Review

A Short Review about the Partial Methane Oxidation in Fuel Cell-Type Reactors for Co-Generation of Energy and Chemicals

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Abstract: The conversion of methane into chemicals is of interest to achieve a decarbonized future. Fuel cells are electrochemical devices commonly used to obtain electrical energy, but can be utilized either for chemicals production or both energy and chemicals cogeneration. In this work, the partial oxidation of methane in fuel cells for electricity generation and valuable chemicals production at the same time is reviewed. For this purpose, different types of methane-fed fuel cells, both low temperature fuel cells, such as PEMFCs and AAEMFCs, and high temperature fuel cells, such as SOFCs. Despite the fact that few studies have been conducted on this subject, the promising results are driving the development of fuel cells that use methane as a fuel source for the cogeneration of power and valuable chemicals.

Keywords: fuel cell; methane to energy; methane to products; methane oxidation reaction

1. INTRODUCTION

Methane is the second most abundant greenhouse gas behind CO_2, but is more potent in trapping heat, having a detrimental impact in the atmosphere [1]. On the other hand, this gas is the major component of natural gas, and has lower overall costs, which par excellence makes it a primary source for energy. There are large reserves of this gas, being the main fraction of natural gas, coal bed gas, shale gas, and biogas, and it is also associated with oil extraction, where it is usually burned when in remote fields [2, 3].

In a world that is geared towards reducing the carbon footprint, methane is identified as a possible source of transition energy, due to its low extraction and logistics costs, which can discourage the use of other fossil fuels [4, 5]. However, even though the energy efficiency of burning liquefied methane is comparable to that of other liquid fuels, it is still used mainly for burning, generating CO_2 [4]. For this reason, the conversion of methane into chemicals is of interest to achieve a decarbonized future [2]. Direct conversion of methane, however, presents some challenges, such as the breaking of the C-H bond, stronger than in any other hydrocarbon (434 kJ·mol⁻¹), and the low polarizability, due to its regular tetrahedron conformation [6-11].

Methanol is an important industrial chemical, widely used in chemical synthesis, for the manufacture of many other chemicals [12-14]. It is also used in automotive antifreezes, in rocket fuels, and as a general solvent. Methanol is also a high-octane, clean-burning fuel that is a potentially important substitute for gasoline in automotive vehicles. Methanol is an alcohol present in nature in small amounts and, obtained anthropologically by pyrolysis or destructive distillation of wood. Demand for methanol is expected to exceed 110 million tons per year (MTY) in the next years and is expected to increase the production capacity [15]. Methanol is commonly obtained from fossil fuels, but it can also be obtained from renewable energy resources, supporting in this way the development of energy

solutions with reduced greenhouse gas emissions. Besides their high-energy content, fossil fuels are hydrocarbon mixtures, that provide low-cost feedstock for the production of various platform chemicals [16], from fossil fuels, there is methane gas.

In most cases, the conversion process from methane to methanol is not completely selective, and, among different compounds, it is possible to find mainly formate. Other compounds with a higher carbon chain, such as ethane, ethanol, and propane, are also found, but less frequently and under more specific experimental conditions [17, 18].

A classical process for conversion of methane into products involves the hydrocarbon and water decomposition to $CO + H_2$ (syngas) at high temperatures and pressures, an extremely energy intensive process due to chemical inertness of the C–H bond. As such, the development of more efficient processes is an active field and a variety of ways has been explored [19-21]. Among others ways, these include homogenous and heterogeneous catalysis, photocatalysis, biocatalysis, plasma technologies, and electrochemical processes [2, 6, 22-28].

All these processes can be conducted in mild conditions, such as the homogeneous catalytic process that consists of partial oxidation of methane by means of strong oxidizing species, H_2SO_4[28, 29] in oleum and H_2O_2 [6, 27, 30-32], enhanced by metal ions, generating reactive oxygenated species.

In the bioconversion of methane in bacterial cells, Methane Monooxygenase (MMO) oxidizes methane to methanol using molecular oxygen and electron donors at room temperature and pressure [26, 33, 34]. This enzyme is biosynthesized by methane-oxidizing bacteria, which are microorganisms that utilize methane as a carbon and energy source [14]. The ability of MMO to cleave the C–H bond of methane under mild conditions is believed to originate from the generation of extremely reactive oxygen species at the catalytic site of MMO. Thus, the structure and properties of the catalytic site in MMO and the reactive oxygenated species involved in the catalysis have been investigated.

The photocatalytic process takes place by the ability of the catalyst to create electron–hole pairs, which generate free radicals [35-37], or reactive oxygenated species [6, 38]. This process can be associated to hydrogen peroxide decomposition, enhancing the conversion [35, 38]. Shi and co-workers [38] synthesized and investigated a fluffy mesoporous graphitic carbon nitride (g-CN), for the partial oxidation of methane to methanol at a mild condition (35°C) in the presence of H_2O_2 under the irradiation of simulated sunlight.

Li and co-workers [39] applied a selective photocatalytic oxidation over graphitic carbon nitride-decorated tungsten bronze cesium nanocomposites to the conversion of low concentration methane under mild conditions into methanol under light irradiation and at room temperature. The superoxide anion radical ($\bullet O_2^-$) first activated the methane and then the photogenerated electrons from nanocomposites in the composite inhibited the peroxidation and increased the generation of methanol [36, 39].

Finally, electrochemical processes play an important role, as they act directly on the electrostatic interactions between electron and atomic nucleus through the direct potential application on an atom or molecule, reducing energy dispersion in the environment [40]. This review presents a perspective of the oxidation of methane by electrochemical ways to obtain products with higher added value, preferably with co-generation of electricity. Discussing how the application of fuel cells as reactors, the methane is consumed, its released electrons are used for electrical work, and products such as methanol are obtained. In a major plan, the potential of the application of crude natural gas ($CH_4 + CO_2$) and we discussed some of the most promising materials to be explored.

2. ELECTROCHEMICAL METHODS FOR METHANE OXIDATION

Electrochemical processes can be carried out at both high and low temperatures, and present the advantage of transfer the energy directly from the hydrocarbon to the system, reducing the dissipation of energy in the form of thermal energy [40-44]. In addition, there are the possibility to select specific reaction products with the adjustment of work

potential. For example, Ramos et al [18] investigated methane oxidation over Pd/C using a polymer electrolyte reactor – fuel cell type at mild condition, to obtain methanol, formic acid, formaldehyde, ethane, ethanol, acetaldehyde, acetic acid and propane, reporting the onset potential for each product.

