Advances in Methane Conversion Processes

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Abstract

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

Keywords: Methane; Heterogeneous catalysts; Electrochemical oxidation; Oxidative coupling; Zeolites; Thermochemical processes.

Short Biographical

Bingwen Wang is currently a third year PhD student in the Department of Chemical Engineering and Materials Science at Wayne State University working under the supervision of Professor Eranda Nikolla. She received her BS from Nankai University in 2006, and a MS degree from Eastern Michigan University in 2013. Her PhD dissertation focuses on the development of active/selective heterogeneous catalysts for chemical conversion processes, such as the oxidative coupling of methane.

Sandra Albarracín-Suazo graduated from the National University of Colombia with a BS in Chemical Engineering. She is currently working towards her MS in chemical engineering at the University of Puerto Rico-Mayagüez under the supervision of Professor Yomaira Pagán-Torres. Her research focus is on the low temperature oxidative conversion of methane in metal-exchanged zeolites.

Yomaira Pagán-Torres is an Assistant Professor in the Department of Chemical Engineering at the University of Puerto Rico-Mayagüez. She received her PhD degree from the University of Wisconsin-Madison in 2011 under the supervision of Professor James A. Dumesic. Prior to her academic position at

the University of Puerto Rico-Mayagüez, she worked for The Dow Chemical Company as a Senior Engineer of the Hydrocarbons R&D group in Freeport, Texas. Her research focuses on the design and synthesis of heterogeneous catalytic materials with tailored active sites for the transformation of carbon resources, such as biomass, carbon dioxide, and methane to chemicals and fuels.

Eranda Nikolla is an Assistant Professor in the Department of Chemical Engineering and Materials Science at Wayne State University. She received her PhD in Chemical Engineering from the University of Michigan in 2009 under the supervision of Prof. Suljo Linic and Prof. Johannes Schwank, followed by a two-year postdoctoral work at California Institute of Technology with Prof. Mark E. Davis. Her research interests lie in the development of heterogeneous catalysts and electrocatalysts for chemical/electrochemical conversion processes, including methane reforming and oxidative coupling of methane using a combination of experimental and theoretical techniques.

1. Introduction

Development of efficient and selective methane conversion processes to electricity, fuels and chemicals has become critical in the recent years due to the emerging number of untapped, unconventional natural gas reserves (e.g., shale gas) and the need to reduced our dependence from limited crude oil resources [1-5]. Recent advancements in hydraulic fracturing have led to access of shale gas reserves that are rich in methane (>70% of the carbon) [3, 5]. Currently, methane is mostly combusted for generation of electrical power and heat [5]. To date, industrial routes for one-step conversion of methane to fuels and chemicals are limited. The most technologically advanced routes are indirect conversion of methane (i.e., methane steam reforming [6]) to fuels and chemicals. For example, steam reforming involves the generation of H_2 and CO mixtures from methane at high temperatures (700 °C to 1000 °C) and pressures (15 to 40 atm) [5], which are then used in the production of methanol and Fischer-Tropsch synthesis. The challenges associated to the one-step conversion of methane to chemicals and fuels arise from the fact that methane is a very stable molecule, comprised of C-H bonds that are weakly polarized. Hence, very aggressive reactants and operating conditions (e.g., temperature and pressures) are required to activate the methane C-H bond, consequently favoring undesired reactions (e.g., complete combustion to CO_2) which lead to loss in activity, selectivity, and yield of desired products.

The schematic in Fig. 1 illustrates some of the main high- and low-temperature methane conversion processes. As indicated in Fig. 1, high-temperature processes mainly involve the partial or total oxidation of methane to CO, H_2 , and CO_2 with the exception of oxidative coupling and non-oxidative conversion of methane that lead to the formation of C_{2+} hydrocarbons [6-12]. While, some of the high temperature processes are technologically advanced, they are energy intensive and high cost [13]. Hence, development of one-step processes for conversion of methane to useful intermediates or fuels and chemicals at low-temperatures would alleviate some of these challenges. To date, low-temperature processes (Fig. 1) have largely focused on partial/total oxidation of methane to valuable intermediates for synthesis of fuels and chemicals, such as methanol and dimethyl ether. However, most of these processes suffer from limited

selectivity to targeted products, since under operating conditions most of the products or intermediates are more reactive than methane and undergo further transformation or decomposition. In this short review, we provide an overview of the latest advancements in methane conversion at high- and low-temperatures to fuels, chemicals, and electricity. In addition, we conclude with a perspective on the promises and drawbacks associated with each of these processes.

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

2. High temperature methane conversion processes

2.1. Thermochemical methane oxidation to CO and H_2

High temperature thermochemical processes for conversion of methane to synthesis gas (a mixture of CO and H_2) are the most developed technologies for the production of valuable intermediates. These processes include methane steam reforming, dry reforming, partial oxidation and autothermal reforming. Below, we discuss the advances and challenges associated with steam and dry reforming of methane. In the case of the partial oxidation and autothermal reforming, we refer to the cited reviews [3, 14-16].

Methane Steam Reforming. Steam reforming of methane is the most developed industrial process for generation of H_2 from methane. This process involves the conversion of methane and water (steam) into

H₂ and CO (rxn 1), and is accompanied by the slightly exothermic water gas shift reaction (WGS) (rxn 2), which converts CO and steam into CO₂ and hydrogen.

