Review

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Review

Recent Advances in the Catalytic Conversion of Methane to Methanol: From the Challenges of Traditional Catalysts to the Use of Nanomaterials and Metal-Organic Frameworks

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Abstract: Methane and carbon dioxide are the main contributors to global warming, being the methane effect twenty-five times more powerful than carbon dioxide. Although the sources of methane are diverse, it is a very volatile and explosive gas. One way to store the energy content of methane is its conversion to methanol. Methanol is liquid under ambient conditions, easy to transport and, apart from its use as an energy source, it is a chemical platform that can serve as a starting material for the production of various higher value-added products. Accordingly, the transformation of methane to methanol has been extensively treated in the literature, using traditional catalysts as different types of zeolites. However, in the last years, a new generation of catalysts have emerged to carry out this transformation with higher conversion and selectivity, and more importantly, under mild temperature and pressure conditions. These new catalysts typically involve the use of a highly porous supporting material such as zeolite, or more recently, metal-organic frameworks (MOFs) and graphene, and metallic nanoparticles or a combination of different types of nanoparticles that are the core of the catalytic process. In this review, the characteristics, the catalytic mechanisms, reactors, and the main results of these catalysts are presented as a way to overcome the challenges found in traditional catalysts.

Keywords: methane oxidation; catalysis; global warming; nanoparticles; metal-organic frameworks; renewable energy; zeolite, methanol synthesis

1. Introduction

Global warming has raised many concerns during the last few decades. Undoubtedly, the major cause is the release of greenhouse gases into the air [1]. Among such gases, methane and carbon dioxide make the biggest contribution to the global problem. Furthermore, when compared by mass, methane has around 25 times more effect on global warming than carbon dioxide. Hence, scientists have given a sharper focus on the conversion of methane to more beneficial chemicals, that is, higher hydrocarbons or liquid fuels [2].

The production of methanol, formaldehyde, propanol, and other compounds through various methods has been gaining more interest to unlink its production from non-renewable sources. So far, diverse studies have been carried out for the catalytic conversion of methane to syngas and methanol on different transition metals including Ir, Pt, Rh, and Ru [3–5], perovskites [6,7] and single metal atoms incorporated in supports of such as graphene [8], metal-organic frameworks [9,10] and metal oxides [11,12]. The conversion of methane into methanol is normally carried out through direct and indirect pathways. While through an indirect route, via a two-step procedure, methanol is formed by a catalytic reaction from syngas ($CO+H_2$), which is produced via oxidation or steam reforming of methane, methane also can be directly converted to methanol through a direct route. Since steam reforming is a thermodynamically unfavorable reaction due to its intrinsic endothermic nature and

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therefore is immensely energy intensive, the indirect route may not be the best option especially when it comes to industrial applications.

Thus, direct conversion of methane under mild conditions has recently become the main objective of researchers' studies. Common direct pathways so far have been partial oxidation of methane (POM) to methanol and acetic acid, conversion of methane to olefins, aromatics through a non-oxidative route (NOCM), and oxidative coupling of methane (OCM). Whereas through OCM and NOCM routes other products rather than methanol are generated, the path which leads to a high methanol yield is stated to be partial oxidation of methane (POM) which is a thermodynamically favorable process since the change in Gibbs free energy for such reactions is negative using oxygen as the oxidant [13–16].

In general, there exist several challenges to the direct conversion of methane to methanol. One is the strong C-H bond in methane, which requires severe conditions such as high temperatures to be cleaved. Due to high costs, this issue questions the industrial applicability of the process. Moreover, it poses the overoxidation of the produced methanol to more thermodynamically favorable products such as carbon monoxide and dioxide. The reason for this phenomenon is the dissociation energy of the C-H bond in methanol is lower than that of methane. In other words, as temperature increases, methanol is more susceptible to oxidation than methane. Consequently, the selectivity for the formation of methanol will decrease due to the generation of other products. In this respect, a catalyst that may activate the C-H bond of methane and simultaneously impede the methanol oxidation would be of significant value [17,18]. In fact, methane monooxygenase enzymes existing in aerobic methanotrophic bacteria are naturally capable of converting methane to methanol under ambient conditions thanks to their intrinsic catalytic system [19]. Hence, emulating such a natural catalytic system for the conversion of methane to methanol has attracted researchers' interest.

For this purpose, scientists have tried to take advantage of zeolite-based catalysts, metal-organic-frameworks (MOFs), and graphene, which inherently have a large number of active sites as well as being perfect hosts for the incorporation of active sites, specifically those existing in nano-catalysts, resembling those found in the monooxygenase enzymes [20–22]. Such materials have gained interest for the catalytic conversion of methane to methanol in the last years. One of the underlying reasons for the incorporation of nano-catalysts into porous media is to overcome a significant obstacle regarding these nano-catalysts high surface energy, which causes their aggregation and instability during the catalytic reaction and consequently their poor catalytic performance at short-medium times.

In this review, a quick revision of the significant factors in the catalytic conversion of methane to methanol (activation of C-H bond in methane and its connection to methanol selectivity, reaction conditions such as temperatures, pressure, and residence time) is presented. Afterward, a deep review of the recent studies that have taken advantage of three emerging supports: graphene, zeolite, and specifically MOFs is developed, especially when they are doped with the proper nanomaterials. These emerging materials have been demonstrated to be the most competent candidates due to their properties, and they will be extensively presented and compared in terms of methanol yield and selectivity as well as the conditions of these emerging catalytic systems such as temperature, pressure and reaction time. Finally, a brief review on catalytic reactors is presented.

2. Conversion of methane to methanol routes

2.1. Direct and indirect routes

As previously commented, conversion of methane into value-added chemicals such as methanol, olefins, aromatics, and oxygenated compounds can be achieved through two different routes as summarized in Figure 1. On one hand, the indirect route for methane to methanol conversion is a two-step process: 1) partial oxidation or steam reforming of methane to syngas ($CO+H_2$), and 2) catalytic conversion of syngas to methanol. It is known that the steam reforming step is an endothermic reaction (ΔH^0_{298K} = +206.2 kJ mol^{-1}), with an operating temperature between 800-1000°C. Therefore, the process is extremely energy demanding. Hence, scientists have attempted to

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circumvent the intermediate syngas production step and directly convert methane at low temperatures. Partial oxidation of methane (POM) to methanol and acetic acid, conversion of methane to olefins and aromatics through a non-oxidative route (NOCM), and oxidative coupling of methane (OCM) are among well-known direct routes for methane conversion reaction.

