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Thermo-Catalytic Methane Decomposition: A Review of State of the Art of Catalysts

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(Received on 12th February 2015, accepted in revised form 6th June 2015)

Summary: The catalytic methane decomposition to produce carbon oxides–free hydrogen and carbon nanomaterial is a promising method feasible for larger production at a moderate cheap price. The produced hydrogen is refined and can be employed straight in fuel cell and in petrochemical industries to produce ammonia and methanol. Auto-thermal reforming of natural gas, partial oxidation, steam reforming are the conventional techniques for hydrogen production in industry, though these processes incur excessive costs for the purification of hydrogen from producing carbon oxides. Current research work on thermo-catalytic methane decomposition has concentrated on promoting the catalytic activity and stability for simultaneous production of pure hydrogen and elemental carbon. The carbon is generated as nanotubes, which are important for the use of this material in numerous new technologies. In the present review, thermodynamics of methane catalytic decomposition are elaborated and extensive considerations are given to the development of catalyst components by emphasizing the role of active particles, effect of catalyst promoters and support. The role of carbon catalyst in decomposing the methane catalytically, the morphology and characteristics of carbon produced and the catalyst deactivation is also discussed. The review also sheds light on the influence of operating parameters of temperature and space velocity. The performances of the frequently used catalysts are tabulated and types of reactors, influences of supports, promoters and preparation methods are outlined. Finally, the iron catalyst perspective towards hydrogen and carbon nanotubes productions by means of catalytic methane decomposition is presented in this work.

Keywords: Methane; Hydrogen; Carbon nanotubes; Iron; Dry reforming

Introduction

Sustainability and environmental impacts have been the two major challenges of the fossil fuel energy in the present era [1-3]. About 85% of the anthropogenic CO_2 emissions produced yearly is from fossil energy use [4]. The fast growth in the consumption of fossil fuels is an indicator for its end in the close future. Additionally, ever growing consumption of fossil fuels has caused environmental problems. Most of the fossil fuel products, CO_2, CxHy, NOx, and SOx might increase acid rain and global warming [5, 6]. Fig. 1 shows the historical production of fossil energy resources in million tons of oil equivalents (Mtoe) [7]. There is a strong need for the development of new technologies and methods for alternative energy sources. High cost and the under developing technology have been the main concerns of the other energy sources such as wind, solar, and biogas to be the replacement of conventional fossil fuels in the near future. Nuclear energy, another, alternating energy source raises a lot of safety concerns. Keeping all these things into consideration, there is consensus among governments, scientific communities and energy industries that fossil fuels will continue as a chief source of energy for predictable future, and the most likely approaches will comprise: (1) to decrease consumption of fossil fuels; (2) to advance renewable energy assets and skills; and (3) to monitor the undesirable environmental effects of fossil fuel utilizations [8, 9]. Hydrogen is presently seen as a halfway point as a promising energy route in both power generation and transport sectors. Water, the only combustion product of hydrogen makes it effective and versatile fuel. The chief benefits of hydrogen utilization as fuel is the substantial mitigation in greenhouse gas emission per unit of mechanical or electrical energy created from hydrogen which makes it the future clean fuel [10]. The other benefit of using hydrogen as a fuel is its higher efficiency in fuel cells compared to the usual
methods of electrical energy production from fossil fuels [11-13]. There is a huge potential for the utilization of hydrogen as a fuel in fuel cell for its usage in residential [14], commercial and industrial sectors [15]. But the method of production is one of the concerns for broader commercial scale production of hydrogen. Nowadays commercial production of hydrogen is largely centred on the processes of steam reforming and partial oxidation of hydrocarbons and carbonaceous feedstock, for instance, coal, natural gas, and petroleum fractions [16-22]. The hydrogen produced by methods, other than methane decomposition such as dry reforming and steam reforming, forms COx; which make severe problems for the further treatment of syngas. The purification of syngas contributes to increased cost and global warming as CO2 is produced from CO in this process [23, 24]. At present steam reforming of methane constitutes 50% of world’s hydrogen production. But to use it in fuel cell it should be COx free even a few ppm of CO is detrimental to low temperature fuel cell and a few ppm of CO2 is toxic to alkaline fuel cells [25] and thus increase the cost of purification of hydrogen. The other ways of getting COx free hydrogen are water electrolysis and ammonia conversion. Electrolysis of water is a high cost process and there are several issues with the utilization of ammonia for the hydrogen production: (1) ammonia produced from hydrogen is not economically and environmentally feasible (2) ammonia gas pollutes the environment, with very unpleasant and harmful effects on human (3) ammonia itself, even at ppm levels, is poisonous to the catalyst of PEMFC [26]. On the other hand, another alternative of steam reforming, partial oxidation and water electrolysis and ammonia decomposition is the thermal/catalytic decomposition of methane [27-30]. The reaction comprises the methane molecule decomposition to produce hydrogen gas and solid carbon:

\[
\text{CH}_4 \rightarrow 2\text{H}_2 + \text{C} \quad \Delta H^\circ = 75.6 \text{ kJ/mole} \quad (1)
\]

The required energy for a mole of hydrogen production in methane catalytic cracking and steam reforming is 37.8 kJ/mole and 63.3 kJ/mole respectively.

\[
\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2 \quad \Delta H^\circ_{298} = 253.2 \text{kJ/mole} \quad (2)
\]

Fig. 1: Global production of fossil energy from 1800 to 2010. Adapted from Höök et al. [7].
The produced hydrogen is mixed with unreacted methane and can be separated easily by membrane separation or absorption. The separation process is less complex than the requirement for additional difficult separation processes that deal with carbon oxides. The production of pure hydrogen would be particularly important in fuel cell technology, as the Pt-based electrocatalyst is poisoned by CO. Reaction (1) eliminates the direct emission of CO₂ to the environment and the carbon produced in this reaction is considered as useful by-product which may have several commercial applications, and has a positive effect on process economy. The advantage of carbon produced depends on its type and properties [31, 32]. In this process, using different catalysts and different reaction conditions generates different carbon species such as, amorphous and graphitic carbon, carbon nanotubes, nanofibres and carbon allotropes as graphene structures [33]. Methane decomposition in the absence of catalyst requires a high amount of energy, i.e. 1200°C for a practically good yield of hydrogen. The difficulty in direct methane conversion by catalytic and/or thermal processes is the strength of the methane C-H bond. The Gibbs free energy of methane is less than that of the products. The employment of catalyst significantly reduces reaction temperature, and also controls properties and type of co-products i.e. carbon species. There are three different types of catalysts for the methane decomposition (1) noble metals such as (Rh, Ru and Pt) [34], (2) metals from group VIII of transition elements [35-38] and (3) carbonaceous materials [39-42]. One of the main challenges accompanying with metal catalysts is the deactivation and recovery; the deposition of carbon formed covers the active sites during the reaction. The carbon formed in this reaction is one of the products, which means its production cannot be stopped. So reaction system and catalyst should be structured to retain good activity and stability despite the formation of substantial amounts of carbon.

Many reviews have been written on the subject with some of them concentrating on carbon nanotube production while others concentrating on hydrogen production. Chai et al. [43], discussed in their reviews the effect of metals, supports and temperature of decomposition, as well as the morphology of the carbon nanotubes produced and its growth mechanisms. Kumar and Ando [44] discussed the use of chemical vapor deposition to obtain carbon nanotubes (CNTs). They elaborated the growth mechanisms and its control. The CNTs have surprising properties: high electrical and thermal conductivity and many-times harder and stronger than diamond and steel respectively. It can be used as a structural material, catalyst, and catalyst support. It can also be used in carbon fuel cell as an anode electrode [44]. Li et al. [45] reviewed current development concerning the reaction mechanism and kinetics of group 8–10 base metal catalysts. Promoters, supports and preparation techniques are discussed. Abbas and Wan Daud [46] examined catalytic decomposition of methane using metal and carbon catalysts. They covered in their review topics such as the effect of operating conditions such as temperature and flow rate, at the rate of hydrogen production and the characteristics of the carbon produced, the types of reactors, operating conditions, deactivation and regeneration and the formation and utilization of the carbon produced. In addition to the topics discussed in the above reviews, Amin et al. [47] presented reaction thermodynamics, mechanism, kinetics, catalyst deactivation and regeneration as well as the use of fluidized beds in effecting the reaction. Ahmed et al. [48] reviewed a more general topic of non-catalytic and catalytic decomposition of hydrocarbons in which methane is a special case. In addition to the use of metallic catalysts, they included carbon as a catalyst and the use of plasmas to effect the decomposition. Abánades et al. [49] discussed industrial challenges for the different options for methane decomposition. They discussed non-catalytic, catalytic and the use of molten metals as a liquid medium to effect the reaction. Solid carbon can thus be skimmed off the surface of the molten metal. The same investigators continued the discussion of the challenges in another publication [50]. Lopez et al. [51] made a comparison between Ni, iron and carbon as a catalyst and found Ni-ex LDH-II as the most active. The least active catalysts in metals were catalysts based on iron. However, iron catalysts are resistant to deactivation. Carbon CB-v was the highest resistant catalyst against deactivation. However, carbon deposited on carbon catalysts is of low quality. Carbon nanotubes of high added value were produced using metal catalysts. This review will consider the thorough discussion of different features associated with methane catalytic cracking, sectioned into various parts; the first section elaborates the basics of the thermodynamics, advances in catalyst development and the role of catalyst and its deactivation. The second part comprises the operating conditions and morphology of carbon nanomaterial formation. The last part summarizes the performances of the frequently used catalysts in tabular form highlighting catalyst employed, types of reactors, preparation methods and conversion and the iron catalyst prospective.
Thermodynamics of Methane Decomposition

Thermal methane decomposition is a famous method that has been used for producing soot and hydrogen. Reaction (1) can be thermally conducted without a catalyst to attain highest hydrogen yield, however, higher reaction temperature is required (>1500 K) [52]. The thermodynamic data show that methane decomposition could be effected at moderate temperatures in the presence of appropriate catalysts. Hence the accomplishment of thermal decomposition of methane at reasonably low temperatures, the employment of catalysts is indispensable [53, 54]. Fig. 2 exhibits the equilibrium volume concentration of hydrogen in H₂ and CH₄ gaseous mixtures amounts to 94% [55, 56].

