steady-state species mass fluxes $\mathbf{j}_k$ through a non-reactive porous membrane may be evaluated by solving a mass-conservation problem as

$$\nabla \cdot \mathbf{j}_k = 0. \quad (42)$$

The DGM is an implicit relationship among the gas-phase species molar fluxes $\mathbf{J}_k$, molar concentrations $[X_k]$, concentration gradients, and the pressure p gradient as,

$$\sum_{\ell \neq k} \frac{[X_\ell] \mathbf{J}_k - [X_k] \mathbf{J}_\ell}{[X_T] D_{k\ell}^e} + \frac{\mathbf{J}_k}{D_{k,\text{Kn}}^e} = -\nabla[X_k] - \frac{[X_k]}{D_{k,\text{Kn}}^e} \frac{B_g}{\mu} \nabla p, \quad (43)$$

where μ is the mixture viscosity and $[X_T] = p/RT$ is the total molar concentration. The mass fluxes $\mathbf{j}_k$ are related to the molar fluxes $\mathbf{J}_k$ as $\mathbf{j}_k = W_k \mathbf{J}_k$, where W_k are molecular weights. $D_{k\ell}^e$ and $D_{k,\text{Kn}}^e$ are the effective ordinary and Knudsen diffusion coefficients, respectively. Knudsen diffusion represents molecular diffusion and mass transport assisted by gas-wall collisions. The Knudsen diffusion coefficients depend upon the porous-media microstructure, including porosity ϕ_g , average pore radius r_p , and tortuosity τ_g . The effective binary and Knudsen diffusion coefficients $D_{k\ell}^e$ and $D_{k,\text{Kn}}^e$ can be evaluated as

$$D_{k\ell}^e = \frac{\phi_g}{\tau_g} D_{k\ell}, \quad D_{k,\text{Kn}}^e = \frac{2}{3} \frac{r_p \phi_g}{\tau} \sqrt{\frac{8RT}{\pi W_k}}. \quad (44)$$

The ordinary multicomponent diffusion coefficients $D_{k\ell}$ and the mixture viscosities μ are determined from kinetic theory [290]. The permeability B_g can be evaluated from the Kozeny-Carman relationship as

$$B_g = \frac{\phi_g^3 d_p^2}{72\tau(1 - \phi_g)^2}, \quad (45)$$

where d_p is the particle diameter. Equation 45 is based on packed spheres. Although the functional forms remain similar, the permeability relationship can vary depending on the material. Porosity is relatively easy to measure and effective particle diameters and pore radii can be reasonably estimated from microscopic images of the membrane. Permeability is also relatively easy to measure. However, transport depends strongly on tortuosity, which is difficult to measure. Thus, tortuosity is often used as an empirical parameter that is adjusted to fit flux measurements. Details about the DGM and the computational implementation have been reported by Zhu et al. [287].

High temperature and humid oxidizing environments can limit the choice of materials that are suitable for OCM membranes. Pore-modified alumina is often used for OCM processes [98, 291, 292]. Readily available porous alumina can have a pore structure that is too open and permits oxygen fluxes that are too high. Silica (SiO₂) or silicon oxy-carbide (SiOC) can be deposited within the pores, restricting the flux [291, 292, 285].

Zeolites are used for separations, and in principle could be used as hydrogen-selective membranes [293–296]. However, the selectivity is not high. Zeolite pore diameters are generally in the range of 0.3–1.3 nm. However, the effective diameters of light gases and H₂ are similar, with the effective diameter of H₂ being 0.289 nm. The effective diameters of CO₂, CO, and CH₄ are 0.33 nm, 0.376 nm, 0.38 nm, respectively. Thus to achieve good selectivity the zeolite cage size would need to be very closely controlled. Recent advances in zeolite technology have enabled the modification of cage sizes without changing the framework and cage structure [297, 294, 298, 295]. Zeolites membranes have been investigated for applications in water-gas-shift processes [299] and hydrocarbon dehydrogenation processes below 550 °C (e.g., isobutane, cyclohexane) [300, 301]. To date, zeolite membranes have apparently not been used in MDA processes. Nevertheless, with continued development of zeolite materials, new zeolites may offer opportunities for small-channel zeolites as alternatives to dense ion-transport membranes.

6.3. Oxide-ion conducting membranes

Materials such as yttria-stabilized zirconia conduct oxide ions O²⁻ via a hopping mechanism within the doped crystal structure. The heterovalent doping creates lattice vacancies, which enable oxide-ion mobility. The ionic conductivity is typically represented as

$$\sigma = \sigma^\circ \frac{1}{T} \exp\left(-\frac{E_a}{RT}\right). \quad (46)$$

For YSZ, $\sigma_0 \approx 3.6 \times 10^5$ S-K/cm and $E_a \approx 8 \times 10^4$ J mol⁻¹ [302]. The oxide-ion flux is dominated by migration (i.e., driven by electrostatic-potential gradients) as

$$J_{O^{2-}} = -\frac{\sigma}{z_k F} \nabla \Phi, \quad (47)$$

where $z_k = -2$ is the charge on O^{2-} , F is the Faraday constant, and Φ is the electrostatic potential. The gas-phase molecular oxygen must react at one membrane surface to incorporate the ion into the membrane lattice and release the $O_2(g)$ back to the gas phase on the opposite side of the membrane. The incorporation process can be represented globally as

where $e^-(ed)$ represents electrons within the electrode and $O^{2-}(el)$ represents the ion within the electrolyte membrane. Thus, a so-called triple-phase boundary is needed where gas, electrode, and electrolyte are coincident. The oxide-ion transport depends on the establishment of an electrostatic potential, and thus an external circuit to provide electrons. There is very little transport associated with oxygen partial-pressure variations across the membrane alone.

6.4. Mixed ionic-electronic conductors, MIEC

Mixed-conducting materials such as $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ (BZY10) or $La_{1-x}Ca_xFeO_{3-\delta}$ (LCF) behave differently from materials such as YSZ. Depending on the particular material, the membrane may perform dominantly as a proton conductor or as an oxygen-ion conductor. Also, depending on the material, any electronic conduction may be dominantly “n-type” (i.e., electrons) or “p-type” (i.e., electron holes).