The electrochemical oxidation of methane can occur in two ways, that is, the direct way, in which the hydrocarbon electron is transferred directly to the electrical system, and the indirect way, involving the electrogeneration of highly reactive species capable of reacting with CH_4 in the interface neighborhoods or/and in the bulk of the solution [45]
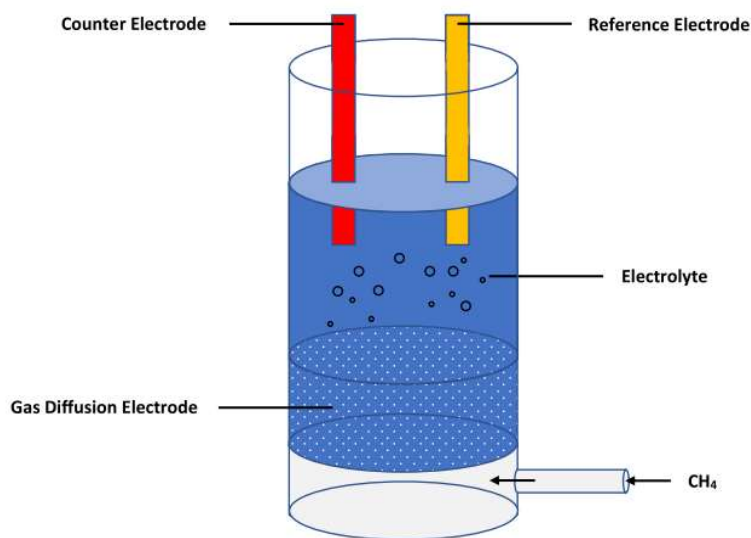
2.1. Faradaic Methane Oxidation

Faradaic methane oxidation is based on the adsorption of methane on the catalyst active site and on the direct electron exchange between the hydrocarbon and the electrode surface. Sustersic *et al* [46] reported the adsorption of methane and its oxidation   at various potentials on platinum in H_2SO_4 solution at 60°C. The existence of two electrosorbed species, COH-type and CO-type, was highlighted through the current/potential characteristics recorded under different perturbation conditions.

Nandenha et al. [47] studied the Pt/C, Pt/C-ATO, Pd/C and Pd/C-ATO catalysts for methane oxidation: cyclic voltammograms of all electrocatalysts after adsorption of methane showed a current increase during the anodic scan, more pronounced for materials supported in C-ATO, related to the adsorption of methane and oxidation of the adsorbed species through the water activation. For all electrocatalysts, adsorbed CO or HCO intermediate species were observed by in-situ Atenued Total Reflectance – Fourier Transformed Infrared (ATR-FTIR) experiments.

Boyd and co-workers[48] investigated the electrochemical conversion of methane to CO_2 on platinum under ambient conditions. Theoretical calculations suggested that methane is thermochemically activated on Pt surfaces ($CH_{4(g)} \rightarrow CH_3^* + H^*$) and that the stable methane-derived surface intermediate was CO*. They observed that catalysts with strong CO* binding and weak OH* binding energy are the most effective for high methane oxidation efficiency, but only at high potentials. These results are in line with those reported by Hahn et al. [49], which through FTIR studies, showed the existence of oxygenated carbonaceous species at potentials greater than 0.55 V over Pt, Au, Pd, Rh and Ru. Arnarson and co-worker [50] identify a surface catalytic limitation of methane oxidation to methanol in terms of a compromise between selectivity and activity, as oxygen evolution is a competing reaction. By investigating two classes of materials, rutile oxides and two-dimensional transition metal nitrides and carbides, they found a linear relationship between the energy needed to activate methane, that is, to break the first C-H bond, and oxygen binding energies on the surface. Based on a simple kinetic model they concluded that to obtain sufficient activity oxygen has to bind weakly to the surface, but there is an upper limit to retaining selectivity.

Various authors, working on faradaic reactions, reported the importance of water activation, as one of the ways to transfer oxygen to the hydrocarbon molecule to obtain methanol [48, 50]. Rocha [42] studied the methane oxidation in a bath reactor with $TiO_2/RuO_2/V_2O_5$ gas diffusion electrode and observed that the reaction occurs by a traditional mechanism in which the discharge of water generates hydroxyl radicals, which, in turn, chemically adsorb onto the oxide surface. This is in agreement with previous reports in the literature [9, 51], however these radicals can not only react with adsorbed species, but also detach themselves from the bulk and react without electron transfer to the electrode. A scheme of the electrochemical reactor described by Rocha et al. [42] is shown in Fig. 1.

Figure 1. scheme of the electrochemical reactor described by Rocha et al. [42].

2.2. Non-Faradaic Methane Oxidation

Methane can be activated by more reactive species originated by faradaic processes, that is, reactive oxygenated species (ROS), such as OH• [18, 52, 53], O_2• [54] and SO_3 [55, 56], these species being capable to activating the C-H bond, without the need to absorb methane on the electrode.

Cui et al. [57] in a recent review reported that the dissociation of H_2O_2 can generate OH• and these radicals produce C_1 compounds and CH_3• radicals. The CH_3• radicals can activate water and other hydrocarbon molecules. Cook et al. [52] reported a cathodic reaction to electrogenerate H_2O_2, then this specie is activated by Fenton reaction to OH• and finally this radical converts the methane into methanol. Neto's group [18, 53, 58] attributed the oxidation of methane at lower overpotential in other products, with co-generation of energy, to the activation of water and the presence of OH• radicals, arising from water activation.

Although ROS are the most commonly applied species for the partial oxidation of methane, other radicals can also be used. The use of a photo-electrochemical system to generate a chlorine radical, that reacts with methane to produce methanol was reported by Ogura [59]. Cl^- is produced by an electrochemical reaction, and then this ion is turned into a radical under UV light. Cl• reacts with CH_4 generating methyl chloride, whose subsequent hydrolysis produces methanol.

Studies demonstrated that the methane-oxygen cyclic operation was not necessary to obtain high selectivity [60, 61]. The active oxygen species responsible for the catalytic conversion of methane into oxygenated products has to be clarified because the reaction could proceed either in the gas phase through a chain propagation mechanism [62-64] and/or on the catalyst surface [58, 65-67].

Frese et al.[54] using an electrochemical cell to convert O_2 into O_2•$^-$ to obtain formaldehyde from methane, reported that there is a correlation between the current density and the selectivity, that is, increasing the current density increases the amount of ROS produced, and these species promote the production of more oxidized chemicals, such as CO and CO_2.

The propagation stage of radical reaction at mild conditions can promote the formation of non-oxygenated radicals, such as the methyl radical (CH_3•), and the detection of C2 and C3 compounds such as ethane and propane by Ramos et al. [18] is evidence of the formation of the methyl radical, these pathways was represented in scheme 1.