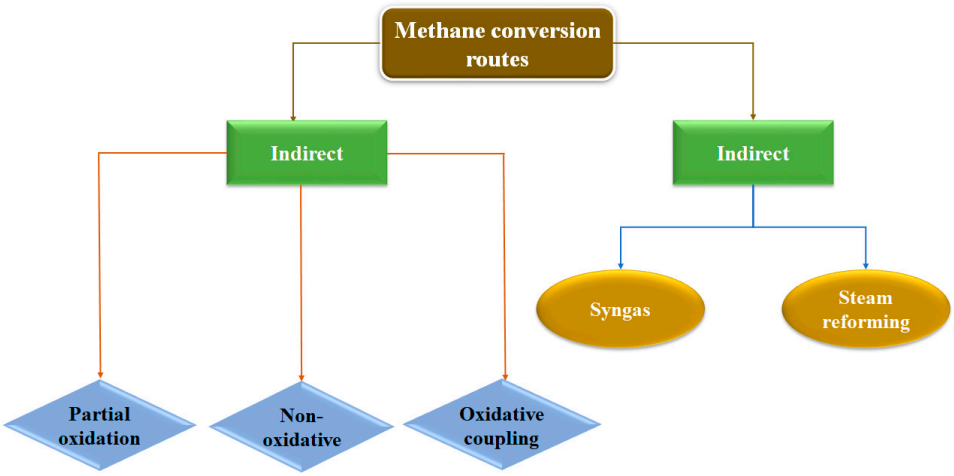

Figure 1. Routes for methane conversion

Partial oxidation of methane is an interesting energy-saving process that converts methane to profitable oxygenates such as methanol, formic acid, formaldehyde, and methanol precursors. This route, using oxygen as an oxidant, is thermodynamically more convenient to be carried out (Equation 1). However, NO and H_2O_2 can be also exploited as oxidants in POM [13–16]:

$$2CH_4 + O_2 \rightarrow 2CH_3OH \ \Delta G^0_{298K} = -223 \text{ kJ mol}^{-1} \quad (1)$$

In addition to this, different works have been published regarding the use of zeolite-based catalysts that can contribute to the formation of methanol and acetic acid at low temperatures by activating methane and oxygen [23], although the reaction needs to be done at low methane conversion to preserve the target products from overoxidation.

Moreover, other studies have been aimed at addressing the challenges of partial oxidation of methane to methanol. Some examples to overcome this phenomenon use different approaches such as the activation of methane in a liquid phase using H_2O_2 as an oxidant for the conversion of methane to methanol over copper-promoted Fe-ZSM-5 [24], a stepwise process for the conversion of CH_4 over Cu-containing zeolite using H_2O as oxidant [25], a new modified Au-Pd/zeolite catalyst for enhanced methanol productivity by *in-situ* generated hydrogen peroxide at low temperature (70 °C) [26], a hybrid system combining metal oxide (MO_x)-coated glass beads as an alternative to thermal catalysis for the production of liquid oxygenates at atmospheric pressure and room temperature [27], a selective formation of methanol as unique oxygenate in a CO-assisted direct catalytic reaction over Cu-CHA zeolite catalyst [28], and the use of water for the mild oxidation of methane to methanol with high methanol selectivity over a gold single atom on phosphorous nanosheets under light irradiation [29].

On the other hand, NOCM (non-oxidative coupling of methane) is a promising route for the direct transformation of methane to hydrogen and ethane despite the thermodynamically unfavorable nature of the reaction (Equation 2):

$$2CH_4 \rightarrow C_2H_6 + H_2 \ \Delta G^0_{298K} = 68.6 \text{ kJ mol}^{-1} \quad (2)$$

As mentioned, OCM (oxidative coupling of methane) is another direct route for methane conversion. During this route through Equations 3 and 4, the methane is primarily converted to C_2H_4 and C_2H_6 in presence of an oxidant (Equation 3):

$$4CH_4 + O_2 \rightarrow 2C_2H_6 + 2H_2O \ DG^0_{298K} = -320.8 \text{ kJ mol}^{-1} \quad (3)$$

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$$2C_2H_6 + O_2 \rightarrow 2C_2H_4 + 2H_2O \quad DG^0_{298K} = -254.9 \text{ kJ mol}^{-1} \qquad (4)$$

As observed, the change in Gibbs free energy is negative and this route is thermodynamically favorable. Regarding OCM and NOCM, many studies have been presented in the literature [30].

2.2. Challenging parameters in methane to methanol catalysis

As previously commented, many catalysts have been developed and used for the direct partial oxidation of methane to methanol. However, there are several challenges regarding this catalytic process such as activation of the C-H bonds of methane, the need for activation of catalysts, and the conditions of temperature and pressure necessary for acceptable methanol productivity and selectivity. In other words, developing a selective and efficient catalyst encounters a major challenge in the simultaneous control of the kinetics of methane transport, activation, hydroxylation, and the desorption and removal of methanol. All these issues will be discussed in this section.

2.2.1. Activation of C-H bonds and its connection to selectivity

The activation of C-H bonds in methane requires high temperatures in the traditional catalytic systems. However, under these conditions, the produced methanol can be overoxidized to thermodynamically more favorable products. In addition, the polar structure of methanol compared to the non-polar methane molecule contributes to the easier oxidation of methanol than methane since methanol molecules are more readily absorbed on the surface of the catalysts and activated for oxidation. Therefore, an ideal catalyst would be one that can facilitate methane activation and, at the same time, hamper methanol oxidation [17,18]. In this regard, a large number of strategies have been proposed in biological, homogenous, and heterogeneous catalytic systems.

