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REVIEW ARTICLE

Advancement in steam reforming of methanol to produce hydrogen: A review

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ABSTRACT

The main deliberation of this review paper is on metallic catalysts, including Cu-based catalysts, with distinct formulations and compositions, utilized for steam reforming of methanol (SRM). The review critically examines the performance of these catalysts, considering the active components, supports, promoters, and their interactions. Additionally, the review identifies and elucidates the various kinds of reaction mechanisms and routes involved in SRM. This comprehensive analysis provides valuable insights into the progress of well-organized and effective catalysts for SRM. To achieve high yields of H_2, it is crucial to conduct a fundamental study of the role of copper as a component in both mono and multimetallic systems, as well as the nature of support. These factors are essential to understand the catalytic mechanisms involved in the steam reforming of methanol and to develop effective strategies for optimizing hydrogen production. Therefore, a thorough investigation of copper-based catalysts and their interaction with the support material is essential for the development of highly efficient steam reforming processes.

Keywords: methanol reforming; hydrogen production; catalyst reaction scheme

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1. Introduction

In the present day, achieving stability between economic evolution, growth, and sustainability while safeguarding the environment poses a monumental challenge to the world. Energy and the environment are intricately linked, and the path toward achieving this balance grows more complex each day. According to a report in 2019 by the International Energy Agency (IEA), a 1% increase in global economic output results in a 0.5% rise in CO_2 emissions annually[1]. In recent decades, there has been a significant focus on using non-carbon renewable sources, such as solar, wind, hydrothermal, and tidal energy, as well as hydrogen energy. However, all of these sources, except hydrogen, experience availability issues throughout the year[2]. Hydrogen is becoming an increasingly popular alternative to traditional energy sources in fuel cells, thanks to its higher energy density and lack of greenhouse gas emissions[3]. Specifically, when it comes to energy sources for transportation, polymer electrolyte membrane fuel cells (PEMFC) are extensively utilized[4]. However, unlike fossil fuels that can be directly extracted from the environment, hydrogen needs to be obtained through different reforming reactions, including steam reforming, auto-thermal reforming, and partial oxidation[5]. Methane is often used as a feedstock for hydrogen generation, but this process has significant drawbacks when it comes to industrial applications. It can be complex, and there are safety concerns related to hydrogen storage and transportation[6]. The majority of hydrogen production worldwide, particularly for the refinery and chemical industries is achieved through steam reforming or partial oxidation of fossil fuels like naphtha or natural gas. This process is well-established and widely used for various feedstocks, including LPG, methanol, diesel and jet fuel[7].

Currently, natural gas reforming is considered more cost-effective and efficient than steam reforming of methanol (SRM) for the production of H_2. However, relying on natural gas reforming is not a sustainable and environmentally friendly solution in the long term[8]. The process reforming of natural gas involves high temperatures, which results in significant CO_2 production and purification requirements for hydrogen production. This translates into higher assets funds, functional charges, and CO_2 radiations[9]. Byun et al.[10] revealed that the lowest cost for hydrogen production was 2.78 USD per kilogram of hydrogen, achieved with a reactant cost of 100 USD per ton and a cost exponent of 0.6, it remains higher compared to the cost of hydrogen produced through SMR (steam methane reforming), which is 2.30 USD per kilogram. However, the analysis of various scenarios provided valuable insights into the steps necessary to achieve economic feasibility in hydrogen production.

In modern centuries, there has been a growing interest in using methanol reforming as an attractive option for hydrogen production. Methanol has several advantages, including its small sulfur content, higher volumetric energy density, higher hydrogen/carbon ratio of 4:1, and biodegradable properties[11]. In the context of hydrogen extraction, methanol stands out as the preferred choice among other alcohols due to its ability to undergo the process at lower temperatures, typically within the range of 200 °C–300 °C. This is attributed to the absence of C–C bonds in methanol's molecular structure. In contrast, the reforming of ethanol and methane necessitates higher temperatures, around 400 °C and 500 °C, respectively[12].

The demand for methanol has been growing at a compound annual growth rate (CAGR) of 6% since 2014, mainly due to its increasing usage in various industries. Recent studies have shown that 40% of the methanol formed is used in the area of energy region[13]. The reforming technologies for hydrocarbons and alcohols have made it possible to generate hydrogen in situ, thereby overcoming the challenges of hydrogen storage and transportation[12,14]. The US Department of Energy (DOE) has established a goal to achieve hydrogen production at a charge of 4 USD/kg or lower, employing emerging technologies[1]. By 2030, it is projected that the cost of hydrogen extraction will see a further reduction to 1.8 USD/kg. Additionally, hydrogen is expected to fulfill approximately 15% of the global energy demand (GED) during that timeframe[15].

During the steam reforming of methanol (SRM) process, in which methanol is converted into hydrogen and other products, the primary product is hydrogen, along with small amounts of carbon dioxide and CO, unreacted H_2O, and CH_4. However, the generation of CO needs to be restricted, as concentrations higher than 10 ppm can damage the catalyst[16]. Therefore, the design and performance of the catalyst play a critical role. An efficient catalyst should have higher activity and selectivity to yield a higher H_2 production, thereby minimizing CO production. Additionally, the catalyst should be resistant to sintering and have the longest feasible stability[17]. Extensive investigations have been carried out on copper and palladium-based catalysts in the field of steam reforming of methanol (SRM). Among these catalysts, copper-based ones are highly favored for their remarkable activity and selectivity. However, a significant concern associated with copper-based catalysts is their susceptibility to catalytic deactivation caused by thermal sintering[18,19].

The attainment of the catalyst through the reforming reaction is dependent on both the metal component and the support material[20]. Promoters, such as acid oxides or metals of alkaline, are critical in removing unwanted reaction products. To increase the efficiency of the reaction, it is also necessary to understand catalyst deactivation caused by coking or sintering[21,22]. In a study by Song and Ozkan[23], it was proposed that employing an improved performance reusable catalyst could offer a cost-effective solution for steam reforming of methanol (SRM). The growing interest in the SRM is apparent from the increasing number of publications on the topic each year (as shown in **Figure 1)**.

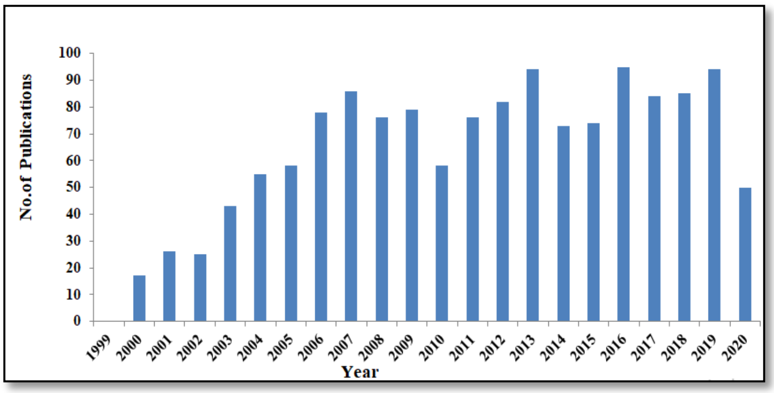

Figure 1. Publications detail on steam reforming of methanol to H_2 production from various databases, modified from Reference [1].

The cost of SRM is impacted by the process of separating hydrogen from the product mixture. Membrane reactors are more efficient than traditional reactors because they allow for the reaction and H_2 separation from CH_4, CO_2, CO, and other known by-products to occur within the same reactor, eliminating the need for additional processing steps. By bypassing the water gas shift (WGS) reaction, membrane reactors are more cost-effective. This is because they can perform both the reaction and separation simultaneously, reducing the cost and time associated with the separation process. This information is supported by research that shows the efficiency and cost-effectiveness of membrane reactors in SRM[24]. Numerous kinds of membrane reactors have been employed for SRM, including fluidized bed membrane reactors (FBMRs), packed bed membrane reactors (PBMRs), micro-porous SiO_2 membranes, and micro membrane reactors[25]. In recent years, research has also focused on disseminated feeding membranes that exhibit selectivity nearby H_2 and CO[26]. This approach has shown promise in enhancing the efficiency and selectivity of hydrogen separation in SRM. These countless varieties of membrane devices have been studied and evaluated, and their effectiveness has been documented in the literature.