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

The major challenges with steam reforming of methane using Ni-based catalysts include: (i) catalyst deactivation due to carbon formation, (ii) catalyst deactivation due to impurities in the methane feed, such as sulfur, and (iii) sintering of the Ni particles at high operating temperatures that leads to a decrease in the active surface area, thus lower catalytic activity over time [22, 23]. The carbon-induced deactivation of Ni has been studied extensively [6, 9, 22, 24-34]. For example, it has been demonstrated using in-situ transition electron microscopy (TEM) and DFT studies that carbon deposits are formed by the diffusion of carbon atoms on surface of the Ni particles and their subsequent binding to carbon nucleation centers [27, 29]. These studies also showed that carbon nucleation originated on under-coordinated, edge surface sites of Ni, which as we discussed above are also the most active for C-H bond activation [27, 29]. An increase in the concentration of steam in the feed can alleviate this problem by enhancing the rate of carbon oxidation, however, this approach introduces a number of operational challenges, including an

increase in the operational cost [6, 9]. Improving the carbon-tolerance of Ni catalysts via promotion with alkaline metals or alloying with other metals have been explored as potential solutions to this challenge [30, 35-42]. A number of efforts that utilize a combined experimental/theoretical approach have been instrumental in determining the mechanism that leads to carbon poisoning, and in providing insights on developing carbon-tolerant catalysts for this process [6, 31, 34, 43]. For example, Nikolla and co-workers have shown that alloying Ni with a small amount of Sn (forming a Sn/Ni surface alloy) can lead to changes in the energetics associated with C-O bond formation versus C-C bond formation on the surface, consequently effecting the C-induced deactivation of the Ni catalyst [31]. Fig. 2a shows the reaction energies associated with methane steam reforming on Ni(111) obtained using DFT calculations [31]. This plot suggests that there are two thermodynamically stable sinks for the adsorbed C* atoms formed on the Ni surface from C-H bond activation in methane: (i) formation of adsorbed CO* and then CO₂ from the reaction with adsorbed O* atoms, or (ii) the reaction with other adsorbed C* atoms on the surface to form extended carbon structures that deactivate the catalyst. Figs. 2b and 2c show that while the paths for formation of C-C and C-O bond on monometallic Ni are energetically comparable; this behavior changes when the Ni surface is modified with Sn atoms. In the case of Ni/Sn surface alloy, the C-C bond formation path becomes less energetically favorable than C-O bond formation leading to preferential removal of the C atoms from the surface forming CO or CO₂ instead of extended carbon structures. Nikolla and co-workers demonstrated experimentally that the Sn/Ni surface alloy led to a more carbon-tolerant catalyst than monometallic Ni during steam reforming of methane [31, 34]. They also showed using energy loss near edge spectroscopy (ELNES), Auger electron spectroscopy (AES) studies along with DFT calculations that the changes in the C and O chemistry on Sn/Ni alloy surface as compared to monometallic Ni were due to Sn-induced electronic changes on the surface Ni atoms, in addition to the Sn-induced geometric effects (breaking the surface ensembles of the Ni particles) [44]. These studies clearly demonstrate that the utilization of the combined experimental/theoretical approaches has been instrumental at obtaining fundamental insights regarding the process of methane steam reforming and in devising ways to improve the activity and stability of steam reforming catalysts.

Fig. 2. a) Reaction energies for the elementary steps associated with steam reforming of methane on Ni(111) obtained using DFT calculations. b) Potential energy surfaces for C–C and C–O bond formation on Ni(111). c) Potential energy surfaces for C–C and C–O bond formation on Sn/Ni(111) alloy. Inserts show the lowest energy pathways for attachment of a C atom to an O atom (in the case of C–O bond formation) and the attachment of a C atom to a carbon nucleation center (modeled as a chain of carbon atoms). Ni is shown as a large blue (light) atom, Sn as a large magenta atom, oxygen as a small red atom, while carbon as small black atoms. Red lines and letters correspond to O diffusion and the C–O bond formation, while black lines and letters correspond to C diffusion and the C–C bond formation. Reprinted from ref [31]. Reproduced with the permission from Elsevier.

While above we mainly discuss the advances related to Ni-based catalysts for steam reforming of methane due to several advantages that Ni provides for this process, a number of studies over the years have explored the activity of different transition metals for this process [10, 21, 45-49]. It has been shown that most of the pure metals that exhibit superior steam reforming activity to Ni are fairly expensive (e.g., Ru, Rh) making their industrial implementation economically challenging.

Methane Dry Reforming. Dry reforming of methane is another important process that involves the reaction of CH₄ with an abundant greenhouse gas, CO₂, to generate synthesis gas (rxn 3).

It is highly endothermic and commonly catalyzed by transition metals supported on oxides. The mechanism of methane dry reforming has been studied by many [10, 50, 51]. It has been established that the rate-limiting step in this process is C–H bond activation in methane, which occurs on the transition metal [50]. In the case of C–O bond activation in CO₂, it has been suggested that if the metal is supported on basic or acidic oxide supports it occurs on the oxide, while on more neutral supports the activation of

C-O bond takes place on the metal. On metals, C-O bond activation occurs with a lowest energy barrier on surface defect sites, such as steps. In the case of metals supported on acidic or basic oxides the mechanism of C-O bond activation depends on the nature of the support [12]. For example, it has been reported that on acidic supports CO₂ dissociative adsorption occurs via the formation of formates, while on basic supports it has been suggested that the mechanism involves the formation of oxy-carbonates [12, 51].

