

A SHORT REVIEW OF TURQUOISE HYDROGEN PRODUCTION VIA METHANE PYROLYSIS OVER CATALYTIC SYSTEMS

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The review provides a short summary of the production of turquoise hydrogen using catalytic methane pyrolysis, focusing on transition metal (Fe, Ni, Co) and carbon-based catalysts. Methane pyrolysis enables the production of CO₂-free hydrogen, with solid carbon serving as a valuable by-product. Fe, Ni, and Co catalysts are highlighted due to their strong C–H activation capacity, high activity, and economic feasibility. In turn, carbon-based catalysts offer high thermal stability and resistance to coking, providing a longer catalyst lifetime. Other materials, such as noble metals or complex oxides, are less considered due to the cost, limited scalability, or lower selectivity in solid carbon formation. Focusing on combined cocatalysts and carbon systems provides a balance between catalytic performance, durability, and economic viability, which is the most practical direction for promoting sustainable turquoise hydrogen production.

Keywords: Carbon catalysts, metal catalysts, methane pyrolysis, turquoise hydrogen.

1. INTRODUCTION

To support global efforts to mitigate climate change, accelerate the decarbonization of the world's energy system, and meet rising demand for affordable clean energy, hydrogen is increasingly recognized as a viable solution, provided its cost becomes competitive. Currently, the most widely used method for hydrogen production is

steam methane reforming (SMR) [1]. Nowadays, 68–76 % of global hydrogen is produced using SMR, despite its high energy demand, large consumption of superheated steam, and the generation of up to 10 kg of CO₂ per kilogram of produced H₂. Such hydrogen is often called “grey” hydrogen [2].

To reduce carbon emissions, there are two options. The first one involves the use of carbon capture and storage technologies (CCS) [3], which produces the so-called “blue” hydrogen. Despite relying on fossil resources, grey and blue hydrogen provide crucial parameters of hydrogen, with a substantially lower cost than fully renewable hydrogen can provide. Additionally, CCS adds complexity and costs to the production of blue hydrogen. This has intensified the search for alternative low-carbon hydrogen pathways. The second option, which is a potentially promising alternative, is methane pyrolysis, where reaction occurs at high temperatures (>1000 °C [1]), and carbon deposits in the reactor, thus mitigating CO_2 emissions and necessity for CCS. The pro-

cess can be further improved using catalysts, which can lower the required reaction temperature and enable the co-production of valuable solid carbon, potentially enhancing both economic and environmental performance. However, no universally optimal catalyst has been identified to date. The field is characterised by diverse catalytic materials, varied reactor conditions, and scattered data on carbon co-products, making systematic comparison challenging.

This review has combined information about Fe, Ni, Co, and carbon-based catalysts in methane pyrolysis to compare their relative performance and support the development of hydrogen production methods with low carbon emissions.

2. METHANE PYROLYSIS

Pyrolysis is the thermal decomposition of methane into hydrogen and carbon, as shown in Reaction 1. Producing one mole of hydrogen via pyrolysis requires an energy input of 37.5 kJ/mol. For comparison, producing hydrogen via SME requires 63.4 kJ

per H_2 mol, whereas water electrolysis requires 285.8 kJ per H_2 mol. The enthalpy diagrams for these reactions are shown in Fig. 1 [1]. Thus, pyrolysis has attracted some interest, but there are challenges.

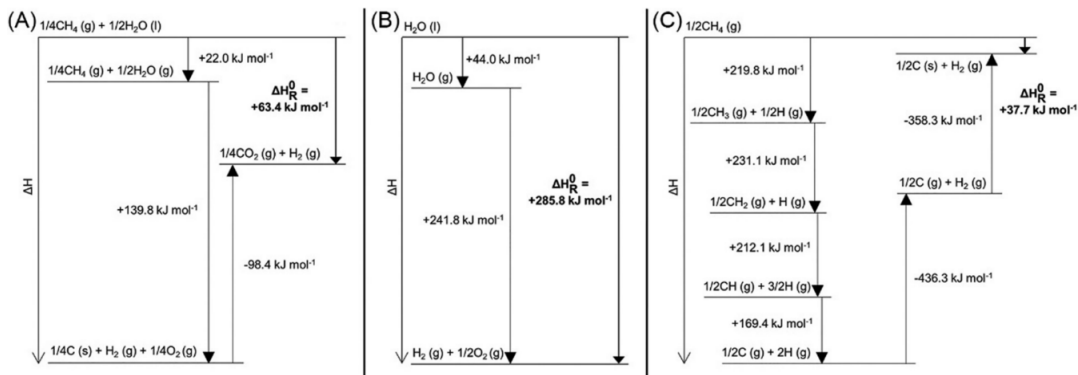
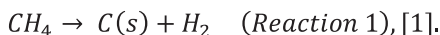


Fig. 1. Enthalpy diagrams of (A) SMR, (B) water electrolysis, (C) methane pyrolysis, adapted from [1].