Concerning its practical implementation, a study conducted by Pashchenko[27] investigated the utilization of low-grade heat for methanol decomposition. The findings demonstrated that the use of low-grade heat for methanol decomposition can lead to an efficiency improvement of up to 5% compared to utilizing the same heat for steam generation. Furthermore, the study highlighted that the efficiency of a combined cycle increases with higher gas turbine inlet temperatures.

Pashchenko et al.[28] conducted a thermodynamic analysis using the Aspen Hysys platform to evaluate the efficiency of various fuels, including methanol, ethanol, n-butanol, and glycerol, in thermochemical recuperation (TCR) systems. The analysis utilized the Gibbs free energy minimization method and investigated a wide temperature range of 400 K to 900 K, with a steam-to-fuel ratio of 1 and a pressure of 1 bar. The study focused on determining the maximum fuel conversion levels achieved. Notably, specific temperatures were found to yield the highest fuel conversion: 600 K for methanol, 730 K for ethanol, 860 K for n-butanol, and 890 K for glycerol.

Similarly, the study revealed that the efficiency of thermochemical heat recuperation systems is significantly influenced by both the composition of the initial reaction mixture and the process temperature. Notably, the maximum efficiency for steam reforming in these systems varied at different temperatures: 600 K for methanol, 700 K for ethanol, and 900 K for methane. These findings underscore the importance of carefully considering the specific reaction mixture and process temperature to optimize the efficiency of thermochemical heat recuperation systems[29].

In the concerning of pressure drop analysis, a combination of numerical simulations and experimental investigations was employed to analyze the pressure drop and loss factor in thermochemical recuperators that incorporated catalysts of varying shapes. The reaction space within these recuperators was modeled as a porous packed bed utilizing a $NiAl_2O_3$ catalyst, and the commercial software ANSYS Fluent was utilized for the simulations. A comparison between the experimental and simulation outcomes for pressure drops revealed a strong correlation, with a discrepancy of less than 8%. Furthermore, it was observed that the pressure loss in the packed bed displayed an approximately linear relationship with the bed depth[30].

Using the RBD algorithm (rigid body dynamics), a numerical calculation was performed to investigate the flow characteristics in a realistic computational domain. The results of the analysis indicated that when the pore size is less than 0.5 mm, the flow through the particle-filled porous medium is negligible. On the other hand, when the pore size exceeds 0.5 mm, a substantial flow occurs through the porous elements of the fixed-bed reactor[31].

The main aim of this paper is to offer a thorough and inclusive examination of the recent progressions in hydrogen production utilizing the steam reforming of methanol technique. The study focuses on Cu-based catalysts and analyzes their performance along with the factors affecting their reactivity. Additionally, the literature review covers the classification of SRM, its usefulness as a hydrogen storage medium, and its potential applications.

2. Literature

2.1. Classification of steam reforming of methanol (SRM)

SRM is a chemical process used to produce hydrogen gas by reacting methanol with steam. This process is highly endothermic, meaning it requires a lot of energy to be supplied in the form of heat. SRM is often preferred over other methods of producing hydrogen such as partial oxidation of methanol (POM), oxidative steam reforming of methanol (OSRM), and sorption-enhanced steam methanol-reforming because it results in a higher yield of hydrogen. There are several categories of SRM as shown in **Figure 2**, including thermo-catalytic reforming, photo-catalytic reforming, aqueous phase reforming, and high-temperature reforming. In general, SRM is represented by the following chemical Equation (1). **Figure 2** shows the various kinds of hydrogen production methods from steam reforming of methanol.

$$\text{SRM: } CH_3OH + H_2O \rightarrow CO_2 + 3H_2;\ \Delta H^{o}_{298\ K} = +49.2 \left(\frac{kJ}{mol}\right) \tag{1}$$

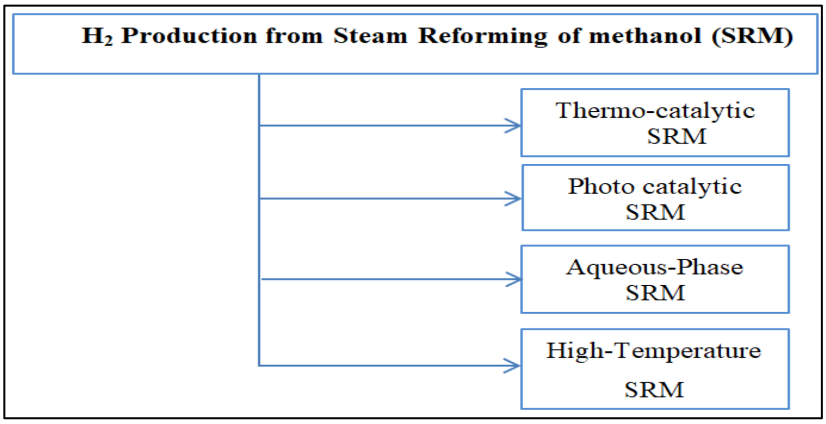

Figure 2. Classification of SRM methods.

2.1.1. Thermo-catalytic SRM

It is a commonly used method in industry for hydrogen production. However, side reactions are a common occurrence, especially when the lower ratio of steam/methanol. These side reactions often include the decomposition of methanol and the WGS reaction, leading to the production of methane, methyl formate, dimethyl ether, and other by-products[32].

$$\text{Dehydration: } 2CH_3OH \rightarrow (CH_3)_2O + H_2O; \Delta H^{o}_{298\ K} = -23\left(\frac{kJ}{mol}\right) \tag{2}$$

$$\text{Methanation: } 2CH_3OH \rightarrow CH_4 + 2H_2 + CO_2; \Delta H^{o}_{298\ K} = -66.9\left(\frac{kJ}{mol}\right) \tag{3}$$

$$\text{Dehydrogenation: } 2CH_3OH \rightarrow HCO_2CH_3 + 2H_2; \Delta H^{o}_{298\ K} = +64.4\left(\frac{kJ}{mol}\right) \tag{4}$$

$$\text{Formaldehyde synthesis: } CH_3OH \rightarrow CH_2O + H_2; \Delta H^{o}_{298\ K} = +84.7\left(\frac{kJ}{mol}\right) \tag{5}$$

$$\text{Carbonation: } CH_3OH \rightarrow C + H_2O + H_2; \Delta H^{o}_{298\ K} = +159.5\left(\frac{kJ}{mol}\right) \tag{6}$$

Wang et al.[33] were involved in a study on the thermodynamic performance of fuel cells via a poly-generation system that incorporated solar, waste heat, fuel cells, and SRM. The simulation results indicated that the system achieved an efficiency of 73.7% during the summer and 51.7% during the winter. In a separate study, Hosseini et al.[34] developed a poly-generation system that utilized a molten carbonate fuel cell (MCFC) system with an SRM, a heat and power cycle, and a methanol generation process using the distillation technique. The system demonstrated the capacity to generate electricity, warm water, and methanol concurrently, resulting in an impressive gross exergy efficiency of 83.7%. Schuller et al.[35] created a new type of heat exchanger reactor specifically for SRM. In their study, it was reported that this reactor employed waste heat from a fuel cell to drive the reforming reaction, leading to the thorough transformation of methanol at a temperature of 180 °C.

2.1.2. Photo catalytic SRM

It is a new type of technology that uses photon energy to reduce the temperature of the reaction. Sun et al.[36] studied SRM by lowering the reaction temperature with photon energy. Through a comparison of process outcomes with and without light, it was found that photon energy promotes the dissociation of formate into CO_2 and H_2. With no evidence of carbon monoxide, the rate of H_2 generation was 50.6 mmol/(g h) at 200 °C and 76.2 mmol/(g h) at 210 °C. Chiarello et al.[37] reported SRM over Pt/TiO_2 retaining in situ diminished entire reflection IR spectroscopy presented that TiO_2 physicochemical were pretentious from Pt nanoparticles.