The main challenge with dry reforming of methane is the deactivation of the catalyst due to carbon poisoning. It has been suggested that the deactivation of the metal catalyst is more pronounced in the case when metals are supported on neutral supports, since both the C-H bond activation in methane and C-O bond activation in CO₂ occur on the metal surface [52]. The use of basic supports or promoters, such as CeO₂ and La₂O₃, has shown to minimize carbon formation by (i) facilitating dissociation of CO₂ with low energy barriers through the formation of oxy-carbonates, and (ii) providing surface oxygen atoms for facilitating the removal of the surface C atoms formed during C-H bond activation in methane [52, 53]. Another approach to suppress carbon formation is to synthesize very small metal particles that are well dispersed on the support [10]. A critical, minimum metal particle size is required for the formation of extended carbon structures. Therefore, synthesizing very small, well-dispersed metal particles destabilizes the formation of extended carbon structures and also enhances the interaction between the support and the metal, increasing the probability of the O atoms formed from CO₂ dissociation on the support to oxidize the C atoms on the metal formed from methane dissociation [10]. While there have been many attempts to minimize carbon formation through the routes discussed above; it still remains a significant challenge for the industrial implementation of the process.

2.2. Oxidative coupling and nonoxidative conversion of methane

Oxidative Coupling of Methane (OCM) with Molecular Oxygen in Packed Bed Reactors. Oxidative coupling of methane has been explored for many years as a potential route for synthesis of C₂₊ hydrocarbons, such as ethylene, directly from methane in the presence of oxygen [54-76]. This process was first reported in the early 1980 by Keller and Basin [7] along with Hinsien and Bearns [8], who

demonstrated direct synthesis of ethylene from methane and oxygen steams at elevated temperatures of greater than 500 °C on oxide catalysts. A detailed mechanism for this process was reported by Lunsford [11] and involved the activation of the first C-H bond in methane through the active oxygen atoms on the catalytic surface, leading to the formation of methyl free radicals (CH_3^*). The methyl radicals were then coupled to form ethane, followed by subsequent dehydration to form ethylene. This process has been widely explored since the early 80s, but inherent limitations in achieving high yields to C_{2+} products have been reported [77, 78]. The limited high selectivities at high conversions are due to the high thermodynamic stability of undesired side products, such as CO_2 and solid carbon, and also to the fact that most heterogeneous catalysts that activate C-H bonds in methane at high rates are also very active toward the activation of the C-H bonds in ethane [77, 78]. As such an inherent barrier for ethylene yields of 30% has been predicted [77]. Theoretical studies have been conducted to elucidate the mechanism of OCM on various metal oxides. It has been shown that an optimal catalyst for this process has to provide a compromise between the energetics associated with C-H bond activation and methyl radical adsorption [54, 79]. Theoretical studies by Janik and coworkers [54] showed that the reducibility of mixed metal oxides played a key role in providing a “tradeoff” between these steps during OCM.

Fig. 3 summarizes some of the best performing catalysts [80] (mainly doped and mixed metal oxides) reported for this reaction. The highest selectivities are reported for Li-doped oxide catalysts. While promising, Li-doped oxides suffer from loss of Li under reaction conditions, which leads to loss in performance over time rendering them unstable for long-term operation under OCM conditions [57, 66, 69, 73, 74].

In addition to molecular oxygen, sulfur has also been used as a “softer” oxidizer for this reaction [81]. DFT calculations were used to identify metal sulfide catalysts that provided the best compromise between the energetics associated with C-H bond activation in methane and CH_2 coupling. While the DFT predicted PbS-based catalysts were shown to exhibit the highest selectivity among the metal sulfides considered; the selectivity was lower than some of the best performing catalysts reported for oxidative coupling of methane with molecular oxygen shown in Fig. 3.

Fig. 3. Plot showing the published data (from references [57, 60, 61, 63, 65-67, 69, 70, 72-74]) for methane conversion versus the selectivity to C₂₊ products on different metal oxide catalysts operated in packed bed reactors. The blue shaded region shows the region appropriate for industrial standards.

OCM with Oxygen Ions through Membrane Reactors. An approach to overcome some of the limitations associated with OCM using molecular oxygen is to implement oxygen ion conducting membranes that control the amount of oxygen that is available to react with methane [78, 82, 83]. In these systems, molecular oxygen and methane are fed on two different sides of an oxygen conducting membrane. On one side of the membrane, oxygen reduction takes place forming oxygen ions (O²⁻) on the oxide, which diffuse to the other side to react with methane. Oxygen ion conduction can be achieved spontaneously at elevated temperatures due to the difference in the oxygen partial pressure on the different sides of the membranes, or it can be controlled via electrochemical pumping, which involves utilization of an outside power sources to direct the amount of charged species through the membrane [82].

Control over the oxygen partial pressure on the methane side of the membrane reactor is critical in achieving high C₂₊ selectivities, since it has been shown that there is a 1/2 order O₂ dependence in the case of reaction steps that lead to C₂₊ products, and a first order O₂ dependence for complete oxidation steps that leads to the undesired formation of CO₂ [78]. Hence, by controlling the partial pressure of oxygen (e.g., operating at low partial pressures) one can favor the formation of C₂₊ products over the complete oxidation to undesired products. Based on this, one would anticipate that membrane reactors would lead to higher selectivities than OCM catalysts in packed bed reactors with molecular oxygen. In general,

while high C_{2+} selectivities have been reported for OCM membrane reactors, they suffer from lower conversions (Fig. 4) when compared to packed bed reactor systems (Fig. 3) [78]. This is due to several factors, including the fact that most literature reports have focused on using standard oxygen conducting oxides that are relatively thick and exhibit limited oxygen conduction rates unless operated at very high temperatures (>800 °C) [82]. Improvements in the performance of membrane reactors can be achieved by using thinner and more efficient oxygen ion conducting oxides, higher surface area membranes [71], and also by controlling the oxygen flux through the membrane using an external power source. Wang and Nikolla are currently exploring the use of mixed ionic/electronic, layered Ruddlesden-Popper oxides [84] as potentially high oxygen conducting membranes, and efficient oxygen reduction and C-H bond activation catalysts for OCM.