When the gas-phase composition varies across the membrane, the electrochemical-potential gradient serves to drive charged defects through the membrane. The result is apparent gas transport through the membrane. At each gas-membrane interface gases must react to form the defects that can be transported through the membrane. Depending on the material and the operating conditions, these defect-incorporation reactions may be equilibrated or they may be kinetically limited. The defect fluxes within the membrane depend on concentration and electrostatic-potential gradients. Mathematically, the defect fluxes are governed by Nernst–Planck–Poisson theory [303–306].

Assuming dilute behavior (i.e., minimal defect-defect interactions), the charged-defect fluxes through MIEC

doped-perovskite materials are governed by the Nernst–Planck relationship as

$$\mathbf{J}_k = -D_k \left(\nabla[X_k] + \frac{z_k F}{RT} [X_k] \nabla \Phi \right), \quad (49)$$

where D_k are defect diffusion coefficients. Defect transport is generally understood to occur via an activated hopping mechanism. The defect diffusion coefficients are typically represented in Arrhenius form as

$$D_k = D_k^0 \exp\left(-\frac{E_k}{RT}\right), \quad (50)$$

where D_k^0 are pre-exponential constants and E_k are activation energies. The Nernst–Einstein equation relates the total conductivity σ to the charged-defect diffusion coefficients as

$$\sigma = \sum_k \frac{z_k^2 F^2}{RT} [X_k] D_k. \quad (51)$$

The MIEC materials typically have several charge-carrying defects. For example, in Kröger–Vink notation, the three mobile defects in BZY are oxygen vacancies $V_O^{\bullet\bullet}$, protons $OH_O^\bullet$, and small polarons $O_O^\bullet$ [19]. The superscripts designate the electronic charge associated with the defects. The “ $\bullet$ ” indicates a positive charge and the “ $\prime$ ” indicates a negative charge.

6.4.1. Protonic ceramic membranes

Consider $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ (BZY10) as a representative proton-conducting ceramic membrane. Incorporation chemistry can be represented with three reactions as

The nomenclature $O_O^\times$ indicates a charge-neutral oxygen at the oxygen lattice site. In a departure with earlier studies [305, 307], Zhu et al. [19] represent the electronic charge carrier as a small polaron $O_O^\bullet$ associated with the oxygen site, rather than an electron hole $h^\bullet$.

The gas-surface chemistry may be equilibrated or may be kinetically rate-limited [306]. In either case, the Nernst–Planck model needs equilibrium constants to establish boundary conditions and in rate-limited circumstances to maintain microscopic reversibility. The equilibrium constants can be evaluated in terms of the reaction thermodynamics (i.e., Gibbs free energy changes).

Figure 19: Composite representation of model-based predictions with the tube side gas being dominantly H₂, but with varying H₂O levels. The shell-side molar composition is fixed at 10% O₂, 10⁻⁶ H₂O, and 90% Ar. The left-hand panel shows defect fluxes and gas-phase fluxes evaluated at the inner radius of the membrane (i.e., the tube side). A positive flux means radially outward. The center panel shows radial profiles of the defect concentrations and the electrostatic potential. The right-hand panel shows defect fluxes and gas-phase fluxes evaluated at the outer radius of the membrane (i.e., the shell side). The colors indicate the shell-side O₂ composition. The solid lines represent vacancy concentration, the short dashed lines represent hole concentration, and the long dashed lines represent proton concentration (the proton profiles for the 10% and 20% O₂ cases are overlapping). Additional solid lines, plotted with respect to the secondary y-axis, represent the electrostatic potential profile across the membrane. This figure is reproduced from Kee, et al. [305].

Although sometimes difficult to obtain, thermodynamic properties can be established experimentally [19].

The Nernst–Planck fluxes must be constrained by site balances and charge neutrality, with details depending on the particular membrane material. For BZY10, the number of oxygen sites in a perovskite lattice (per formula unit) must be maintained as 3. Thus,

$$[V_{\text{O}}^{\bullet\bullet}]_{\text{L}} + [\text{OH}_{\text{O}}^{\bullet}]_{\text{L}} + [\text{O}_{\text{O}}^{\bullet}]_{\text{L}} + [\text{O}_{\text{O}}^{\times}]_{\text{L}} = 3. \quad (55)$$

Charge neutrality requires that

$$2[V_{\text{O}}^{\bullet\bullet}]_{\text{L}} + [\text{OH}_{\text{O}}^{\bullet}]_{\text{L}} + [\text{O}_{\text{O}}^{\bullet}]_{\text{L}} - [Y'_{\text{Zr}}]_{\text{L}} = 0. \quad (56)$$

Considering BZY10 (BaZr_{0.9}Y_{0.1}O_{3-δ}), the yttrium doping concentration is 10%, in which case $[Y'_{\text{Zr}}]_{\text{L}} = 0.1$.

An interesting aspect of mixed-conducting membranes is so-called “uphill diffusion” [308–310]. That is to say, the apparent transport of some gas-phase species may be proportional to the partial pressure gradient across the membrane (i.e., not proportional to the usual negative partial-pressure gradient as in Fick’s law). For example, the apparent flux of water vapor may be in the direction from low partial pressure on one side of

the membrane to high partial pressure on the other side. However, all the charged-defect transport must be proportional to the negative gradient in electrochemical potential,

$$\mathbf{J}_{\mathbf{k}} = -\frac{D_{\mathbf{k}}}{RT} [X_{\mathbf{k}}] \nabla \tilde{\mu}_{\mathbf{k}}. \quad (57)$$

The defect electrochemical potentials may be expressed as

$$\tilde{\mu}_{\mathbf{k}} = \mu_{\mathbf{k}}^{\circ} + RT \ln[X_{\mathbf{k}}] + z_{\mathbf{k}} F \Phi, \quad (58)$$

where $\mu_{\mathbf{k}}^{\circ}$ are the standard-state chemical potentials. The Nernst–Planck flux (Eq. 49) follows directly from these relationships [305]. Because of the role played by the internal electrostatic-potential gradient, the apparent gas-phase transport can sometimes appear to be going in a direction opposite from what would be expected by Fickian diffusion.