Fig. 2: Thermodynamic diagram showing isopotential curves for CH₄-H₂ gas mixtures [55].

In Fig. 2, \( u_c \) is the gas phase thermodynamic activity of carbon. Equation (3) states the definition of the thermodynamic carbon activity. The equilibrium constant in the process of cracking is commonly stated in terms of H₂ and CH₄ partial pressures [57-59]. The carbon activity is usually assumed one as shown in equation (4). Nevertheless, Fig.2 designates its impact on the equilibrium and the activity of the catalyst. Catalytic decomposition of methane encompasses the formation of solid carbon, such that the carbon atom dissociated from methane diffuses and reacts to form graphite layers.

\[
\frac{P_{CH_4}^2}{P_{H_2}} \times K_c
\]

(3)

It was observed that the carbon in the gas phase adsorbs on the active phase of the catalyst and diffuses through the catalyst as a result of existing diffusion driving force [60, 61]. The driving force for the bulk diffusion of carbon through the metal particle is attributed either to a concentration gradient or to a temperature gradient [62, 63]. Thermal reactions are commonly kinetically controlled and their products taken away from thermodynamic equilibrium while catalytic reactions are usually equilibrium controlled and their products near equilibrium. The overall reaction equilibrium constant which is a function of catalyst type can be stated in terms of hydrogen and methane partial pressures as [57]:

\[
K_{eq} = \frac{\left( \frac{P_{H_2}}{P_{CH_4}} \right)_{eq} L^3}{\left( \frac{P_{H_2}}{P_{CH_4}} \right)_{eq}}
\]

(5)

(Where \( L^3 \) the carbon solubility in the active phase)

This equilibrium constant equation is for a gas phase in equilibrium with a solution of carbon in the active metal. The graphite solubility of particle differs from at the support. For instance, Yang et al. [64] accomplished carbon solubility in nickel in contact with a mixture of hydrogen and methane and obtained that the carbon quantity at saturation was 35% greater than for a mixture at equilibrium with graphite. The solubility of filamentous carbon is the equilibrium concentration of carbon dissolved in the active phase at the supporting side, which, determines the gas-phase composition at the coking threshold. Therefore, the threshold constant can be obtained from the formula:

\[
K_m = \frac{P_{H_2}^2}{P_{CH_4}}
\]

(6)

The Gibbs energy of catalytic decomposition of methane changes in the temperature according to the following formula [65]:

\[
\Delta G^0 (J/mole) = 89658.88 - 102.27T - 0.00428T^2 - 2499358.99 T^{-1}
\]

(7)

(Where T is temperature in Kelvin)
However, the expression provides approximate values since its derivation is based on graphitic carbon formation. In fact, the Gibbs free energy (Eq.7) demands values of temperatures above 819K for the formation of carbon. Nevertheless, many researchers obtained carbon formations below that temperature indicating the impreciseness of Eq. (7). Dent et al. exhibited that the gas-phase composition of systems forming carbon on transition metal catalysts differed considerably from the equilibrium values predicted for the reaction forming graphite (Eq.1). On the other hand, the study of Rostrup-Nielsen (57) on Ni based catalyst suggested that the Gibbs energy of catalytic decomposition of methane ($\Delta G^{cd}$) can be obtained by subtracting the expression for catalytic decomposition of methane that forms carbon deposit as graphite (Eq. 7) from the actual Gibbs free energy ($\Delta G^a$) of methane cracking.

$$\Delta G^{cd} = \Delta G^a - \Delta G^0$$  \hspace{1cm} (8)

![Graphical representation of the mechanism of filamentous carbon formation](image)

The determination of rate constants in (Eq. 4) and $K_m$ (Eq.6) indicates that no cracking will take place ($K_c > K_m$) as $K_m$ is measured at no gasification and at no carbon formation. When $K_c < K_m$, it is predicted that encapsulated carbon or carbon filaments are produced. A threshold constant $K_{mf}$ for the formation of filamentous carbon on catalytic decomposition of methane was postulated by Zhang and Smith [66]. The constant has defined the value of $K_c$ at which catalyst deactivation rate equals zero as a result of the filamentous carbon formation. Therefore, stable activity and formation of filamentous carbon in the methane decomposition over supported Ni and Co catalysts can be guaranteed by choosing $K_m$ such that:

$$K_{mf} < K_c < K_m$$  \hspace{1cm} (9)

![Graphical representation of rate against time in methane cracking](image)

**Role of Active Metal**

In this section, the discussion covers mainly different catalysts employed for catalytic decomposition of methane. The main function of the catalyst is to lower the operating reaction temperatures, which results by the reduction of the activation energy required for methane decomposition reaction. Since non-catalytic methane decomposition requires as high as 1200°C, the sluggishness of this reaction without catalyst employment leads to the fact that this reaction has no practical application at temperatures below 1000°C. However, catalytic methane decomposition can be carried out at temperatures as low as 500°C [68]. For instance, Ni/SiO$_2$ catalyst, being highly active for methane decomposition, presented optimal performance in the temperature range of 500-550°C [69]. Transition metals such as Ni, Co and Fe are known to be the most active for hydrocarbon decomposition. Among these transition metals, nickel has been recognized to have higher activity for the highly stable methane [70]. Co has the potential, as well, to be used as a catalyst for decomposition of methane, but there are some disadvantages associated with it such as less activity, toxicity issues, and higher cost. Additionally, Fe based catalysts have also been investigated for methane decomposition, but they showed lower activity as compared to Ni based catalysts [68]. Based upon the above discussion, comparison among above mentioned transition metals shows that the catalytic performance order is: Ni>Co>Fe [71].

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The metal based catalysts have been extensively investigated as reported in the literature [72-80]. Pudukudy and Yaakob [72] studied the role of Ni, Co and Fe based monometallic catalysts for methane decomposition and inferred that Ni based catalyst was more active than Co and Fe based catalysts. Similarly, SBA-15 supported Ni, Co and Fe based bimetallic catalysts were investigated for hydrogen production and it was found that NiCo/SBA-15 was active while CoFe/SBA-15 was more stable than other catalysts [73]. Methane cracking at moderate temperature 550-600°C was studied over Ni/Y zeolite catalysts and long term stability and carbon yield as high as 614.24 gC/gNi was observed [74]. Fakeeha et al. [80] reported Ni-Co-Al catalysts for methane decomposition for the production of hydrogen and carbon nanofibers. They concluded that the catalyst containing 25wt% each of Ni and Co presented the best activity among the tested catalysts. The crystalline size of the Ni after reduction, in case of pure Ni based catalysts, was linked significantly to the catalytic activity of these catalysts for CH₄ decomposition reactions. Moreover, the highest carbon as well as H₂ yields was reported over the crystalline size of around 10.8 nm while relatively lower yields were reported in case of crystalline size of 20 nm and further increase in crystalline size to about 24 nm showed very low activity while crystalline size of 26 nm led to total deactivation. A novel catalyst based on Ni was investigated for CH₄ decomposition and carbon yields as high as 354–398 gC/gNi was reported before complete deactivation after 75 h showing maximum CH₄ conversion of about 10% [81].

Cai et al. [82] studied CH₄ decomposition over NiO nanoparticles for a reaction temperature of 300–500°C. The advantage associated with the use of NiO after reduction without any support material was to operate the reaction at lower temperature. Prior to the requirement of carbon removal during 2–3 h, uniform CH₄ conversion of around 50% were observed. The carbon in the form of fibers or filaments was well lodged with un-supported NiO particles. The NiCl₂ based NiO having 7.5 nm particle size exhibited the best catalytic performance at 500°C which was attributed to higher carbon deposition capacity i.e. C/Ni ratio. NiO particles generated from nickel nitrate with an average size of 9 nm showed an intermediate activity and stability. The nickel acetate based 10 nm sized NiO particles presented the lowest catalytic performance in terms of both activity and stability. Ni catalysts with high concentrations up to 90 wt.% were employed for the direct CH₄ decomposition for the production of H₂ and filamentous carbon [83]. However, lower CH₄ conversions were observed, i.e. at 500°C, 8% conversion was obtained, 15% at 550°C, and complete deactivation was observed at 600°C.

Rahman et al. [84] investigated 5-wt.% Ni/Al₂O₃ for CH₄ decomposition reaction using a thermo balance. They showed that faster deactivation was observed at 600–650°C due to faster carbon deposition rates. Moreover, use of lower catalyst weights (0.1–0.2 g) produced same results as well. Finally, they proposed a promising way to regenerate catalyst using partial gasification.