Fig. 4. Plot showing the published data (from references [58, 59, 62, 64, 68, 70, 71, 75, 76]) on methane conversion versus the selectivity to C_{2+} products on different membrane reactors. The blue shaded region shows the region appropriate for industrial standards.

While there have been a number of advancements in packed bed and membrane reactor systems for OCM, operation within the industrial standards (blue regions in Fig. 3 and 4) is still a challenge for most of the systems reported.

Nonoxidative Conversion of Methane. Nonoxidative conversion of methane to ethylene, aromatics and hydrogen at high temperatures is considered to be another direct route for conversion of methane to useful chemicals and fuels [85]. The advantage of nonoxidative conversion of methane is that it prevents irreversible overoxidation, which leads to thermodynamically stable undesired products, such as CO_2 and

H₂O. Fe and Mo supported on zeolites have shown promising selectivities to hydrocarbon (e.g., naphthalene) formation during this process [85-87]. The proposed mechanism involves C-H bond activation in methane on the metal sites forming CH_x species followed by dimerization to C₂H_y. While, nonoxidative coupling of methane is advantageous since it eliminates the formation of CO₂, a greenhouse gas, coke formation on the catalyst surface and the relatively high reaction temperatures as compared to oxidation processes are still a challenge.

3. Low temperature methane conversion processes

The development of processes for the partial oxidation of methane to methanol through a low-temperature direct route from an inexpensive and abundant feedstock is a long-standing challenge, stimulated by the numerous applications of the chemical as a solvent and a precursor for the production of commodity chemicals, such as formaldehyde, methyl *tert*-butyl ether, acetic acid, chloromethanes, methyl methacrylate [88, 89]. Current industrial methanol synthesis from methane involves a high-temperature and energy-intensive process involving the formation of synthesis gas by autothermal reforming, followed by the conversion of the synthesis gas to methanol over Cu/ZnO/Al₂O₃ catalysts [90, 91]. Although the current industrial process produces methanol in high yields it requires high temperatures and pressures at various stages, in addition to large-capital intensive reforming facilities [90, 91], which limit the implementation of this technology in remote and inconveniently located untapped natural gas reserves [90]. Therefore significant interest in the development of direct low-temperature methane to methanol processes, that circumvent the production of synthesis gas, has emerged to exploit the transformation of abundant and remotely located sources of natural gas [92]. Inspired by the remarkable activity and selectivity of methanotrophic bacteria to convert methane at mild reaction conditions over methane monooxygenase enzymes (MMO) [93-96], transition metal-exchanged zeolites, with active sites analogous to those in MMO have been studied as reactive materials for the activation of the highly stable C-H bond (438.8 kJ mol⁻¹) of methane at low temperatures (< 250 °C) [97-99]. The active site of these enzymes for methane oxidation have been elucidated as bis(μ-oxo)diiron complexes in soluble methane

monooxygenase (sMMO) and as bis(μ -oxo)dicopper complexes in particulate methane monooxygenase (pMMO) [93, 100].

The first efforts in developing inorganic heterogeneous materials for the oxidation of methane to methanol, with active sites similar to sMMO enzymes, were Fe-ZSM-5 zeolites activated with nitrous oxide (N_2O) [101, 102]. The N_2O assisted in the formation of an active bridging Fe-oxo complex for hydrogen atom abstraction from methane [101, 102]. A bis(μ -oxo)diiron cluster similar to the active center in sMMO was elucidated by in-situ Mossbauer spectroscopy studies of Fe-exchanged ZSM-5 [103]. In addition to Fe-exchanged zeolites, Cu-exchanged ZSM-5 has received considerable interest for methane oxidation to methanol. The elucidation of the active Cu species in ZSM-5 has been subject of numerous spectroscopic and theoretical studies [104-106]. Pioneering work on Cu-exchanged ZSM-5 was conducted by Groothaert et al., which demonstrated the partial oxidation of methane by a stepwise and stoichiometric reaction with molecular oxygen at low temperatures [104]. A bis(μ -oxo)dicopper complex has been proposed as the active site by a number of studies [104, 105, 107], however some have identified the site by resonance Raman spectroscopy and DFT studies as a bent mono-(μ -oxo)dicopper cluster located at the intersection of two 10-membered rings [108, 109].

Although a number of Cu-oxo species in ZSM-5 have been identified as active sites for methane oxidation to methanol, most suggested species are comprised of more than one Cu atom [97]. In a very recent work, a comprehensive theoretical study based on DFT and *ab initio* thermodynamic analysis was conducted by Li et al. on the structure, stability, and reaction mechanism of extra-framework Cu complexes in ZSM-5 (e.g., bi- and trinuclear Cu-oxo species) as a function of activation and reaction conditions [110]. The formation of extra-framework trinuclear Cu-oxo species in ZSM-5, $[Cu_3(\mu-O)_3]^{2+}$, was shown to take place under oxygen-rich environments at high temperatures, whereas the formation of binuclear Cu species, $[Cu(\mu-O)Cu]^{2+}$, are formed and stabilized in low oxygen partial pressure environments during catalyst activation. Theoretical studies indicated that both the binuclear Cu complex $[Cu(\mu-O)Cu]^{2+}$ and trinuclear Cu-complex $[Cu_3(\mu-O)_3]^{2+}$ were reactive for C-H bond activation, however

the trinuclear Cu-complex exhibited the lowest energy pathway as shown in Fig. 5 [110]. It is important to note that after reaction, the trinuclear Cu-species $[\text{Cu}_3(\mu\text{-O})_3]^{2+}$ was transformed to a partially reduced Cu complex, $[\text{Cu}_3(\mu\text{-O})_2]^{2+}$, hence regeneration of the active site was essential for the next methane conversion cycle [110].