To illustrate aspects of proton-conducting membrane behavior, Fig. 19 shows a representative model-predicted result [305]. In this case a tubular 20 μm thick membrane is positioned on a 10 mm diameter support. The inside of the tube is dominantly H₂, but with varying low levels of H₂O. The outside of the tube has a gas atmosphere of 90% Ar and 10% O₂ and trace steam.

Figure 20: Predicted defect concentrations (formula units) for $\text{La}_{1-x}\text{Sr}_x\text{Ca}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ at 850 °C.

Figure 21: Measured O_2 flux through an $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-\delta}$ membrane that is 0.95 mm thick. The figure is reproduced from Hunt, et al. [316].

The right- and left-hand panels show defect fluxes and effective gas-phase fluxes at the membrane surfaces. The effective gas-phase fluxes are in the range of $10^{-3} \text{ mol s}^{-1} \text{ m}^{-2}$. Under the operating conditions shown, gas-phase H_2 leave the central tube but, because of reaction with oxygen, emerges from the membrane exterior as H_2O . The central panel illustrates defect profiles as well as electrostatic potential profiles. Note that internal electrostatic potential variations on the order of 100 mV are needed to preserve charge neutrality. Of course, details of the defect transport and apparent gas-phase fluxes depend on operating conditions. Sanders, et al. [310] developed maps that explore large ranges of operating space.

6.4.2. Oxygen-ion transport membranes

Consider the behavior of $\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$ (LCF) as an MIEC oxide-ion conducting membrane. This material is important for application in hydrocarbon membrane reactors because, unlike many other MIEC oxide-ion conductors, it is stable in both oxidizing and reducing environments [311–316].

Because LCF does not have the ability to incorporate protons, the incorporation chemistry is different from materials such as BZY10. As reported by Geary and Adler [317], the incorporation and disproportionation chemistry can be represented in Kröger-Vink notation as

The B-site Fe in this material can be simultaneously present in three oxidation states, Fe^{2+} , Fe^{3+} , and Fe^{4+} . Thus, at the surface and within the bulk, Eq. 60 represents the interactions between three Fe oxidation states. Geary and Adler [317] reported thermodynamic proper-

ties from which the equilibrium constants can be evaluated.

As is the case with the BZY10, the equilibrium composition must be constrained by site and charge balances. For the LCF materials, the charge balance (electroneutrality) requires that

$$[\text{Ca}_{\text{La}}']_{\text{L}} + [\text{Fe}_{\text{Fe}}']_{\text{L}} = [\text{Fe}_{\text{Fe}}^{\bullet}]_{\text{L}} + 2[\text{V}_{\text{O}}^{\bullet\bullet}]_{\text{L}} \quad (61)$$

The iron site balance requires that

$$[\text{Fe}_{\text{Fe}}^{\bullet}]_{\text{L}} + [\text{Fe}_{\text{Fe}}^{\times}]_{\text{L}} + [\text{Fe}_{\text{Fe}}']_{\text{L}} = 1 \quad (62)$$

The oxygen site balance requires that

$$[\text{O}_{\text{O}}^{\times}]_{\text{L}} = 3 - [\text{V}_{\text{O}}^{\bullet\bullet}]_{\text{L}} \quad (63)$$

For $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-\delta}$, it may be assumed that $[\text{Ca}_{\text{La}}']$ is fixed by the doping level as

$$[\text{Ca}_{\text{La}}']_{\text{L}} = 0.1 \quad (64)$$

Also, the “non-stoichiometry” is assumed to be $\delta = [\text{V}_{\text{O}}^{\bullet\bullet}]_{\text{L}}$.

Using the thermodynamics reported by Geary and Adler [317], Fig. 20 shows the defect concentrations (formula units) as functions of oxygen partial pressure and at 850 °C. At very low p_{O_2} , the vacancies (i.e., δ) approach the Ca doping concentration. Also at very low p_{O_2} the $[\text{Fe}_{\text{Fe}}^{\bullet}]$ concentration becomes negligible small, but the $[\text{Fe}_{\text{Fe}}']_{\text{L}}$ concentration approaches that of the vacancies. At high p_{O_2} the $[\text{Fe}_{\text{Fe}}^{\bullet}]_{\text{L}}$ concentration is the dominant charge-carrying defect. The reduced $[\text{Fe}_{\text{Fe}}']_{\text{L}}$ and oxidized $[\text{Fe}_{\text{Fe}}^{\bullet}]_{\text{L}}$ defects behave as small polarons.

Figure 21 shows measured oxygen fluxes through a 0.95-mm thick $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-\delta}$ membrane as a function of temperature. These fluxes were measured in a stagnation-flow reactor configuration [316]. The paper also reports a range of other measurements, considering membrane thickness and sweep-gas flow rates.

Table 2: Representative membrane materials

Material	Mobile Species/defects	Electronic conduction	Effective gas	Flux law
Lanthanum ferrite $\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$, LCF	$\text{V}_{\text{O}}^{\bullet\bullet}, \text{Fe}_{\text{Fe}}^{\bullet}, \text{Fe}_{\text{Fe}}'$	Yes	O_2	Nernst–Planck
Doped barium zirconate $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$, BZY10	$\text{V}_{\text{O}}^{\bullet\bullet}, \text{OH}_{\text{O}}^{\bullet}, \text{O}_{\text{O}}^{\bullet}$	Low	$\text{H}_2, \text{O}_2, \text{H}_2\text{O}$	Nernst–Planck
Doped ceria $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$, GDC10, LCF	$\text{V}_{\text{O}}^{\bullet\bullet}, \text{Ce}_{\text{Ce}}'$	Low	O_2	Nernst–Planck
Yttria-stabilized zirconia $(\text{Y}_2\text{O}_3)_{0.08}(\text{ZrO}_2)_{0.92}$, YSZ	O^{2-}	No	O_2	Migration
Meso-porous alumina Al_2O_3	Gases	No	All	Dusty gas
Palladium and alloys Pd and Pd alloys	H	Yes	H_2	Sieverts law

6.4.3. Ion-transport membrane conductivity

The electrical conductivity is an important measure of charged-defect mobility within ion transport membranes. Although ITMs are generally all polycrystalline oxides, their properties vary greatly. Kreuer's 2003 review of proton-conducting ceramics showed that conductivity varies by orders of magnitude as functions of material composition and temperature, with doped barium cerates and barium zirconates having the highest conductivities [318].