2.1.3. Aqueous-phase SRM

It is an innovative technology that converts various compounds such as alcohol, sugar, and polyol into H_2 and CO_2 by placing them in an aqueous solution. The utilization of this process is regarded as an environmentally friendly technique for converting biomass into H_2 and CO_2 at lower reaction temperatures[38]. The key factor for the successful aqueous phase of methanol-reforming is the creation of a durable catalyst that can produce high hydrogen yields while minimizing the absorption of alkanes and CO[39]. The hydrogenation process of CO and CO_2 can lead to methane development.

$$CO + 3H_2 \rightarrow CH_4 + H_2O; \Delta H^{o}_{298\ K} = -253.70\left(\frac{kJ}{mol}\right) \tag{7}$$

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O; \Delta H^{o}_{298\ K} = -165\left(\frac{kJ}{mol}\right) \tag{8}$$

Davda et al.[40] utilized the catalyst (Pt/Al_2O_3) in their research on ethylene glycol and the methanol aqueous phase reforming. Their findings indicated that hydrogen had maximum activity and selectivity, with nearly 100% efficiency. Similarly, the catalyst $Ni/25\%CeO_2{-}ZrO_2$ was employed in investigating aqueous phase SRM. The research showcased a methanol conversion rate exceeding 50% and a hydrogen efficiency surpassing 40%[41]. Cortright et al.[42] also reported on the feasibility of H_2 extraction from alcohols at approximately 227 °C via aqueous phase SRM. These studies suggest the potential for efficient hydrogen production through AP-SRM using various catalysts.

2.1.4. High-temperature SRM

This technique explores the utilization of bimetallic catalysts, specifically iron and copper supported on Al_2O_3-Zn-ZrO_2, for the extraction of hydrogen. The investigation revealed that hydrogen extraction without any detectable carbon monoxide could be achieved at a temperature of 500 °C. The catalytic activity was evaluated across a temperature range of 150 °C to 500 °C. The research team observed an intriguing synergy that led to a decrease in particle size and improved reducibility for a bimetallic catalyst with an equal Fe/Cu ratio of 1:1. Furthermore, when the copper content exceeded 75%, the selectivity towards CO was practically eliminated. By conducting DRIFTs analysis, the researchers were able to identify that the existence of Fe_2O_3 as the surface species on the catalyst played a key role in the transformation of produced CO to CO_2. The results of the analysis indicated that Fe_2O_3 acted as an active component in facilitating the chemical transformation of CO into CO_2. These findings suggest the potential for efficient H_2 production using bimetallic catalysts through iron and copper[42,43].

2.2. Chemical hydrides as methanol

Chemical hydrides and metal hydrides share the characteristic of chemically bonding hydrogen, but their properties differ significantly due to the presence of lighter elements in chemical hydrides. Significantly, chemical hydrides exhibit a liquid state under normal conditions, which offers several advantages. It simplifies the transportation and storage of these hydrides and facilitates heat and mass transfer through dehydrogenation and hydrogenation approaches. Some chemical hydrides, including formic acid, methanol, and ammonia are already commonly produced through natural gas and used for purposes beyond hydrogen storage. This pre-existing infrastructure for production, handling, and transport is advantageous. Furthermore, utilizing hydrogen obtained through water electrolysis instead of natural gas reforming for the production of these bulk chemicals can contribute to a reduction in fossil fuel consumption. While certain chemical hydrides have been proposed as substitutes for hydrogen, this article does not aim to compare these fundamentally distinct pathways[44].

Methanol (CH_3OH) exhibits hydrogen storage capacities of 12.5% (wt) and 99 kg/m^3 in terms of gravimetric and volumetric measurements, respectively, making it the simplest alcohol with the potential for hydrogen storage. One of the most widely discussed methods for producing renewable methanol is over-carbon dioxide (CO_2) hydrogenation[45]. There are several ways to release hydrogen from methanol, including through steam reforming where it reacts with water, partial oxidation where it reacts with oxygen, or via methanol thermolysis (decomposition)[46]. Among these methods, steam reforming stands out as advantageous because it yields 3 moles of H_2 per mole of CH_3OH, whereas the other two reactions result in only 2 moles of H_2 per mole of CH_3OH[46,47].

To facilitate the methanol steam reforming, external heating is required due to the endothermic nature of the reaction and the evaporation of water and methanol. Typically, a catalyst ($Cu/ZnO/Al_2O_3$) is employed at temperatures ranging from 230 °C–330 °C[46]. The production of methanol through the synthesis of CO_2 and hydrogen has reached a commercial stage, and the "George Olah Renewable Methanol Plant" has been operational in Iceland since 2011, making it the world's first facility of its kind. The same type of catalyst used in conventional natural gas-based development can be used in the CO_2-based process[45]. The reaction to form methanol from CO_2 and hydrogen is exothermic, and temperatures around 220 °C–280 °C and pressures (10–80 bar) are normal reactor conditions. The methanol-water mixture produced from this process can be used to hydrogen yield directly through the reaction of steam reforming, without the need for the energy-intensive separation of developed methanol and water by distillation[48]. In this scenario, the overall process can be streamlined, resulting in a significant surplus of heat during the synthesis of methanol.

2.3. Utilization of hydrogen production in associated sectors

Hydrogen can be viewed as a feasible substitute fuel for engines originally intended to operate on different fuels due to its broad flammability range, which allows for precise regulation of engine power[49]. Chehade et al.[50] have stated that, although the reactivity of liquids is not a concern, the high density of liquid hydrogen makes it a more desirable option compared to lightweight hydrogen gas. However, due to its compressibility in smaller reservoirs, hydrogen gas offers greater storage capacity[50]. In terms of storage efficiency, high-pressure reservoirs are preferred for storing hydrogen gas over liquid nitrogen because gas molecules can be packed into a smaller space, whereas liquid nitrogen requires refrigeration units and takes up more space in its liquid state. Fuel combustion can only occur in the vaporized or gaseous states, and H_2 can reach its state of gaseous form at a relatively lower temperature. The flashpoint, which is the temperature at which a fuel can ignite in the occurrence of an ignition source, is typically lower than its boiling point[51] However, low temperatures can reduce vaporization, which may result in the fuel flame not lasting without an ignition source. Consequently, it is anticipated that engines utilizing hydrogen as fuel would necessitate less sophisticated ignition and starting equipment in comparison to engines operating on alternative fuel types[52]. Moreover, hydrogen-powered engines can operate effectively in severe conditions. For example, a hydrogen-fueled vehicle was reported to continue functioning even after being stored in lower temperatures for multiple days, without the need for ignition[53]. Furthermore, hydrogen has a unique flammability range, which presents several opportunities for its use in turbine or combustion engines. This is due to the significant disparity between its lower flammability level (LFL) and higher flammability level (HFL)[54].

3. Cu-based catalyst

Copper-based catalysts are widely used in the steam reforming of methanol. To improve their selectivity and prevent deactivation, various methods have been proposed in the literature. Some of these methods involve investigating the configuration, properties, and preparation of the catalyst, including the accumulation of promoters and supports, while others focus on optimizing preparation methods. Furthermore, numerous scientists have underscored the significance of examining the interfacial synergy between supported metal catalysts and the interactions among their constituents. This approach is crucial for acquiring a comprehensive comprehension of the reaction mechanisms and deactivation processes[55].

3.1. Composition and active components

It is widely recognized that $Cu/ZnO/Al_2O_3$ serves as the commercial catalyst for the SRM reaction and the associated water-gas-shift (WGS) process employed in industrial hydrogen production. The catalyst ($Cu/ZnO/Al_2O_3$) is widely recognized as the commercial catalyst used in the SRM reaction and the associated water-gas-shift (WGS) process, which are integral to industrial hydrogen production.

As per prior research papers, copper is typically recognized as the primary energetic ingredient of the metal compound, implying that the catalytic characteristics are sturdily influenced by the chemical properties and structure of copper. Though, it is important to note that higher copper loading does not necessarily result in better activity and selectivity. The performance of the catalyst greatly depends on the synergy with supports and the interaction between various components. ZnO, for instance, is known to enhance the surface catalytic properties of Cu by promoting its reducibility, which plays an essential role play in the process of reforming.

Moreover, the process can be influenced by the acid/base characteristics of ZnO and its capacity to enhance copper dispersion while inhibiting sintering. Utilizing porous alumina as catalyst support offers the advantage of generating a large surface area, resulting in enhanced copper dispersion, increased loading capacity, and reduced particle size. Furthermore, recent studies have focused extensively on investigating various dopants and support to enhance the overall performance of Cu-based catalysts, leading to promising advancements[56–58].