Fig. 5. Minimum reaction energy paths for methane conversion to methanol over binuclear Cu-oxo complex, $[\text{Cu}(\mu\text{-O})\text{Cu}]^{2+}$, and the trinuclear Cu-oxo complex, $[\text{Cu}_3(\mu\text{-O})_3]^{2+}$, in Cu-ZSM-5. Reprinted from ref [110], Copyright 2016, with permission from Elsevier.

Markovits et al. studied the effect of the location and distribution of Al sites in ZSM-5 on the formation of Cu-oxo species to understand the structure and chemical environment required for the stabilization of these active sites [111]. A number of Cu-ZSM-5 materials with high concentrations of Al pairs and different loadings of Cu were synthesized and studied in the stepwise oxidation of methane to methanol. From a combination of IR spectroscopy, extended X-ray absorption fine structure (EXAFS) studies, and DFT computed geometrical parameters of Cu-oxo complexes [110], the authors proposed structures for the Cu-oxo complexes in ZSM-5. Trinuclear Cu-oxo complexes $[\text{Cu}_3(\mu\text{-O})_3]^{2+}$ bonded to two paired framework Al as active sites for Cu-exchanged ZSM-5 for Cu/Al ratios of 0.2 to 0.5 and a combination of Cu monomers and dimers $[\text{Cu}_2(\mu\text{-O})]^{2+}$ for Cu/Al ratios below 0.2 were proposed [111]. The highest yield obtained for methane oxidation was of $89 \mu\text{mol g}_{\text{cat}}^{-1}$ over Cu-ZSM-5 catalyst with

Cu/Al ratios of approximately 0.5. Although the synthesized zeolites by Markovits et al. displayed high yields for methane oxidation, it should be noted that only 50% of the sites were active [111]. In addition to the nature of the extra-framework Cu-oxo cluster, it was concluded that the size and shape of the zeolite environment where the embedded Cu cluster is localized impacts its reactivity in methane conversion.

Interestingly, Cu-oxo species in other zeolite frameworks such as mordenite (MOR) have demonstrated higher methanol yields for the oxidation of methane compared to Cu-exchanged H-ZSM-5 materials [112]. Vanelderen et al. conducted detailed Raman spectroscopy studies to elucidate the structure of Cu active sites in MOR [113]. The sites were identified as two different $[\text{Cu}_2\text{O}]^{2+}$ clusters located in the 8-membered ring (MR) side pockets of MOR [113]. Depending on the framework environment in which the $[\text{Cu}_2\text{O}]^{2+}$ sites were located, differences in methane oxidation reactivity were observed [113]. Besides $[\text{Cu}_2\text{O}]^{2+}$ clusters being identified as active species for methane conversion, trinuclear Cu-oxo species in MOR have recently demonstrated high reactivity for C-H bond activation [112]. The combination of in-situ X-ray adsorption spectroscopy (XAS) and DFT calculations determined the active site as a trinuclear Cu-oxo cluster, $[\text{Cu}_3(\mu\text{-O})_3]^{2+}$, bonded to two Al atoms located at the entrance of the 8-MR side pocket. The barrier for methane C-H bond activation of 74 kJ mol^{-1} was determined for the $[\text{Cu}_3(\mu\text{-O})_3]^{2+}$ complex in MOR, comparable to the 78 kJ mol^{-1} barrier obtained for methane C-H bond activation over binuclear $[\text{Cu}(\mu\text{-O})\text{Cu}]^{2+}$ complex in ZSM-5 [112]. On the other hand, Zhao et al. performed DFT studies on the formation and reactivity of extra-framework $[\text{CuOCu}]^{2+}$ and $[\text{CuOOCu}]^{2+}$ complexes as active centers in MOR for methane to methanol oxidation [114]. Results suggested that the $[\text{CuOCu}]^{2+}$ complex is the most stable to be formed in MOR and is also the most reactive in activating methane between the two moieties studied [114].

Grundner et al. optimized the synthesis of Cu-exchanged MOR zeolites for the deposition of a high number of uniform trinuclear Cu complexes in H-MOR resembling the structure and reactivity of active sites in pMMO, while minimizing the formation of Cu spectators [115]. Heterogeneous speciation of Cu

(e.g., tri-, di-, and mononuclear species) in MOR was shown to be affected by synthesis conditions, including solution pH and the cation in the parent zeolite. The presence of Na^+ and other alkaline earth cations in the 8-MR side pockets were shown to hinder the formation of trinuclear Cu-oxo species. For Cu-exchanged H-MOR a stoichiometry of 3:1 Cu to activated methane confirmed that all extra-framework trinuclear Cu-oxo species formed were reactive for methane conversion. Despite that fact that a similar trinuclear Cu-oxo complex $[\text{Cu}_3(\mu\text{-O})_3]^{2+}$ has been identified in both Cu-H-MOR and Cu-H-ZSM-5, the methane oxidation activity of Cu-H-ZSM-5 is almost 50% that of Cu-H-MOR [111]. It has been hypothesized that in H-ZMS-5 the Cu-oxo species are located in more than one environment and in some cases the $[\text{Cu}_3(\mu\text{-O})_3]^{2+}$ is in a less constrained local environment exhibiting higher free energy barrier for C-H bond activation. Whereas in Cu-H-MOR, most of the $[\text{Cu}_3(\mu\text{-O})_3]^{2+}$ complexes are stabilized in a highly constrained local environment in the 8-MR side pockets with a lower free energy barrier [111-113].