Figure 22 illustrates measured conductivities for two perovskite materials that are relevant for membrane reactors [19, 319]. The BZY10 is primarily a proton conductor that is suitable for MDA processes. The $(\text{La}_{0.8}\text{Ca}_{0.2})_{0.95}\text{FeO}_{3-\delta}$ (LCF) is primarily an oxide-ion conductor that is suitable for OCM processes. There is a great difference in functional behaviors between these two materials. The BZY10 conductivity is approximately four orders of magnitude smaller than that of the LCF. The BZY10 conductivity is a strong function of oxygen partial pressure in the oxidizing environments, but nearly constant in reducing environments. The LCF conductivity shows relatively weak pressure and temperature dependence. The high conductivity of the LCF is primarily the result of high electronic conductivity relative to the oxide-ion conductivity. By contrast, the BZY10 has low electronic conductivity, with the total conductivity being dominated by the partial conductivities of protons and oxide ions.

The electronic conductivity has important implications in membrane technology. Because materials such as YSZ or BZY have low electronic conductivity, they can be polarized to establish an electrostatic-potential field within the membrane. The field then can be used to promote ion transport (cf., Eq. 49).

Figure 22: Measured total conductivities for a proton-conducting BZY10 and an oxide-ion conducting LCF. The BZY10 conductivities were reported by Zhu et al. [19] and the LCF conductivities were reported by Yoon et al. [319].

6.4.4. Nernst–Planck–Poisson model

The spatial and temporal variations in defect concentrations are governed by conservation equations as

$$\frac{\partial [X_k]}{\partial t} + \nabla \cdot \mathbf{J}_k = 0, \quad (65)$$

where $[X_k]$ are defect concentrations and $\mathbf{J}_k$ are the Nernst–Planck defect fluxes (Eq. 49). The electrostatic-potential profiles Φ are determined by solving the Gauss

equation,

$$\nabla \cdot (\epsilon_r \epsilon_0 \nabla \Phi) = -\rho_e = -F \sum_{k=1}^K z_k [X_k]. \quad (66)$$

The relative and vacuum permittivities are represented as ϵ_r and ϵ_0 , respectively. The local charge density is represented as ρ_e .

Imposing strict charge neutrality is a widely practiced alternative to solving the Gauss equation. Although slightly less accurate, imposing charge neutrality is usually easier to implement computationally. Charge neutrality means that $\rho_e = 0$. However, interestingly, it *does not follow* that

$$\nabla \cdot (\epsilon_r \epsilon_0 \nabla \Phi) = 0. \quad (67)$$

Based on small-parameter-expansion analysis, Bazant and colleagues have shown that second-order (i.e., very small) variations in the charge density cause leading-order (i.e., large) variations in the electrostatic potential [320, 321].

Equations 65 and 66 form a coupled system of non-linear partial differential equations that can be solved computationally. The solution depends on initial and boundary conditions. The boundary conditions depend upon the defect-incorporation chemistry at the gas-membrane interfaces, which establish the boundary defect concentrations. The boundary conditions for the electrostatic potentials depend on circumstances such as if the membrane is polarized by an external circuit. The governing equations and boundary conditions are further constrained by imposition of site balances and electroneutrality, the details depending on the particular materials.

Details of the Nernst–Planck–Poisson (NPP) model and the computational solution can be found elsewhere [19, 304–307, 320–324].

6.5. Ion-catalyst interactions

If a catalyst is placed directly onto an ion-conducting membrane, then there is the possibility that the catalytic chemistry may be influenced by electrochemistry. In a great many papers, Vayenas and colleagues, as well as others, developed theory and discussed processes that are labeled as “non-faradaic electrochemical modification of catalytic activity” (NEMCA) or “electrochemical promotion of catalysis” (EPOC) [325–330]. Early research by Gür and Huggins considered NO decomposition in a solid-state electrochemical cell [331]. Electrochemical promotion is based on the idea that ionic species emerging from a mixed-conducting electrolyte membrane are catalytically more reactive than

the equivalent charge-neutral species in the gas phase. Thus, in addition to effective and selective gas transport to and from the catalysts, ion-conducting membranes may offer additional benefits in enhancing the catalytic behavior.

A comprehensive review paper in 2000 by Stoukides [332] discussed NEMCA effects for a wide range of processes, including methane CPOX, OCM, CO and H₂ oxidation, NO_x decomposition, alkane and alkene oxidation, oxidation and decomposition of sulfur oxides, methanol oxidation, oxidation and dehydrogenation of aromatics, oxidation, decomposition and synthesis of ammonia. An earlier review by Eng and Stoukides [333] considered NEMCA effects for methane partial oxidation to CO and H₂, discussing interactions with solid-oxide fuel cells. This paper also discussed NEMCA effects for OCM processes. A later review by Vayenas et al. [334] discussed the concepts of electrocatalysis, electrochemical promotion, and metal-support interactions for methanol and ethylene oxidation processes.

6.6. Membrane summary characteristics

Table 2 summarizes some of the salient characteristics of alternative membranes, especially as they may affect membrane-reactor applications.

Despite their potential benefits, all the membrane approaches must deal with some practical difficulties. For example, at high operating temperatures sealing can be very challenging. Especially in the cases of ceramic membranes, a ceramic-metal seal is usually needed. A range of glass based seals have been developed and used in fuel-cell applications, but long-term leak-free reliability remains elusive. In the case of thin-film membranes (e.g., palladium or ion-conducting ceramics) the fabrication of large-area defect-free materials is difficult. Even small pinholes or micro-cracks can significantly degrade membrane performance. Beyond the initial defect-free fabrication, the thin membranes (typically on the order of tens of microns) must remain mechanically, chemically, and thermally stable on their underlying support structures.