Direct pyrolysis is an endothermic reaction that requires high reaction temperature ($>1000\text{ }^{\circ}\text{C}$) due to the stable, non-polar tetrahedral molecular geometry of CH_4 and its high C–H bond dissociation energy [1]. Recently, Koshi et al. have extensively discussed the mechanisms of methane pyrolysis separating the process into various components with and without surface influence and/or soot formation. They have compared the models with known experimental data and concluded that there is still no clear model to describe the process. One major challenge is the variability of pyrocarbon deposits; many models assume graphene-like structures, although not all deposits exhibit graphene structure, among other aspects. On the other hand, existing models such as CRECK-Polimi and NUIK-Polimi can explain shock wave decomposition with pyrocarbon deposits and negligible surface influence [4]. Further research is being carried out to develop more accurate models, while there is certain amount of experimental work.

Given the large global reserves of methane and its relatively low cost, as well as availability of biomethane in the future,

methane pyrolysis could serve as a viable low-carbon alternative to SMR with a lower carbon footprint. Most of the carbon footprint from this process comes from electricity generation and from extracting and transporting natural gas [5], [6]. Reactor parameters as pressure can significantly influence reaction efficiency. Furthermore, reactor materials and configuration affect product distribution. For example, experiments in corundum tube at various temperatures have shown that soot has different elemental content and pyrolysis gas composition, ranging from 28.64 to 92.74 % H_2 with CH_4 flow of 1 L/min at 1000–1200 $^{\circ}\text{C}$, respectively [7].

To further reduce the carbon emissions of methane pyrolysis and improve its energy efficiency, the use of catalysts is crucial. Catalytic methane pyrolysis offers lower reaction temperatures, reduced energy demand, and improved overall process economics compared to non-catalytic methods; therefore, this study focuses on catalytic systems, with particular attention to cost-effective and high-performing catalysts and the mechanisms proposed for their activity.

3. CATALYTIC METHANE PYROLYSIS

Two reaction mechanisms have received the greatest attention in literature: the molecular adsorption mechanism [8] and the dissociative adsorption mechanism [9]. In the molecular adsorption mechanism, methane adsorbs intact onto the catalyst surface, Fig. 2A a), then it dissociates in a series of dehydrogenation reactions as shown in Fig. 2A from b) to e). In contrast, during the dissociative adsorption mechanism (Fig. 2B), methane is split into CH_3 and H fragments upon adsorption (Fig. 2B I) at the active sites on the surface. Then,

dehydrogenation steps follow (Fig. 2B II to IV), analogous to those in the molecular adsorption mechanism. At present, there is no consensus regarding the dominant reaction pathway or the rate-limiting steps of methane pyrolysis [10], [11]. Conventionally, catalysts are expected to deactivate over time due to carbon deposition (coking) on their surfaces [12], [13]. However, in some cases, deposited carbon grows into structured materials such as carbon nanotubes. Both the form of the deposited carbon and the catalytic activity appear to be

strongly catalyst dependent. In the literature, catalytic materials are generally classi-

fied into two main groups: metal-based and carbon-based catalysts [1].

