tungsten

titanium

Metal (Mo, W, Ti) Carbides for Dry Reforming

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Dry reforming of hydrocarbons (DRH) is a pro-environmental method for syngas production. It owes its proenvironmental character to the use of carbon dioxide, which is one of the main greenhouse gases. Transition metal carbides (TMCs) can potentially replace traditional nickel catalysts due to their stability and activity in DR processes.

molybdenum

dry reforming catalysts metal carbides

1. Introduction

Synthetic gas, called syngas, is one of the most important intermediates for the production of fuels, acetic acid, ammonia, and methanol, and the Fischer–Tropsch process. It is a mixture of carbon monoxide and hydrogen, and very often carbon dioxide. Among the technologies for syngas production, steam reforming, dry reforming (DR), partial oxidation (PO), and autothermal reforming (ATR) can be distinguished ^[1]. Among the mentioned technologies, steam and dry reforming are highly endothermic processes. Their standard enthalpies are +206 kJ/mol and +247 kJ/mol, respectively. In contrast to DR and ST, the enthalpies of ATR and PO are negative as a result of the ongoing oxidation reaction. Each of the processes is characterized by other process parameters and the hydrogen-to-carbon monoxide ratio in the outlet stream (see **Table 1**). Dry reforming of hydrocarbons (DRH) is a pro-environmental technique for synthetic gas generation. DR processes involve the processing of hydrocarbons, mainly methane, and carbon dioxide, which are the most important greenhouse gases. Furthermore, dry reforming is a suitable method to manage biogas emitted during biomass fermentation or digestion of anaerobic microorganisms ^[2]. The hydrogen-to-carbon monoxide ratio in the outlet stream is around 1.0. A ratio of n = 1 is favorable in many processes, such as ammonia, methanol, dimethyl ether, and selective Fisher–Tropsch synthesis. Furthermore, DR progresses under atmospheric pressure, allowing the use of an apparatus that does not have to withstand high pressures ^{[3][4][5][6]}.

 Table 1. Important parameters of syngas technologies.

Process	Main Reaction	Enthalpy _∆ H ⁰ _{298 K} [kJ/mol]	Pressure [bar]	H ₂ /CO Ratio
Dry reforming of methane (DRM)	$CH_4 + CO_2 = 2CO + 3 H_2$	+247	1	1:1
Steam reforming of methane (STM)	$CH_4 + H_2O = CO + 3H_2O$	+206	3–25	3:1

Process	Main Reaction	Enthalpy _∆ H ⁰ _{298 K} [kJ/mol]	Pressure [bar]	H ₂ /CO Ratio
Partial oxidation of methane (POM)	CH ₄ + ½ O ₂ = CO + 2H ₂	-35.2	100	2:1
Autothermal reforming (ATR)	$CH_4 + H_2O = CO + 3H_2O$ $CH_4 + \frac{1}{2}O_2 = CO + 2H_2$	+206 -35.2	1–50	1:1 or 1:2

on metal oxides such as aluminum oxide, magnesium oxide, silicon oxide, zirconium oxide, lanthanum oxide, and magnesium-aluminum spinel with alkali metal promoters ^{[3][7][8]}. The use of nickel catalysts is economically justified because of their relatively low price and high activity, comparable to the activity of noble metals. The endothermic character of the DRM reaction (+247 kJ/mol) requires a large amount of heat to be provided, which causes sintering and growth of agglomerates of active phase particles, leading to a reduction in the specific surface area, a reduction in the number of active sites, and increased deposition of carbon structures including coke and unsaturated polyaromatic hydrocarbons with H/C ratios less than unity ^[7]. With regard to the above factors, current worldwide research in the field is focused on the development of new catalysts with higher activity and stability in the dry reforming process ^[8].

Transition metal carbides (TMCs) have attracted much interest because of their high thermal stability, good electronic properties, and catalytic activity. TMCs are a wide group of catalysts currently developed for many catalytic processes, such as hydrocarbon reforming, hydrogenation, and CO oxidation. Under DRM conditions, they participate in recarburization–oxidation cycles. In the oxidation reaction, carbon dioxide is reduced into carbon monoxide. On the other hand, during the recarburization reaction, carbon atoms from methane cracking and carbon monoxide disproportionation are built into the carbide structure, thus preventing the formation of carbon deposits on the surface of the catalyst ^{[9][10]}.