Besides MFI and MOR, other zeolite topologies such as ferrierite [104], Beta [104], Y [104], SSZ-13 [116], SSZ-16 [116], SSZ-39 [116], and SAPO-34 [116] exchanged with Cu have shown methane oxidation activity to methanol. Smeets et al. demonstrated that Cu-Beta and Cu-ferrierite are reactive materials containing active copper species different to those identified in Cu-MOR and Cu-ZSM-5 zeolites [104]. Cu-exchanged in 8-MR small pore zeolites (e.g., Cu-SSZ-13, Cu-SSZ-16, Cu-SSZ-39, Cu-SAPO-34) synthesized by Wulfers et al. produced higher methanol per Cu atom yields in comparison to Cu-ZSM-5 and Cu-MOR [116]. Kulkarni et al. investigated the active site in Cu-SSZ-13 through DFT calculations. A mono-copper species $[\text{Cu}^{\text{II}}\text{OH}]^+$ was proposed based on their results and previously reported spectroscopic and experimental studies [117]. Furthermore, the need of water for methanol extraction and the effect of the Si/Al ratio of Cu-SSZ-13 on reactivity were investigated by *ab-initio* molecular dynamics simulations. The presence of extra water molecules for the extraction of intermediate species was shown to hydrate the Cu atom, causing the detachment of a $[\text{Cu-2}(\text{H}_2\text{O})\text{-CH}_3]^+$ species from

the framework Al [117]. The authors proposed that the formation of the mobile hydrated-Cu species gave a possible alternative route for methanol extraction through a more favorable energy path.

Ni-ZMS-5 [118], Co-ZSM-5 [119, 120], and Zn-ZSM-5 [121, 122] have also shown reactivity in the oxidation of methane to methanol with molecular oxygen. Shan et al. have reported that Ni-ZSM-5 converts methane with molecular oxygen to a mixture comprised of methanol, formaldehyde, and ethylene glycol at 150 °C and atmospheric pressure [118]. The total oxygenated product yield was of 14.9 $\mu\text{mol g}_{\text{cat}}^{-1}$ [118]. Based on UV-vis, XANES, and EXAFS studies, the nature of the active site was proposed as a bent mono(μ -oxo)dinickel species. The oxidation of methane to a mixture of oxygenates, methanol and formaldehyde, has also been observed for Co-ZSM-5 materials using air [120]. The product distribution was strongly dependent on the nature of the active Co center and the synthesis method conditions. Co-oxide particles (e.g., CoO, Co₃O₄) deposited by impregnation favored the formation of methanol, whereas cobalt present in ion-exchange sites favored the formation of formaldehyde. Beznis et al. were able to increase the selectivity of Co-ZSM-5 towards methanol production by altering the micro- and meso-porosity of the parent ZSM-5 material by alkaline treatments, with the aim of depositing higher loadings of Co-oxide species [120]. Zn modified zeolites, such as ZSM-5, can also activate CH₄ at low temperatures through homolytic and heterolytic mechanisms. Xu et al. studied the room temperature activation of methane over Zn-ZSM-5 by solid-state NMR, spectroscopy studies, and DFT calculations [121]. Dinuclear Zn-oxo species were shown to favor the homolytic cleavage of the methane C-H bond, whereas, the isolated Zn²⁺ favored the heterolytic cleavage of methane. Hence, surface bound methoxy and zinc methyl species were formed upon C-H bond activation on the two different types of active sites. Extraction with water of the surface bound methoxy species in Zn-ZSM-5 led to the successful formation of methanol. Pagán-Torres and Albarracín-Suazo are analyzing, through DFT calculations and experimental studies, the formation, stability, and reactivity of Zn²⁺ and dinuclear Zn-oxo complexes in different zeolite topologies for the direct oxidation of methane to methanol.

Numerous research groups in recent years have developed first row transition metal-exchanged zeolites for the direct oxidation of methane to methanol stepwise and stoichiometrically with molecular oxygen [97, 98, 123-125]. For most of these processes the treatment of the exchanged zeolite and the direct oxidation of methane requires three stages consisting of: (i) the oxidation of the transition metal exchanged zeolite with oxygen at high temperatures (≥ 400 °C), (ii) the addition of methane for C-H bond activation at low temperatures (< 250 °C), and (iii) the introduction of a solvent (e.g., water) for the extraction of surface-bound intermediates to yield methanol [126]. A significant disadvantage of these systems is that after extraction of surface-bound intermediates the sites deactivate, hence requiring high temperature treatments for site regeneration for the subsequent methane oxidation cycle. Furthermore, studies by Bozbag et al. have shown that the long-term performance of Cu-exchanged zeolites (e.g., Cu-MOR) requires more than one complete reaction cycle to obtain maximum methanol yields from methane oxidation [127].

Fig. 6. Stoichiometric and catalytic oxidation regimes for methane to methanol over Cu-Na-ZSM-5 and Cu-H-ZSM-5. Catalysts were pretreated and contacted with a flow of methane for reaction, followed by the introduction of a mixture of He/H₂O/O₂ for the stoichiometric production of methanol over Cu-Na-ZSM-5 (blue open squares) or the introduction of a continuous feed of a CH₄/H₂O/O₂ mixture over Cu-Na-ZSM-5 (black solid squares) and Cu-H-ZSM-5 (red solid triangles). Reprinted with permission from ref [128]. Copyright © 2016 American Chemical Society.