In nature, methane monooxygenase enzymes are existing in aerobic methanotrophic bacteria that directly convert methane to methanol under ambient conditions due to their ability to control the transport of oxygen, methane, and protons to the active centers. Hydrophobic cavities linked together in the methane monooxygenase open the access gate to the oxygen and methane into the active center via the hydrophobic passage. Then, the activation of the oxygen in the metal center of the monooxygenase proteins leads to the formation of an oxidative intermediate being able to perform the cleavage of the strong C-H bonds of methane [19]. When the enzymes rearrange their conformation, cavities dissociate from each other resulting in the blockage of the hydrophobic passage and consequently restricting back diffusion and overoxidation of methanol while simultaneously opening separated hydrophilic pores for methanol to be removed. This biological system leads to an exceptionally high selectivity for methanol and can be an example of the control of mass transfer to and from the active sites. Therefore, it can be concluded that the presence of a hydrophobic cavity in the proximity of catalytic sites might lead to a higher affinity towards methane than methanol [31]. However, such interesting ideas cannot be simply translated into simple homogenous catalysts [32]. In a homogenous catalytic system, the approach adopted is to functionalize methane in form of methyl ester that is more stable in this reaction environment. Afterward, this methyl ester is easily hydrolyzed for the recovery of methanol [33]. Regarding heterogeneous catalysis, the published studies have been focused on the investigation of materials that have a reactivity and a morphology resembling those found in methane monooxygenases. The exploitation of zeolite-based catalysts and incorporation of different types of MOFs and graphene supports are among these attempts, and they will be discussed later.

2.2.2. Activation of catalyst

One of the principal challenges in methane conversion to methanol is that the reaction has a stoichiometry 1:1 [34]. This has originated the so-called “stepped conversion” process. In this procedure, the catalysts are firstly activated with an oxidant at a high temperature and then exposed to methane to form methanol at a lower temperature. Finally, methanol is extracted utilizing steam flow. In this way, methanol selectivity is higher since the catalyst is exposed to the oxidant and methane separately. However, there exist inevitably considerable obstacles such as the fact that the

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industrial technologies need high reaction energy barrier for methane conversion, so there are energy-intensive processes when it comes to practical and industrial terms. [35].

2.2.3. Temperature and pressure

Temperature and pressure are crucial parameters for methane oxidation to methanol in terms of the activation of catalysts and the cleavage of the methane C-H bond. In addition to the cost of having high temperatures, the issue of overoxidation of methanol at high temperatures is also noteworthy. Hence, developing catalysts that may directly convert methane to methanol under mild conditions is essential. As reported in the literature, various catalysts including zeolites, MOFs, and graphene, jointly with nanomaterials immobilized in these supports, are the most used systems to achieve this goal. These catalysts and their working conditions are presented in Tables 1 and 2. It can be observed that many novel catalysts are using relatively low temperatures. However, maintaining high catalytic activity and a methanol selectivity under these mild conditions is a field of the present research, and new findings are regularly published.

3. Traditional catalysts

Inspired by the natural methane monooxygenase mechanism in methanotrophic bacteria, zeolites have gained popularity as catalysts for the direct conversion of methane to methanol (Table 1). In 1997, Kudo et al. investigated the catalytic activity of ZSM-5 as the first zeolites used for the partial oxidation of methane[36]. The maximum selectivity for methanol was not more than 10% and the major product of the catalysis was carbon dioxide with a selectivity of more than 80% at 0.01 bar methane partial pressure and 600-700°C after 1 hour. Fe-ZSM-5 is among the pioneer zeolites that have been extensively investigated by researchers during the last two decades for the catalytic conversion of methane to methanol [37–45]. Michalkiewicz studied both sodium and hydrogen forms of Fe-ZSM-5 at atmospheric pressure and 350-650°C using oxygen as the oxidant and achieved 74% selectivity for methanol using Fe-NaZSM-5 [37]. Panov et al. investigated the catalytic activity of FeZSM-5 by increasing the concentration of α-sites at 160 °C and sub-ambient pressure using N_2O as oxidant and achieved a methanol yield ranging from 34 to 160 μmol/g_{cat} and a 76 to 95% methanol selectivity [38]. Hammond et al. investigated Fe-containing MIF-type zeolites more deeply and showed that these zeolites can be used for oxidation of methane at high catalytic rates and high selectivity at mild temperatures in the aqueous phase using hydrogen peroxide as oxidant [42]. Xu et al. could accomplish iron and copper modified ZSM-5 catalysts through chemical vapor impregnation, which demonstrated excellent selectivity (92%). In addition, they showed that the catalysts do not deactivate during continuous reaction while maintaining a high selectivity [40]. Over the last decade, copper-exchanged zeolites are the ones that have been more extensively studied [46–57]. Lobo et al. investigated the catalytic performance of Cu-SSZ-13 for methanol production using oxygen and nitrous oxide as oxidants at temperatures ranging from 300 to 450°C and achieved the maximum methanol yield of 13 μmol/g_{cat} at 200°C when N_2O was used for peroxidation. They attributed such results to higher concentrations of active species formed by N_2O at lower temperatures [58]. Tomkins et al. studied the effect of methane activation temperature with oxygen and methane partial pressure on methanol yield in the isothermal cyclic conversion of methane to methanol over Cu-exchanged zeolite at low temperatures [52]. The maximum methanol yield obtained was reported to be more than 100 μmol/g_{cat} at 36 bar and 450°C. Sushkevich et al. took advantage of water as the oxidant and proved that water molecules played two important roles in the catalytic procedure. Water facilitates the regeneration of active sites and the desorption of methanol while achieving 97% of methanol selectivity [25]. Ohyama et al. examined the catalytic performance of several Cu zeolite catalysts using oxygen and water as oxidants at 300°C for 24 hours [51]. Recently, Fang et al. overcame the main obstacle regarding the activation of methane, demonstrating the ability of $[Cu_2(\mu\text{-}o)]^{+2}$-ZSM-5 active sites for the activation of methane towards high selectivity to methanol. They investigated the significant role that water plays in enhancing methanol formation as well as the role of chlorine in promoting the production of active sites and facilitating the production of methanol through enhancing desorption [59]. Yu et al. achieved high

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methanol yields of 431 $mol_{MeOH}.mol^{-1}_{Fe}$ per hour at low temperatures with 80% methanol selectivity over a Cu-Fe(2/0.1)/ZSM-5. They realized that Cu species in these catalysts facilitate the formation of OH radicals which react rapidly with CH_3 radicals to form CH_3OH [46]. In summary, using traditional zeolites, a maximum methanol yield of 5866 $\mu mol/g_{cat}$ has been obtained with a high (79.7%) methanol selectivity at 50 ºC and 30 bar [59].

Table 1. Catalytic conditions of methanol yields and selectivity for various traditional zeolites used as catalyst for the conversion of methane to methanol.