2. Metal Carbides

2.1. Tungsten Carbide

Tungsten carbide contains two separate crystalline phases, W_2C and WC, which, due to a different structure, are characterized by different ranges of temperature stability ^[11]. The β -W₂C phase is stable at lower temperatures compared to α -WC and contains several structural modifications due to the different arrangement of carbon atoms ^[11]. Meanwhile, the α -WC phase has a hexagonal structure in which the carbon atoms are in the center of the tungsten trigonal body. Thus, in its most basic form, the crystals of WC have a hexagonal structure, and it is a fine gray powder. It is characterized by high strength, fracture resistance, and resistance to high temperature and abrasion, as well as high melting (2600–2850 °C) and boiling points (6000 °C) ^[12]. Due to its properties, WC is widely used, among others, in the chemical, armament, and electronics industries, in the production of cutting mechanical tools, and in abrasives and surface coatings ^[13]. In addition, tungsten carbide exhibits catalytic properties, and the efficiency of WC as a catalyst is similar to that of platinum ^[14], its use being associated with much higher costs. Therefore, the subject of many studies is the use of WC in chemical and electrochemical

catalysis, which allows one to reduce the cost of the process by partially or completely replacing noble metals with tungsten carbide.

2.2. Molybdenum Carbide

Molybdenum carbide is characterized by high thermal stability, good thermal and electrical conductivity, resistance to corrosion, hardness, and a melting point above 2000 °C. Due to their properties, molybdenum carbides have found applications in catalysis, electrocatalysis, anti-creeping alloys, and as cutting tool parts. Molybdenum carbide has already found application in the synthesis and decomposition of ammonia, hydrocarbons, oxidation, hydrogen generation, hydrogenation, photocatalytic oxidation, water splitting, hydrodesulfurization, methane aromatization, and hydrocarbon reforming. The catalytic properties of molybdenum carbide are very comparable to the activity of noble metals [15][16][17][18].

2.3. Titanium Carbide

TiC, similar to WC, is one of the high-melting compounds, which is widely applied in many industries as a component of carbidosteels, hard-alloy and cutting tools, and abrasive materials, as well as in the manufacture of ceramics and alloys ^[19]. Titanium carbide-supported catalysts are used in CO₂ hydrogenation and methanol synthesis ^{[20][21]}, electrochemical reduction of CO₂ to CH₄ ^[22], oxygen reduction reactions ^{[23][24]}, water–gas shift reactions ^[25], CO oxidation ^[26], and many others. Generally, the use of TiC as a support has been shown to be effective in improving the stability of Pt-based electrocatalysts ^[27]. It has been reported that titanium carbide can also be used as a catalyst in dry reforming.

3. The Use of Metal Carbides for Dry Reforming

3.1. Tungsten Carbide

Compared to noble metals, nickel-based catalysts have a lower cost; therefore, they are commercially used in the methane reforming ^[28]. However, their major disadvantage is that during the decomposition of CH₄ and CO disproportionation, they can be deactivated by forming coke ^{[29][30]}. Therefore, alternative catalysts are sought, the use of which would eliminate the existing problems. Transition metal carbides such as WC have been shown to be good catalytic materials. They have a very high catalytic activity (at a level similar to that of noble metals such as Ru and Pt) ^[31], are stable and highly selective in a wide range of reactions, and are also resistant to the presence of contaminants such as sulfur and chlorides in the reaction medium. They are also highly resistant to carbon deposition ^[32]. Generally, the order of stability of group V and VI transition metal carbides in the case of methane dry reforming is as follows: Mo₂C ≈ WC > VC > NbC > TaC, at the reaction pressure of 8 bar, and Mo₂C > Ir > WC > Pd >Pt, in the case of 2 bar ^{[31][33]}. Therefore, it should be noted that carbides of the Mo₂C and WC types show stable activity only at relatively high pressures ^[33]. At atmospheric pressure, a significant limitation is the deactivation of such catalysts through oxidation with carbon dioxide ^[34], which occurs through dissociative CO₂ adsorption and oxidation of the carbide with oxygen atoms ^[35]. Thus, the stability of the catalyst is determined by

the ability to convert the oxide back to carbide, which is assisted by high temperatures. Consequently, tungsten or molybdenum carbide can act as redox catalysts in dry methane reforming, but it is worth bearing in mind that at atmospheric pressure, the reaction of CO_2 with this type of carbide is more favorable than the reaction of CH_4 with the oxides formed ^[33].