To overcome this challenge, in very recent work, Román-Leshkov et al. developed the first catalytic direct oxidation of methane to methanol process using molecular oxygen at low temperatures (210-225

°C) and atmospheric pressure over Cu-exchanged zeolites [128]. The Cu-exchanged zeolites (e.g., H-ZSM-5, H-Beta, MCM-41, H-mordenite, H-ferrierite, Na-ZSM-5, Na-Y, Na-SAPO-34, Na-SSZ-13) studied were subjected to an initial catalyst pretreatment, followed by introduction of pure methane for 0.5 hr, and a subsequent continuous feed of a gas mixture comprised of water, oxygen, and methane [128]. Production rates for the stable and continuous production of methanol were $0.88 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$ and $1.81 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$ for Cu-Na-ZSM-5 (Cu/Al = 0.37) and Cu-H-ZSM-5 (Cu/Al = 0.31), respectively as shown in Fig. 6 [128]. Furthermore, these studies demonstrated steady state methanol production rate of $88 \mu\text{mol g}_{\text{cat}}^{-1}$ for Cu-Na-ZSM-5, which is approximately five times higher than that observed by previous researchers in the stepwise and stoichiometric oxidation of methane over similar zeolites [116]. The catalytic turnover of Cu-Na-ZSM-5 was confirmed based on results obtained from kinetic and isotopic labeling studies.

Román-Leshkov et al. also studied the catalytic oxidation of methane over other zeolite topologies exchanged with Cu, including H-ferrierite, H-Beta, H-mordenite, Na-Y, and MCM-41 [128]. All of these materials showed catalytic activity toward methanol production, but at lower specific activities compared to Cu-H-ZSM-5. Zeolites with CHA topology exhibited the highest site time yields compared to zeolites with MFI topology at similar Cu/Al ratio [128]. For methane oxidation reactions conducted at higher temperatures (e.g., 260 °C) with Cu-Na-SSZ-13 site time yields were shown to increase to $31.6 \times 10^{-3} \text{mol}_{\text{CH}_3\text{OH}} (\text{mol Cu})^{-1} \text{h}^{-1}$ [128]. Based on these findings, which indicated that small pore zeolites or cage-like structures have higher performance for methanol production compared to larger pore zeolites, the authors hypothesized that the structure of the catalytic sites or transition states are influenced by the zeolite topology. Although, the catalytic reaction rates for the Cu-exchanged zeolites studied by Román-Leshkov et al. are relatively low, the discovery of pretreatment and reaction conditions favoring oxidation of methane is of significant contribution to the development of technologies for the catalytic direct production of methanol from methane [128].

The recent advances in the low temperature conversion of methane to methanol discussed in this short review have predominantly focused on the use of transition metal exchanged-zeolites and molecular oxygen. However, pioneering studies on methane oxidation processes using metal organic frameworks [129, 130], covalent triazine frameworks [131, 132], homogeneous metal complexes [133], and various oxidizing agents (e.g., hydrogen peroxide, N_2O , oxygen) have been discussed in more comprehensive reviews [97-99].

4. Other methane conversion processes

Electrochemical Oxidation. Electrochemical oxidation of methane has been considered as a direct route for generation of electrical energy from methane. The most commonly used electrochemical systems for direct electrochemical methane oxidation are solid oxide fuel cells (SOFCs). SOFCs are solid-state electrochemical devices that can in principle convert the chemical energy of combustible fuels (H_2 , CO and hydrocarbons (such as methane)) directly into electrical energy. The SOFC cathode is responsible for reducing gas-phase oxygen into oxygen ions in the presence of electrons. Oxygen ions are then transported through an ion-conducting oxide (such as yttria stabilized zirconia - YSZ) to the SOFC anode, the electrode where the fuel is fed and oxidized in the presence of the oxygen ions to CO_2 and H_2O , releasing electrons to an external circuit. While direct electrochemical oxidation of methane using SOFCs is an appealing approach for the direct generation of electrical energy from methane, there are a number of operational challenges that have been impeding its industrial implementation [25, 134-141]. One challenge is the deactivation of the conventional anode electrocatalyst (Ni) due to carbon poisoning [25, 134, 135, 139]. An approach to alleviate this problem is to develop SOFC anode electrocatalysts that are inherently resistant to carbon poisoning [142, 143]. An attempt toward this direction was made by Gorte and coworkers, who showed that replacing Ni/YSZ with Cu/ CeO_2 /YSZ anodes led to improvements in the carbon-tolerance during on-cell, electro-oxidation of methane [35, 37, 134, 144-146]. Nikolla and co-workers also showed that Sn/Ni surface alloy-based SOFC anode electrocatalysts exhibited improved tolerance to carbon-induced deactivation as compared to conventional monometallic

Ni electrocatalysts [147]. Other attempts in identifying carbon-tolerant anode electrocatalysts for direct electro-oxidation of methane in SOFCs have focused on the use of mixed ionic-electronic conducting oxides as anode electrocatalysts [143, 148-152]. While some mixed ionic-electronic conducting oxides have shown promise, their activity toward methane electro-oxidation is much lower when compared to Ni-based anodes.

Low Temperature Total Oxidation. Low temperature total oxidation or combustion of methane is a process that plays a critical role in automobile emissions. While not directly related to generation of fuels, chemicals and electricity from methane, this process is critical for minimizing methane emissions from automotive exhaust. The commonly used catalysts for this process are Pd-based supported on oxides to facilitate operation at temperatures lower than 400 °C. It has been recently shown that encapsulation of Pd nanocatalytic particles with reducible oxides, such as ceria, can significantly improve the activity and stability of these catalysts [153, 154]. The enhancement in the activity was attributed to the structural and chemical features of the ordered Pd-O-Ce moieties [154].