Methyl radical formation occurs by H abstraction from CH_4 by hydroxyl radicals. Gaseous methane first binds to the metallic sites [61], then hydrogen atoms are gradually

abstracted by the adjacent surface M-O sites and yield M-OH. The reverse reaction of hydroxyl recombination is favored by H_2O [6, 37, 61, 64, 68, 69].

Methane activation chemistry and oxidative coupling of methane remain to date a subject of interest related to the initial methyl radical formation site and the role of surface-initiated gas-phase radical reactions [64, 70-73].
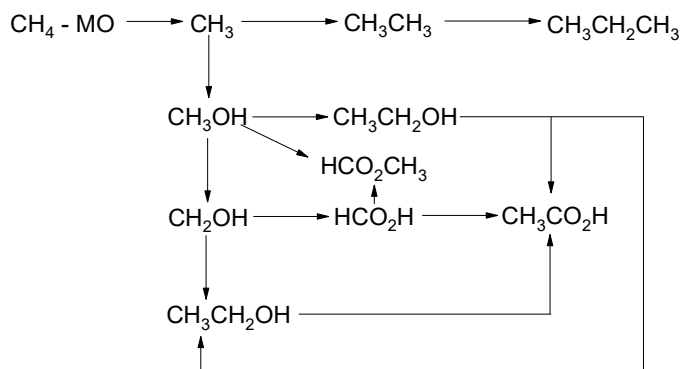
Scheme 1. methane partial oxidation pathway proposed by Ramos et al. [18].

3. FUEL CELLS

Fuel cells are a tool commonly used to convert chemical energy into electrical energy, and are also used as a reactor for chemical transformations. Therefore, they can generate only energy (classic use), only valuable chemicals or both energy and valuable chemicals. While a previous review on methane-fed fuel cells was addressed to the production of only chemicals [10], this review deals with both energy and chemicals generation.

Vayenas et al. [74] compared the suitability of a cogeneration solid oxide fuel cells (SOFC) with respect to a chemical reactor of the same capacity giving the same product composition. Their model showed that such a relative suitability depends on the value of the dimensionless number, v, defined as:

$$v = [24\alpha(K\text{E} - K\text{H})t\text{C}/\alpha C\text{C} - C\text{R}] \qquad (1)$$

where KE is the unit electrical energy price (in $ kWh^{-1}), KH the price per thermal unit produced in ($kWh^{-1}), tC the cogenerative SOFC useful lifetime (in days), CC the co-generative fuel cell capital investment per unit installed power (in $ kW^{-1}), CR the chemical reactor capital investment per unit installed capacity (in $ day kW^{-1}) and α is a conversion factor given in the economical model. On these bases, a cogeneration fuel cell is more advantageous than a chemical reactor if $v > 1$.

At the beginning of the second half of the twentieth century, the use of hydrocarbons as fuel for fuel cells was considered, and the adsorption and oxidation characteristics of hydrocarbons were investigated [75-78]: it was reported that hydrocarbons adsorb slowly while undergoing dissociation on platinum electrodes in a narrow potential range around the final cathodic part of the double layer region and can be oxidized in an anodic potential sweep. Since the 1960s, with the observation that methane oxidation occurred only at high overpotentials, studies for non-protic electrolytes led to ceramic systems and subsequently to the use of hydrocarbon as fuel for SOFCs [79]. In the 21st century, with the improvement of proton exchange fuel cell (PEMFCs), CH_4 started to be considered as fuel under mild conditions.

The performance of a methane-fueled proton exchange fuel cell was reported by Tyagi et al.[80], applying a Nafion membrane doped with phosphoric acid, obtaining an open circuit value of ~0.55 V using Pt catalysts. Nandenha et al. [47] using Pd/C as the anode catalyst obtained a power density of 0.5 mW cm^{-2} in a PEMFC fueled by methane at 80°C. In a later work, Nandenha et al. [81] obtained a power density of *ca.* 0.6 mW cm^{-2}, due to the effect of Zn addition to Pd, that enhances the water activation and the
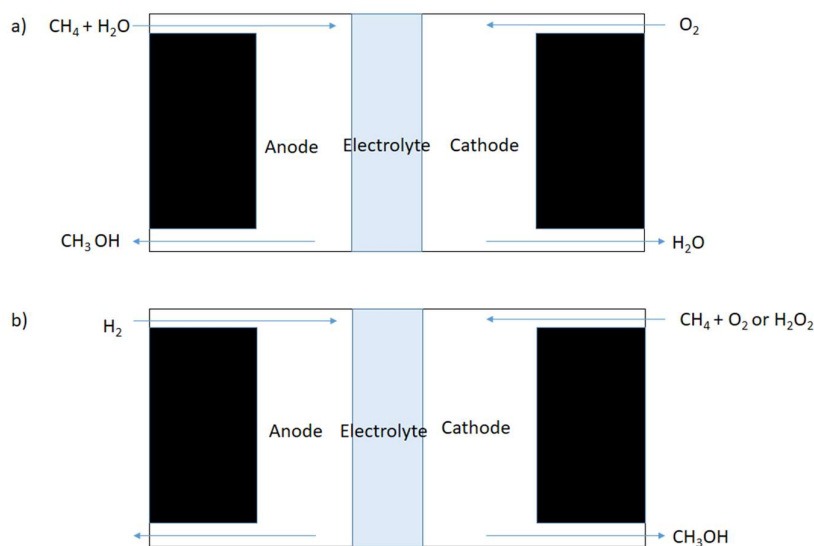
production of methanol and formate, which are more easily converted into energy than methane itself. Among different Pd-based catalysts, a power density of *ca.* 1 mW cm^{-2} was obtained using PdAu as the anode catalyst, due to the methane interaction with the noble metals in the region of hydrogen adsorption; the formation of methanol and formate at water activation potentials was observed [82].

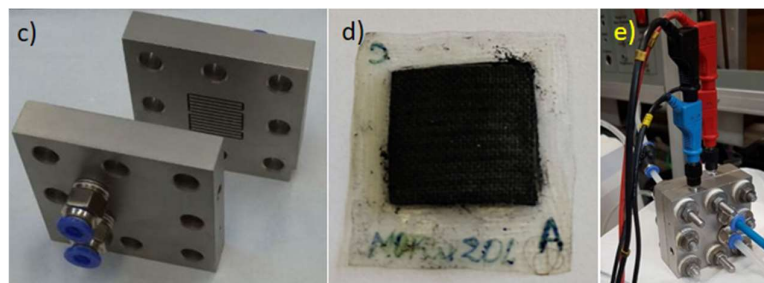## 4. FUEL CELLS FOR COGENERATION OF ENERGY AND CHEMICALS

The fuel cells can be applied to methane oxidation for obtain energy, added value products, and both, and in all cases the differential is the material and operation conditions. As can be seen in Fig. 2, methane oxidation can occur both at the anode or cathode side. Otsuka and Yamanaka [83] reported the partial oxidation of alkenes at low temperatures (< 100 °C) using gaseous alkene–O$_2$ fuel cell systems and for hydroxylation of alkanes and aromatics applying H$_2$–O$_2$ fuel cell reactions, which control the reaction rate and selectivity by a variable resister or potentiostat in the outer circuit. On this basis, Hibino's group [9, 84] used a fuel cell as an electrolytic reactor to convert methane into methanol at different temperatures (50 – 250 °C), and attributed the high conversion to the production of O$_2$*- obtained from the activation of water over vanadium and tin oxides.