Comparing the phases of WC that occur, it may be concluded that the hexagonal close-packed β -W₂C is the most active, while the hexagonal α -WC is slightly less active, and the fcc WC_{1-x} is twofold less active ^[36]. β -W₂C nanoparticles are characterized by a disordered structure and the presence of carbon vacancies ^[37], as a result of which they have greater stability compared to α -WC nanorods ^{[36][38]}. According to research conducted by Zhang et al. ^[39], during dry methane reforming, oxidation of β -W₂C by CO₂ readily occurs, resulting in phase transformation to α -WC. The following steps of β -W₂C oxidation can be described by Equations (1)–(4).



However, according to Yan et al. ^[40], two-sided reactions are possible when using tungsten carbide in the dry methane reforming process. The first reaction is the oxidation of WC by CO_2 (Equation (5)), and the second is the reverse gas–water shift reaction (Equation (6)).



In addition, an increasing amount of research is currently focused on discovering new methods of tungsten carbide synthesis leading to various types of morphologies such as nanoparticles ^[41], nanosheets ^[33], and nanorods ^[42].

The results of these studies indicate a definite relationship between the characteristics of the obtained particles and the catalytic activity. However, there are very few works that try to explain this relationship. This may be due to significant synthetic limitations, especially since a large part of this research is not experimental ^{[43][44]}.

3.2. WC Combined with Nickel and Cobalt Particles

Tungsten carbide is used as a catalyst in dry methane reforming, usually in combination with nickel or cobalt, because the addition of a second metal can modify the catalytic performance and structure of this carbide ^{[45][46]}. Despite the unique properties of WC, this compound has a surface with a strong oxygen affinity. As a consequence, this leads to blockage of the surface in the event of irreversible adsorption of oxygen-containing substances, which, in turn, results in a reduction in catalytic activity ^[47]. Therefore, to avoid this problem, core–shell systems are used, that is, WC cores covered with a metallic coating that prevents oxidation of the carbide surface, thus promoting structural stability ^[48]. Co-WC and Ni-WC are stable, active, and selective catalysts in dry methane reforming ^[49].

According to Barbosa et al., higher CO₂ conversion values compared to CH₄ conversion in dry methane reforming are obtained using Ni-Mo₂C and Ni-WC catalysts ^[50]. This is probably due to the reactions occurring, including the Boudouard reaction (Equation (7)), as a result of which the forming CO₂ is activated in the carbide (Equation (8)), leading to the oxidation of WC (Equations (9) and (10)) and the conversion of CO with steam (Equation (11)), in which part of the hydrogen obtained reacts with CO₂, resulting in a lower H₂/CO ratio and in increased CO₂ conversion. However, regardless of the presence of nickel and the Ni/W ratio, the less stable β -W₂C is transformed into α -WC during dry methane reforming, according to Equations (3)–(6) ^[39].



In the case of cobalt tungsten carbide (Co_6W_6C), the addition of carbon in the early stages of the catalytic reaction results in the conversion of the bimetallic carbide to a stable form containing active sites for dry methane reforming [46], according to Equation (12).



3.3. Molybdenum Carbide

Molybdenum carbide is the most widely used transition metal carbide. In the dry reforming of hydrocarbons, Mo_2C exhibits superior catalytic activity and stability. The mechanism of dry reforming of methane is based on the oxidation–recarburization cycle and noble metal-type mechanisms ^{[51][52][53][40][54]}, as presented in Equations (13)–(22).



(20) $2H + MoO_3 = MoO_2 + H_2O$ (21) $3C + 2MoO_2 = Mo_2C + 2 CO + CO_2$ (22)

An overwhelming number of research reports on the catalytic activity of molybdenum carbides in the dry reforming of hydrocarbons refer to catalysts prepared using TPR method. The physicochemical properties and resulting catalytic activity of molybdenum carbide catalysts are influenced by the molybdenum-to-carbon ratio. Gao et al. ^[55] reported a series of molybdenum carbide catalysts that differ in the weight content of Mo in order to use carbon nanotubes as a carbon source (Mo 0, 5, 10, 15, 30, 60, and 100 wt.%). Along with an increasing proportion of molybdenum in the catalyst, a decrease in the specific surface area, diameter, and pore volume was observed. A correlation was observed between the molybdenum content and catalytic activity in the dry methane reforming process. The highest activity was observed for the catalyst containing 30 wt.% of Mo. Another of the key structural parameters of the carbide for catalytic activity is the excess unbound carbon formed during the synthesis process. Roohi et al. ^[56] found that the amount of excess carbon depends on the carburization temperature and the concentration of carbon-containing gas during the synthesis. Catalysis with lower contents of excess carbon exhibited an initial higher activity in the DRM reaction; however, during the long-term test, the molybdenum loading was a crucial factor.