7. Membrane reactor technology

As noted in the foregoing discussion, membranes can potentially play important roles in the spatially distributed introduction of oxygen or the removal of hydrogen to improve the process performance [335]. However, the close integration of membranes and catalysts

Figure 23: Illustration of an annular packed-bed reactor with a polarized ion-conducting membrane.

in different reactor configurations remains an active research topic. This is especially the case for mixed-conducting and ion-transport membranes. In addition to simply shifting reaction equilibrium, membranes that can achieve spatially varying fluxes can beneficially affect the interactions between chemistry and transport within a catalyst bed.

Membrane reactors for direct methane conversion processes are typically implemented in a co-annular configuration with packed-bed catalysts. As illustrated in Figs. 1 or 23, the catalyst bed is in the annular space and the sweep gas flows through an inner tube. The tube is usually fabricated as a porous support with a thin membrane applied to the outside of the tube. However, reactors can also be configured with the catalyst bed being housed within the interior tube and the sweep gas flowing through the annular region.

Figure 23 illustrates a co-annular membrane reactor in which the membrane may be electrically polarized. In this case, electrodes must be attached to both

Figure 24: Button-cell, stagnation-flow, reactor design with membrane-coupled OCM process [336].

sides of the membrane. Assuming that the membrane is dominantly an ion conductor with minimal electronic conductivity (e.g., BZY10), an external power source can be used to impose an electrostatic-potential gradient within the membrane [324]. As is evident from the form of the Nernst–Planck flux (Eq. 49), the ion fluxes can be increased by increasing the electrostatic-potential gradient $\nabla\Phi$.

Although the mixed-conducting ceramics are ionic conductors, the ion conductivities are usually low, which is manifested as a high ionic resistance. Thus, polarization can be a significant operational cost (i.e., buying electricity) associated with using the external power source to drive ions through the membrane. Moreover, because electrode design and attachment can be difficult and complex, there can be significant capital cost. Nevertheless, depending on the process, improvements in flux rates and process control may offset the cost and complexity.

If electrodes (such as in Fig. 23) are configured with segmented electrical connections, then it may be possible to control the axial profiles of ion fluxes through the membrane. The opportunity to control fluxes by electrical polarization is only possible with ion-conducting membranes. Metal membranes such as palladium, which are electrical conductors, cannot be polarized. Similarly, membranes fabricated from insulating materials, such as ceramic nano-filtration membranes, offer no benefits from polarization.

As illustrated with the expanded balloon in Fig. 23, it is possible with mixed ionic-electronic ceramic (MIEC) membranes, to have protons being transported in one direction and oxide ions being transported in the other direction [310]. Thus, for membrane-assisted MDA processes it is possible to have the benefits of hydrogen flux from the catalyst bed and steam flux into the catalyst bed. Polarized membranes can be helpful in realizing this circumstance.

Membrane reactors typically incorporate the catalysts as packed-beds. However, the catalyst could also be washcoated onto a membrane or the support structure. Such washcoated catalysts can be found in laboratory-scale experiments [337, 338, 284]. Washcoated monoliths are common in many industrial processes and in applications such as automotive catalytic converters.

At the laboratory scale, membrane reactors can also be configured in a stagnation-flow configuration [336, 339, 312, 313]. In these configurations, such as shown in Fig. 24, the membrane takes the form of a disk. The catalyst may be either washcoated on the membrane or packed with the catalyst particles above the membrane. Such reactors can also be polarized. In this case, the experimental setup is very much the same as is common for so-called button-cell fuel-cell experiments. Figure 24 shows an oxygen-transport membrane as might be used in converting methane to ethylene via a membrane-assisted OCM process. Although stagnation-flow reactors are especially valuable in studying reaction chemistry and membrane properties, upscaling to commercially viable reactors is usually impractical.

8. Hydrogen-membrane assisted processes

Although hydrogen-permeable membranes can play significant beneficial roles in dehydrogenation processes, there are potentially deleterious competing effects. For example, as H_2 is removed from hydrocarbon streams, there is significant propensity for catalyst-deactivating carbon deposits. Additionally, even though conversion of the parent fuel (e.g., CH_4) may increase, the product selectivity may shift toward less desired products. In MDA, as H_2 is removed, the product selectivity shifts toward naphthalene (and higher PAH) and away from the desired benzene. Thus, simply increasing H_2 flux through the membrane is not always desirable. Because they can also transport oxygen defects, membranes such as the perovskite protonic ceramics may offer advantages compared to membranes that are purely hydrogen selective (e.g., palladium).

In principle, hydrogen membranes can be used to assist direct conversion of methane to ethylene under non-oxidizing environments (i.e., Eq. 2). However, although conversion may increase, removing the excess H_2 can cause severe catalyst deactivation. The high temperatures needed for the direct conversion to ethylene promote more carbon deposits than is the case for MDA process that operate at relatively lower temperature (cf., Fig 3). Hence, the use of hydrogen membranes in non-oxidizing environments is usually impractical.

8.1. Pd-based H_2 membranes

Larachi and co-workers studied membrane-coupled MDA processes using Pd-alloy membranes with porous stainless-steel supports [255–257]. These studies used packed-bed catalysts in a shell-and-tube configuration at temperatures between 500–700 °C. The HZSM-5 catalysts used 3 wt.% Mo and 0.5 wt.% Ru. Although H_2 removal via the membrane nearly doubled the C_6H_6 yield, the carbon deposits caused severe catalyst deactivation [255]. In a subsequent publication, this group showed that the carbon deposits are in the form of both graphitic carbon and polyaromatic hydrocarbons. The catalyst could be regenerated by flowing hydrogen. However, although the short-term C_6 yield could be increased using the membrane, the productive time-on-stream decreased [256].