Awadallah et al. [27] studied the effectiveness of the combination of group VI (i.e. 25% each of Cr, Mo or W) and 25% Co supported over MgO for catalytic decomposition of methane to CO₂ free hydrogen and carbon nanotubes. They revealed that group VI metal addition helped in improving catalyst surface properties due to inducing stronger interaction with the support i.e. MgO and CoO, crystals. Additionally, they attributed the longer catalytic stability to the higher dispersion and stabilization of Co particles via formation of CoMoO₄ and CoWO₄ species.

Lua et al. [85] investigated Ni-Cu-Co alloy particles for hydrogen production via (catalytic decomposition of methane) CDM. They showed that Ni-Cu-Co alloy catalysts, with different atomic compositions and crystalline sizes ranging from 12.6 to 15.9 nm presented good catalytic activities for 650 to 775 °C. Co addition to Ni-Cu alloy inhibited the quasi-liquid phenomenon, thus catalyst stability, enhanced at higher temperatures, but further increase in Co contents resulted in phase separation.

Wang and his co-workers [86] tested sol-gel based active and stable Ni-Fe–SiO₂ catalysts for the direct decomposition of undiluted methane to produce hydrogen and carbon filaments at 823 K and 923 K. They indicated that the Ni–Fe–SiO₂ catalysts retained activity for a longer time than that of Ni–SiO₂ catalyst at higher reaction temperature, i.e. 923 K, while at a lower temperature the same catalyst showed a reverse trend. They attributed this catalytic behavior to iron atoms that entered into the Ni lattice forming Ni–Fe alloy.

Venugopal et al. [87] studied the performance of a Ni/SiO₂ catalyst with nickel loadings in the 5-90% range in a fixed-bed reactor. The results revealed that initially increase in nickel loading affected catalytic activity and stability positively up to 30% Ni loading. However, further
increase in Ni loading resulted in poor catalytic performance.

Suvelles et al. [88] used Ni based commercial catalyst and reported that hydrogen concentration was around 80% at a temperature of 700°C. He added that the value of conversion attained corresponded to the theoretical equilibrium value. Oghiara et al. [89] investigated M/Al2O3 (M=Fe, Co, Ni and Pd) and Pd-based alloys containing Ni, Co, Rh or Fe. They concluded that Fe, Co and Ni/Al2O3 catalysts deactivated quickly at 700°C, while Pd/Al2O3 catalyst showed the initial methane conversion of 15% which gradually decreased to <15% after 270 min. The Pd-alloy based catalysts presented high activity and stability above 700°C, especially, Pd–Ni/Al2O3 and Pd–Co/Al2O3 produced the highest hydrogen yields.

Co-doped Al2O3 catalysts having porous structures and high surface areas were tested for methane decomposition. The catalytic activity and stability results showed that the prepared catalysts were reported to be active and stable, and this performance was related to catalyst characteristic properties as well as the operating conditions used for decomposition reaction. In addition, the increase in methane conversion was observed with respect to feed (N2:CH4) ratio, metal loading and reaction temperature [90].

Jana et al. [91] studied the behavior of cobalt catalysts, for hydrogen production via decomposition of methane, prepared by different precipitating agents including sodium carbonate, ammonium hydroxide and urea. They revealed that precipitating agent employed influenced physicochemical properties of the catalysts which, in turn, affected catalytic performance. The results indicated that Na2CO3 or CO(NH2)2 based catalysts remained significantly active even at lower temperatures. Smaller metal particle size and lower degree of aggregation were the main factors influencing metallic Co catalytic performance. Moreover, the urea based Co catalyst produced the highest H2 at 600°C for over 12 h time on stream while the catalyst prepared by Na2CO3 exhibited notable activity even at a temperature as low as 400°C.

Cobalt based catalysts having 48 wt% Co supported over MgO were investigated for the production of carbon via methane decomposition at a reaction temperature of 900°C as a function of the calcination temperature Tc [92]. Transmission electron microscopy results for carbon produced showed that carbon presented three structural forms, including shapeless tangles, shell-like materials, and carbon filaments. Temperature-programmed reduction (TPR) and X-ray diffraction (XRD) results revealed that the calcination temperature at 700°C (Tc<700°C) generated Co3O4, CoMgO4, and (Co, Mg)O (solid solution of CoO and MgO); at Tc=800°C, Co3O4 and (Co, Mg)O were located while only (Co, Mg)O was identified for Tc=900°C. Furthermore, the filamentous carbon formation was well favored by the metal particles which were originated from the reduction of the solid solution.

Jana et al. [93] studied methane decomposition for the production of hydrogen using urea precipitation based cobalt catalysts. After drying, calcination of the prepared catalyst changed it to metal oxide. Moreover, use of different reducing environment converted metal oxide to actual metallic cobalt catalyst. The results indicated that catalytic activity and deposited carbon type were fairly influenced by the reduction ambiance. In addition to reduction ambiance, catalyst pre-treatment had a strong influence in the H2 production as well. Thermal treatment of the catalyst using nitrogen as pre-treatment gas presented the best catalytic activity. The better performance for nitrogen atmosphere was associated with smaller size of Co nanoparticles (i.e. higher surface area) in the bulk in comparison to the other two pre-treatment atmospheres used. The results also showed that the possible product, in addition to hydrogen, generated from Co based catalyst was graphene and this was observed when reducing gas employed was methane.

Piao et al. [94] investigated the performance of cobalt aerogel catalyst supported over alumina, prepared by sol-gel and supercritical drying method, for catalytic methane decomposition. The characterization and activity results as well as the effect of calcination and reaction temperature showed that the CoAl2O4 spinel structure was formed in the calcined catalyst. Increase in cobalt loading increased the quantity of the nanotubes deposited over catalyst surface and higher rate of reaction was observed with increased reaction temperature which led to faster catalyst deactivation. The deposited carbon nanotubes were having smooth walls and uniform diameter distribution.

Cobalt based catalysts were employed in catalytic decomposition of methane with reaction temperature in the range of 475–600°C and pressure nearly 1 bar. The findings inferred that influencing factors for the process included a catalyst method of preparation, support material nature and temperature regimes and 60–75 wt% Co catalysts supported over alumina and prepared by co-precipitation showed the
best catalytic performance at reaction temperature of 500°C. Characterization techniques such as XRD, EXAFS and TEM indicated that the results were close to previously investigate Co and Ni catalysts. However, as compared to Ni catalysts, Co catalysts generated hollow-like core morphology carbon filaments [95].

Co based catalysts supported over SiO₂ with metal loading varying from 5 to 30 wt.% were investigated for CH₄ decomposition reaction [96]. In addition, the effect of different parameters, such as metal (Co) dispersion, reaction temperature and introducing CO or H₂ in the feed, on the kinetics of CH₄ decomposition was reported as well. The results indicated that decreasing Co dispersion from 13% to 5% increased initial catalytic activity and decreased catalyst deactivation rate. Since increased reaction temperature led to more carbon deposition, thus the deactivation rate increased with increasing reaction temperature. The study of CH₃ migration from the metal to the support presented the fact that the formation of filamentous carbon played important role in carbon removal from the metal surface and thus contributing to the catalyst stability during CH₄ decomposition reaction. Moreover, addition of H₂ or CO to the feed decreased carbon formation rate and carbon removal rate increased because of increased carbon diffusion through the Co.

Abdullahi et al. [97] reported methane decomposition over Fe-MgO catalyst for the selective production of single-walled carbon nanotubes (SWCNTs) having narrow chirality and diameter distribution. They employed different characterization techniques to clarify the structure and chemical state of the species which contributed to SWCNT growth as well as reaction selectivity, SWCNT chirality and diameter distribution, purification protocols effectiveness and carbon yield were characterized by High resolution electron microscopy, Raman and optical absorption spectroscopy, temperature programmed oxidation, energy dispersive X-ray spectroscopy and nitrogen physisorption. Effect of reaction temperature studied implied that carbon increased with an increase in temperature, although above the optimum reaction temperature, SWCNTs’ selectivity decreased. The results indicated that catalyst selectivity towards SWCNT growth was well affected by the iron oxide dispersion degree inside the support *i.e.* MgO.

Fe based catalysts were tested in a fixed bed reactor for the production of hydrogen and filamentous carbon via methane decomposition [98]. The results indicated that catalyst performance was well affected by the addition of textural promoter as well as Mo as a dopant. Al₂O₃ based Fe catalyst presented slightly better catalytic performance than that of catalysts based on MgO. On the contrary Mo addition to Al₂O₃ based catalysts showed poor performance while improved performance was observed for Mo doped MgO based catalysts. Additionally, the effect of different parameters, such as catalyst reduction temperature, the reaction temperature and the space velocity, showed that at temperatures higher than 800°C Fe based catalysts yielded higher methane conversion with filamentous carbon having interesting properties. Moreover, the formation of multiwall carbon nanotubes was observed at temperatures higher than 700°C.