Catalyst	Reaction time (min)	Temp. (˚C)	Pressure (bar)	Oxidant	Methanol yield ($\mu mol/g_{cat}$)	Selectivity (%)	Side products	Ref.
ZSM-5	60	600-700	0.01	O_2	-	10	CH_2O CO_2 O_2	[36]
FeHZSM-5	2.5 s (Contact time)	630	atmosphere	O_2	-	16.51	CO_2 HCHO	[37]
FeNaZSM-5	0.5 s (Contact time)	390	atmosphere	O_2	-	74.37	CO_2 HCHO	[37]
FeZSM-5	8-165	160	0.1	N_2O	160 34	76 95	C_2H_5OH C_2H_4O	[38]
Fe-ZSM-5 (84)	30	50	30.5	H_2O_2	74.4	10	HCOOH CH_3OOH	[42]
ZSM-5 (86)	30	50	30.5	H_2O_2	5.55	72	HCOOH CH_3OOH	[42]
Fe-silicalite-1 (86)	30	50	30.5	H_2O_2	65.18	19	HCOOH CH_3OOH	[42]
Fe-Cu-ZSM-5 (30)	Steady state = 60 min	50	20	H_2O_2	81 ($\mu mol\ g_{cat}^{-1}\ h^{-1}$)	92.2	CO_2	[40]
Cu-SSZ-13	60	200	0.3	N_2O	13.1	24	CO_2 HCHO	[58]
Cu-MOR	30	200	36	O_2	56	100	-	[52]
Cu-MOR	30	200	7	H_2O	0.204 mol/mol_{Cu}	97	H_2O H_2	[25]
Cu-ZSM-5-Cl	30	50	30	H_2O_2 H_2O	5866	79.93	CH_3OOH $HOCH_2OOH$	[59]
Cu-ZSM-5-N	30	50	30	H_2O_2 H_2O	3216	73.31	CH_3OOH $HOCH_2OOH$	[59]
Cu-ZSM-5-Ac	30	50	30	H_2O_2 H_2O	2851	74.78	CH_3OOH $HOCH_2OOH$	[59]
Cu-Fe(2/0.1)/ZSM-5	30	50	30	H_2O_2	431 mol/mol_{Fe}	80	$HOCH_2OOH$ CH_3OOH CO_2	[46]

4. Nanoparticles-based novel catalysts

Metal nanoparticles have gained a strong interest for catalytic purposes during the last few years. However, nanoparticles possess high surface energy resulting in thermodynamically

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instability and susceptibility to aggregation during the catalytic reactions. To achieve satisfactory performance, critical parameters such as size, shape, and dispersion need to be controlled. In this regard, a variety of surface capping agents such as polyvinylpyrrolidone (PVP), dendrimers, and oleyl amine have been exploited. However, these capping molecules have been shown to attach to metal nanoparticles with very strong interactions that adversely affect the catalytic process. One promising solution to have properly dispersed metal nanoparticles with a clean surface in comparison to traditional zeolite is their incorporation in porous materials such as zeolites, graphene, or MOFs as shown in Table 2 and Figure 2 [20–22].

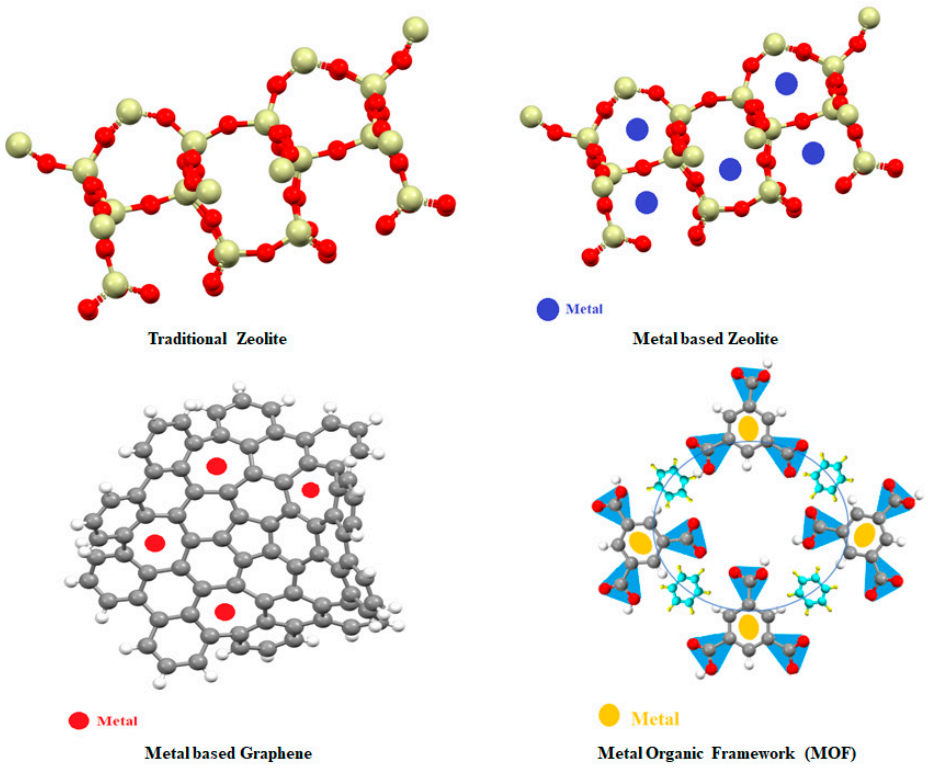

Figure 2. Catalysts based on nanomaterials for methane conversion to methanol.

4.1. Nanomaterials used with zeolite

Metal nanoparticles have been tried to be loaded on the solid supports surface to achieve more efficient heterogeneous catalysts. The solid supports can electronically and geometrically alter the nanoparticles through strong metal-support interactions and provide a high surface area for metal species to disperse [60–62]. A majority of the solid supports used so far are Al_2O_3, SiO_2, MgO, ZrO_2, TiO_2, and CeO_2. However, the supported metal oxide nanoparticles have also demonstrated several negative effects such as low activity and selectivity. In addition to this, their deactivation can occur due to sintering, leaching, and coke formation under harsh conditions. On the contrary, fixing metallic nanoparticles within zeolite crystals brings the advantage of satisfactory catalytic activity with high selectivity. This happens through several mechanisms. For instance, immobilizing metal nanoparticles within a stable framework such as zeolite would lead to the stability of these metal nanoparticles against sintering and leaching. Additionally, the diffusion of reactant and product can be controlled: the reactant adsorption on the metal nanoparticles can be adjusted and the reactant and product can be sieved through the pores of the zeolite. When metal nanoparticles are localized in zeolites, their micropores can function as diffusion channels for the reactant and product. This results in shape selectivity [63,64]. So far, very few studies have been carried out regarding nanoparticles supported by zeolite structures for methane to methanol conversion. Shan et al. introduced rhodium supported on ZSM-5 zeolite for oxidation of methane to methanol under mild conditions [65]. In a batch water system, with CH_4, CO, and O_2 pressure of 30 bar at 150°C, this material was tested for catalytic performance evaluation. After an hour, an exceptional methanol