Wang et al. [340] used a Pd-Ag membrane coupled with an MDA packed-bed reactor with a Re/HZSM-5 catalyst. The temperature and gas-hourly space velocities were relatively low ($T = 585$ °C, $120 \leq GHSV \leq 1440$). Although the membrane increased methane conversion by as much as to 50%, the maximum methane conversion was still low at less than 7.5%.

Kinage et al. [341] coupled a Pd membrane disk in a packed-bed reactor loaded with 3 wt.% Mo/ZSM-5 catalyst operated at 610 °C. The results showed that the hydrogen-permeable membrane increased methane conversion as well as the aromatic (benzene, toluene, and naphthalene) yield. However, they also reported that carbon deposits on the Pd membrane significantly decreased the hydrogen flux through the membrane.

A study by Natesakhawat et al. [258] reported the results of membrane-coupled MDA reaction in an annular packed-bed reactor with a 4 wt.% Mo/HZSM-5 catalyst. Using a 125 μm thick Pd membrane and operating at 700 °C, they reported severe catalyst deactivation rates with or without the membrane. The coke also deposited on the Pd membrane, significantly decreasing the hydrogen transport rate. At the reaction conditions studied, the membrane lost 75% of the initial H_2 permeability. Nevertheless, the results showed that the membrane

could increase the C_6H_6 yield by up to 360%, but with a very low overall yield below 2%. They reported that the membrane efficiency was strongly effected by gas-hourly space velocities within the catalyst bed.

8.2. Protonic-ceramic membranes

Beginning in 1998, Iglesia and co-workers studied membrane coupled MDA proceses [342, 216, 18, 254]. Liu et al. [254] coupled a dense thin-film $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ proton-conducting membrane with a Mo/H-ZSM-5 catalyst in a packed-bed reactor. The study showed that at temperatures below 677 °C the hydrogen membrane removed less than 7% of the catalytically produced H_2 , but did significantly increase the CH_4 conversion. As the temperature increased to 720 °C, the hydrogen removal increased to approximately 16%. At the higher temperature the methane conversion rate increased modestly, but also increased the yield of undesired C_{12+} hydrocarbons. The catalyst deactivation rate also increased at higher temperatures. Co-feeding 2% CO_2 enhanced the catalytic stability and beneficially reduced the C_{12+} formation rate.

The Iglesia group developed a membrane-coupled packed-bed model to predict reactor performance, including the effect of hydrogen removal on methane conversion as well as benzene and naphthalene selectivity [216, 18]. The model showed that methane conversion can be increased as the hydrogen permeation fraction increases. However, the effect on product distribution is non-linear. In an MDA system, the production of undesired naphthalene competes with desired benzene yield. Thermodynamic considerations show that removing hydrogen shifts the product selectivity toward naphthalene. However, kinetics and transport considerations show that there are useful tradeoffs between the hydrogen removal rate (i.e., membrane flux), residence time in the catalyst bed, and the benzene yield. At long residence times the MDA process is kinetically controlled, favoring naphthalene formation. In the kinetically limited regime, the hydrogen removal rate should be low. As the residence time decreases the process is increasingly mass-transport controlled, allowing more hydrogen permeation and favoring selectivity toward benzene [18].

In addition to MDA processes, hydrogen membranes can play roles in non-oxidative conversion of methane to ethylene. Woldman and Sokolovskii [343] developed an electrochemical button cell using a proton-conducting electrolyte membrane made of $SrO(CeO_2)_{0.95}(YbO_{1.5})_{0.05}$ (SCY). The electrolyte membrane could be polarized using an external power supply. Methane was supplied to the anode side

and nitrogen on the cathode side of the membrane. Even without polarization, and operating at 800 °C, the cell produced ethane and ethylene. Upon polarization the C_2 yield increased greatly. Apparently the SCY electrolyte membrane also acted as the catalyst. When steam was mixed with the methane feed, the C_2 yield increased. No evidence of carbon deposits was reported. However, in all cases the C_2 yields were impractically low at less than 0.01%.

Langguth et al. [344] also studied the use of $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ (SCYO) as a high-temperature proton-conducting membrane in an electrochemical button cell. Methane (and moist methane) was supplied on the anode side with air supplied on the cathode side. The system did produce ethane and ethylene, but also produced CO and CO_2 . The SCYO membrane is a mixed conductor. Thus, hydrogen can be removed from methane side, but oxygen also enters the methane side. Water vapor was found to decrease the C_2 yield because of competitive reforming chemistry.

Liu et al. [27] incorporated a $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ (SCYb) mixed-conducting perovskite into a hollow-fiber membrane reactor. Methane was introduced into the central tube of a co-annular reactor, with air flowing in the outer annular space. No other catalysts were used. The methane conversion was attributed to electrochemical reactions at the membrane surfaces. In addition to the experiments, the paper also reported a model that represented the proton and electron hole transport within the membrane and the electrochemical methane conversion chemistry at the membrane surfaces. The results showed that the membrane increased the methane conversion as well as the C_2H_4/C_2H_6 ratio in the product stream.

With or without membranes, MDA processes are not yet commercially viable. Nevertheless, there appears to be some industrial interest. BASF recently patented an MDA application using a ceramic-protonic conducting membrane [345]. The membrane hydrogen flux could be driven entirely by H_2 partial-pressure differences across the membrane or the flux could be increased by electrically polarizing the membrane. By introducing oxygen in the sweep gas, H_2 entering the sweep stream is rapidly converted to H_2O , thus decreasing the H_2 partial pressure in the sweep and maintaining a large H_2 gradient across the membrane. Ceramatec, Inc. recently submitted a patent application describing a protonic-ceramic membrane coupled with an MDA reactor [346]. This application used a Re/ZSM-5 catalyst and operated in the temperature range $700 \leq T \leq 900$ °C [347].