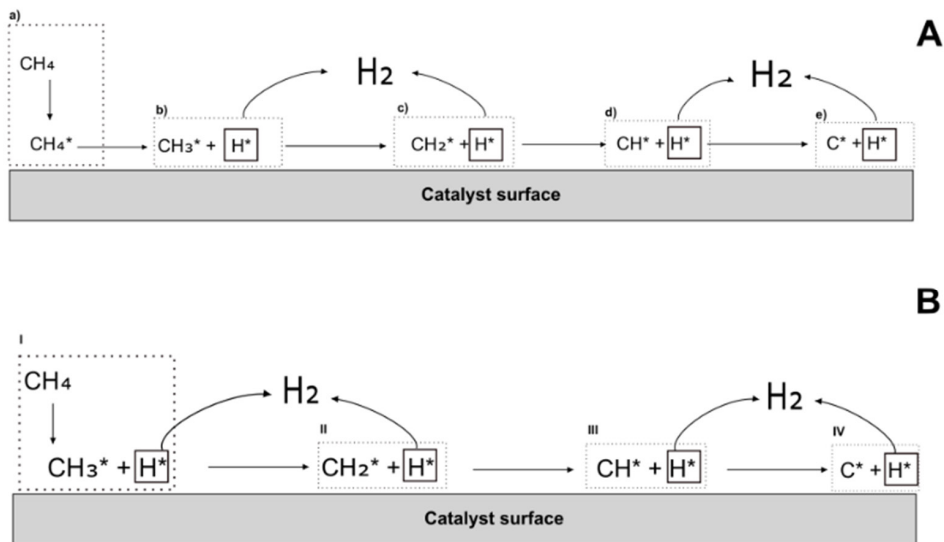


Fig. 2. The proposed pyrolysis reaction mechanisms adapted from [5].

3.1. Metals

Metal catalysts such as transition metals Fe, Ni, Co are supported by various oxides SiO₂ [14], Al₂O₃ [15], MgO [16], CeO₂ [17], [18], Fe₂O₃ [19]. The key reason for using these metals is their partially filled 3d orbitals, which facilitate the breakage of C–H bonds. Metal catalysts for methane pyrolysis have been extensively studied, with nickel, iron, and cobalt showing diverse catalytic performances. Nickel-based catalysts, especially supported on activated carbon, are known for high methane conversion, but suffer from carbon deposition that limits their lifetime [20].

Two metals can be combined into a bimetallic system. For example, nickel and iron or cobalt can improve both activity

Iron (Fe)

Iron is used as a catalyst because it is widely available and cheaper than pre-

and catalyst stability. Iron catalysts offer high methane conversion rates, approaching 90 % under certain conditions, and they bring the advantages of low cost and thermal robustness. However, they also face deactivation due to carbon formation. Cobalt catalysts typically exhibit methane conversion efficiencies between 7 % and 12 % at moderate temperatures (475–600 °C), forming filamentous carbon that influences catalyst durability [1], [21]. For high process efficiency, the catalyst should be abundant, low cost, or high recoverability from the process. Let us focus on a couple of abundant and available catalysts – Fe, Ni, and Co – as possible additives despite their higher costs [22].

cious metals like platinum or palladium [23], [24]. Iron-based catalysts demonstrate

significant catalytic activity within the temperature range of 650–950 °C [23], [25] with hydrogen yields by catalysts supported on alumina reported between 60 and 62 % [26]. At these temperatures, iron oxides reduce and transform into active iron and iron carbide phases. The cyclic formation and decomposition of these carbide phases facilitate methane decomposition and carbon formation, thereby increasing H₂ yields [25].

Iron catalysts also promote the growth of carbon deposits, which can lead to the formation of carbon nanotubes that can break down larger particles of iron catalyst, creat-

Nickel (Ni)

Nickel catalysts are widely regarded in methane pyrolysis due to their higher catalytic activity compared with Fe or Co [1]. Primarily supported forms, such as nickel on activated carbon (Ni/AC), have demonstrated a methane conversion rate of about 46 % at ~ 800 °C [27], [28]. However, this high activity of nickel comes with a significant drawback: rapid carbon deposition on the surface of the catalyst, which leads to deactivation [1].

To increase catalyst lifetime, bimetallic catalyst systems can be used, for exam-

Cobalt (Co)

Cobalt is one of the most active catalysts for methane pyrolysis; however, it is more expensive and toxic than alternatives (Fe or Ni) [1]. Reported performance of cobalt catalysts varies, largely due to differences in support material. The catalytic activity and stability of supported cobalt catalysts follow the order Co/Al₂O₃ > Co/MgO > Co/TiO₂ > Co/SiO₂ [31]. For example, cobalt oxide on alumina (CoO/Al₂O₃), containing 10 wt% of cobalt, has shown methane conversion

ing additional catalytic surfaces [24]. Eventually, carbon accumulation will fully cover the catalyst surface and will lead to its deactivation. Nevertheless, the thermal stability of iron allows it to withstand both pyrolysis conditions and regeneration. Regeneration can be done with small amounts of CO₂ and H₂O by cycling iron carbide phases [1]. When all these factors are considered, iron is one of the most economical and effective catalyst for the methane pyrolysis reaction. However, the limited lifetime and the form of deposited carbon constrain the practical application of this catalyst.

ple, Ni-Fe/AC, which leads to a slightly lower methane conversion rate (~37 %), but increases resistance to carbon buildup [29]. Nickel catalysts can also benefit from microwave irradiation, which significantly enhances methane conversion and hydrogen yield compared to conventional heating methods [27]. Furthermore, research on nanocomposites and supported nickel catalysts with various promoters shows improved performance with lower activation energies and better catalyst stability [30].

of 9.3 % at 550 °C and 6.5 % at 700 °C, with notable carbon-holding capacity (mass of solid carbon produced per mass of catalyst during pyrolysis), indicating methane decomposition [32].