Fu et al.[59] conducted a study showcasing the effective adsorption of both CO and water through Cu doping of the Fe_3O_4 (111) surface, which in turn facilitated the steam reforming process. Furthermore, recent advancements highlighted the remarkable enhancement in the specific surface area achieved by the 2D Cu-Fe-Al-O nanosheet structure, leading to the creation of additional active sites for metallic Cu[60]. This innovative structure not only contributed to the stability of the catalyst but also enhanced its catalytic activity, showcasing the potential of Cu-Fe composite materials[61].

3.2. Effects of promoters on catalytic activity and selectivity

Copper, as the energetic element, can be easily influenced by various promoters to enhance its catalytic performance. The desirable objectives in producing highly active catalysts are achieving well-dispersed and small copper particles, as well as maintaining stable physicochemical properties. In addition, these promoters can also lead to improved selectivity, which is an added benefit[55]. **Table 1** presents the impact of these promoters on the performance of SRM catalysts. The impact of zirconia as a structural promoter has been studied extensively over the years. Recent research has led to a better understanding of the synergistic effects of zirconia, revealing that it can improve both the stability of the catalyst and the dispersion of the active phase. As a result, this structural promoter has been shown to significantly enhance both the activity and selectivity of SRM[55].

Azenha et al.[62] conducted a study to examine how the SRM behavior is affected by the structure of the ZrO_2 support, specifically comparing the impacts of the monoclinic and cubic forms. The utilization of ZrO_2-monoclinic as a support in CuePd/ZrO_2-monoclinic catalyst resulted in significantly improved metal phase dispersion, leading to a remarkable increase of up to 13 times in activity and a doubling of selectivity compared to the CuePd/ZrO_2-cubic catalyst, as observed in the study. By incorporating zirconia into the conventional $CuO/ZnO/Al_2O_3$ catalyst, the researchers observed enhanced stability, which was attributed to the presence of surface oxygen sites on zirconia clusters and an improved ability to adsorb methanol. This finding indicates that the addition of zirconia has beneficial effects on the catalyst’s performance[63]. The inclusion of zirconium was found to induce microstrain in CuO and ZnO, resulting in a decrease in their crystallite size and limiting their growth. Moreover, Zr-based catalysts exhibited a higher quantity of metallic copper during the reduction process, even at lower temperatures. These observations highlight the influence of zirconium on the structural and chemical properties of the catalyst[64].

Table 1. Promoters effect on various categories of catalyst (Cu-based) for SMR.

Catalyst	**T (ºC)**	**GHSV, LHSV or WHSV (h^{-1})**	**X_{MeOH} (%)**	**Activity (mmol/g_{cat}/h)**	**S_{H2} (%)**	**S_{CO} (%)**	**Reference**
$Cu_{33}Fe_{19}Al_{15}O_{33}$	240	1760 (g)	94.3	225	100	-	[60]
$CuPd/ZrO_2$-m	260	2400 (g)[a]	>80	40	87	5	[62]
$Cu/ZnO/ZrO_2$	250	21,600 (g)[a]	88.6	806.41[b]	75	NA	[64]
$CuMnO_x$	400	12,000 (g)[a]	75	414	-	5	[65]
$CuZn_3GaZr$	275	2200 (g)	75	836	-	0.3	[66]
CueGa/ZnO	320	3600 (g)	96	720	74	NA	[67]
$CuO/ZnO/CeO_2/Al_2O_3$	260	1000 (g)[a]	98	-	65	NA	[68]
$CuO/ZnO/Al_2O_3/ZrO_2/CeO_2$	220	10,000 (g)[a]	100	-	75	1	[69]
$CueMgO/Al_2O_3$	220	2923 (g)[a]	100	-	99.4	<0.15	[70]

Table 1. (*Continued*).

Catalyst	**T (ºC)**	**GHSV, LHSV or WHSV (h^{-1})**	**X_{MeOH} (%)**	**Activity (mmol/g_{cat}/h)**	**S_{H2} (%)**	**S_{CO} (%)**	**Reference**
$Cu/Ni/Zr/Ce_{0.1}$	330	172 (g)	60	1000	100	NA	[71]
Cu/SiO_2	400	2400 (g)^a	97	-	72–77	<11	[72]
$CueNi/LaZnAlO_4$	300	20.8 (w)	90	-	>80	<2	[73]
CueFe/ATP	300	3.52 (w)	100	-	98.25	2.55	[74]

The unit for “a” is mL/gcat/h (milliliters per gram of catalyst per hour).
The unit for “b” is mol/molmetal/h (moles per mole of metal per hour).

3.3. Effects of Cu-based catalyst preparation methods

Apart from utilizing various promoters and combinations of active metals, the method of preparation has also been found to significantly impact catalytic performance, a wide range of preparation approaches have been informed via literature for different types of materials. While co-precipitation, sol-gel synthesis, hydrothermal synthesis, and impregnation are commonly used methods, some authors have also proposed novel approaches or modifications to conventional methods to improve the catalytic activity and selectivity of the synthesized materials[50]. Hosseini et al.[75] systematically investigated the effects of the preparation method on the surface area and performance of their materials. They studied ZrO_2/CeO_2 doped $CuO/ZnO/Al_2O_3$ without specifying it as a catalyst.

Investigations have been conducted by researchers to examine the influence of various preparation techniques on factors such as surface area, metal dispersion, and particle size of catalysts containing copper. One method that has received attention is the urea nitrate combustion (UNC) method, which is known for its fast and easy synthesis of nano-catalysts. Several studies have shown that this method can result in catalysts with improved metal dispersion, smaller particle size, and greater surface region, which can lead to enhanced catalytic performance[76]. Yang et al.[77] examined different preparation methods for CuO/CeO_2 catalysts, emphasizing the importance of ceria morphology in influencing catalytic performance. This underscores the importance of selecting appropriate synthesis methods to optimize active site size, dispersion, and morphology to achieve desired properties.

3.4. Catalyst performance by supports

It should also be noted that the quality of the support material plays a crucial role in ensuring the effectiveness and stability of catalysts. Properly designed supports, when combined with specific modification techniques, can lead to the development of catalysts with extremely high surface area and metal dispersion[78,79].

In the study conducted by Tajrishi et al.[78], SBA-15 mesoporous substantial was produced using a hydrothermal arrangement and utilized as a support for Cu-based catalysts. The research findings highlighted that SBA-15 is a highly suitable support material for promoting the dispersion of Cu due to its exceptional stability and maximum surface region. Opting for suitable support materials with a high surface area is vital to enhance the dispersion of active metals. Support materials like MCM-41, SBA-15, carbon nanotubes (CNTs), spinel, and silica possess surface areas nearly ten times larger than those of compound catalysts. A previous study reported that an MCM-41-supported Cu-based catalyst, with a surface area of 662 m^2/g, demonstrated excellent stability and resistance to deactivation[79].

Acetic acid modification of MCM-41 before metal impregnation is effective in reducing particle size, leading to a significant improvement in dispersion and reduction behavior, as demonstrated in previous research[80].

Optimizing the catalytic performance of SRM relies on the careful selection of suitable support material with a high surface-to-volume ratio. This characteristic plays a pivotal role in facilitating the improved dispersion of active components on the surface of the support. The uniform mesopores, high BET surface area, and exceptional thermal stability of mesoporous molecular sieves like SBA-15 and MCM-41 have contributed to their widespread acceptance[80].

Moreover, the surface area and pore volume of 3D metal foam, felt, and porous ceramics can be modified to suit various catalyst loadings. However, it is imperative to conduct additional investigations into the size and pores distribution, considering the dimensions of reactant molecules and their transport characteristics. An illustration of this is seen in the case of SBA-15, which possesses mesopores with sizes ranging from 3 to 30 nm, making it well-suited for the reforming of larger molecules such as tars. In contrast, traditional microporous catalysts are not suitable for this application[78]. Additionally, the thermal conductivity and permeability of catalysts can be influenced by gradient and cascading structures, ultimately affecting their performance. Therefore, it is important to consider the current application scenarios and not generalize that porosity and higher specific surface zone always lead to improved catalyst performance.