Halogenation and Oxyhalogenation of Methane. Another route for the activation of the C-H bond in methane is based on halogenation and oxyhalogenation processes [5, 155-158]. The reaction chemistry for halogenation consists of reacting methane with a halogen (preferably Cl_2 or Br_2) under mild reaction conditions to yield methyl halides (CH_3X), which can then undergo catalytic hydrolysis reactions to produce oxygenates, alkanes, olefins, and aromatics. In oxyhalogenation, the C-H bond in methane is activated by a reactive halogen that is formed by oxidation of a hydrogen halide with O_2 . The alkyl halide formed then reacts to produce aromatics or olefins through coupling reactions [158-161]. Olah et al. showed that halogenation of methane to methyl halide over supported acidic catalysts under mild reaction conditions (e.g., 180-250 °C) led to selectivities of > 90% [162]. Although halogenation processes are attractive owing to the relatively low energy barrier for methane C-H bond activation via the halogen, drawbacks exist to these processes, such as the regeneration of the halogen to close the catalytic cycle. To overcome such limitation, Li et al. demonstrated the one-pot catalytic partial oxidation of methane to methanol and dimethyl ether over supported $\text{MoO}_2\text{Br}_2(\text{H}_2\text{O})_2$ on Zn-MCM-48 [157]. The process involves

the formation of Br_2 by decomposition of $\text{MoO}_2\text{Br}_2(\text{H}_2\text{O})_2$ in the presence of O_2 , followed by the halogenation of methane to form a CH_3Br species, which is then converted to oxygenated products by reaction with MoO_3 in-sync with the regeneration of the MoO_2Br_2 species. This process presents a closed catalytic cycle for partial oxidation of methane, however, the efficiency of each step in the process must be optimized to increase product selectivity. Recently, Pérez-Ramírez et al. demonstrated a highly attractive process integrating alkane bromination and oxidation steps [4]. The selective route consisted of the gas-phase bromination of methane coupled with the oxidation of the HBr by-product to bromine over a vanadium phosphate (VPO) catalyst. The VPO catalyst assisted in providing a continuous source of bromine through the regeneration of HBr by oxidation over the catalyst surface. In the studies conducted by Pérez-Ramírez et al. selectivities to CH_3Br of up to 95% were obtained with stable operation of the catalyst with time on stream [4]. The high selectivity toward CH_3Br was attributed to the high activity of the catalyst for HBr oxidation and low activity toward the oxidation of methane and the methyl halide. In more recent work, Pérez-Ramírez et al. demonstrated the one-step production of CO from methane by selective oxychlorination, yields of up to 35% at 96% selectivity of CO were obtained over stable VPO catalyst at mild reaction conditions [163]. The process involved an approach combining C-H bond activation in the presence of HCl and O_2 yielding CH_3Cl and CH_2Cl_2 , followed by the in-situ oxidation of halogenated products to CO and the regeneration of HCl over the VPO catalyst. This methane conversion strategy presents an alternative to the use of steam-reforming processes for the production of CO from methane.

5. Perspective

The conversion of the simplest but most unreactive hydrocarbon molecule, methane, remains one of the most significant and promising challenges in chemical/electrochemical catalysis research. With the advent of abundant untapped natural gas reserves, the direct transformation of methane as a feedstock for chemicals and fuels has become key in the current society, which is highly dependent on limited resources of crude oil. Despite the number of products (e.g., ethylene, aromatics, methanol,

formaldehyde, etc.), that could be obtained from the direct conversion of methane, large-scale industrial processing still relies on its conversion to chemicals and fuels through the production of synthesis gas. Hence, development of technologies for the industrial production of chemicals and fuels from direct conversion of methane has not made substantial progress in the recent years. However, progress in fundamental knowledge on catalysts design, synthesis, in-situ and ex-situ characterization, and theoretical work as presented in this short review has shed light into important aspects in the pursuit for active and selective catalytic materials for direct methane conversion processes.

The area of high temperature methane conversion has been mainly dominated by processes that lead to generation of synthesis gas from methane. A promising high temperature route for direct conversion of methane to valuable fuels and chemicals is through oxidative coupling (OCM) and nonoxidative conversion of methane. While promising, OCM with molecular oxygen in packed bed reactors has inherent limitations in the yields of C_{2+} hydrocarbon products. Whereas, strategies in improving the performance of heterogeneous catalysts and reactor design have been pursued, methane conversions and selectivities toward C_{2+} products are still far from industrial standards. An approach to improve C_{2+} product selectivity during OCM is to use membrane reactors. While high C_{2+} product selectivity has been demonstrated for these systems, methane conversions are low, leading to low overall yields to the desired products. Development of membrane systems with high surface area and improved oxygen conductivity is important toward achieving industrially relevant conversions and yields. Direct electrochemical oxidation of methane to electricity is another approach for efficient conversion of methane. This process has been successfully demonstrated using SOFCs, but long-term stability of these systems has presented challenges. Combined experimental and theoretical approaches have provided the initial important steps toward improving the stability of SOFC electrocatalysts when operating on methane, but further optimization of the electrocatalytic materials is necessary for large-scale implementation.

In low temperature oxidation of methane to methanol a number of active site structures have been suggested including mono metal-oxo species, multinuclear metal-oxo species, large metal-oxide clusters, and metal cations. Scientific findings discussed in this short review have also indicated that zeolite

topology, Si/Al ratio, and zeolite exchange preparation methods can affect the formation and stabilization of catalytic sites. Hence, future studies aimed at synthesizing metal-exchanged zeolites with well-defined active sites to create a single site type of catalyst will be imperative to establish relationships between reactivity and active site structure. In addition, determining active site stability, formation, and regeneration conditions will be essential for the direct oxidation of methane through a truly catalytic process. Therefore, identifying the nature of the active sites under relevant reaction conditions by in-situ and in-operando spectroscopy studies, combined with kinetic studies and DFT calculations will be essential for the further engineering of materials for the catalytic production of high-value chemicals from methane conversion processes discussed herein.

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