Several articles have been published to investigate the effect of the crystal structure on catalytic activity in DRM ^[57] [58]. Liang et al. ^[57] investigated the catalytic activity of β -Mo₂C and α -MoC_{1-x} phases in DRM. Both phases were characterized by a narrow size distribution of up to 5 nm. Better activity was observed for the -MoC_{1-x} phase. Oshikawa et al. ^[58] observed the dependence of the η -Mo₃C₂ phase on the methane decomposition rate. They reported the key role of the η -Mo₃C₂ phase among other molybdenum carbide phases as an active species for methane reforming. During the DRM process, the molybdenum carbide may be partially oxidized to the form of an oxycarbide. Kurlov et al. ^[59] reported that the oxycarbidic phase Mo₂C_xO_y exhibits high stability toward further oxidation to MoO₂, and the increase in β -Mo₂C/ Mo₂C_xO_y active sites correlates with higher efficiency in the DRM reaction.

3.4. Molybdenum Carbide Modified with Nickel Particles

Molybdenum carbide catalysts during DRM at atmospheric pressure may suffer from deactivation due to oxidation with carbon dioxide. The carbide structure is reconstructed with the carbon element from the dissociation of methane; however, oxidation with CO_2 is more favorable ^[60]. The combination of molybdenum carbide with other metals: Ni ^[61], Co ^[62], and Fe ^[63], allows controlled dissociation paths of CO_2 and CH_4 , ensuring appropriate conditions for oxidation–recarburization cycles ^{[16][64]}. The introduction of other metals into the carbide catalyst

results in the generation of more moles of hydrogen, leading to a higher H_2/CO ratio in the outlet stream. Carbide and the introduced metal (Ni, Co) act as an active center for the dissociation of CO_2 and methane, respectively.

It is generally accepted that the catalytic activity of nickel catalysts is strictly connected with the size of the nickel particles: the smaller the Ni particles, the better the catalytic activity, resulting from the stronger active metalsupport interactions, delayed sintering, and a lower rate of formation of carbon deposits [3][5][65][66]. However, in the case of molybdenum carbide supported nickel catalysts, the ratio of Ni/Mo to the size of nickel particles plays a predominant role [19][67]. The nickel-to-molybdenum ratio affects the morphology and catalytic activity of Mo₂C. Moreover, too high a dissociation of CH_4 promotes the formation of coke on the surface of the catalysts [55][61]. Zhang et al. ^[61] observed that with an increasing nickel content in nickel-modified Mo₂C supported on carbon nanotubes, the crystallite size of Mo₂C for Ni/Mo ratios = 0.5, 1, 1.5, and 2 was equal to 53, 38, 35, and 28 nm, respectively. Moreover, the increase in the Ni content resulted in an increase in the particle size. Catalytic activity increased with an increasing Ni/Mo ratio to the optimal value (1:1). After this value was exceeded, the activity decreased despite the higher content and smaller particle size of nickel. The DRM process is carried out mainly at temperatures above 800 °C. The performance of processes at lower temperatures results in lower methane and carbon dioxide conversions, as well as a lower H_2/CO ratio ^{[68][69]}. However, Diao et al. ^[70] recently reported the high catalytic activity of a Ni-Mo₂C/Al₂O₃ catalyst at 470 °C in a catalytic bed coupled with non-thermal plasma treatment. The molybdenum-nickel-alumina catalyst exhibited superior activity compared to Ni/Al₂O₃. The H₂/CO ratio was equal to 0.9, and the conversions of CH₄ and CO₂ were around 80% and 85%, respectively.