9. Oxygen-membrane assisted processes

Oxygen-permeable membranes are most relevant for OCM processes. As expressed globally by Eq. 3, OCM processes are intended to produce ethylene from methane. Membrane assisted OCM reactors can potentially improve thermal management and product selectivity. When oxygen is premixed into the methane feed stream, controlling local temperature excursions associated with the exothermic oxidation chemistry can be difficult. Thus, because the chemistry is highly temperature-sensitive, controlling the product selectivity and unwanted production of total-oxidation products CO_2 and H_2O can be challenging.

By spatially distributing the introduction of the limiting reactant O_2 via a membrane, the process temperature, and hence the product selectivity, can be controlled. In 1985 Otsuka et al. first introduced the idea of using oxygen-permeable membranes to improve OCM processes [348]. In these studies the catalysts were Ag and $\text{Ag-Bi}_2\text{O}_3$. The O_2 was electrochemically pumped through a dense ceramic yttria-stabilized zirconia membrane at 700 °C. The membrane reactor was configured in a co-annular arrangement where the membrane was supported on the tube side (similar to the configuration shown in Fig. 23). They demonstrated that membrane-coupled packed-bed reactor increased the C_2 yield and the selectivity compared to a typical packed-bed reactor with premixed O_2 (e.g., Fig. 12).

In a typical co-annular OCM packed-bed reactor, the pressure drop along the length of the catalyst bed can be significant. Thus, the local pressure drop across membrane can vary, leading to local variations in the oxygen flux into the catalyst bed. Locally high oxygen concentrations can lead to deleterious local hot spots and full oxidation.

9.1. Ion-transport membranes for OCM

Oxygen-permeable ITM membranes are usually doped-perovskite polycrystalline ceramics, such as $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ (LSCF) or $\text{La}_x\text{Ca}_{1-x}\text{FeO}_{3-\delta}$ (LCF). The oxide-ion conductivity of these materials is highly activated, with practical oxygen fluxes requiring temperatures of 700 °C and higher. An additional, and possibly valuable, attribute of the oxygen-transport membranes is that they can serve a dual purpose of in-situ air separation as well as controlled oxygen dosing into the reactor. However, material stability in reducing environments is a practical limitation for many oxide-ion conducting membranes. The $\text{La}_x\text{Ca}_{1-x}\text{FeO}_{3-\delta}$ perovskites are stable in both oxidiz-

ing and reducing environments and have good oxide-ion conductivity [311, 312, 314, 317, 313, 315].

To achieve needed fluxes, ceramic ITM membranes usually need to be very thin, often in the range a few tens of micrometers. Thus, they needed to be supported on some sort of much thicker porous ceramic structure, such as a porous tube. The mechanical strength and structural stability of such thin oxygen-permeable ITM membranes can be problematic.

Thin hollow-fiber membranes provide a structure with good mechanical stability [349–353, 337]. The hollow-fiber structures are fabricated using an immersion induced phase inversion technique [350]. As shown in Fig. 25, tapered radial microchannels are open to the tube's inner surface [337].

Othman et al. [337] developed a Catalytic Hollow Fiber Membrane MicroReactor (CHFMMR) for OCM applications. The hollow-fiber tube is fabricated from $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ (LSCF), which is an oxide-ion conducting perovskite. The outer surface of the tube forms a thin dense LSCF membrane. A thin layer of the OCM catalyst composed of $\text{Bi}_{1.5}\text{Y}_{0.3}\text{Sm}_{0.2}\text{O}_{3-\delta}$ (BYS) is washcoated onto the interior radial microchannels. The reactor is fabricated in a co-annular configuration, where air flows in the outer annulus and methane is introduced into the tube interior. The LSCF membrane separates air and delivers oxygen to high-surface-area BYC catalyst. The design also provides good heat and mass transfer between the gas and solid phases. The CHFMMR reactor delivers good performance, reported as 39% C_{2+} yield and 79% C_{2+} selectivity at 900 °C.

Zhu et al. [354] developed a mixed-conducting multichannel hollow fiber membrane (MCMHF) using $\text{SrFe}_{0.8}\text{Nb}_{0.2}\text{O}_{3-\delta}$ (SFN). The “multi-channel” nomenclature means that there are four axial interior channels within each rod of the SFN. This structure enables high oxygen fluxes ($0.38 \text{ ml cm}^{-2} \text{ min}^{-1} \text{ cm}^{-2}$ at 800 °C) in CO_2 -rich environments, and exhibits good thermal and mechanical stability. The intended application was for oxyfuel combustion, not membrane reactors. Nevertheless, such an approach may be useful for OCM processes.

Bhatia et al. [284] measured the performance of two different membrane-assisted OCM reactor configurations. The reactors were all implemented in a co-annular configuration. The so-called catalytic membrane reactor (CMR) used a mixed-conducting perovskite membrane ($\text{Ba}_{0.5}\text{Ce}_{0.4}\text{Gd}_{0.1}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, BCGCF) supported on a porous ceramic tube. The Na-W-Mn/ SiO_2 catalyst was coated on the inner surface of the membrane tube. The so-called packed-bed membrane reactor (PBMR) used a packed-bed catalyst instead of the thin catalyst

Figure 25: Two microscopic images of the CHFMMR hollow-fiber tube, prior to catalyst introduction [337]. a) Tube cross-section, b) Tube inner surface.

coating that was used in the CMR approach. Compared to the PBMR, the CMR approach achieved significantly better methane conversion, C_{2+} selectivity, and C_{2+} yield. The study suggested that reducing pressure drop through the catalyst bed could improve performance of the PBMR. In both cases, with the membrane delivering distributed oxygen flux to the catalyst, the membrane-assisted processes have the potential to deliver better results than can be achieved with a typical packed-bed reactor.

9.2. Porous membranes for OCM

Micro- and nano-porous membranes have the potential advantage of producing higher oxygen fluxes than dense ion-transport membranes. Moreover, fluxes through porous membranes are less temperature-dependent than are the fluxes through ITMs. However, the selectivity for oxygen flux is lower than it is for dense ion transport membranes. The oxygen fluxes are proportional to the oxygen partial-pressure differences

across the membrane. Because of its chemical and thermal stability, porous alumina is often a material of choice. The pore microstructure can be modified to achieve desired oxygen fluxes.