3.5. Catalyst deactivation

Despite exhibiting high catalytic activity, Cu-based catalysts are prone to deactivation due to various factors such as changes in oxidation state, sintering of the catalyst, or deposition of coke[57], as depicted in **Figure 3**. Furthermore, the presence of foreign species such as chloride and sulfur in the feed mixture can lead to the poisoning of the catalyst[81]. The research conducted by Fasanya et al.[82] demonstrated that the selectivity of side reactions was significantly influenced by the ratio of methanol to water. When the feed mixture lacked sufficient water, there was a higher selectivity towards CO and CH_4, and coke formation occurred at temperatures exceeding 300 °C.

Tonelli et al.[83] perceived that the deactivation of Cu-based catalysts can result from two concurrent processes. Firstly, the deposition of carbonate species, which is a reversible phenomenon. Secondly, the sintering of the active phase, which is an irreversible process that is more likely to occur at higher temperatures. The catalytic system, however, can undergo a simple regeneration process using either a 400 °C air flow or an inert flow at the reaction temperature. This regeneration procedure leads to nearly identical initial conversion rates, indicating the effective restoration of catalytic activity.

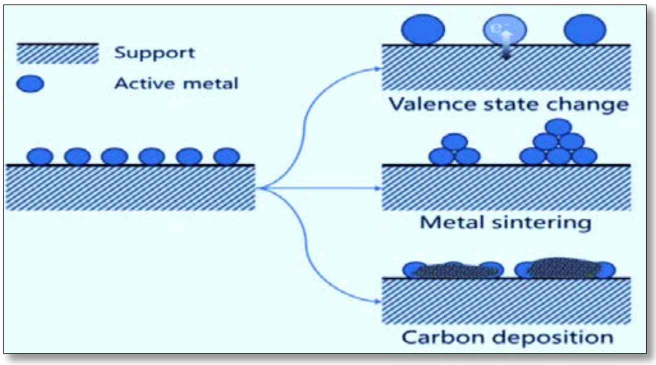

Figure 3. Various kinds of catalysts deactivation[55].

3.6. Reaction mechanism

Extensive research has been conducted on the reaction mechanism of SRM over Cu-based catalysts over a prolonged period. Initially, it was believed that the MD and WGS reactions were responsible for the reaction process[81,84].

$$CH_3OH \leftrightarrow CO + 2H_2 \tag{9}$$

$$CO + H_2O \leftrightarrow 2H_2 + CO_2 \tag{10}$$

Contrary to the initial assumption that the steam reforming of methanol (SRM) reaction is solely driven by the reaction of water gas shift and methanol decomposition, it has been discovered that the resulting product should have a higher concentration of CO, which is not observed as the produced hydrogen is nearly pure. Subsequent investigations have indicated that the steam reforming of methanol (SRM) reaction exhibits a low yield of carbon monoxide (CO) at lower temperatures, which is influenced by factors such as the steam-to-carbon ratio and catalyst properties. Further research suggests the involvement of alternative reaction pathways, including the participation of methoxy species, methyl formate, dioxymethylene, and formate intermediates[85].

Takezawa et al.[86] proposed a potential pathway for the SRM reaction mechanism involving a stepwise dehydrogenation process leading to the establishment of formaldehyde and formic acid.

$$\mathrm{CH_3OH \rightarrow HCHO + H_2} \tag{11}$$

$$\mathrm{HCHO + H_2O \rightarrow HCOOH + H_2} \tag{12}$$

$$\mathrm{HCOOH \rightarrow H_2 + CO_2} \tag{13}$$

The reaction rate may be restricted by the dehydrogenation step of methanol to form formaldehyde[85]. Nevertheless, there is some inconsistency in the explanations for how CO is formed. While Shishido et al.[87] supported a pathway where CO_2 is produced directly and provided evidence for a stepwise dehydrogenation pathway of methanol to form formaldehyde and formic acid, ultimately resulting in the production of H_2 and CO_2. However, there are differing opinions on the origin of CO. Some scientists argue that adsorbed formaldehyde is directly decomposed to generate H_2 and CO, which then participates in the water-gas shift reaction[85].

$$\mathrm{HCHO \rightarrow CO + H_2} \tag{14}$$

It is worth noting that while decomposition occurs at a slower rate compared to reforming, it still needs to be considered in most kinetic models. The endothermic nature of the decomposition reaction has a more significant impact in the presence of water, especially at higher temperatures as predicted by thermodynamics. Another proposed mechanism involves a complex process that includes a methyl formate intermediate[81].

$$\mathrm{2CH_3OH \rightarrow HCOOCH_3 + 2H_2} \tag{15}$$

$$\mathrm{HCOOCH_3 + H_2O \rightarrow CH_3OH + HCOOH} \tag{16}$$

The Langmuir-Hinshelwood mechanism proposes that the initial step in methanol conversion involves the breaking of the O–H bond, leading to the formation of surface methoxy species. Subsequently, the methoxy species undergo dehydrogenation to generate formaldehyde[85].

In their work, Frank et al.[88] presented a comprehensive catalytic cycle that encompasses two types of active sites, one responsible for hydrogen adsorption and the other for the adsorption of all other intermediates. Hammoud et al.[89] illustrated a potential pathway, shown in **Figure 4**, for the production of methyl formate. In this process, formaldehyde, produced through dehydrogenation, reacts with a methoxy group. This interaction gives rise to an intermediate, which subsequently decomposes with the involvement of hydroxyl groups, resulting in the formation of methoxy and formate groups. Another pathway involves the dimerization of methoxy groups, leading to the synthesis of methyl formate.

Despite numerous studies, a clear consensus on the kinetics and reaction mechanism of SRM has yet to be reached. However, significant progress has been made in utilizing these studies to develop specialized catalyst formulations. In recent years, the pathway through a methyl formate intermediate has gained widespread acceptance as the most feasible mechanism for SRM.

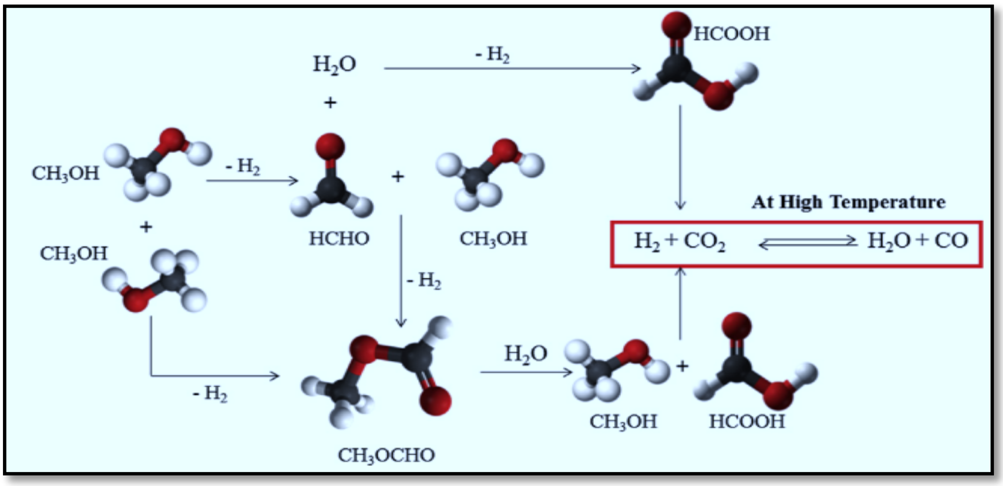

Figure 4. Reaction pathways of steam reforming of methanol[55,89].

4. Future research

The primary hurdle encountered in the SRM process is the deactivation of the catalyst caused by coking or metal sintering. To address this concern, it is crucial to develop and fabricate a catalyst that exhibits, reduced coke formation, enhanced catalytic activity, smaller particle size prolonged stability even distribution of metal particles. These catalyst properties are essential for achieving optimal hydrogen yield at lower temperatures. This requires advanced research focused on developing such catalysts using various promoters and supports. Additionally, reducing the reforming temperature and producing pure hydrogen can make the process more cost-efficient. Advanced materials like CNT (Carbon nanotubes) and SAA (single-atom alloys) can be explored to achieve these objectives, along with amalgamating various reforming reactions to enhance economic viability, for example, by utilizing heat produced through an exothermic reaction for SRM. To achieve high yields of hydrogen, it is of utmost importance to gain a deep understanding of the fundamental role played by copper in both mono and multimetallic systems, as well as the characteristics of the supporting material. The interactions between the metal and the support, specifically the transfer of oxygen from reducible oxides to the metal sites, need to be thoroughly investigated to assess their impact on catalyst performance, selectivity, and stability. Moreover, advanced characterization techniques should be employed to gain insights into the effects of alloying on selectivity in multimetallic catalysts utilizing mixed metal oxides.