Spinner and Mustain [85], used a CO$_3$$^{2-}$ exchange polymer in a fuel cell type reactor, to convert methane to CH$_3$OH, HCHO, CO, HCOO and other low molecular weight oxygenate species at room temperature. The methane was activated electrochemically on a NiO-ZrO$_2$ electrocatalyst and the carbonate anions were used as an oxygen donor to facilitate methane activation.

Nandenha and co-workers [86], generated methanol through partial oxidation of methane at the cathode of   a solid membrane reactor-PEMFC type (H$_2$ /H$_2$O$_2$ + CH$_4$) at room temperature. CH$_4$ was injected into the cathode together with a H$_2$O$_2$ solution. They observed that the catalytic layer adsorbed methane and H$_2$O$_2$ in the active sites, generating OH• radicals, that reacted with the methane, giving rise to methanol formation. Methanol production was higher at the potential range of 600–400 mV.

Figure 2. Fuel Cell Basic architecture: oxidation of methane a) at the anode side and b) at the cathode side. c) reactor plates, d) Membrane- electrode assemble, e) reactor type fuel cell.

Santos *et al* [58] carried out the partial oxidation of methane for cogeneration of power and chemicals on Pt/C, Pd/C and Ni/C in an alkaline anion exchange membrane fuel cell (AAEMFC). FTIR data suggests that methane was converted into small organic molecules such as methanol and formate at different potentials for Pt/C, Pd/C, and Ni/C. The highest conversion efficiency was about 20% at 0.3 V using a Pt/C catalyst, the maximum conversion over Pd/C was 17.5% at 0.15 V, associated with the formation of a thin layer of PdO on the catalytic surface.

In later work, Neto's Group [87] investigated the effect of Ni content in PdNi/C catalysts used as anode materials in AAEMFCs on the fuel cell performance and methanol selectivity. They observed that the increase Ni content enhances the energy generation and the formation of products more oxidized than methanol, probably due to the high ability of NiO_x to activate water monitored by electrochemical experiments with Raman spectroscopy *in situ* using a electrochemical cell shown in figure 3.
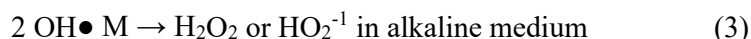

Figure 3. electrochemical cell for Raman spectroscopy in situ, described in Santos [87].

For partial oxidation of methane by the electrochemical method, water activation is necessary [48, 50], in which the hydroxyl radicals can be produced directly by the oxidation of water (equation 2) [88].

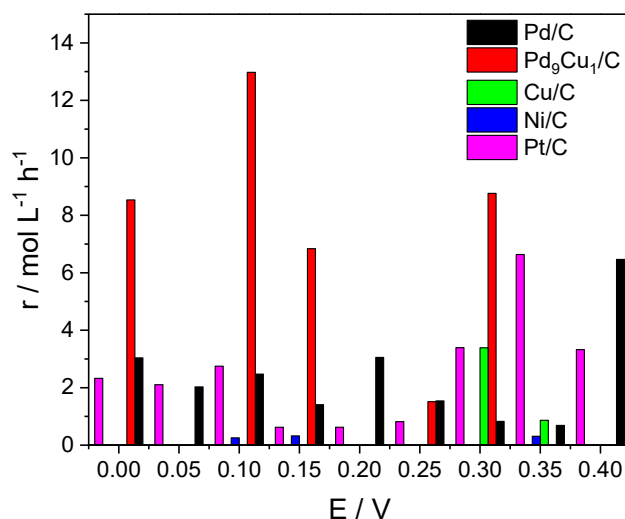$$M + H_2O \rightarrow M(OH\bullet) + H^+ + e^- \tag{2}$$

This radical can be detected indirectly by the formation of hydrogen peroxide generated by the chemical equilibrium of this radical, according to equation (3) [89]:

$$2\ OH\bullet\ M \rightarrow H_2O_2 \text{ or } HO_2^{-1} \text{ in alkaline medium} \tag{3}$$

The detection of H_2O_2 electrochemically is carried out by rotation ring disk electrode (RRDE) experiments. Garcia et al [53] used RRDE to give an indication of the most suitable percentage of Cu-complex, that should be used for the conversion of methane to methanol in alkaline medium. Godoi and co-workers [90] used this methodology to evaluate Pd_x-Cu_y/C electrocatalysts for methanol production from methane partial oxidation, and observed that the most active materials showed a content of H_2O_2 of about ~5 – 6 %,
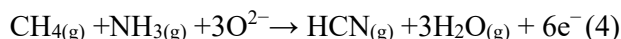
similar to that reported by Garcia [53]; materials generating a H_2O content higher than 6%, however, presented lower methanol production. For high H_2O_2 content, carbonate was detected in the products, inferring that the excess of ROS can lead to more oxidized products. The dependence on water activation alters the rate of reaction for methanol formation as shown in figure 4

Figure 4. Rate reaction for methanol production in potential function of transition metals electrocatalyst, Data extracted by [58, 87, 91].

5. HIGH TEMPERATURE FUEL CELLS

Solid oxide fuel cells (SOFCs), operating at high temperatures, thus minimizing polarization losses and of the effect of impurities, are good candidate for the cogeneration of electricity and chemicals. Kiratzis et [92] used a SOFC for the chemical cogeneration of hydrogen cyanide, used in the synthesis of adiponitrile, in fumigation, as insecticide, in electroplating, metallurgy and photography. This cell is formed by a tube of YSZ enclosed in a quartz tube, containing a porous Pt electrode as the cathode and a porous rhodium and platinum electrode as the anode, operating in the range 800-1000 °C, and using a mixture of methane and ammonia as the fuel, as the following anodic reaction:

$$CH_{4(g)} + NH_{3(g)} + 3O^{2-} \rightarrow HCN_{(g)} + 3H_2O_{(g)} + 6e^- \quad (4)$$

HCN selectivity depends on the fuel composition, temperature and current density. The cell selectivity to HCN could exceed 75%. The addition of oxygen to the fuel positively affects the cell selectivity to HCN. For the currents tested, the only by-products formed were CO and N_2 and a power density of *ca.* $0.01 Wcm^{-2}$ was generated. Selective oxidation of methane in SOFC was studied for co-generation of C2 hydrocarbons and synthesis gas.