Lafarga et al. [291] used a porous Al_2O_3 membrane for distributing the oxygen into an OCM process. The reactor was a co-annular configuration, with the oxygen flowing in the annular space and a packed-bed catalyst within the central tube. Experiments were conducted at $800^\circ C$ and the oxygen pressure in the annular space was 6 bar. The high pressure was used to impede back diffusion of hydrocarbons onto the annular oxygen flow. The membrane itself was composed of a support structure and a much-less-permeable thin membrane. The support layer was approximately 1.5 mm thick with an average pore size of $10\ \mu m$. The separation layer was approximately $10\ \mu m$ thick with an average pore size of approximately 200 nm. OCM processes need low oxygen fluxes to achieve high performance. To reduce the membrane permeability even further, silica was deposited within the pores. In a related subsequent study, Coronas et al. [292], used the silica-modified porous membrane and reported greater than 40% C_{2+} yield at $750^\circ C$ with a Li/MgO catalyst. No deactivation was reported over 34 h of time on stream. More recently, Godini et al. [285] implemented a silicon-oxycarbide-modified Al_2O_3 porous membrane in an OCM packed-bed reactor and reported high temperature stability up to $1000^\circ C$. Measured results using a Mn- Na_2WO_4 catalyst with varying CH_4/O_2 ratios showed 18.5% C_2 yield and good temperature uniformity.

Based on plug-flow models, Kiatkittipong et al. [283] compared OCM reactors with and without membranes. The membrane-assisted reactors were all co-annular packed-bed configurations. The membrane structures included porous-alumina, oxide-ion-conducting perovskite ($La_{0.4}Sr_{0.6}Ga_{0.4}Fe_{0.6}O_{3-\delta}$), and electrically polarized yttria-stabilized zirconia (YSZ). The study explored pros and cons of the alternative reaction configurations, but did not reach unambiguous conclusions about the best approach.

9.3. Oxygen membranes for MDA

Although most MDA research considers hydrogen-permeable membranes, there is also some interest in oxygen-transport membranes. Caro and co-workers [32] studied the incorporation of a $20\ \mu m$ thick $Ba_{0.5}Sr_{0.5}Ca_{0.8}Fe_{0.2}O_{3-\sigma}$ perovskite as an oxygen-conducting membrane. The process was implemented in a packed-bed reactor at $750^\circ C$ and 1 bar with a 6 wt.% Mo/H-ZSM-5 catalyst. The desired global reac-

tion can be represented as

Compared to premixing O_2 with CH_4 , feeding the oxygen through a membrane increases methane conversion, aromatic selectivity, and catalyst durability [32]. The increased methane conversion can be explained by hydrogen removal via oxidation to produce H_2O at the membrane-catalyst interface. Low concentrations of water play a beneficial role on catalyst stability [192, 193, 173]. However, there is still catalyst deactivation owing to carbon deposits. In the Caro et al. experiments, the methane-to-oxygen ratio in the reaction zone was not fully controlled. Thus any excess oxygen may have caused a Mo_2C to oxycarbide (MoO_xC_y) phase change, which would also contribute to catalyst deactivation.

10. Summary and outlook

The direct conversion of natural gas to fuels and chemicals has the potential to be much more efficient than first reforming to produce intermediate synthesis gas. Assuming a hydrocarbon product is desired, there is an inherent inefficiency associated with first making an oxidation product (i.e., carbon monoxide) and then reducing to produce final product. However, direct routes such as oxidative coupling of methane (OCM) and methane dehydroaromatization (MDA) are far less mature than commercially practiced processes such as reforming followed by Fischer–Tropsch synthesis.

Although far less mature than traditional routes via methane reforming, there is certainly promise for OCM, MDA, and related processes. However, there are significant challenges that must be overcome before laboratory-scale demonstrations can be scaled to commercially viable processes. Broadly speaking, these challenges include finding ways to improve catalyst performance, mitigate of catalyst deactivation, reduce coke and carbon deposits. In addition to designing and developing new catalysts, innovative reactor and process design are surely needed.

Any process that involves the dehydrogenation of methane to produce hydrocarbons faces at least two challenges. One is that hydrogen accumulation tends to limit conversion. Another is that carbon and polyaromatic hydrocarbon deposits are thermodynamically favored over desired gas-phase products such as small olefins (e.g., ethylene) or small aromatics (e.g., benzene). Hydrogen-permeable membranes promote

increased conversion, but tend to exacerbate catalyst-deactivating deposits.

The two most-studied direct methane-conversion processes have two different objectives. The MDA process seeks to produce benzene and the OCM process seeks to produce ethylene. The OCM process is probably closer to commercial practice than is the MDA process. The low oxygen levels in OCM tend to mitigate, but not eliminate, the carbon-deposition problems. Compared to benzene, ethylene is probably a more flexible product in terms of further downstream processing.

It is reasonable to expect that commercially viable implementation of both OCM and MDA will use some sort of membrane. The oxygen-transport membranes are generally more mature, and several alternative membrane technologies are available. The perovskite mixed-conducting protonic ceramics that could be used for MDA offer the interesting possibility of simultaneous hydrogen removal from the catalyst and low levels of steam introduction onto the catalyst bed. Nevertheless, these membranes are less well developed than are the ceramic oxide-ion membranes.

Both the OCM and MDA processes can use a range of catalysts. To date, the most successful OCM catalysts are in the family of Na-W-Mn/ SiO_2 . The most successful MDA catalysts are bifunctional Mo/zeolites. However, there is continuing active research on improving catalyst selectivity and yield for numerous catalysts and catalyst combinations.

Commercially viable direct conversion will likely depend on process intensification. Thus, innovative reactor and process design and development is important. Integrating thermal control with catalytic chemistry is certainly important. The innovative development and use of membranes will likely assist process improvement.

As evidenced by 350 papers and patents cited in this review, it is clear that there is significant and current interest in direct methane conversion. At the same time, it is also evident that there is not yet any direct-conversion process that has been scaled to viable commercial practice. Substantial advances in catalyst performance and reactor technology are needed.

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