5. Conclusion

The diminishing availability of fossil fuels and the growing environmental apprehensions underscore the urgent demand for clean and sustainable alternative energy sources. Hydrogen, being the most ample component on earth, holds great promise as an energy solution due to its superior energy density compared to fossil fuels on a mass basis. However, addressing the cost of production and transportation, improving energy conversion efficiency, ensuring safety, and managing the transition period for energy infrastructure requires in-depth research to develop and examine a comprehensive hydrogen supply-demand network that simultaneously meets economic, efficient, and feasible standards.

The present study undertook a comprehensive review of the literature on various approaches for steam methanol reforming (SRM) in hydrogen production. Based on the analysis conducted, the following conclusions can be drawn from this research investigation.

- Hydrogen production has traditionally depended on conventional sources such as coal, natural gas, and naphtha using steam reforming processes. However, the sustainability of these sources presents a challenge in the present era.
- In upcoming years, hydrogen is projected to have a substantial impact on carbon-neutral and carbon-negative economies. This has spurred extensive research into developing new and environmentally friendly technologies for H_2 production.
- Steam reforming methanol (SRM) has emerged as a highly promising technology that has gained significant attention. This review offers an in-depth analysis of different catalysts, their supports and promoters, the interactions among them, and the effects of various operating conditions on the performance of SRM.
- The analysis of SRM catalysis utilizing different Cu-based catalysts, as well as alternative catalysts, revealed their susceptibility to deactivation caused by coking and sintering.
- Among the Cu catalysts, catalysts (Cu/ZnO) have received significant attention, with the formation of Cu-Zn alloy considered critical for high activity. To enrich the catalytic activity and stability, different kinds of promoters such as ZrO_2, Al_2O_3 and CeO_2 have been utilized.
- The existing literature addresses different types of methanol-reforming reactions, focusing on their application in specific mobile devices powered by internal combustion engines (ICEs) with in-cylinder thermochemical fuel reforming (TFR) processes, solid oxide fuel cells (SOFCs), and polymer electrolyte membrane fuel cells (PEMFCs). The discussions consider the varied temperature requirements and inlet gas compositions associated with each technology.
- The analysis utilized the Gibbs free energy minimization method and investigated a wide temperature range of 400 to 900 K, with a steam-to-fuel ratio of 1 and a pressure of 1 bar. The study focused on determining the maximum fuel conversion levels achieved. Notably, specific temperatures were found to yield the highest fuel conversion: 600 K for methanol, 730 K for ethanol, 860 K for n-butanol, and 890 K for glycerol.
- Future investigations should prioritize achieving a consistent system output and instantaneous hydrogen yield to enhance hydrogen production and utilization.
- It is worth noting that methanol benefits in the reforming process, production, and storage making it a crucial component of the entire hydrogen network.

Author contributions

Conceptualization, RK and AK; methodology, RK; software, RK; validation, RK and AK; formal analysis, RK; investigation, RK; resources, AK; data curation, RK; writing—original draft preparation, RK; writing—review and editing, AK; visualization, AK; supervision, AK.

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Conflict of interest

The authors declare no conflict of interest.

References

1. Ranjekar AM, Yadav GD. Steam reforming of methanol for hydrogen production: A critical analysis of catalysis, processes, and scope. *Industrial & Engineering Chemistry Research* 2021; 60(1): 89–113. doi: 10.1021/acs.iecr.0c05041
2. Olah GA. Towards oil independence through renewable methanol chemistry. *Angewandte Chemie International Edition* 2013; 52(1): 104–107. doi: 10.1002/anie.201204995
3. Wang J, Wang H, Hu P. Theoretical insight into methanol steam reforming on indium oxide with different coordination environments. *Science China Chemistry* 2018; 61: 336–343. doi: 10.1007/s11426-017-9139-x
4. Cacciola G, Antonucci V, Freni S. Technology up date and new strategies on fuel cells. *Journal of power sources* 2001; 100(1–2): 67–79. doi: 10.1016/S0378-7753(01)00884-9
5. Xu X, Liu X, Xu B. A survey of nickel-based catalysts and monolithic reformers of the onboard fuel reforming system for fuel cell APU applications. *International Journal of Energy Research* 2016; 40(9): 1157–1177. doi: 10.1002/er.3509
6. Kaftan A, Kusche M, Laurin M, et al. KOH-promoted Pt/Al_2O_3 catalysts for water gas shift and methanol steam reforming: An operando DRIFTS-MS study. *Applied Catalysis B: Environmental* 2017; 201: 169–181. doi: 10.1016/j.apcatb.2016.08.016
7. García L. Hydrogen production by steam reforming of natural gas and other nonrenewable feedstocks. In: Subramani V, Basile A, Veziroğlu TN (editors). *Compendium of Hydrogen Energy*. Woodhead Publishing; 2015. pp. 83–107.
8. Sun P, Young B, Elgowainy A, et al. Criteria air pollutants and greenhouse gas emissions from hydrogen production in US steam methane reforming facilities. *Environmental science & technology* 2019; 53(12): 7103–7113. doi: 10.1021/acs.est.8b06197
9. Cormos AM, Szima S, Fogarasi S, Cormos CC. Economic assessments of hydrogen production processes based on natural gas reforming with carbon capture. *Chemical Engineering Transactions* 2018; 70: 1231–1236. doi: 10.3303/CET1870206
10. Byun M, Lee B, Lee H, et al. Techno-economic and environmental assessment of methanol steam reforming for H_2 production at various scales. *International Journal of Hydrogen Energy* 2020; 45(46): 24146–24158. doi: 10.1016/j.ijhydene.2020.06.097
11. Ribeirinha P, Mateos-Pedrero C, Boaventura M, et al. CuO/ZnO/Ga_2O_3 catalyst for low temperature MSR reaction: Synthesis, characterization and kinetic model. *Applied Catalysis B: Environmental* 2018; 221: 371–379. doi: 10.1016/j.apcatb.2017.09.040
12. Basile A, Parmaliana A, Tosti S, et al. Hydrogen production by methanol steam reforming carried out in membrane reactor on Cu/Zn/Mg-based catalyst. *Catalysis Today* 2008; 137(1): 17–22. doi: 10.1016/j.cattod.2008.03.015
13. Ott J, Gronemann V, Pontzen F, et al. Methanol. In: *Ullmann's Encyclopedia of Industrial Chemistry*. American Cancer Society; 2012. doi: 10.1002/14356007.a16_465.pub3
14. Ahmed S, Krumpelt M. Hydrogen from hydrocarbon fuels for fuel cells. *International Journal of Hydrogen Energy* 2001; 26(4); 291–301. doi: 10.1016/S0360-3199(00)00097-5
15. Staffell I, Scamman D, Abad AV, et al. The role of hydrogen and fuel cells in the global energy system. *Energy & Environmental Science* 2019; 12(2): 463–491. doi: 10.1039/c8ee01157e
16. Dhar HP, Christner LG, Kush AK. Nature of CO adsorption during H_2 oxidation in relation to modeling for CO poisoning of a fuel cell anode. *Journal of the Electrochemical Society* 1987; 134(12): 3021. doi: 10.1149/1.2100333
17. Kubacka A, Fernández-García M, Martínez-Arias A. Catalytic hydrogen production through WGS or steam reforming of alcohols over Cu, Ni and Co catalysts. *Applied Catalysis A: General* 2016; 518: 2–17. doi: 10.1016/j.apcata.2016.01.027
18. Karim AM, Conant T, Datye AK. Controlling ZnO morphology for improved methanol steam reforming reactivity. *Physical Chemistry Chemical Physics* 2008; 10(36): 5584–5590. doi: 10.1039/b800009c
19. Papavasiliou J, Avgouropoulos G, Ioannides T. Steady-state isotopic transient kinetic analysis of steam reforming of methanol over Cu-based catalysts. *Applied Catalysis B: Environmental* 2009; 88(3–4): 490–496. doi: 10.1016/j.apcatb.2008.10.018
20. Kubacka A, Martínez-Arias A, Fernández-García M. Role of the interface in base-metal ceria-based catalysts for hydrogen purification and production processes. *ChemCatChem* 2015; 7(22): 3614–3624. doi: 10.1002/cctc.201500593
21. Hardiman KM, Ying TT, Adesina AA, et al. Performance of a Co-Ni catalyst for propane reforming under low steam-to-carbon ratios. *Chemical Engineering Journal* 2004; 102(2): 119–130. doi: 10.1016/j.cej.2004.03.005
22. Alenazey F, Cooper CG, Dave CB, et al. Coke removal from deactivated Co-Ni steam reforming catalyst using different gasifying agents: An analysis of the gas-solid reaction kinetics. *Catalysis Communications* 2009; 10(4): 406–411. doi: 10.1016/j.catcom.2008.10.010