Oxidative coupling reactions of methane, such as the synthesis of ethylene and ethane, aroused a lot of interest. Oxidation coupling of methane using a SOFC is an effective way to obtain C2 compounds and to generate energy at the same time [79, 93-95]. The use of SOFC reactor for co-generation of C_2 hydrocarbons and electrical power was first reported by Pujareand Sammells [93], in which a high selectivity to C_2 hydrocarbons (>90%) was achieved but with low conversion.

Otsuka et al. [94] used a SOFC with yttria-stabilized zirconia (YSZ) as a solid electrolyte for the oxidative coupling of methane. Among various catalysts, the most active and selective was $BaCO_3$ (86% C2 selectivity) deposited on Au anode. The effects of temperature on the rates of products and C2 selectivity was investigated: the formation rate of C2 compounds and C2 selectivity showed maxima at 1073 K. The higher the pressure of methane, the better for the cogeneration of C2 hydrocarbons and electricity. An increase in

the pressure of oxygen at the cathode also enhanced the rate of C2 formation and current, but the C2 selectivity did not change appreciably.

However, the conversion of methane and C2 yield are still very low (< 2%). Guo et al. [95] utilized a SOFC with 1 wt% $Sr/La_2O_3-Bi_2O_3-Ag-YSZ$ membrane for the oxidative coupling of methane. An increase in the current generated was accompanied by a decrease in C2 selectivity and an increase in methane conversion. Methane conversion decreased, C2-selectivity increased and current generated decreased slightly with a rise in total flow rates. CH_4 conversion and the current generated increased with a rise in oxygen concentration. High methane concentrations are the more suitable conditions for the cogeneration of electrical energy and ethane and ethylene.

Tagawa et al. [79] used a SOFC for a selective oxidation reactor and for the conversion of the energy of oxidation into electric power. $La_{1.8}A_{10.2}O_3$ anode catalyst was effective not only to prevent the total oxidation of methane, but also to prevent carbon deposition. A thin thickness YSZ composite was used as the electrolyte in the SOFC reactor. A temperature higher than 1200 K the yield of valuable chemicals (CO and C_2) were much higher than that of CO_2. The selectivity of CO_2 was always below 20%. Thus, this reactor can be regarded as a high selective oxidation reactor. The free energy change of the oxidation reaction has been directly converted into electric power with high efficiency.

The production of C2 hydrocarbons and electricity from oxidative coupling of methane in an SOFC reactor was simulated [96]. $La_{0.85}Sr_{0.15}MnO_3/8mol\%Y_2O_3-ZrO_2/La_{1.8}A_{10.82}O_3$ (LSM/YSZ/LaAlO) were used as a cathode, electrolyte and an anode, respectively. A plug flow reactor model (PFRM) was developed using kinetic parameters of the oxidative coupling of methane and the oxygen permeability through LSM/YSZ/LaAlO from the previous work [79]. Good agreements of power generation between experimental and simulation results were obtained. The effect of operating conditions was investigated. Methane conversion and C2 selectivity increase with increasing operating temperature. In this system, most of C2 production is ethylene, which is more favored than ethane. Methane conversion decreases with increasing methane feed flow rate while C2 selectivity slightly increases. Higher methane feed concentrations on the anode give higher power. The reactor performance increases at higher pressures. The results suggest that this SOFC system is an excellent reactor for C2 production and power generation simultaneously.

Wiyaratn et al. [97] evaluated chemicals and power cogeneration in an $Au/LaSrMnO_3//YSZ//LaSrMnO_3$ SOFC reactor. The e.m.f. and closed-circuit current increased to 0.86 V and 9.8 mA, (4.4 mW cm^{-2}) respectively at 850 °C. The e.m.f. was also close to the theoretical value of oxidation of methane. A 7% methane conversion and a 5.7% C2 hydrocarbons selectivity were observed when the air flow rate was 30 ml/min at 850 °C.

Some works were addressed to syngas production and electrical power generation from methane-fed SOFCs [98-101]. Syngas can be used as feedstock for hydrocarbon and methanol production. In particular, methane partial oxidation expressed by the following reaction:

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad\qquad (5)$$
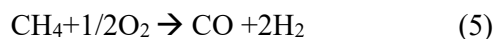
is attractive since it yields a synthesis gas with a molar ratio of 2. Synthesis gas with molar ratio of H_2 to CO of 2 is the most useful for the hydrocarbon and methanol synthesis. First, Yamada et al. [98] used a SOFC to obtain syngas by partial oxidation of methane. Co doped $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ was chosen as the electrolyte, since it was observed that doping small amount of Co was effective in increasing the oxide ion conductivity. The optimized composition for this electrolyte was $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.115}Co_{0.085}O_3$ considering the power density and the amount of oxygen leakage. Although the thickness of electrolyte with the above composition was as thick as 0.5 mm, a maximum power density and yield of synthesis gas were obtained at 242 mW cm^{-2} and 16%, respectively at 800 °C.

Then, Ishihara et al. [99] investigated the co-generation of syngas and electricity by using a single planar type SOFC. The electrolyte is a $LaGaO_3$-based oxide. $La_{0.6}Sr_{0.4}CoO_3$ and Ni were used as the cathode and the anode, respectively. A gaseous mixture of CH_4

and N_2 was employed as the fuel, while O_2 was used as the oxidant. The SOFC gave at 1000 °C a maximum power density of 526 mWcm^{-2}, which could be higher depending on doping, increasing the oxide ion conductivity. It was observed that doping $LaGaO_3$ based oxide with small amount of Fe or Co was highly effective for increasing oxide ion conductivity. Thus, the use of Fe or Co doped $LaGaO_3$ as electrolytes in SOFCs for methane partial oxidation would increase the power density and the yield of synthesis gas. The yield of synthesis gas was around 20% in all the cases studied.