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yield of 1224 μmol g_{cat}^{-1} was obtained. However, the selectivity of methanol was low (8.78%), and the reaction seemed to favor the production of acetic and formic acid. Lewis et al. supported nanoparticles of gold and palladium on HZSM-5 and used them for the oxidation of methane to methanol under 30 bar methane pressure and at 50°C of temperature in an aqueous system containing H_2O_2 for 30 minutes and achieved a methanol yield of 51.1 μmol g_{cat}^{-1} and relatively low methanol selectivity of 33.6% [66]. Therefore, metal nanoparticles loaded on the surface of zeolite proved several advantages such improvement of metal sinter resistance and enhancement of the selectivity. In addition, the catalysis of metal nanoparticles incorporated into zeolites has the capability of regeneration performance [67].

4.2. Graphene-based catalysts

Graphene, a single or a few layers of two-dimensional (2D) sp^2 bonded carbon sheets, possesses a unique structure and extraordinary properties such as high electrical and thermal conductivity, mechanical flexibility, charge-transport mobility, and extremely high surface area, excellent chemical stability, and optical transparency [68,69].

Over the last two decades, graphene has been exploited by scientists for various purposes [70–73]. Among them, a single individual atom anchored on graphene-based materials has been tested as a novel catalyst since it fulfills the expectations regarding cost-effective catalysis and high surface activity while reducing the use of noble metals. Recently, single metal atoms doped in monolayer graphene surfaces have been used in catalytic reactions for different purposes because of their well-defined site, unsaturated coordination environment, and high atom efficiency [74,75]. Traditionally, supporting noble metal atoms such as Pt and Pd on metal oxides or metal surfaces has been the focus of researchers' investigation [76,77]. In the case of graphene, Fe, Pd, Pt, Ni, P, and Si are typically dopants that can substitute carbon atoms in graphene sheets to boost their properties [78–85]. In addition, graphene sheets can be tailored by introducing defects in form of heteroatoms (e.g., N, B or P) in their structure to accelerate the catalytic reactions occurring on the surface and adjust the electronic properties of the catalysts [78,86–90].

Regarding the conversion of methane to methanol, many materials such as metal nanoparticles have been immobilized in the different forms of graphene. Despite these advances, the activity and productivity of the methane to methanol seemed to be still dissatisfactory, although considering their unique properties, as graphene should be an ideal support. This is what is reported in other applications. Although graphene has been utilized for a great variety of applications, very few works have been carried out using graphene-based catalysts for methane to methanol oxidation. Wang et al. embedded several metal atoms of Co, Mn, Ni, W, and V in graphene based on density functional theory (DFT) calculations and showed that Co atoms enhanced the catalytic performance in comparison to other metals [91]. Impeng et al. [92,93] investigated theoretically the direct oxidation of methane to methanol on Fe-O modified graphene using N_2O as an oxidant with results being comparable to the other previous catalysts. Sanjubala et al. studied the usage of free and graphene-supported single transition metal Cr, Mn, Fe, Co, and Cu atoms for the activation of methane, and discovered that Co atoms supported in graphene could be highly effective in the activation of methane [94]. Yuan et al. presented a two-step reaction mechanism for the direct oxidation of methane to methanol on a single atom C-embedded in graphene using N_2O as oxidant and they could conclude that the catalysts would be highly active and will possess good selectivity under mild conditions [95]. Chang et al. exploited DFT to study the catalytic reaction mechanism of methane oxidation to methanol on Bi-functional graphene-oxide-supported platinum nanoclusters. They concluded that this catalyst would have a good performance for the methane to methanol reaction and showed that graphene oxide plays an improving role in the catalysis reaction by tuning the interactions between the surface and the adsorbed species [96]. Cui et al. discovered that on O-FeN_4-O active sites of graphene-confined single iron atoms, methane can be converted to methanol at room temperature. They showed that the O-FeN_4-O can activate the C-H bond of methane to form methyl radicals with a very low reaction energy barrier that can be further converted to CH_3OH and CH_3OOH [97]. Recently, He et al. studied the direct conversion of methane to methanol on Pd-Au

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nanoparticles supported on carbon materials such as carbon nanotubes (CNTs), activated carbon (AC), and reduced graphene oxide (rGO) using a gas mixture of oxygen and hydrogen as oxidant under moderate water aqueous condition and achieve methanol productivity of 139 μmol g_{cat}^{-1} and methanol selectivity of 73.2% [98]. Since few studies in this regard have been conducted for methane to methanol oxidation and some of them are exclusively theoretical, more investigation and experimental studies on graphene utilization as a support for various nano-catalysts to improve the catalytic activity are necessary. Up to date, the best yield obtained using graphene and nanoparticles is 139 μmol/g_{cat} at 50 ºC and 33 bar [98].

4.3. Nanomaterials used with MOFs

4.3.1. General characteristics

MOFs offer considerable opportunities for the incorporation of active sites for catalysis that mimic methane monooxygenases, with high tailorability of the pore structures and environmental conditions in the proximity of the active sites. In this regard, there is already a considerable amount of literature in which various aspects of MOF are well reviewed: synthesis and post-synthetic modifications [99–101], actives sites and their characterization [102], structure [103–106], the inclusion of defects [107–110], water stability [111,112], scale-up of synthesis [113–115], multiple functionalities [116,117], application for CO_2 and biomass conversion [118–120]. In this review, a deep comparison of the MOF-based catalysts for the conversion of methane to methanol is performed in terms of methane conversion, methanol selectivity, and space-time yield (STY) (Table 2). Most of the published works on MOFs are based on their porous crystalline structure that can be manipulated in terms of size, geometry, and functionality. The structure of MOFs has been reported to have a high porosity of more than half of the MOF volume. These advantages, together with their high surface area ranging from 1000 to 10000 m^2/g, that exceeds the traditional porous materials like zeolite and carbon-based materials, make them an excellent candidate for various purposes, especially in catalysis applications [121].