23. Song H, Ozkan US. Economic analysis of hydrogen production through a bio-ethanol steam reforming process: Sensitivity analyses and cost estimations. *International Journal of Hydrogen Energy* 2010; 35(1); 127–134. doi: 10.1016/j.ijhydene.2009.10.043
24. Zhang G, Jin W, Xu N. Design and fabrication of ceramic catalytic membrane reactors for green chemical engineering applications. *Engineering* 2018; 4(6): 848–860. doi: 10.1016/j.eng.2017.05.001
25. Gallucci F, Fernandez E, Corengia P, van Sint Annaland M. Recent advances on membranes and membrane reactors for hydrogen production. *Chemical Engineering Science* 2013; 92: 40–66. doi: 10.1016/j.ces.2013.01.008
26. Liuzzi D, Fernandez E, Perez S, et al. Advances in membranes and membrane reactors for the Fischer-Tropsch synthesis process for biofuel production. *Reviews in Chemical Engineering* 2022; 38(1): 55–76. doi: 10.1515/revce-2019-0067
27. Pashchenko D. Low-grade heat utilization in the methanol-fired gas turbines through a thermochemical fuel transformation. *Thermal Science and Engineering Progress* 2022; 36: 101537. doi: 10.1016/j.tsep.2022.101537
28. Pashchenko D, Gnutikova M, Karpilov I. Comparison study of thermochemical waste-heat recuperation by steam reforming of liquid biofuels. *International Journal of Hydrogen Energy* 2020; 45(7): 4174–4181. doi: 10.1016/j.ijhydene.2019.11.202
29. Pashchenko D. Thermochemical waste-heat recuperation as on-board hydrogen production technology. *International Journal of Hydrogen Energy* 2021; 46(57): 28961–28968. doi: 10.1016/j.ijhydene.2020.11.108
30. Pashchenko D. Pressure drop in the thermochemical recuperators filled with the catalysts of various shapes: A combined experimental and numerical investigation. *Energy* 2019; 166: 462–470. doi: 10.1016/j.energy.2018.10.084
31. Pashchenko D, Karpilov I, Mustafin R. Numerical calculation with experimental validation of pressure drop in a fixed-bed reactor filled with the porous elements. *AIChE Journal* 2020; 66(5): e16937. doi: 10.1002/aic.16937
32. Thattarathody R, Artoul M, Digilov RM, Sheintuch M. Pressure, diffusion, and S/M ratio effects in methanol steam reforming kinetics. *Industrial & Engineering Chemistry Research* 2018; 57(9): 3175–3186. doi: 10.1021/acs.iecr.7b05033
33. Wang J, Wu J, Xu Z, Li M. Thermodynamic performance analysis of a fuel cell trigeneration system integrated with solar-assisted methanol reforming. *Energy Conversion and Management* 2017; 150: 81–89. doi: 10.1016/j.enconman.2017.08.012
34. Hosseini SS, Mehrpooya M, Alsagri AS, Alrobaian AA. Introducing, evaluation and exergetic performance assessment of a novel hybrid system composed of MCFC, methanol synthesis process, and a combined power cycle. *Energy Conversion and Management* 2019; 197: 111878. doi: 10.1016/j.enconman.2019.111878
35. Schuller G, Vázquez FV, Waiblinger W, et al. Heat and fuel coupled operation of a high temperature polymer electrolyte fuel cell with a heat exchanger methanol steam reformer. *Journal of Power Sources* 2017; 347: 47–56. doi: 10.1016/j.jpowsour.2017.02.021
36. Sun Z, Fang S, Lin Y, Hu YH. Photo-assisted methanol steam reforming on solid solution of Cu-Zn-Ti oxide. *Chemical Engineering Journal* 2019; 375: 121909. doi: 10.1016/j.cej.2019.121909
37. Chiarello GL, Ferri D, Selli E. In situ attenuated total reflection infrared spectroscopy study of the photocatalytic steam reforming of methanol on Pt/TiO_2. *Applied Surface Science* 2018; 450: 146–154. doi: 10.1016/j.apsusc.2018.04.167
38. Fasolini A, Cucciniello R, Paone E, et al. A short overview on the hydrogen production via aqueous phase reforming (APR) of cellulose, C6-C5 sugars and polyols. *Catalysts* 2019; 9(11): 917. doi: 10.3390/catal9110917
39. Huber GW, Dumesic JA. An overview of aqueous-phase catalytic processes for production of hydrogen and alkanes in a biorefinery. *Catalysis Today* 2006; 111(1–2): 119–132. doi: 10.1016/j.cattod.2005.10.010
40. Davda RR, Shabaker JW, Huber GW, et al. A review of catalytic issues and process conditions for renewable hydrogen and alkanes by aqueous-phase reforming of oxygenated hydrocarbons over supported metal catalysts. *Applied Catalysis B: Environmental* 2005; 56(1–2): 171–186. doi: 10.1016/j.apcatb.2004.04.027
41. Stekrova M, Rinta-Paavola A, Karinen R. Hydrogen production via aqueous-phase reforming of methanol over nickel modified Ce, Zr and La oxide supports. *Catalysis Today* 2018; 304: 143–152. doi: 10.1016/j.cattod.2017.08.030
42. Cortright RD, Davda RR, Dumesic JA. Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. *Nature* 2002; 418(6901): 964–967. doi: 10.1038/nature01009
43. Sharma R, Kumar A, Upadhyay RK. Bimetallic Fe-promoted catalyst for CO-free hydrogen production in high-temperature-methanol steam reforming. *ChemCatChem* 2019; 11(18): 4568–4580. doi: 10.1002/cctc.201901062
44. Andersson J, Grönkvist S. Large-scale storage of hydrogen. *International Journal of Hydrogen Energy* 2019; 44(23): 11901–11919. doi: 10.1016/j.ijhydene.2019.03.063
45. Goeppert A, Czaun M, Jones JP, et al. Recycling of carbon dioxide to methanol and derived products-closing the loop. *Chemical Society Reviews* 2014; 43(23): 7995–8048. doi: 10.1039/c4cs00122b
46. Guczi L, Erdôhelyi A (editors). *Catalysis for Alternative Energy Generation*. Springer; 2012.
47. Richards N, Needels J, Erickson P. Autothermal-reformation enhancement using a stratified-catalyst technique. *International Journal of Hydrogen Energy* 2017; 42(41): 25914–25923. doi: 10.1016/j.ijhydene.2017.08.050