Both bare and nickel-modified molybdenum carbide catalysts are used, both supported and unsupported. Deposition on an inert substrate allows for dilution of the catalyst, thus eliminating channeling, and retarding heat transfer limitations and pressure drop across the catalytic bed ^[34]. As a support, metal oxides: La_2O_3 ^[64], Al_2O_3 ^[71] ^{[72][67]}, SiO_2 ^[10], ZrO_2 ^[73], MgO ^[74], biochar ^[75], carbon nanotubes ^[61], zeolites ^[76], and silicon carbide ^[10], have been examined. Silva et al. ^[10] investigated the effect of the support (SiO₂, Al_2O_3 , and SiC) Ni-Mo₂C on catalytic activity and stability in the DRM reaction. The lowest DRM substrate conversions and H₂/CO ratios were observed for the silica support. As a reason for the low activity observed for the SiO₂-supported samples, there were weak interactions between Ni and SiO₂, leading to movement of Ni species at the surface of the catalysts, retarding the interface contact between Ni and Mo₂C responsible for the oxidation–recarburization cycle, Ni aggregates, and the formation of filamentous carbon.

3.5. MAX and MXenes for Dry Reforming of Hydrocarbons

A special family of transition metal carbides is constituted by multilayer metal carbides with a 2D nanosheet structure similar to that of graphene, belonging to the group of compounds called MXenes. The term MXenes denotes carbides and nitrides of transition metals, with the general formula $M_{n+1}X_nT_x$, where n = 1, 2, 3, or 4, M refers to the transition metal (M = Sc, Ti, V, Cr, Mn, Y, Zr, Nb, Mo, Hf, Ta, and W ^[77][78]</sup>), and X refers to the p-block element (silicon, aluminum, gallium), while T describes the type of terminal groups (–O, –OH, –F, –Cl) in the amount of x per selected unit. They are obtained by selectively removing component A from the ternary MAX matrix. The MAX matrix consists of the elements of the transition metal M, a p group element (A), and carbon or

nitrogen (X). MXene compounds are gaining importance due to their metal-like conductive properties, thermal and chemical stability, and the ability to manipulate properties through simple and effective modification of terminal groups ^{[79][80]}. Their unique properties allow for application in various branches of science: energy storage ^{[80][81]}, electrocatalysis ^{[82][83]}, photocatalysis ^{[84][85]}, and heterogeneous catalysis ^{[77][81][82][83][86]}.

Despite a broad examination in electrocatalysis, heterogeneous photocatalysis, and catalysis, to our best knowledge, to date, among titanium, molybdenum, and tungsten MXenes or MAX matrices, the catalytic activity in dry reforming of hydrocarbons has been reported only in a few articles. Ronda-Lloret et al. reported the catalytic activity of Co_3O_4 supported on Ti₂AlC in the dry reforming of butane ^[87]. The levels of butane and carbon dioxide conversions for Co_3O_4/Ti_2AlC were 20% and 25% after 18 h of testing, respectively. The efficiency of butane conversion was higher compared to Co_3O_4/TiO_2 ; however, it was lower than that for Co_3O_4/Al_2O_3 . Despite the lower activity, the Co_3O_4/Ti_2AlC catalyst exhibited higher stability and anticoking properties compared to the metal oxide-supported catalysts.

Kurlov et al. ^[88] reported the catalytic activity of a 2D-Mo₂CO_x/SiO₂ catalyst in the dry reforming of methane. The catalyst was prepared by incipient wetness impregnation of multilayered m-Mo₂CT_x on a SiO₂ support in a colloidal alcoholic suspension, followed by reduction in hydrogen (20 vol.% H₂/N₂, 800 °C) and oxidation with CO₂. The authors found that the deposition on silica particles prevents the thermal sintering and oxidation of the Mo₂C and MoO₂ phases, respectively, while activation with CO₂ is crucial to protect the catalysis from complete oxidation. Furthermore, they found that long-term storage of 2D-Mo₂CO_x/SiO₂ leads to partial fragmentation of nanosheets and thus to deactivation of the catalyst.

Among others, the catalytic activity of $V_2O_3-V_8C_7/m-V_2CT_x$, obtained from the V_2AIC matrix, belonging to the MAX/MXene family, in the dry reforming of methane was reported ^[67]. The $V_2O_3-V_8C_7/m-V_2CT_x$ catalyst exhibited catalytic activity comparable to the nickel catalyst supported on ZSM-5 zeolite. After the catalytic process, the remaining $V_2O_3-V_8C_7/m-V_2CT_x$ catalysts' layered structure was slightly oxidized into an oxycarbide. The thermal stability at high temperatures, anti-oxidation properties under mild oxidants (CO₂), and ability to participate in oxidation–carburization cycles are crucial factors in terms of potential application in the dry reforming of hydrocarbons.

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