Sobyanin and Belyaev[100] investigated methane-to-syngas oxidation and power generation over Pt electrodes in an SOFC reactor. The experiment was performed at a constant ratio of methane and oxygen flows ($CH_4/O_2 \approx 1.8$), so that an increase in methane flow rate was equivalent to an increase in the current (oxygen flow). Syngas productivity increases linearly with the increase of CH_4 flow rate (or current), whereas electric power passes through maximum. Zhang et al. [101] carried out the partial oxidation of methane to syngas at 700–800 °C in a SOFC with an Ni–SDC anode and an Sr- and Mg-doped lanthanum gallate in the composition $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) electrolyte. They observed that the co-generated syngas at H_2/CO ratio of 1.4–2.0 varied with applied current densities, CH_4 flow rates and operating temperatures. The cell voltage at 100 mA cm^{-2} and 800 °C was 0.90 V, i.e. about 90 mW cm^{-2} power density could be obtained. The cell operating at 50 mA cm^{-2} for 24 h almost showed no degradation of the cell performance.

Zhan et al. [102] used direct-methane SOFC (air,LSM-YSZ|YSZ|Ni-YSZ,CH$_4$) for power and syngas production simultaneously. Thermodynamic equilibrium analysis indicated that efficient methane conversion to syngas takes place for SOFC operating temperature >700 °C and O^{2-}/CH_4 ratios of ≈1. Fuel cells operated at $T \approx 750$ °C, $V \approx 0.4$ V, and $O^{2-}/CH_4 \approx 1.2$ yielded electrical power output of ~700 mW cm^{-2} and syngas production rates of ~20 sccm cm^{-2}. Stable cell operation without coking for >300 h was observed.

Pillai et al. [103] used direct-methane SOFCs to produce electricity and syngas. During initial operation at 750 °C, the cells produced 900 mW cm^{-2} and ≈90% methane conversion to syngas at a rate of 30 sccm/cm^2. However, the methane conversion decreased continuously over the first 30–40 h of operation, even though the solid oxide fuel cells (SOFC) electrical performance was stable. An additional catalyst layer on the anode yielded more stable methane conversion to syngas. Finally, the possibility of synthesis gas and power production from partial oxidation of CH_4 in SOFC was studied by Paloukis et al. through a numerical simulation [104]. By using a simple mathematical model, they showed the technological potentiality to cogenerate synthesis gas and electricity through the autothermal operation of an SOFC and its high performance with overall thermodynamic efficiency far above unity. This can be obtained by the SOFC operating under transient conditions by periodically reversing the flow through the monolithic reactor. Thus, the energy can be accumulated and trapped inside the reactor, maintaining the reactor at high temperatures (above the adiabatic temperature rise): in this way the electrochemical partial oxidation of methane into synthesis gas can proceed autothermally.

Brousas et al. [105] compared a regular SOFC plant (complete oxidation of methane to CO_2 and H_2O) with co-generation SOFC plants, producing ethylene and syngas. They observed that the rate of return for the regular fuel cell exceeded 25%, whereas that for the ethylene plant was about 21%, and that for the syngas plant was well behind at about 17%.

6. CH$_4$/CO$_2$ MIXTURES

CO_2 and CH_4 largely contribute to the greenhouse effect. Conversely, conversion of CH_4 into syngas using CO_2 not only provides a useful feedstock for hydrocarbon and methanol synthesis but also contributes to the mitigation of greenhouse gases. The dry reforming of CH_4 with CO_2, an endothermic reaction ($CO_2 + CH_4 = 2CO + 2H_2$), is a viable method to convert CH_4 into syngas. Commonly, SOFCs directly convert the chemical energy of the fuels into electricity with H_2O and CO_2 as the products, which is very promising in terms of the energy efficiency yet leads to CO_2 emission in practice.

On the other hand, SOFCs are able to perform in situ CO_2-CH_4 reforming and H_2 selective electro-oxidation, enabling a sustainable path to produce electrical power and syngas from CO_2 CH_4 mixtures. Hua et al. [106] developed an innovative CH_4–CO_2 dry reforming process to co-produce electricity and CO-concentrated syngas, which benefits the selective oxidation of H_2 in high performance proton-conducting solid oxide fuel cells (H-SOFCs). An additional layer, consisting of a $Ni_{0.8}Co_{0.2}$–$La_{0.2}Ce_{0.8}O_{1.9}$ (NiCo–LDC) composite, was incorporated into the anode support, forming a layered SOFC configuration. The multiple-twinned bimetallic nanoparticles showed enhanced activity towards in situ methane dry reforming. Compared to the conventional cell design, this layered SOFC demonstrated drastically improved CO_2 resistance as well as internal reforming efficiency (CO_2 conversion reached 91.5% at 700 °C), and up to 100 h galvanostatic stability in a CH_4–CO_2 feedstream at 1 A cm^{-2}. More importantly, H_2 was effectively and exclusively converted by electrochemical oxidation, yielding no CO_2 but CO concentrated syngas in the anode effluent. The maximum power density exceeded 910 mW cm^{-2} at 700 °C. The heat released by H_2 electrochemical oxidation fully compensated for that required by the extremely endothermic dry reforming reaction, making the entire process thermally self-sufficient. Moreover, the layered structure was beneficial in terms of decreasing coking and increasing CO_2 resistance of the SOFC in the mixed CO_2 and CH_4 feedstock. Summarizing, this H-SOFC showed outstanding electrochemical performances in CH_4–CO_2 feedstream, coproducing CO-enriched syngas with few CO_2 by-products.

Chen et al. [107] developed a multi-physical model to investigate the dry methane reforming (DMR) integrated SOFC running on CH_4 and CO_2 mixture to obtain the cogeneration of syngas/power. From the base case simulations at SOFC voltage of OCV and 0.7 V, they observed that the integration of proton conducting SOFC at 0.7 V could effectively enhance the syngas production than the OCV condition (4.8% improvement for CO_2 conversion and 21.6% for CH_4 conversion) and generate electricity (1.5 W) at the same time. The decrease of the voltage leads to higher electricity output, higher syngas production efficiency, and lower H_2:CO ratio of the product. However, the operating voltage is suggested to be higher than 0.5 V to prevent the undesired large temperature gradient. The inlet fuel flow rate showed a significant influence on the CO_2 and CH_4 conversion ratio.

The increase of flow rate gave rise to a low H_2 fraction, reducing the current density, and thus the temperature in DMR-SOFC. A collection of literature data on methane-fueled fuel cells including intrinsic parameters (catalysts and electrolyte), operational parameters (fuel composition and temperature), produced chemicals and maximum power density (MPD) values is reported in Table 1.

Table 1. A collection of literature data on methane-fueled fuel cells including intrinsic parameters (catalysts and electrolyte), operational parameters (fuel composition and temperature), produced chemicals and maximum power density.