Tang et al. [99] investigated the catalytic performance of ceria supported iron catalysts (Fe–CeO₂) for the production of hydrogen by methane decomposition. The Fe–CeO₂ catalysts exhibited better activity than the catalysts based on iron alone. The catalyst containing 60 wt.% Fe₂O₃ and 40 wt.% CeO₂ presented optimal catalytic activity as well as the highest iron metal surface area. The better metal dispersion helped in maintaining the active surface area for the reaction. Reaction temperature increase from 600°C to 650°C increased methane conversion. The formation of high mobility lattice oxygen in the solid solution within the vicinity of catalyst helped in the oxidation of carbonaceous species resulting in continuous CO trace amount formation. This oxidation could help in a longer catalyst lifetime as it minimized catalyst deactivation caused by carbon deposition. Additionally, the formation of filamentous carbon also helped to extend the catalyst life.

**Effect of Support**

Conversion of methane depends upon the catalyst matrix which comprises the active material and the support [87, 100]. In this section the role of support on the catalytic performance for methane decomposition will be discussed in detail. The support material affects the conversion and the researchers have been reported that unsupported catalysts are less active than the supported catalysts. For example, Li et al. [101] prepared two samples with and without support using co-precipitation method. They reported that unsupported NiO was not active under study conditions while Ni supported over Al₂O₃ showed good activity and stability for the same reaction conditions. In a similar way, Toebes and co-workers [102] found negligible carbon nano fibres over an unsupported Ni catalyst for methane decomposition. However, unsupported Ni catalyst presented very stable and active performance for C₂H₄ decomposition which they associated with
higher activity demand for CH$_4$ dissociation than C$_2$H$_4$ decomposition.

The interaction between active metal and support plays a vital role in catalytic activity of the catalyst. Echegoyen and his co-workers [103] showed that methane conversion increased with a decrease in the interaction between the active component and the support. Additionally, the surface area and electronic state of metal influenced methane activity as well. For instance, the study of Ni catalyst supported over magnesia and silica concluded that the formation of solid solution between Ni and Mg lowered methane conversion while the higher methane conversion, in case of silica, was attributed to the possible formation of unstable nickel silicates which, at higher temperature during reduction, might decompose [68]. Ermakova and Ermakov [70] studied Ni/SiO$_2$ and Fe/SiO$_2$ and showed that silicate free Ni catalyst presented the maximum yield (384 g C/g Ni) while the yield decreased to 40 g C/g Ni when 1.5 to 2% of the nickel was converted to nickel silicate. In case of Fe, silica addition, depending upon silica loading, decreased or increased methane conversion. Takenaka, along with his team mates, [104] investigated nickel catalyst supported over different supports (SiO$_2$, TiO$_2$, graphite, Al$_2$O$_3$, MgO and SiO$_2$-MgO) calcined at 600°C for 5 h. In addition, they employed X-ray diffraction to characterize the catalysts. The results concluded that methane conversion increased for the catalyst which had lower metal to support interaction even with the equivalent surface area. At the end, among all tested supports for the same operating conditions, silica and titania supports showed the highest methane conversions.

Among different important factors affecting methane conversion, the structure of the support material and its textural properties e.g., porosity also influence methane conversion. Ermakova et al. [68] investigated nickel based catalysts having different support promoters i.e., silica, magnesia, alumina, and zirconia. They inferred that the pore structure of the catalyst significantly affected its catalytic performance and stability. Moreover, using silica as promoter instead of support, highest methane conversion with longer catalyst lifetime was observed and this performance was associated with the higher pore width for silica promoted nickel catalyst. The outlet gas composition and deposited carbon morphology could also be affected by the support structure. For instance, the high oxygen capacity supports such as ceria could produce oxides of carbon e.g., carbon monoxide unless surface oxygen of the catalyst made to be immobilized so as to prevent the reaction between oxygen and deposited carbon [105].

Takenaka along with his team workers [106] studied Co based catalysts supported over different supports, including MgO, Al$_2$O$_3$, SiO$_2$ and TiO$_2$, and showed that using MgO and Al$_2$O$_3$ as support for Co metal catalysts resulted in higher activity as compared to the rest of the supports investigated. Additionally, they came across the fact that better catalytic performance in case of Co/Al$_2$O$_3$ and Co/MgO was due to smaller particle sizes of active metal. Moreover, they showed that carbon nano fibers grew with more ease for Co particle diameters of 10–30 nm while Co particle diameters more than 30 nm presented no activity. Finally, characterization techniques including K-edge XANES and EXAFS, confirmed the presence of Co in the form of metal during the reaction irrespective of catalyst support type and reaction temperature. Temperature programmed catalytic reaction technique was used to study the catalytic performance of the supported Ni catalyst. The results revealed that the onset temperature of methane decomposition reaction got influenced by the nature of the supports employed [107].

Hu and Ruckenstein [108] suggested that nickel particles with very small size were obtained when the solid solution of NiO and MgO was reduced. This concept was reconfirmed recently in the work of Gac et al. [100]. They proved that the high initial decomposition rate was attained by using catalyst having small nickel crystallite strongly interacting with magnesia. Ismagilov et al. [109] investigated silica glass fiber supported Ni catalyst for the growth of carbon nano fibers via methane decomposition reaction. They employed washcoat and ion exchange methods to prepare catalysts and found that carbon nano fibers having diameter 20–50 nm and carbon capacity as high as ca.55 g C/g Ni were produced for washcoat based catalyst. Recently, catalysts with structure based supports, such as Perovskite structured oxides, have been used for decomposition reaction [110–113]. Smaller metal particles with stronger metal support interaction enhanced catalytic activity and carbon formation with improved structure. The reduction of LaFeO$_3$ produced Fe nanoparticles, which, in turn, generated single wall carbon nano tubes (SWCNTs) with diameters in the narrow range of 0.8–1.8nm [114]. The factor responsible for SWCNTs growth was uniform and close distribution of Fe fine nanoparticles over LaFeO$_{3-x}$. Chen et al. [110] inferred that good activity and carbon yield was attained with Ni–Co/La$_2$O$_3$ catalyst employed, without any pre-treatment, in decomposition reaction. Kuras et al. [111] reported better stability at higher temperature for perovskite precursor based Ni
catalyst. They also showed that Ni particle size was not much affected by the reduction and the reaction temperatures. Self-combustion preparation method was employed to prepare LaNiO₃ type perovskite which was subsequently tested for methane decomposition at reaction temperature of 873 and 973 K [112]. The excellent activity results showed that catalyst used for the simultaneous production of carbon nanotubes (CNTs) and hydrogen remained stable even after 22 h of reaction at 973 K. The main reason behind the stable catalytic performance of Ni catalyst originated from LaNiO₃ precursor’s activation was the high degree of metal crystallites dispersion over La₂O₃ matrix [113]. The higher metal dispersion degree helped in controlling the metal particle sintering as well. In addition, La₂O₃, being textural promoter or support, increased the BET surface area and also exhibited as an electronic promoter [115, 116]. The addition of La₂O₃ to Raney Fe improved activity and stability of the catalyst.

In addition to metal oxides, carbon based materials such as nano fibers have been reported as support for methane decomposition reaction catalysts. Since carbon nano fibers possess a mesoporous structure with high surface area varying from 100–300 m²/g, these fibers are a good choice for decomposition reaction catalyst system [117]. Carbon nano fibers, produced from methane decomposition over Ni, Ni–Cu, Ni–Fe, Co and Fe–Co supported on alumina, were used as support for Ni catalysts [118–120]. The secondary carbon (carbon produced from methane decomposition over carbon supported Ni catalyst) yield remained 224 g/g Ni over Ni/CNF (Ni–Cu) catalyst and 268.5 g/g Ni on Ni/CNF (Ni–Fe) catalyst, respectively. Zeolites have also been reported to be the support for decomposition reaction catalysts [120–124]. Ashok et al. [120] tested different supports such as HY, USY, SiO₂ and SBA-15 to estimate their catalytic performance for Ni based catalyst. The catalyst comprising 30 wt.% of Ni supported on HY exhibited the best activity and stability. The performance was ascribed to the acidic nature of the support as well as the Ni metal particle size. Guevara et al. [122] employed surfactant-assisted method to prepare mesoporous Ce-MCM-41 for Ni based catalysts and showed that the catalyst presented a very stable performance in the decomposition reaction.

Ni based catalyst supported on ZSM-5 was utilized to produce MWCNTs in the lower temperature range of 673–823 K [123]. The decomposition reaction was found to take place mainly in the zeolite channels at 673 K as suggested in TEM characterization images. However, at temperature over 673 K, the formation of carbon on the catalyst surface was observed as well. Jehng and his research fellows [124] investigated the performance of Ni/MCM-41 catalyst. They discussed the MWCNTs’ deposition on catalyst surface and suggested tip-growth mechanism for the formation of MWCNTs in which catalyst particles detached from support is found at the tips of the CNTs formed. Choudhary et al. [125, 126] investigated the effect of support on the carbon formed and CO evolved during methane decomposition. They found that both carbon morphology and CO produced were well influenced by the support. No filamentous carbon formed over Ni/H-ZSM-5 catalyst in the temperature range of 723–873 K, while Ni/HY and Ni/SiO₂ catalysts produced filamentous carbon in tested temperature range (723–873 K).