4.3.2. Potentials and limitations

In general, MOFs offer benefits when used for catalysis. Catalysis by manifold functional groups and also bifunctional or simultaneous catalysis owing to MOFs potential for synthesis and post synthesis modifications, high catalytic reaction rates per unit volume due to their high internal surface area and active sites density, their potential for shape selective catalysis and having large pores to allow fast transport of product molecules and large reactants due to their pore structures tailorability, and also their Potential for large scale catalytic applications are among the most significant ones [122–124]. Despite these significant advantages, the types of active sites in the structure of MOF are limited, which leads to a limited catalytic activity [125]. However, in addition to their inherent active sites, MOFs porous structure can be a host for the incorporation of catalytically active sites.

Metal nanoparticles have become more and more interesting for catalytic purposes during the last few years. However, as commented before, nanoparticles have high surface energy resulting in their thermodynamically instability and susceptibility to aggregation during the catalytic reactions. One promising solution to achieve properly dispersed nanoparticles with a clean surface is their incorporation in porous materials [20–22]. In this case, MOFs have been the best choice for this purpose. Here, we review the studies that use nanoparticles embedded in MOFs as catalysts for the partial oxidation of methane to methanol. Osadchii et al. incorporated isolated Fe units into Al-based MOF which successfully imitated the catalytic behavior of soluble methane monooxygenase (sMMO) enzyme for C-H activation of methane [126]. Through two different synthesis routes, they prepared two different MOF catalysts. The catalytic activity of catalysts was tested under mild conditions in an aqueous environment of water using H_2O_2 as the oxidant at temperatures lower than 80 °C for 1 hour leading to highly selective methanol and with only negligible amounts of overoxidized products such as methyl peroxide, formic acid, and carbon dioxide. Ren et al. proposed the in-situ formation of Cu

oxides clusters in UiO-bpy channels and achieved methanol space-time yield and selectivity of 24.33 μmol/g_{cat}, and 88.1% with the side product of ethanol, under ambient pressure at 200°C after 3 hours. This work included three steps which were the activation of the catalyst by O_2 followed by loading of methane and finally extraction of methanol with steam [127]. Xia et al. took good advantage of the combination of catalytic activities of platinum and polyoxometalate via their immobilization into UiO-67 and achieved methanol (12.4%), ethanol (71.3%), and acetic acid (15.9%) under conditions of CH_4 pressure of 50 bar and temperature 60 °C after 2 hours [128]. They reported 3.5% methanol and 74.9% ethanol after 4 hours which indicates that methanol is oxidized over time. In addition, the low methane conversion was reported to be due to methane's low solubility in an aqueous solution. Yang et al. introduced an extraordinary MOF-derived mixed hybrid oxide, IrO_2/CuO, which they synthesized using a bottom-up tactic. Firstly, Ir nanoparticles were synthesized and then a Cu-containing MOF, Cu-BTC, was utilized as a CuO precursor as well as a host for Ir nanoparticles to be encapsulated to achieve Ir@Cu-BTC which was further calcinated in the air at 500 °C to produce the final catalyst. IrO_2 is reported to play a methane activation role being capable of facilitating the C-H bond cleavage. After the catalysis of methane by this catalyst under the conditions of feeding 3 bar CH_4 / 1 bar air at 150 °C after 3 hours, they achieved 872 μmol/g_{cat} of methanol. Also, they reported a methanol yield of 1937 μmol/g_{cat} when increasing the CH_4 pressure to 20 bars [129]. Xu et al. loaded AuPd nanoparticles to ZIF-8, Zn(2-methylimidazole)$_2$ to achieve AuPd@ZIF-8 catalyst, and the methanol yield and selectivity were reported 21.7 μmol g_{cat}^{-1} per hour and 21.9% under CH_4/Ar pressure of 30 bar and an average temperature of 50 °C after 30 minutes [130]. In addition, the catalytic activity of AuPd@ZIF-8 was compared to the nanoparticles of Au, Pd, AuPd, as well as Au@ZIF, and Pd@ZIF. The earlier comparison well proved the effective role MOFs play in the catalytic performance of the catalyst. Baek et al. synthesized three different MOF catalysts by incorporating three different metal binding ligands into MOF-808 and obtained methanol productivities of 31.7, 61.8, and 71.8 μmol g_{cat}^{-1} per hour after methane oxidation at 150 °C for 1 hour. The catalysts were reported to have been pretreated with 3% N_2O/He for 2 hours at 150 °C [10]. As reported, at temperatures below 150 °C, methanol was the only product of the methane oxidation, while increasing the temperature seemed to have pushed the methanol to be overoxidized into CO_2. Moreover, the catalysts appeared to fail in their recyclability, which is attributed to the strong bond that water molecules form with the active sites, which leads to the catalyst's deactivation. Zheng et al. stabilized Cu-Oxo dimers into NU-1000 MOF for methane oxidation. The catalytic tests for methane to methanol oxidation by this catalyst were carried out at 150-200 °C under pressure varying from 1 to 40 bar and the reaction time range of 30-180 minutes to observe the effect of contact time, temperature, and pressure on the catalytic activity of the catalyst. As a result, methanol yield and selectivity varied from 1.5 μmol g_{cat}^{-1} and 70% (150°C, 1 bar, 30 min) to 15.81 μmol g_{cat}^{-1} and 90% (200°C, 40 bar, 180 min) [131]. Zheng et al. also used NU-1000 MOF to stabilize Cu-Oxo clusters and used it as a catalyst for methane oxidation. The conditions of the catalytic test were approximately the same and the results were 17.7 μmol g_{cat}^{-1} methanol and 46% selectivity for methanol and dimethyl ether altogether [132]. Hall et al. presented for the first time, the roughly exclusive formation of methanol on the Fe^{2+} active sites of MIL-100(Fe) as a heterogeneous catalyst at mild temperature and sub-ambient pressure with only a trace amount of carbon dioxide produced [133]. In this study, the catalyst was pretreated for 12h with N_2O at 250 °C and then methane and N_2O were introduced (0.015 bar methane/ 0.016 bar N_2O) at 200 °C. Almost every Fe^{2+} sites were reported to contribute to the catalytic conversion of methane to achieve a methanol yield of 0.2 μmolg_{cat}^{-1}. Imyen et al, interestingly, proposed a catalyst by the simultaneous exploitation of MOF and zeolites (Fe-ZSM-5@ZIF-8), in which the zeolite is responsible for the methane catalysis while the MOF adsorbs the methane [134]. primarily, the catalyst was heated at 100 °C to eliminate the surface moisture and then methane gas (3% CH_4/He) at 1 bar was fed at 4 ml/min at 50 °C for 2 hours to adsorb the methane. Then, the methane feeding was stopped, and the reaction was allowed to continue at 150 °C for the conversion of methane to methanol on the catalyst's surface for 0.5 h. To collect the produced methanol, the catalyst is said to be flushed by N_2 (10 mL/min) for 2 hours. The methanol was also gathered through steaming, 40 mL/min of N_2 bubbling into deionized water at 50 °C. The maximum methanol yield was reported to be 0.12