Unsupported cobalt catalyst can be synthesized, such as those prepared by using the Pechini method. Cobalt-based catalysts typically operate in the temperature range of 475–600 °C and near atmospheric pressure, achieving methane conversion rates in

the range of 7–12 %, depending on catalyst type and reaction conditions [31], [33]. Still, compared to Fe or Ni, cobalt, in some cases, shows lower hydrogen production yields.

Co catalysts have also been investigated as bimetallic combinations with nickel and iron to improve hydrogen yields and stability. For instance, a 25% Fe–25% Co/MgO catalysts achieved more than 80 % hydro-

gen yield over 550 minutes on stream, demonstrating high performance among bimetallic formulations. These findings establish cobalt as a viable catalyst option for methane pyrolysis, especially when optimised with suitable supports or combined in bimetallic systems, to justify higher production and purification costs associated with Co-based materials [30].

3.2. Carbon-Based Catalysts

Carbon-based catalysts for methane pyrolysis have attracted considerable attention as a cost-effective alternative to metal catalysts, although their methane conversion efficiencies tend to be lower than those of Ni, Fe, or Co-based systems. Studies show that surface area plays a crucial role in the initial catalytic activity of carbon materials. Activated carbon, with a very high surface areas up to 2200 m²/g, demonstrates some of the highest initial activities among carbon catalysts [1], [33]. Studies show approximately 30 % increase in initial activity over other carbon-based catalysts [35]. However, carbon catalysts generally experience deactivation over time due to carbon deposition that blocks pores [1], [36]. These deposits block physical access to active catalytic sites, not allowing methane to adsorb and hydrogen to desorb, lowering overall process efficiency [37]–[40]. Interestingly, the carbon formed during the reaction can itself act as an active catalytic phase, producing an autocatalytic effect under certain conditions. For example, during induction heating, methane conversion may initially decrease but subsequently increase, reaching a stable state around 40–50 % conversion at 800 °C [36].

The crystal structure and lattice defects

Activated Carbon (AC)

Activated carbon is commonly used as

of carbon catalysts exert a significant influence on their catalytic performance. Higher lattice defects, indicated by Raman spectroscopy intensity ratios (I_D/I_G), correlate with greater catalytic activity, as seen in comparisons between different carbon blacks and mesoporous carbons [1]. Amorphous carbons with abundant defects and large surface areas tend to be more active. Mesoporous carbon structures outperform microporous carbons due to improved mass-transfer characteristics. The carbon produced during methane pyrolysis is often graphitic or nanotube-like, having reduced catalytic efficiency compared to the initial catalyst's surface. Despite these limitations, carbon catalysts offer advantages such as low cost, wide availability, and the ability to be regenerated and recycled. Operationally, carbon-based catalysts require relatively high temperatures, typically above 800 °C, to achieve meaningful methane conversion, which is higher than some metal catalysts but may still be acceptable depending on process design and economics. The main challenge remains maintaining a long-term activity through effective regeneration strategies that mitigate pore blockage and surface structural changes [1], [33], [36], [41].

a catalyst support but can also be used as

a catalyst in methane pyrolysis due to its high surface area and good thermal stability. Studies on activated carbon-supported nickel catalysts (Ni/AC) report methane conversion rates of around 46 % at 800 °C under microwave heating [27]. While these catalysts exhibit a high initial activity, they suffer from rapid deactivation caused by carbon deposition, which limits their operational lifetime.

Bimetallic catalysts, such as nickel and iron supported on activated carbon (Ni-Fe/AC), exhibit lower methane conversion rates, approximately 37 %, but offer significantly improved resistance to carbon

Carbon Nanotubes

Carbon nanotubes (CNTs) have also emerged as promising catalysts for methane pyrolysis, with their catalytic activity strongly linked to their unique structural and electronic properties. CNT-based pyrolysis generally requires higher temperatures (600–1000 °C) than metal-based systems. The presence of residual or intentionally added metal catalysts (Fe, Ni, and Co) enhances the decomposition of methane and increases the yield of carbon nanostructures [42], [43]. Catalysts supported by CNTs not only produce hydrogen but also facilitate the formation of high-quality carbon materials [13], [44].