Fuel Cell Type	Anode // cathode	Methane input	Eletrolyte	T / °C	Chemicals	MPD[a] / mW cm^{-2}	Ref
PEMFC[b]	Pd/C // Pt/C $Pd_{(10\%)}Au_{(10\%)}$ /C // Pt/C	Anode	Phosphoric acid doped Nafion membrane	110	-	0.8 2.5	[80]
PEMFC	Pd/C // Pt/C	Anode + $H_2O_{(g)}$	Nafion	80	Formate	0.55	[47]
PEMFC	PdZn/C // Pt/C	Anode+ $H_2O_{(g)}$	Nafion	80	Methanol, formate, formic acid	0.6	[81]
PEMFC	PdAu/C // Pt/C	Anode+ $H_2O_{(g)}$	Nafion	80	Methanol, formate, formic acid	1.0	[82]
PEMFC	Pt/C // PdAu/C	Cathode+ H_2O or O_2	$Sn_{0.9}In_{0.1}P_2O_7$	50-250	Methanol and CO_2	-	[84]

PEMFC	Pt/C // Pd–Au–Cu/C	Cathode + H_2O or O_2	$Sn_{0.9}In_{0.1}P_2O_7$	50-450	methanol	-	[108]
PEMFC	Pt/C // Pt/C	Anode + H_2O	$Sn_{0.9}In_{0.1}P_2O_7$	100-300	Methanol	-	[9]
PEMFC	Pt/C // Pt/C	Cathode + H_2O_2	Nafion	80	Methanol, formic acid and formaldehyde	70	[86]
AAEMFC [c]	Pt/C // Pt/C	Anode + KOH	KOH doped Nafion membrane	25	Methanol, formate	0.3	[58]
AAEMFC	PdNi/C // Pt/C	Anode + KOH	KOH doped Nafion membrane	25	Methanol, formate	0.13	[87]
AAEMFC	[6,6′-(2,2′-Bipyridine-6,6′-Diyl)bis(1,3,5-Triazine-2,4-Diamine)](Nitrato-O)Copper(II) Complex/C // Pt/C	Anode + KOH	KOH doped Nafion membrane	25	Methanol, formate	-	[53]
AAEMFC	Pt/Cu // Pt/C	Anode + KOH	KOH doped Nafion membrane	25	Methanol, formate	0.12	[90]
SOFC[d]	Pt or Rh // Pt/C	Anode + NH_3	YSZ	800-1000	HCN	10	[92]
SOFC	Sm_2O_3-LaSrMnO_2 // LaSrMnO_3	Anode	YSZ	760	C2 hydrocarbons	-	[93]
SOFC	Sr/La_2O_3-Bi_2O_3-Ag // Ag	Anode	YSZ	730	C2 hydrocarbons	6	[95]
SOFC	$Au/LaSrMnO_3$ // $LaSrMnO_3$	Anode	YSZ	850	C2 hydrocarbons	4.4	[97]
SOFC	Ni// $La_{0.6}Sr_{0.4}CoO_3$	Anode + N_2	$LaGaO_3$	1000	Syngas	526	[99]
SOFC	Ni–SDC// $Sm_{0.6}Sr_{0.4}CoO_3$	Anode	$La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$	800	Syngas	90	[101]
SOFC	Ni-YSZ// $La_{0.8}Sr_{0.2}MnO_3$	Anode	YSZ	750	Syngas	700	[102]
H-SOFC	Ni//$NdBa_{0.75}Ca_{0.25}Co_2O_{5+d}$	Anode + CO_2	$BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-d}$	700	CO-enriched syngas	910	[106]

[a] Maximum Power density. [b] proton exchange membrane fuel cell [c] alkaline anion exchange membrane fuel cell [d] solid oxide fuel cell.

7. MATERIALS FOR METHANE PARTIAL OXIDATION REACTION

The activation of methane is influenced by the characteristics of the catalysts, such as surface, structure, and composition. Transition metal oxides are the most commonly used in the conversion of methane-to-methanol [14, 109].

The surface-catalyzed activation of C-H bonds of methane for its selective oxidative coupling into ethane and ethylene or for its partial oxidation into methanol and formaldehyde is a subject of increasing interest. Many metal oxides have been claimed to be effective catalysts for these direct conversions of methane into the functionalized chemicals.

Nickel is a frequently used metal catalyst for methane conversion due to its availability and low cost. There are different strategies for stabilizing Ni particles in catalytic reactions against coking and sintering. Some of them include modifications of Ni particles by addition of a second metal, such as Co or Cu. Nematollahi and Neyts [110] by density functional theory (DFT) computations compared the reaction and activation energies of

Ni and NiN_4 embedded graphene on the methane-to-methanol conversion near room temperature. Thermodynamically, conversion of methane to methanol is energetically favorable at ambient conditions. Santos and co-workers [58] attributed the conversion of methane to methanol on a NiO catalyst in a solid electrolyte reactor – alkaline fuel cell type to the low potential for water activation, behavior not observed for Pt or Pd. Their oxides were appointed as a site for methane adsorption and activation [85].

Platinum is one of the most efficient catalysts used in the oxidation of small organic molecules due to its excellent catalytic properties. When considering the electrochemical properties of Pt, it should be remembered that Pt surface structure alters the rate of adsorption and oxidation of the adsorbed molecules [48, 69, 111], i.e., terraces on Pt (100) can active C-H bond at low energy [112]. Hsieh and Chen [113] studied Pt black for methane oxidation to CO_2 and report the shift of onset potential for methane oxidation in function of pH.

Boyd and co-workers [48] found platinum to be the most active catalyst for the electrochemical oxidation of methane under ambient conditions. To understand the reaction mechanism and the factors that determine catalyst activity, they used experimental and theorical studies and found that methane activation step is thermochemical (i.e., $CH4_{(g)} \rightarrow CH3^* + H^*$). Nandenha et al. [86] used a Pt cathode catalyst in a solid electrolyte reactor – fuel cell type to activate H_2O_2 species and convert methane to methanol.

The catalytic activity of palladium can be enhanced by supporting it on carbon materials. Carbon materials such as carbon nanotubes (CNTs), activated carbon (AC), and reduced graphene oxide (rGO) were employed as the catalyst support, and palladium-gold (Pd-Au) nanoparticles were used as active center. The Pd-Au/CNTs catalyst showed outstanding methanol productivity and selectivity [111]. Compared with the PdAu/CNTs, Pd-Au supported on functionalized carbon nanotubes (CNTs-n) by a treatment of nitric acid enhances the methanol selectivity, but decreases the methanol productivity [73].

Serra-Maia and co-workers [109] observed that methane oxidation to methanol occurs in a significant excess of hydrogen peroxide by inhibiting the activity of AuPd nanocatalysts. Jin and co-workers [114] reported a catalyst system formed by Pd and Au strengthened by hydrophobically covered zeolite, to generate hydrogen peroxide for immediate reaction with methane at mild temperatures. Santos and co-workers attributed the Pd activity for methanol electrosynthesis to the formation of a thin layer of PdO on the catalytic surface [58].