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μmol.g_{cat}^{-1} when steaming was used for the methanol collection. In summary, using nanoparticles embedded in MOF's, the best yield is71.8 μmol/gcat at 150 °C.. Although metal nanoparticles such as copper and iron based zeolite can oxidize methane at temperature range of 200 to 600 °C, the product is complex from gas-phase reaction. Even thought, the use of platinum based complexes can oxidize methane at milder conditions, but the disadvantages of this type of catalyst are the sensitivity to water and the difficulty of methanol extraction from aqueous solutions. Hence, metal- organic frameworks overcome these problems due to the large surface area, tolerability, pores structures, excellent steward to catalyst as well as the conversion of methane to methanol at low pressure and temperatures [130].

Table 2. Catalytic conditions and methanol yields and selectivity for metal organic frameworks (MOF), and zeolite used as supports and nanomaterials as active catalyst in the conversion of methane to methanol.

Catalyst	Reaction time (min)	Temp. (°C)	Pressure (bar)	Oxidant	Methanol yield (μmol/g_{cat})	Methanol selectivity (%)	Side products	Ref
Rh-ZSM-5	60	150	30	O_2	1224	8.78	CH_3COOH HCOOH	[65]
1%Pd/HZS-5 (30)	30	50	30.5	H_2O_2	51.1	33.6	CH_3OOH HCOOH CO_2	[66]
MIL-53 (Fe, Al)	60	≤60	30.5	H_2O_2	-	-	CH_3OOH CH_2O_2 CO_2	[126]
Cu_xO_y@UiO-bpy	180	200	1	O_2	24	88.1	C_2H_5OH	[127]
Uio-67-Pt-Z	120	60	50	H_2O_2	-	12.4	C_2H_5OH CH_3COOH	[128]
MOF derived IrO_2/CuO	180	150	3	H_2O	872	95	C_2H_5OH CH_3COOH	[129]
AuPd@ZIF-8	30	90	15	H_2O_2/O_2	10.85	21.9	CH_3OOH HCOOH	[130]
Au@ZIF-8	30	90	15	H_2O_2/O_2	0.7	-	CH_3OOH HCOOH	[130]
Pd@ZIF-8	30	90	15	H_2O_2/O_2	1.2	-	CH_3OOH HCOOH	[130]
MOF-808-His-Cu	60	150	-	N_2O	31.7	100	-	[10]
MOF-808-Iza-Cu	60	150	-	N_2O	61.8	100	-	[10]
MOF-808-Bzz-Cu	60	150	-	N_2O	71.8	100	-	[10]
CU-NU-1000	30-180	150-200	1-40	O_2	1.5 -15.81	70-90	C_2H_5OH CO_2	[131]
CU-NU-1000	180	200	1	O_2	17.7	≤46	C_2H_5OH CO_2	[132]
MIL-100(Fe)	120	200	0.015	N_2O	0.2	≥98	CO_2	[133]
Fe-ZSM-5@ZIF-8	300	150	1	-	0.12	-	-	[134]

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5. Stability and reusability of catalysts

An undoubtedly significant issue is the question of stability and reusability of the catalyst. As observed, in most of the studies of this review, the stability and reusability of the catalyst have not been investigated except for a few works [126,127,129–131,133]. Generally, these studies showed good results for long operation times in a range of few hours. Although this operation time may seem low, it is equivalent to thousands of residence times. However, in industrial applications, the catalyst needs to be stable under the catalytic procedure circumstances for more than one cycle of catalytic reaction for batch mode and longer times for continuous systems while maintaining a good product yield and selectivity. Hence, it is a matter to study in further research, and a clear lack of this topic.

6. Reactors used for methane to methanol catalysis

Methane conversion to methanol and valuable products is normally carried out using different types of reactors. The most widely used are fixed-bed, fluidized-bed, well-coated and membrane reactors as illustrated in Figure 3.