The ability to improve metal support interaction and active metal dispersion has attracted the researchers to employ CeO₂ as support in methane decomposition reaction. Li et al. [105] investigated Ni/CeO₂ catalysts and reported the effect of different preparation methods as well. Tang et al. [99] employed Fe supported over CeO₂ was used in decomposition reaction and the results indicated that the catalyst containing 60 wt.% Fe₂O₃ on 40 wt.% CeO₂ exhibited the best catalytic performance. However, the product stream showed CO₂ detection, which was attributed to the lattice oxygen, originating from CeO₂, reaction with deposited carbon. Odier et al. [127] reported improved H₂ production by using Pt/CeO₂ catalyst. They suggested that the spillover of noble metal’s carbylons towards partially reduced CeO₂ hydroxyl groups was the main reason behind improved catalytic performance. Moreover, the reverse spillover of lattice oxygen towards active metal helped in gasifying deposited carbon which was confirmed with CO₂ detection in the product stream.

Different support materials such as Al₂O₃, MgO, or SiO₂, has been used as catalyst surfaces with high dispersion for (Single walled carbon nanotubes) SWCNT growth [35–38]. MgO has been more attractive than that of SiO₂ and Al₂O₃. MgO-supported catalysts may be a better choice because of their efficiency for SWCNT and (Double walled carbon nanotubes) DWCNT growth as well as ease of MgO separation from the carbon product through acid leaching without any loss or damage to carbon structure, while in case of SiO₂ or Al₂O₃, it is very difficult to remove these support materials from carbon product. Li et al. [132] investigated SWCNTs growth via chemical vapor deposition over porous MgO support based on thermal decomposition of its salts (Mg(NO₃)₂ and MgCO₃) and showed that MgO presented excellent results. Ning and his team [133]
reported formation of a uniform \( \text{MgFe}_2\text{O}_4/\text{MgO} \) solid solution structure as a result of calcination at 1173 K for 12 h and concluded that the reduced structure facilitated several active sites, having a diameter around 4 nm, which helped in generating SWCNTs and DWCNTs. Hydrothermal treatment was applied to produce porous and lamella-like Fe catalysts supported over MgO which became a simple approach for high yield of DWCNTs [134]. The hydrothermal treatment method was also found promising in preparing hydrophilic oxides supported metal catalysts. Ethanol-thermal treatment was employed to prepare a porous MgO supported Fe catalyst [135]. The resulting catalyst having pores in the range of (50 nm to 5 μm) was used to produce SWCNTs with a quality better than that of originating from the previously reported catalysts. Direct growth of SWCNTs on a flat support surface, e.g. SiO\(_2\)/Si wafer, has also been reported to be applied in the micro-electronics or nano-scale research on physico-chemical properties [136]. In another study, Wang et al. [137] used chemical reduction with microwave irradiation to produce Fe/Ru and Fe/Pt based bimetallic catalysts supported over the SiO\(_2\) flat surface. Li et al. [138] utilized carbonyl complexes decomposition to prepare Fe–Mo nanoparticles with sizes ranging from 3 to 14 nm via different protective agents. These nanoparticles were subsequently precipitated from propanol and redispersed in n-heptane. SWCNTs were grown by dropping or spin coating the solution onto Al\(_2\)O\(_3\)/Si or SiO\(_2\)/Si substrates. Kong et al. [139] reported individual SWCNT production over silicon wafers having a micro level well defined pattern of catalytic material. The CNTS generated were perfect with individual CNTs having 1–3 nm diameter and up to tens of micron length.

**Role of Carbon Catalysts**

Catalyst plays a significant role in generating methane thermal decomposition and determining its performance. The adaptability of carbon as a catalyst was recognized a long time ago [140]. In recent years, carbon material has become a hot research area, and carbon-based catalysts are developing rapidly [141-144]. Generally, two different types of catalyst have been developed for thermo-catalytic methane reforming; they comprise metal and carbonaceous catalysts [46]. Carbon based materials are considered as ideal catalysts due to desirable features such as low material cost, high surface area and thermal stability [145-148]. Moreover, they offer certain advantages over metal catalysts due to tolerance to sulfur and other potentially harmful impurities in the feedstock [148]. In addition, the carbon based catalyst can be easily separated from reaction system, which is very convenient for recovery and reuse. Different kinds of carbon materials have been developed for methane catalytic decomposition. These include carbon black, glassy carbon, activated carbon (AC), diamond powder, graphite, fullerene, carbon nanotubes and acetylene carbon [142, 148-150]. The factors influencing the performance of a catalyst include the number of active sites available for reaction, reactant chemisorption capacity and capability to form surface intermediates having suitable strength [151]. Indeed, most of the previous studies have shown that the activity of carbon catalysts relates to their structural and textural surface properties [41].

Abanades et al. [152] investigated the solar thermo-catalytic decomposition of methane employing carbon black catalysts for the production of pure hydrogen in a packed-bed reactor. Solar power supplied the required heat to derive endothermic reaction. The rate of the heterogeneous decomposition reaction was improved by carbon particles. Several operating parameters such as temperature and residence time of the feed gas through the catalyst bed were tested to measure the performance of thermochemical properties of the reactors. The parameters affected the chemical conversion and hydrogen yield. Indeed, A very high methane conversion to hydrogen was attained with negligible side products. Nevertheless, gradual catalyst deactivation was seen due to carbon formation on the surface, with acetylene as the chief developing by-product.

Rechnia et al. [153] reported the suitability of carbon catalyst for the methane decomposition to generate hydrogen. In their study, they tested the addition of methanol as a promoter that generates potentially active carbonaceous deposits for suppressing the catalyst deactivation. Activated carbon gained from the hazelnut shells was tested at different reaction temperatures. The use of the ethanol lengthwise the methane boosted the yield of hydrogen produced and maintained at a high level the catalyst activity.

Muradov et al. [148] studied the carbon materials and in particular the role of carbons during decomposition reaction which is related to the relation between their surface and structural properties. The concentration of active sites over the surface is the governing factor affecting the activity of the carbons. Moreover, the activation energy of methan decomposition reaction over carbon based catalysts is estimated to be between the activation energy of the decomposition reaction over transition metal based catalysts and activation energy of
methane decomposition without using catalyst (non-catalytic).

Serrano et al. [154] studied a range of carbon materials which include ordered black carbons, carbon nanotubes, mesoporous carbons, activated carbon, graphite and coke as catalyst for thermo-catalytic methane decomposition to produce hydrogen. They investigated the activities of different carbon materials by means of temperature programmed conditions. No conclusive correlations were observed for minimum temperature for activation of the process and parameters such as crystallinity, surface area, and the oxygenated groups concentration. Nevertheless, a decreasing linear relationship has been found to exist between the minimum activating temperature and the proportion of defects in the graphene layers. Thus, carbon materials having a high defect concentration, such as an ordered and interconnected mesoporosity, followed by activated carbon or carbon blacks, show higher activity. Alternatively, highly ordered carbon catalysts exhibit little activity. Al-Hassani et al. reported the production of hydrogen via catalytic methane decomposition using as catalyst two different types of activated carbon [42]. Rates of ethane decomposition at 820, 860, 900, and 940°C were conducted. The Pore structure of the catalyst was observed to have negligible effect on the initial rate of decomposition, but had a significant effect on the time required for full catalyst deactivation. Higher temperatures increased rate of decomposition of methane and decreased the deactivation time. The mesopores activated carbon catalysts showed high resistance to catalyst deactivation, whereas the micropores ones resulted in fast and complete catalyst deactivation.

Lee et al. [155] studied methane decomposition at high temperatures ranging from 1,293-1,443 K using carbon black catalyst. Nearly total methane conversion and stable condition for two and half hours’ time on stream was attained at 1,443 K, and the activation energy of the catalytic reaction over carbon black was 198 kJ/mol. In addition, it was observed that the specific surface area decreased as the amount of deposited carbon increased. Fig. 1 Global production of fossil energy from1800 to 2010, Microporous activated carbon catalyst was used for production of hydrogen from decomposition of methane [156]. No appreciable catalytic activity effect of surface area was observed, but as the surface area and the pore volumes increased, the resistance of the catalysts to deactivation increased. Carbonaceous deposit formed during the reaction block the micropores and hence was responsible for the catalyst deactivation.

Guil-Lopez et al. made comparative examination in terms of initial activity and stability of methane decomposition via metal based catalysts (Ni and Fe) and carbon based catalysts (activated carbon, carbon black, carbon nanotubes and graphite) [157]. They found that activity of carbon catalysts was similar to that of the non-pre-reduced metal catalysts and the carbon black were shown to be the most resistant catalyst against deactivation. Table-1 displays the principal catalytic parameters of metal catalysts for methane decomposition while Table-2 presents the literature summary for carbon catalysts in the thermo-catalytic decomposition of methane. Abbas and Wan Daud studied the apparent kinetics of methane decomposition and the deactivation kinetics of activated carbon catalyst using various reactant residence times in the temperature range of 775–850°C in a fixed bed reactor [46]. The authors’ apparent kinetics gave the reaction order of 2 and activation energy of 163 KJ/mol instead of 0.5 as reported by other investigators and deactivation order of 0.5 and the deactivation energy of approximately 177 KJ mol/ [53, 158, 159]. In an earlier work, the investigators studied the catalyst deactivation kinetic due to carbon deposition with time and found that the catalyst activity decreased almost linearly with the amount of carbon deposited at 800°C, while the substantial diffusion effect took place at higher temperatures [46]. Methane decomposition over carbon catalyst was investigated kinetically and the apparent reaction order was found to be 0.5 for both activated and carbon black-based catalysts [53,158, 159]. Hence, the rate equation for carbon-catalyzed decomposition of methane can be expressed as follows:

\[
\frac{dCH_4}{dt} = k P_{CH_4}^{0.5}
\]

(10)

Considerable work has been carried out in the catalytic methane decomposition using metal catalysts like Ni, Fe Co and carbon materials. Customarily metal exhibit higher catalytic activities and the need for a lower reaction temperature than carbon catalysts, however the carbon catalysts reveal their own benefits. It is expected for catalysts to lose the activity with time on the stream because of the constant carbon formation during catalytic methane decomposition. Lately, attractive topic research is developed in the area of catalytic methane decomposition using carbon materials, like activated carbon, as the support for metal catalyst. The utilization of carbon-assisted catalysts provides certain advantages over metal catalysts.
Table 1: Review summary of metal catalytic decomposition of methane.