Reaction kinetic studies show deviations from ideal behaviour when CNTs are used as catalyst support. Reported reaction orders of approximately 0.6 suggest a complex interaction between the methane molecules and the active sites on the CNT

buildup and enhanced long-term stability. They also require lower power input to maintain reaction temperature, improving overall energy efficiency.

Carbon depositions on activated carbon-supported catalysts frequently form filamentous carbon, which has a potential commercial value as a co-product. In contrast, pure activated carbon catalysts exhibit lower catalytic activity, the need for metal incorporation to achieve high performance. Nevertheless, catalyst deactivation due to carbon accumulation remains a key challenge that necessitates continued research [27], [37], [42]–[44].

surface [45], [46]. CNTs can be supported by various metals, including Ni, Co, and Fe. Jiang et al. showed that the reaction order varies with catalyst composition, generally remaining below one, which is attributed to the catalytic characteristics of CNT-supported metals [45]. Density functional theory studies further demonstrate favourable methane adsorption energies on metal-decorated CNTs, supporting their ability to activate CH₄ for decomposition [47], [48].

It has been reported that microwave heating presents an alternative route to enhance the catalytic activity of CNTs, utilising the dielectric heating properties of CNTs, by increasing the temperature of the catalyst and accelerating methane decomposition [46], [49]. Also, the thermal conductivity and stability of CNTs leads to more uniform heating of the catalyst, which can help reduce carbon deposition [50].

3.3. Alternative Pyrolysis Methods and Competing Results

Even when effective catalysts are used, variations in reactor design, catalyst delivery methods, and operating pressure can significantly influence methane pyrolysis outcomes. As summarised by Becker et al.

[51], research has been conducted using diverse reactor configurations, including bubble column, capillary, liquid metal, and molten salt reactors [52]–[54].

In addition to conventional thermal

pyrolysis, the primary focus of this review, several alternative methods exist. These include microwave assisted pyrolysis [51], solar thermal pyrolysis [52], and plasma assisted pyrolysis [53]. These competing technologies and approaches aim to the same goal of lower hydrogen costs, and economic analyses have been reported for specific configurations, such as bubble reactors by Angikath et al. [54] and broader comparison with SMR and water electrolysis by Hyun Seung Kim [55]. Kim’s analysis indicates that coupling methane pyrolysis with renewable energy sources (e.g., solar) can improve productivity and reduce environmental impact by leveraging electrification. However, these economic assessments

often do not incorporate catalyst efficiency, which remains crucial. More active and durable catalysts could significantly reduce energy requirements, improve process viability, decrease mineral and material intensity, and enable catalyst recovery or recycling – factors that must be considered in any comprehensive evaluation of methane pyrolysis technologies.

Summary of reported conversion rates are depicted in Table 1. As we can see, single catalysts can provide substantial CH₄ conversion rates, but optimisation of catalysts should be carried out to further improve yields and carbon materials grown on catalysts in pyrolysis reaction.

4. CONCLUSIONS

Methane pyrolysis is a promising route for low-carbon hydrogen production, offering the advantage of generating solid carbon instead of CO₂. This review highlights the main metal-based (Fe, Ni, and Co) and

carbon-based (activated carbon, and carbon nanotubes) catalysts and their role in methane conversion, hydrogen yield, and formation of carbon structures. These values are summarized in Table 1.

Table 1. Methane Conversion Rates and Hydrogen Yield by Catalyst Type

Catalyst type	CH ₄ conversion, %	H ₂ yield, %	Reference
Iron (Fe)	~ 60	60–62	[24], [26], [56]
Nickel (Ni)	~ 46	~ 37	[27]–[29]
Cobalt (Co)	~ 80	7–12	[30], [31], [33]
Activated carbon (AC)	10–50	20–60	[27], [32]
Carbon nanotubes (CNTs)	30–80	60–90	[56]–[58]

Iron catalysts are cost-effective and thermally stable, making them suitable for large-scale applications, while nickel and cobalt catalysts offer higher activity, but face challenges related to rapid carbon deposition and higher costs. Carbon-based catalysts, including activated carbon and carbon nanotubes, are widely available and recyclable, although they require higher

operating temperatures and often benefit from metal promotion. Reactor design, heating methods, and alternative pyrolysis approaches, such as microwave, solar, and plasma-assisted pyrolysis, further influence efficiency and hydrogen yield, emphasising the importance of process optimisation.

This short review has shown a primary comparison of catalyst types and operating

strategies, which provides a basis for cost-effective and high-performance catalysts. By combining optimised catalysts with advanced reactor designs and renewable

energy integration, methane pyrolysis can become a practical, low-carbon hydrogen production route, supporting the transition to a sustainable energy future.

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