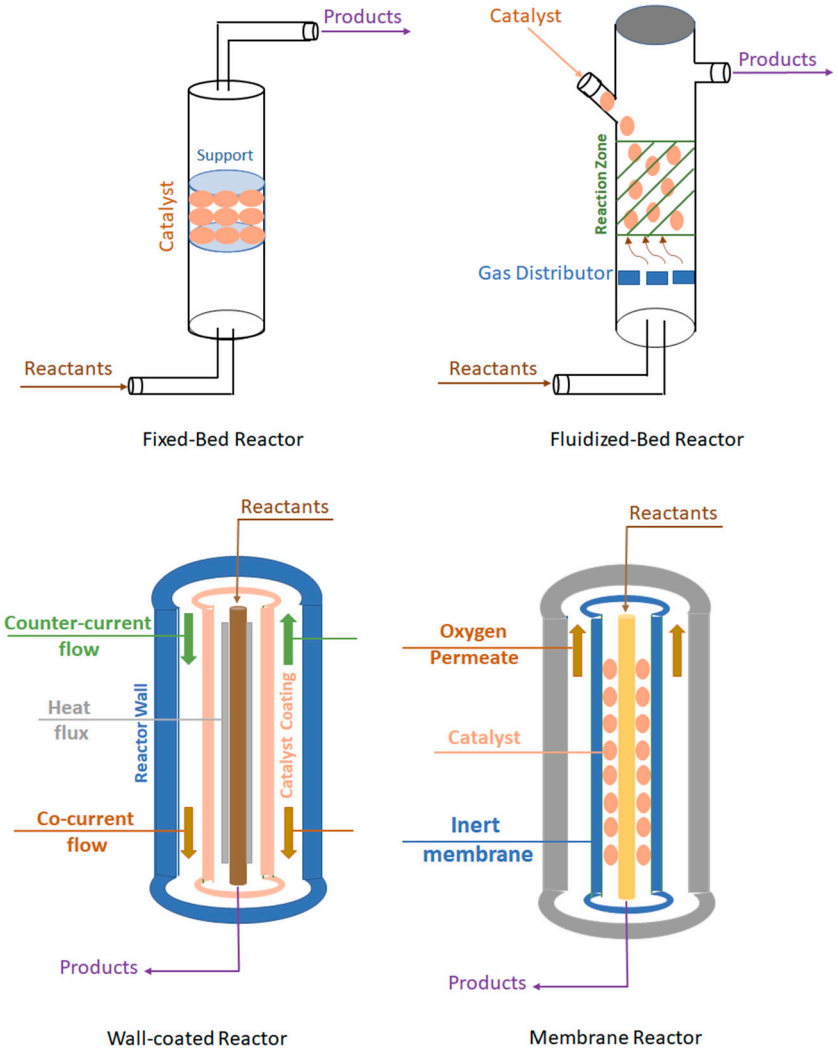

Figure 3. Reactors used for the catalytic conversion of methane to methanol.

6.1. Fixed-bed reactor

Fixed-bed reactor is the most commonly used reactor where a certain amount of the catalyst is fixed in a defined location inside the cylindrical tube of the reactor [135]. This type of reactor can be used in industrial processes as well as for kinetic and catalyst activity studies [136]. Based on one or

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more catalysts application in the reactor, this type can be used as a single or multi stages reactor. In addition, spherical, cylindrical, powder, or randomly shaped catalysts can be used in this reactor. So, the fixed-bed reactor has benefits such as low-cost, high catalyst spatial density, and ease of operation [137]. However, drawbacks of this type are the drop of high pressure, low surface area, and poor distribution of the temperature. Therefore, further studies are performed in recent decades using the reversal flow mode to improve the capability of heat transfer while maintaining the catalyst activity without overheating the catalyst. Recovering the heat from the reversal flow reactor was found the most efficient way for methane conversion by optimizing the catalyst bed position, the flow, and the heat exchanger [138].

6.2. Fluidized-bed reactor

This is also a very common type of catalytic reactor where the catalysts are fluidized during the reaction. The materials inside the reactor are supported by the porous plate so that an efficient contact between the catalyst and the reactants is achieved due to the high gas flow. The main benefits of this type of reactor in comparison to the fixed-bed reactor are the uniform temperature distribution and high methane conversion with the increase of the temperature [139]. However, the methane conversion seems to decrease by increasing the initial concentration of methane and an increase in the gas velocity causes the weight loss of the catalyst after the long-term operation increases [140].

6.3. Wall-coated reactors

The enhanced mass/heat transfer, lower pressure drops and increased catalyst contact surface area by depositing a catalyst layer on the reactor wall surface are the main benefits of the so-called wall-coated reactor [137]. Four sub-types of wall-coated reactors are studied in literature: tubular, monolithic, plate-type and micro/mini channel plate type reactors.

6.3.1. Tubular reactor type

The performance of this reactor is based on the heat transfer flux, which is normally cold air to remove the release of reaction heat, and the fins are coated with the catalyst that are located at the end of the tube reactor [141]. This design could reach up to 100% conversion of methane when either a 16-finned-tube reactor with high gas velocity or 10-finned-tube reactor with lower velocity are used. Moreover, the catalytic efficiency of the reactor and the improvement of the diffusion rate of the reactants can be controlled using thinner catalysts and suitable surface area [142].

6.3.2. Monolithic reactor type

The monolithic reactor is suitable for power generation in gas turbines and purification of the emitted pollutants due to its high thermal stability, high rate of mass/ heat transfer and high surface-to-volume ratio [143]. Various types of substrates such as metallic fibers or foams and different shapes of the interconnected channels as triangles or squares could be adapted in different applications. For instance, a high specific surface area could be obtained using a monolithic reactor with triangle interconnected channels [144].

6.3.3. Plate-type reactor type

In this reactor, the co-current and the counter-current flow modes occur on the opposite sides of the same plate reactor, combining methane combustion and methane steam reforming reactions. The overlapped temperature zone with the proper co-current mode eliminates hot spots. Besides, the use of folded sheet reactors with rectangular adjacent channels proved the improvement of the heat transfer and avoided high heat loss [145].

6.3.4. Microchannel plate type reactor

In the last years, better catalytic performance has been reported using the microchannel reactor where the methane conversion takes place on the wash-coated catalyst deposited on the multiple straight channels due to the excellent heat/ mass transfer and high surface area of the microchannel [146,147]. Also, the reactants can more easily access the inner surface of the microreactor using the porous catalysts that are prepared by the electrodeposition method [148]. The main drawback of this reactor type is the need for extra heat to compensate for the heat loss.

6.4. Membrane reactor

Here, the catalysts are deposited on the surface of the membrane and this type is one of the most common reactors for methane oxidation due to the efficiency of oxygen permeation, which reacts with methane when it passes through the membrane with air [149]. The efficiency of the reactor depends on the oxygen permeability, flow rate of methane and air and temperature [150]. Improvement of the methane conversion was conducted using two-pass ion transport where the oxygen permeation was performed in two stages. In addition, the methane conversion was found to be higher when the configuration of the counter-current flow in this mode of ion transport is used in comparison to the co-current flow configuration [151]. Although high conversion of methane could be achieved using this type of reactor varying the partial pressure of oxygen permeability, it has a limitation in industrial applications due to its high cost.

7. Conclusions

The present review highlights the main items related to the chemical conversion of methane to methanol. This reaction has gained progressive interest because of the properties of methanol, which are, to be easy to store and use as an energy source and as a platform chemical for a multitude of other reactions in organic chemistry. This chemical conversion presents a main bottleneck: finding a suitable catalyst that can provide satisfactory results in terms of conversion and selectivity. Regarding this, a new generation of catalysts based on nanomaterials embedded in novel support materials such as MOFs seems to be the best candidates to be explored, also in terms of durability and reuse of the catalyst, which, jointly with economic issues, should be a topic of further research. One significant matter which needs to be considered is the stability and reusability of the catalysts. Most of the studies have not investigated the reusability of the catalyst. Therefore, the author recommends researchers consider this important issue in future studies.

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