<table>
<thead>
<tr>
<th>Catalyst constituents</th>
<th>Method of forming catalyst</th>
<th>Reactor type</th>
<th>Operating conditions</th>
<th>Product/conversion</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>La₂O₃ doped Ni and Ni-Cu Raney-type promoter amount 0.03 - 0.06 g</td>
<td>leaching out the aluminium with a concentrated NaOH solution</td>
<td>tubular reactor</td>
<td>Activ.=600°C</td>
<td>nanofibers and multiwall carbon nanotubes 79% CH₄ conversion 22hr</td>
<td>[166]</td>
</tr>
<tr>
<td>75% Ni-12% Cu/Al₂O₃, 70% Ni-10% Cu-10% Fe/Al₂O₃</td>
<td>mechanochemical activation</td>
<td>rotating flow reactor</td>
<td>Enhanced T=700-750°C 600-650°C</td>
<td>Nanofibers Carbon Y= 150-160 g/g. HY&gt;70</td>
<td>[167]</td>
</tr>
<tr>
<td>Mo doped Fe(Al₂O₃) or Fe/MgO</td>
<td>Fusion</td>
<td>fixed-bed reactor</td>
<td>T=800-900°C</td>
<td>filamentous carbon, ast=900°C 87% CH₄ conversion &amp;93% yield H₂, Conc. Space velocity =1L/g/h</td>
<td>[89]</td>
</tr>
<tr>
<td>Ni-Cu-Al 78/6/16 ratio</td>
<td>co-precipitation vs fusing of the metallic nitrates</td>
<td>fluidized bed</td>
<td></td>
<td>60 l/1f hydrogen and 15 g/h carbon nanofibers</td>
<td>[168]</td>
</tr>
<tr>
<td>cobalt acetate in ethylene glycol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-based catalysts doped</td>
<td>fusion method</td>
<td>a thermobalance</td>
<td>Maximum performance of Fe-Mo catalysts 700-900</td>
<td>Methane (70%) MWCNTs (5.3 g/h).</td>
<td>[169]</td>
</tr>
<tr>
<td>NiSiO₂</td>
<td>incipient wetness impregnation</td>
<td>fixed-bed quartz micro reactor</td>
<td></td>
<td>15 wt.% Ni/SiO₂ At 650°C</td>
<td>Fully regenerated</td>
</tr>
<tr>
<td>Ni metal foam wash-coated with SiO₂</td>
<td>wet impregnation</td>
<td>quartz tube reactor</td>
<td>T=550-750°C</td>
<td>MWCNTs Optimum 20% wt Ni at 650°C</td>
<td>[171]</td>
</tr>
<tr>
<td>Fe/HZSM-5 zeolite, HBETA zeolite, and porous precipitated Al₂O₃</td>
<td>microwave assisted impregnation method.</td>
<td>quartz tube</td>
<td>T=800°C</td>
<td>H₂ 10-30 vol% CNT</td>
<td>[162]</td>
</tr>
<tr>
<td>Ni-Mo and Co-Mo/Al₂O₃</td>
<td>Commercial</td>
<td>fixed bed horizontal reactor</td>
<td>T=700°C</td>
<td>Ni-Mo catalyst (CNTs) Co-Mo catalyst (Amorphous carbon).</td>
<td>[172]</td>
</tr>
<tr>
<td>Nickel-copper based catalysts textural promotes with SiO₂, Al₂O₃, TiO₂, MgO</td>
<td>Fusion method</td>
<td>fluidized bed reactor</td>
<td>T=700°C For 7h</td>
<td>CNTFs</td>
<td>[173]</td>
</tr>
<tr>
<td>NiO-M/SiO₂ (where M=AgO, CuO, CoO, FeO, MnO, and MoO)</td>
<td>impregnation method</td>
<td>fixed-bed reactor</td>
<td>T= 700°C</td>
<td>8.2 ratio NiO/SiO₂ promoted with CatO give the highest hydrogen yield</td>
<td>[174]</td>
</tr>
<tr>
<td>Ni, Ni:Cu, Fe or Fe:Mo / Al₂O₃ or MgO</td>
<td>rotary bed reactor</td>
<td></td>
<td></td>
<td>H₂ yields 14.4 Ndm³ (h·g cat)⁻¹ Initial CH₄ conversion of 82% 3hr reaction Carbon nanofilament</td>
<td>[30]</td>
</tr>
<tr>
<td>NiAl₂O₃, Ni-Cu,MgO, Fe/Al₂O₃, Fe-Mo/MgO</td>
<td>fusion method</td>
<td>rotary bed reactor</td>
<td>Space velocity 2 Nm³ (h·g cat)⁻¹</td>
<td>Carbon nanofilaments</td>
<td>[175]</td>
</tr>
</tbody>
</table>
Table 2: Literature summary for carbon catalysts in the thermo-catalytic decomposition of methane.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>b</th>
<th>VHSV/(L/h•gcat)</th>
<th>CH4 (%)</th>
<th>CCH4</th>
<th>Carbon deposits</th>
<th>td</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-micro (AC)</td>
<td>950</td>
<td>504</td>
<td>50.4</td>
<td>-</td>
<td>0.13</td>
<td>1.42</td>
<td>[146]</td>
</tr>
<tr>
<td>AC-meso (AC)</td>
<td>950</td>
<td>1115</td>
<td>111.5</td>
<td>-</td>
<td>0.34</td>
<td>1.42</td>
<td>[146]</td>
</tr>
<tr>
<td>CG (AC)</td>
<td>850</td>
<td>0.6</td>
<td>0.6</td>
<td>51</td>
<td>0.45</td>
<td>8</td>
<td>[133]</td>
</tr>
<tr>
<td>SUPRA (AC)</td>
<td>850</td>
<td>0.6</td>
<td>0.6</td>
<td>25</td>
<td>0.35</td>
<td>3</td>
<td>[133]</td>
</tr>
<tr>
<td>GAC (AC)</td>
<td>850</td>
<td>0.6</td>
<td>0.6</td>
<td>25</td>
<td>0.40</td>
<td>8</td>
<td>[133]</td>
</tr>
<tr>
<td>CMK-5 (OMC)</td>
<td>950</td>
<td>545-2000</td>
<td>54.5-2000</td>
<td>-</td>
<td>-8</td>
<td>24</td>
<td>[41]</td>
</tr>
<tr>
<td>CMK-5 (OMC)</td>
<td>1000</td>
<td>400-3000</td>
<td>40-300</td>
<td>1.5-3.5</td>
<td>-20</td>
<td>48</td>
<td>[176]</td>
</tr>
<tr>
<td>CB-bp (CB)</td>
<td>1100</td>
<td>1911</td>
<td>191.1</td>
<td>-</td>
<td>5.0</td>
<td>3</td>
<td>[146]</td>
</tr>
<tr>
<td>CB-b (CB)</td>
<td>1100</td>
<td>1361</td>
<td>136.1</td>
<td>-</td>
<td>8.5</td>
<td>4</td>
<td>[146]</td>
</tr>
<tr>
<td>DCC-N1083 (CB)</td>
<td>850</td>
<td>15</td>
<td>15</td>
<td>13</td>
<td>-</td>
<td>2</td>
<td>[177]</td>
</tr>
<tr>
<td>DCC-N2200 (p) (CB)</td>
<td>850</td>
<td>15</td>
<td>15</td>
<td>7</td>
<td>-</td>
<td>2</td>
<td>[177]</td>
</tr>
<tr>
<td>XC72 (CB)</td>
<td>900</td>
<td>100</td>
<td>100</td>
<td>-</td>
<td>2.74</td>
<td>20</td>
<td>[178]</td>
</tr>
<tr>
<td>BP2000 (CB)</td>
<td>900</td>
<td>100</td>
<td>100</td>
<td>-</td>
<td>6.13</td>
<td>20</td>
<td>[178]</td>
</tr>
<tr>
<td>RC (AC)</td>
<td>850</td>
<td>15</td>
<td>15</td>
<td>19</td>
<td>&gt;4.32</td>
<td>&gt;5</td>
<td>[140]</td>
</tr>
<tr>
<td>CC (AC)</td>
<td>850</td>
<td>15</td>
<td>15</td>
<td>21</td>
<td>2.45</td>
<td>5</td>
<td>[140]</td>
</tr>
<tr>
<td>AIRC (AC)</td>
<td>850</td>
<td>15</td>
<td>15</td>
<td>61</td>
<td>&gt;36</td>
<td>&gt;10</td>
<td>[140]</td>
</tr>
<tr>
<td>SIRC (AC)</td>
<td>850</td>
<td>15</td>
<td>15</td>
<td>26</td>
<td>&gt;4.90</td>
<td>&gt;5</td>
<td>[140]</td>
</tr>
<tr>
<td>BP2000 (CB)</td>
<td>850</td>
<td>15</td>
<td>15</td>
<td>12</td>
<td>1.31</td>
<td>5</td>
<td>[140]</td>
</tr>
</tbody>
</table>

a: Carbon catalyst, with the type marked in the parentheses. AC, OMC and CB means activated carbon, ordered mesoporous carbon and carbon black, respectively.
b: Reaction temperature
c: Maximum methane conversion on the catalyst
d: Deactivated time of the catalyst

Jin et al [194] investigated catalytic methane decomposition for hydrogen production employing Fe-Al2O3 supported on activated carbon catalysts. Their characterization results displayed the straight reduction of ferric nitrate upon carbon support to metallic iron at 870 °C. The effect of Fe/Al2O3 weight ratio was shown to influence the textural properties and catalytic methane decomposition. In addition, Fe and Al2O3 loading decreased the surface area and pore volume of the catalyst. Mesopores formation of catalyst enhanced the catalytic activity and stability.