The methane activation with in-situ H_2O_2 formation was successfully demonstrated in a microcapillary containing Au-Pd nanoparticles embedded in its silica-coated walls using a microchannel reactor. The direct methane activation with in situ generation of H_2O_2 promoted methanol formation [32, 66]. The high affinity for oxygen of gold facilitates the breakdown of H_2O_2 in OH•, which would be the activator of the C-H breakage [73, 115, 116].

A bifuncional catalyst, with a carbophilic site and sites capable of activating water, as exemplified in figure 5 can be used for maximize the conversion of the hydrocarbon into products, as a cited by Godoi [90].

A screening of different metal oxides for the oxidative coupling of methane (OCM) by lattice oxygen, using first and second transition metal oxides (V, Cr, Co, Cu, Zr and Mo) and some lanthanide oxides (La and Ce) was carried out by Hassan and co-workers [71] . The OCM activity was correlated with the surface amount of a low 1s binding energy (O1s, 526–527 eV) oxygen species on the catalyst, as well as its energy separation from the lattice oxygen.

Iron is extensively applied as a catalyst for the conversion of methane to formaldehyde [117], however, mild conditions make it more selective for less oxidized products such as methanol [118]. Yang et al [6], in a study of visible-light-driven selective oxidation of methane to methanol on amorphous FeOOH coupled m-WO_3, reported the active role of Fe in the H_2O_2 decomposition mechanism. The same role was attributed to Fe by Zuo et al[119] in a study about selective oxidation of methane with H_2O_2 over Fe-silicalite-1.

Copper is   active for partial oxidation of methane into methanol, due to its high activity   for water dissociation at 177 – 227 °C, a key process to C-H break [120], and the direct conversion increases in the presence of zeolites [14].

Sushkevich and co-workers[25] studied methane oxidation over copper-exchanged zeolites *via* chemical looping. Methoxy species and carbon monoxide are the primary reaction products formed directly from methane. Partial poisoning with water after the oxygen activation and before the methane reaction leads to the decrease of methanol yield, which is associated with the blockage of at least two copper atoms in the active site per one water molecule. In addition, they found that the poisoning is reversible and the increase in methane pressure increases CuMOR (copper mordenite) activity due to competitive adsorption on active sites. Alvarez and coworkers[19] also studied the   partial oxidation of methane to methanol over a Cu-MOR catalyst at 200 °C. They observed that at the optimum reaction conditions 52 % of the adsorbed methane is converted to methanol. Metal organic frameworks (MOFs) are a class of hybrid crystalline materials, composed of metal ions/clusters linked together by organic ligands [121] which have a high surface area, microporosity that would act as reaction zones, limiting the residence time of the molecules of interest in the catalytic site, making the reaction more specific [122].   These materials have been applied for methane oxidation: Garcia et al. [53] used a [6,6'-(2,2'-Bipyridine-6,6'-Diyl)bis(1,3,5-Triazine-2,4-Diamine)](Nitrato-O)Coppe r(II) complex for the   cogeneration of chemicals and power from methane.
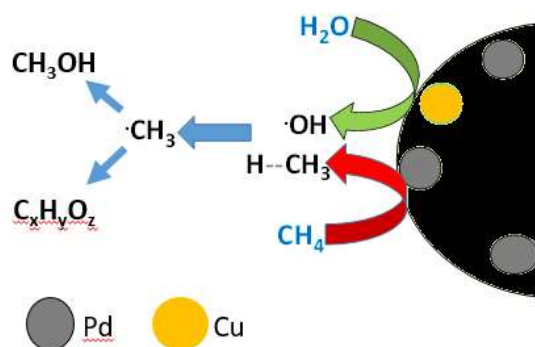
Figure 5. Partial methane oxidation with bifunctional PdCu/C electrocatalyst.

Another material very active for water dissociation is   ceria[120]; this oxide also acts as an oxygen buffer [123] in a thermoprocess. Lustemberg et al. [123] showed that low-loaded Ni/CeO$_2$ (111) system activates CH$_4$ at 25 °C and then, with the help of water, which prevents sequential cleavage of C−H bonds and at 177 °C   methanol was obtained with a conversion of about 35%.

Metal-exchanged zeolite has been reported as efficient catalyst to partial oxidation of methane to methanol using only oxygen and water at low temperatures [62, 124]. Kang and co-workers carried out selective oxidation of methane into methane oxygenates, including methanol and formic acid, over Fe-zeolites and Pd/activated carbon in the presence of molecular hydrogen as a reducing agent using a liquid-phase with molecular oxygen[125].

Kang and co-workers. [125] observed the partial oxidation of methane using Fe-zeolites prepared via an ion-exchange method to immobilize the homogeneous Fe catalysts into the zeolite matrix. Rocha et al [42] applied the bismuth vanadate (BiVO$_4$) microcrystals for conversion of methane preferencially in methanol, explain that this selectivity is echoed in reports for the same reaction via photocatalyzed pathways.

8. OPPORTUNITIES AND OUTLOOK

This review highlighted the ability of fuel cells to convert the chemical energy of methane in valuable chemicals and electric power. Also if it is an interesting field related to the commercial development of fuel cells, few works are present in the literature. Although knowledge has been obtained on different types of electrocatalytic systems capable of catalyzing the selective conversion of methane, the tailoring of electrocatalytic systems for methane conversion to value-added chemicals such as C2 compounds and methanol with high efficiency and high selectivity still remains a challenge. An improvement of catalyst activity and stability and reduced cost of catalysts are a challenge in fuel cell reactors for opening the opportunity in commercialization. Moreover, as SOFCs are operated at 800-1000 ºC, materials with high activity and stability at high temperatures are required. Thus, a development of anode catalysts for an oxidative coupling of methane in SOFC becomes an important goal to improve the conversion, selectivity, yield and stability of the reactor. For example, it is necessary to develop suitable catalysts capable of generating reactive oxygen species to activate the conversion of methane to methanol with a low over-potential and a high current at the same time. The understanding into the active sites and phases resulting from the selective oxidation or oxidative coupling of methane are useful to develop more efficient catalysts for the electrocatalytic methane conversion. However, a deep knowledge into the roles of electrochemical reaction environments in the conversion of methane and the formation of products are still lacking.

Economic studies showed that exothermic reactions involving inexpensive raw materials and products with respect to the cost of electricity are good candidates for electro-cogeneration. Different electrocogeneration processes have been identified to be interesting from a commercial point of view. Further studies in such fields are desirable because the advantage of different electrocogeneration processes depend on the relative value of chemicals to power of the historical moment, with probable better suitability than in chemical or electrolytic reactors.

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