Zhang et al. [160] studied the catalytic methane decomposition for hydrogen production, using Ni doped carbons obtained from raw coal and direct coal liquefaction residue. Their results exhibited that the Ni doped carbon performed better stability and activity at 850°C reaction temperature when compared to corresponding metal and carbon catalysts. Moreover, the procedure for preparing Ni doped carbons influenced the reducibility of the carbon composition. Simialrly, the catalytic activity was affected by the amount and the morphology of the formed carbon.

Operating Conditions

The catalytic decomposition of methane into carbon oxides–free hydrogen and carbon is viable method of reforming. The potentiality of the useful carbon co-product rests on its characteristics, which depends on the process and conditions used. Carbon can be used in the production of fibers, plastics, composites, metal carbides and metal–carbon composites. The value of the carbon formed in the catalytic methane decomposition depends on the operation conditions and the type of catalyst used. Reactors used include fixed and fluidized beds. Fixed bed reactors could suffer from reactor plugging due to the growth of carbon on the catalyst surface. Fluidized bed reactors and rotary bed reactors show promise for continuous operation whereby carbon can be separated in cyclones. Catalyst regeneration is carried out using air or steam. Employment of metal-based catalysts generates high-quality forms of carbon that compensate the cost of the catalyst. The work of Suvelles et al. [88] investigated commercial catalyst based on Ni for catalytic decomposition of methane for CO2-free hydrogen production employing different operating conditions. They have stated that operating conditions dictate the time for catalyst deactivation i.e., a shorter lifetime of the catalyst was observed when higher temperature and methane flow were used. Fig. 5 shows the reaction temperature effect in which increase in temperature leads to increased methane conversion and hydrogen production. Similarly Fig. 6 exhibits the dependence of CH4 conversion and hydrogen production on catalyst amount.
Fig. 5: Hydrogen production and CH\textsubscript{4} conversion versus reaction temperature.

Run 1: 550°C; run 2: 650°C; run 3: 700°C. Amount of catalyst: 2 g; Flow: 20 ml/min.

Fig. 6: Effect of catalyst amounts on production of hydrogen and CH\textsubscript{4} conversion.
Run 3 = 2 g; run 5 = 0.3 g. T = 700 °C; Flow = 20 ml/min.

Nuernberg et al. [90] examined the effect of operating conditions for thermo-catalytic decomposition of methane using Co/Al\textsubscript{2}O\textsubscript{3} catalyst. They found that the catalytic performance is well affected by characteristics of the catalyst as well as the operating conditions used. The increase in methane conversion was observed with respect to molar ratio (N\textsubscript{2}/CH\textsubscript{4}), reaction temperature and metal loading. The best conditions for hydrogen production included 20 wt% loading of Co, molar ratio of 6:1 and 800°C reaction temperature. Fig. 7 displays the catalyst activities in dealing with different N\textsubscript{2}/CH\textsubscript{4} molar ratios. The results inferred that increase in a molar ratio increased average methane conversion. When the amount of the inert gas was very high in the feed, the catalyst gave the highest conversion value (22%). Alternatively, the increase in methane concentration in the feed i.e., employing N\textsubscript{2}/CH\textsubscript{4} molar ratios of 2.5:1; 1:9 and 4.5:1, lowered the conversion values. The lesser amount of catalyst active sites may be responsible for this effect.

Fig. 7: Methane decomposition over 9-Co/Al\textsubscript{2}O\textsubscript{3} catalysts. Performance of the 9-Co/Al\textsubscript{2}O\textsubscript{3} catalyst in the CH\textsubscript{4} conversion with time-on-stream at 700 °C at different N\textsubscript{2}/CH\textsubscript{4} molar ratios.

The laboratory scale bubbling fluidized bed reactor was used to investigate →-alumina baed copper catalyst for thermo-catalytic decomposition of methane [162]. The influence of different operating parameters including reaction temperature, contact time, total flow rate and CH\textsubscript{4} inlet concentration was studied. From Fig. 8, it can be seen that shorter deactivation times with lower methane conversions (even lower than equilibrium conversions) were observed when higher concentrations of methane were employed. This may be ascribed to the intrinsic kinetics of decomposition reaction, i.e., more carbon deposition leads to lower activity with respect to reaction time. Nonetheless, lower methane conversion is observed and this conversion does not drop directly to zero.

Fig. 8: Influence of methane concentration on methane conversion at T=800°C; mcat =25g; Q= 45Nl/h.
The deposited carbon perhaps plays a role in the catalytic activity [163]. In Fig. 9, it can be seen from carbon formation rate curves that rapid growth reaching its maximum is observed in the initial period. After that a decline from maximum takes place which leads to a residual constant value. The methane concentration affects the carbon formation rate in that increase in methane concentration increases carbon formation. It can be concluded that, depending upon operating conditions employed, type as well as the amount of carbon formed contribute to catalyst deactivation [65, 88,164].

**Catalyst Deactivation**

The employment of a catalyst facilitates the reaction to take place at lower temperatures much below the required value of 1200°C. The catalyst activity decreases over time. The catalytic activity and/or selectivity loss over time is an extreme difficult and a continuing problem in the course of catalytic reactions. The variation of the activity due to deactivation is concisely reported [165].

![Fig. 9: Influence of methane concentration on carbon formation rate at T=800°C; mcat =25g; Q= 45Nl/h.](image)

The activity of a catalyst at any time may be expressed as

$$ a = \frac{\text{rate at which reactant} \text{A is converted by the catalyst}}{\text{rate of reaction of A using a fresh catalyst}} $$  \hspace{1cm} (11)

While the rate at which the catalyst deactivates may be written as

$$ \frac{da}{dt} = k_d \cdot c^m_1 \cdot a^d $$  \hspace{1cm} (12)

where $k_d$ is the deactivation rate constant, $d$ the order of deactivation, $m$ measures the concentration dependency.

In the catalytic methane decomposition using carbon catalysts, the kinetic profiles of methane decomposition over activated carbon and carbon black catalysts display fast catalytic activity initially, followed by a fairly mild drop in methane decomposition rates. Due to carbon deposition, loss of the catalyst surface deactivated the catalyst [159]. Catalyst deactivation, which is mainly due to surface area reduction and pore obstruction arising from carbonaceous deposits from methane decomposition reaction, is responsible for the loss of catalytic activity. Probably, the total rate of CH₄ decomposition is the combination of carbon nucleation rate and carbon crystalline growth rate. In the activated carbon catalysts, the blockage of the pore mouths by carbonaceous deposits significantly reduces the micro pore volume and BET surface area and thus the loss of catalytic activity prevails [166]. The catalytic activity of deposited carbon is less than that of the original carbon and hence methane conversion has decreased with time [144]. Fig. 10 shows the surface area and total pore volume versus reaction time for methane decomposition using carbon black catalyst. In the case of metal catalysts, gas-side of the metal surface is covered by excess carbon. Encapsulating carbon decreases the available metal surface area for methane cracking to take place. Moreover, the reduction of the active surface area brings about reduction of heat input to the metal which in turn diminishes the carbon solubility and its diffusion through the metal and consequently, the rate of carbon encapsulation escalates [61]. Suelves et al. [88] investigated the catalytic methane decomposition in a fixed bed reactor at different operating conditions employing a commercial Ni-based catalyst to obtain pure hydrogen. They investigated the mechanism of catalyst deactivation, and obtained hydrogen concentration of about 80% at 700°C, which is close to the thermodynamic values. It has been displayed that operating conditions influence the time for catalyst deactivation. Higher temperature and higher methane flowrate reduce the catalyst life. In Fact, using 700°C reaction temperature and space-time of 1 s, the catalyst activity was maintained over 8 h in the stream. On the contrary, the catalyst became deactivated after 90 min using 0.2 s space-time while the amount of carbon deposited was reduced to half.
Morphology and Characteristics of Carbon Formed

Hydrogen and different carbon nanomaterial are produced from the catalytic methane decomposition depending on the type of catalyst and reaction conditions used. The carbon products include carbon nanotubes (CNTs), carbon fibers (CFs), carbon blacks (CBs), and carbon flakes [168-173]. There is a strong relationship between the morphology of the formed carbon and its performance. For instance, for CNTs, the open end has prospective applications in heterogeneous catalysis as the inner surface of the tubes avails room for reactant molecules and also form irregular and varying configurations due to their sharp ends and dangling bonds when used in the emission devices, whereas the CNTs require pretreatment to take away the cap in the case of close end [174]. Li et al. [175] performed methane catalytic decomposition in a tubular using porous supported iron catalyst such as zeolite HZSM-5, zeolite HBETA and precipitated Al2O3. They found CNTs with different morphologies. The CNTs formed on zeolites were short and had close ends and catalyst particles did settle on the CNTs tips. While with zeolite HBETA, CNTs formed on HZSM-5 showed more turns and discontinuities. Moreover, complex CNTs with various morphs and a wide range of size were grown on precipitated Al2O3; In fact, catalyst particles rested at the CNTs tips. Their study of CNTs on zeolites and Al2O3 revealed two different growth mechanisms for similar reaction conditions, which are the tip growth mode for Al2O3 and the base growth mode for zeolites. Fig. 11 depicts the morphology of carbon products. Saraswat and Pant investigated thermal catalytic methane decomposition using a nano-size Ni-Cu-Zn/MCM-22 catalyst [176]. Their result indicated the formation of CNTs which looks like interlaced nano filaments emerging from nickel particles over catalysts. Fig. 12 displays the morphology of carbon formed via SEM Characterization.

Cunha et al. [177] studied the effectiveness of Ni–Cu alloyed Raney-type catalysts for the hydrogen production via catalytic methane decomposition. They found different structures of carbon were formed due to the different active phases. The SEM micrographs of the Ni30Cu50 obviously display lengthy carbon nanofibers (CNF) after decomposition reaction at 600°C. Fig. 13 presents a TEM picture, displaying filaments with narrow hollow cores.

Pinilla et al. [30] investigated Ni and Fe-based catalysts for catalytic methane decomposition. Their results exhibited the carbon nano filaments formation of the order of 12–14 gC·gcat⁻¹ for the Ni-based catalysts and 1.5–2.3 gC·gcat⁻¹ for the Fe-based catalysts. In Fig. 14, Ni-based catalysts generated fishbone-like carbon nanofibres whereas Fe-based catalysts produced chain-like carbon nanofibres.

Zhang et al. [178] studied catalytic methane decomposition employing Ni/MgO and NiO-D catalysts. Their results revealed that catalyst kinds and reaction conditions influenced not only the methane conversion, but also microcosmic morphology of carbon.
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Fig. 11: Morphologies of carbon products over (a and b): HBETA zeolite; (c and d): HZSM-5 zeolite; (e–h): Al₂O₃ (TEM graphs) [162].

Fig. 12: SEM micrographs of as grown CNTs over the catalyst (a) catalyst 50%Ni-10%Cu-10%Zn/MCM-22 (b) catalyst 50%Ni-15%Cu-5%Zn/MCM-22, and (c) catalyst 50%Ni-15%Cu-15%Zn/MCM-22 after a CDM run at 750°C [163].

Fig. 13: TEM micrograph of the carbon deposit obtained on Ni30Cu50 at 600 °C [164].
A huge interest has been granted to the development of iron-based catalysts for their cheaper, non-toxic properties than Ni catalysts. Indeed, iron-based catalysts are one of the least expensive catalysts used for the thermo-catalytic methane decomposition. Muradov studied thermo-catalytic decomposition of methane over an iron oxide catalyst [54]. The author concluded that the catalytic activity of iron catalyst was high at temperatures above 600°C and the yield was near equilibrium values at 800°C. The alumina supported iron catalysts were explored by Shah et al. [192] at a temperature range of 400-1200°C. First, they studied pure iron catalysts and concluded that their effectiveness decreased with decreasing reactor temperatures. Better activity was obtained using binary molybdenum-iron catalysts and binary palladium-iron catalyst. The authors also investigated the effects of temperature on hydrogen production and found that, above 800°C production decreased with most of the active catalysts, likely due to the thermal deactivation of the catalyst. Although Fe-based catalyst has lower catalytic activity than Ni-based one at a low reaction temperature [193] it is likely to find higher methane conversion on Fe catalyst at high temperatures (above 700°C), because high temperature enhances the methane decomposition reaction equilibrium and making use of the catalytic activity of AC itself as the catalysts. A comparison between Ni and Fe based catalysts were performed by Pinilla et al. [30] in a rotary reactor. Although Ni-based catalysts are more active at a given temperature, the use of iron-based catalysts allows for the use of higher temperature and thus obtains methane conversion above 80 %. The type of nano-carbon obtained is different. The use of Al₂O₃ as a support gives better results than MgO. Pinilla et al. [98] studied the addition of Mo as a promoter to Fe-based catalyst. It improves the performance if MgO is used as a support and there is a little effect if Al₂O₃ is used. Methane Conversion up to 87% is obtained if the temperature is increased to 900°C. Tang et al. [99] tested the use of ceria as a support giving improved performance. Optimal catalytic activity was obtained for a catalyst of composition 60 wt% Fe₂O₃ + 40 wt % CeO₂. Reshetenko et al. [195] studied the effect of adding Ni or Co to Fe-based
catalysts from 600 to a 650°C reaction temperature. The investigators concluded that the temperature range was effective for methane decomposition. The best performance was for a catalyst of the composition, 50–65 wt.% Fe, 5–10 wt.% Co (or Ni) and 25–40 wt.% Al₂O₃. Torres et al. [182] found that the addition of Mo to Fe based catalysts led to the increase of the rate and amount of deposited carbon. Chesnokov and Chichkan found that by adding Fe to Ni-Cu/Al₂O₃ catalyst, it was possible to increase the reaction temperature from 700 to a 750°C and thus increase the conversion [180]. Cunha et al. [177] found that the addition of Cu to Raney type iron catalyst improves catalyst performance. Takenaka et al. [196] found that Al₂O₃ is a better support than SiO₂ for Fe catalysts. Koneczny et al. [197] studied preparation methodology for Fe based catalysts. Avdeeva et al.[71] examined catalyst preparation effects on the amount of filamentous carbon produced. Fe-Co-Al₂O₃ catalysts gave the most effective carbon formation. Ermakova et al. [198] investigated the reaction temperature effect of the Fe-based catalyst. They used a temperature range of 650-800°C. They found that temperature should be higher than 680°C for the catalyst to be stable and to operate for a long period of time. Oliveira et al. [199] found that Sn hinders methane decomposition in chemical vapor deposition reaction to produce carbon. Wang et al. [86] found that Ni-Fe-SiO₂ has a better performance than Ni-SiO₂ when the reaction temperature is 650°C. The reverse happens when reaction temperature is 550°C. Yamaguchi et al. [200] suggested using a cycle in which methane decomposition is carried out in one step. Steam is used in the second step to remove carbon deposited. The catalyst is iron based. The simultaneous addition of CeO₂ and ZrO₂ improved catalyst activity and stability. Polymer-based composites were prepared by Suelves et al. [188] using different concentrations of nano carbons produced from methane decomposition in a rotary. The study revealed the possibility of using nano carbons in polymer composites. Pinilla et al. [201] investigated using solar energy as a source of the heat for the decomposition reaction. Nano-carbon is formed using Ni/Al₂O₃ and Fe/Al₂O₃ and amorphous carbon is formed when using carbon as a catalyst.

Conclusions

In the nearest future, hydrogen production most probably will continue to rely on fossil fuels, chiefly, natural gas. Presently, hydrogen production technologies produce considerable amounts of CO₂ emissions. An environmentally smart technique for producing valuable carbon and pure hydrogen without (or with significantly reduced) CO₂ emissions is the thermo-catalytic decomposition of methane Carbon blacks, carbon fibers, carbon flakes and carbon nanotubes are the carbon products associated with hydrogen.

The valuable carbon byproducts could be sold, thus decreasing the net price of hydrogen production. The operating conditions and the type of catalyst used affect the value of the carbon formed in the catalytic methane decomposition. There is a strong relationship between the morphology of the formed carbon and its performance. Catalytic methane decomposition produces carbon nanotubes that possess surprising properties: high thermal and electrical conductivities, harder than diamond and many-times stronger than steel. It can be used as a structural material, catalyst, and catalyst support. It is also useful to the carbon fuel cell in forming the consuming anode.

The endothermicity reaction of methane decomposition is not very high. The thermodynamic data exhibit that the methane decomposition could be effected at moderate temperatures in the presence of appropriate catalysts. Comparison among transition metals shows that the catalytic performance order comes as: Ni > Co > Fe

At the beginning of the catalytic methane decomposition very high methane conversions could be obtained from the Fe-based catalyst by operating at a sufficiently high temperature. The formation of well-arranged graphitic carbon at 600°C benefits from Cu inclusion in the incipient alloyed Ni–Cu Raney-type catalysts.

Support structure and its textural features affect the conversion process so that unsupported catalysts are less active than the supported catalysts.

Carbon-based materials are considered as ideal catalysts for catalytic methane decomposition due to desirable features such as low material cost, high surface area, thermal stability, resistant to sulfur and other potentially detrimental impurities in the feedstock and can be easily separated from reaction system. A pore blockage and surface area reduction carbonaceous deposit of methane is commonly related to the loss of catalytic activity of carbon catalysts.

Acknowledgements

The authors thankfully acknowledge their appreciation to King Abdul-Aziz City for Science...
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