48. Klankermayer J, Wesselbaum S, Beydoun K, Leitner W. Selective catalytic synthesis using the combination of carbon dioxide and hydrogen: Catalytic chess at the interface of energy and chemistry. *Angewandte Chemie International Edition* 2016; 55(26): 7296–7343. doi: 10.1002/anie.201507458
49. Emami SD, Kasmani RM, Hamid MD, et al. Kinetic and dynamic analysis of hydrogen-enrichment mixtures in combustor systems—A review paper. *Renewable and Sustainable Energy Reviews* 2016; 62: 1072–1082. doi: 10.1016/j.rser.2016.05.029
50. Chehade G, Lytle S, Ishaq H, et al. Hydrogen production by microwave based plasma dissociation of water. *Fuel* 2020; 264: 116831. doi: 10.1016/j.fuel.2019.116831
51. Niermann M, Beckendorff A, Kaltschmitt M, Bonhoff K. Liquid organic hydrogen carrier (LOHC)—Assessment based on chemical and economic properties. *International Journal of Hydrogen Energy* 2019; 44: 6631–6654. doi: 10.1016/j.ijhydene.2019.01.199
52. Dimitriou P, Tsujimura T. A review of hydrogen as a compression ignition engine fuel. *International Journal of Hydrogen Energy* 2017; 42(38): 24470–24486. doi: 10.1016/j.ijhydene.2017.07.232
53. Yan F, Xu L, Wang Y. Application of hydrogen enriched natural gas in spark ignition IC engines: From fundamental fuel properties to engine performances and emissions. *Renewable and Sustainable Energy Reviews* 2018; 82: 1457–1488. doi: 10.1016/j.rser.2017.05.227
54. Mazloomi K, Gomes C. Hydrogen as an energy carrier: Prospects and challenges. *Renewable and Sustainable Energy Reviews* 2012; 16(5): 3024–3033. doi: 10.1016/j.rser.2012.02.028
55. Li H, Ma C, Zou X, et al. On-board methanol catalytic reforming for hydrogen production—A review. *International Journal of Hydrogen Energy* 2021; 46(43): 22303–22327. doi: 10.1016/j.ijhydene.2021.04.062
56. Yong ST, Ooi CW, Chai SP, Wu XS. Review of methanol reforming-Cu-based catalysts, surface reaction mechanisms, and reaction schemes. *International Journal of Hydrogen Energy* 2013; 38(22): 9541–9552. doi: 10.1016/j.ijhydene.2013.03.023
57. Kubacka A, Fernández-García M, Martínez-Arias A. Catalytic hydrogen production through WGS or steam reforming of alcohols over Cu, Ni and Co catalysts. *Applied Catalysis A: General* 2016; 518: 2–17. doi: 10.1016/j.apcata.2016.01.027
58. Li J, Mei X, Zhang L, et al. A comparative study of catalytic behaviors of Mn, Fe, Co, Ni, Cu and Zn-based catalysts in steam reforming of methanol, acetic acid and acetone. *International Journal of Hydrogen Energy* 2020; 45(6): 3815–3832. doi: 10.1016/j.ijhydene.2019.03.269
59. Fu Z, Wang J, Zhang N, et al. Effect of Cu doping on the catalytic activity of Fe_3O_4 in water-gas shift reactions. *International Journal of Hydrogen Energy* 2015; 40(5): 2193–2198. doi: 10.1016/j.ijhydene.2014.12.063
60. Wang L, Zhang F, Miao D, et al. Preparation of Cu-Fe-Al-O nanosheets and their catalytic application in methanol steam reforming for hydrogen production. *Materials Research Express* 2017; 4(3): 035005. doi: 10.1088/2053-1591/4/3/035005
61. Zhang F, Guo H, Wang L, et al. Porous $Al_{63}Cu_{25}Fe_{12}$ quasicrystals covered with $(Al_{11.5}Fe_{13.9}Cu_{19.7})O_{54.9}$ nanosheets. *Materials Characterization* 2019; 147: 165–172. doi: 10.1016/j.matchar.2018.10.026
62. Azenha CSR, Mateos-Pedrero C, Queirós S, et al. Innovative ZrO_2-supported CuPd catalysts for the selective production of hydrogen from methanol steam reforming. *Applied Catalysis B: Environmental* 2017; 203: 400–407. doi: 10.1016/j.apcatb.2016.10.041
63. Ahmadi F, Haghighi M, Ajamein H. Sonochemically coprecipitation synthesis of $CuO/ZnO/ZrO_2/Al_2O_3$ nanocatalyst for fuel cell grade hydrogen production via steam methanol reforming. *Journal of Molecular Catalysis A: Chemical* 2016; 421: 196–208. doi: 10.1016/j.molcata.2016.05.027
64. Sanches SG, Flores JH, da Silva MIP. Cu/ZnO and $Cu/ZnO/ZrO_2$ catalysts used for methanol steam reforming. *Molecular Catalysis* 2018; 454: 55–62. doi: 10.1016/j.mcat.2018.05.012
65. Gac W, Słowik G, Zawadzki W. Structural and surface changes of copper modified manganese oxides. *Applied Surface Science* 2016; 370: 536–544. doi: 10.1016/j.apsusc.2016.02.136
66. Liu X, Toyir J, de la Piscina PR, Homs N. Hydrogen production from methanol steam reforming over Al_2O_3- and ZrO_2-modified $CuOZnOGa_2O_3$ catalysts. *International Journal of Hydrogen Energy* 2017; 42(19): 13704–13711. doi: 10.1016/j.ijhydene.2016.12.133
67. Toyir J, de la Piscina PR, Homs N. Ga-promoted copper-based catalysts highly selective for methanol steam reforming to hydrogen; relation with the hydrogenation of CO_2 to methanol. *International Journal of Hydrogen Energy* 2015; 40(34): 11261–11266. doi: 10.1016/j.ijhydene.2015.04.039
68. Shokrani R, Haghighi M, Jodeiri N, et al. Fuel cell grade hydrogen production via methanol steam reforming over $CuO/ZnO/Al_2O_3$ nanocatalyst with various oxide ratios synthesized via urea-nitrates combustion method. *International Journal of Hydrogen Energy* 2014; 39(25): 13141–13155. doi: 10.1016/j.ijhydene.2014.06.048
69. Bagherzadeh SB, Haghighi M, Rahemi N. Novel oxalate gel coprecipitation synthesis of ZrO_2-CeO_2-promoted CuO-ZnO-Al_2O_3 nanocatalyst for fuel cell-grade hydrogen production from methanol: Influence of ceria-zirconia loading. *Energy Conversion and Management* 2017; 134: 88–102. doi: 10.1016/j.enconman.2016.12.005
70. Li H, Tian H, Chen S, et al. Sorption enhanced steam reforming of methanol for high-purity hydrogen production over Cu-MgO/Al_2O_3 bifunctional catalysts. *Applied Catalysis B: Environmental* 2020; 276: 119052. doi: 10.1016/j.apcatb.2020.119052

71. Lytkina AA, Orekhova NV, Ermilova MM, Yaroslavtsev AB. The influence of the support composition and structure ($M_XZr_{1-X}O_{2-\delta}$) of bimetallic catalysts on the activity in methanol steam reforming. *International Journal of Hydrogen Energy* 2018; 43(1): 198–207. doi: 10.1016/j.ijhydene.2017.10.182
72. Sarafraz MM, Safaei MR, Goodarzi M, Arjomandi M. Reforming of methanol with steam in a micro-reactor with Cu–SiO_2 porous catalyst. *International Journal of Hydrogen Energy* 2019; 44(36): 19628–19639. doi: 10.1016/j.ijhydene.2019.05.215
73. Khani Y, Bahadoran F, Soltanali S, Ahari JS. Hydrogen production by methanol steam reforming on a cordierite monolith reactor coated with Cu–Ni/$LaZnAlO_4$ and Cu–Ni/γ-Al_2O_3 catalysts. *Research on Chemical Intermediates* 2018; 44: 925–942. doi: 10.1007/s11164-017-3144-8
74. Cao L, Lu M, Li G, Zhang S. Hydrogen production from methanol steam reforming catalyzed by Fe modified Cu supported on attapulgite clay. *Reaction Kinetics, Mechanisms and Catalysis* 2019; 126: 137–152. doi: 10.1007/s11144-018-1493-y
75. Hosseini T, Haghighi M, Ajamein H. Fuel cell-grade hydrogen production from methanol over sonochemical coprecipitated copper based nanocatalyst: Influence of irradiation power and time on catalytic properties and performance. *Energy Conversion and Management* 2016; 126: 595–607. doi: 10.1016/j.enconman.2016.07.056
76. Talkhoncheh SK, Haghighi M, Minaei S, et al. Synthesis of $CuO/ZnO/Al_2O_3/ZrO_2/CeO_2$ nanocatalysts via homogeneous precipitation and combustion methods used in methanol steam reforming for fuel cell grade hydrogen production. *RSC Advances* 2016; 6(62): 57199–57209. doi: 10.1039/C6RA03858A
77. Yang S, Zhou F, Liu Y, et al. Morphology effect of ceria on the performance of CuO/CeO_2 catalysts for hydrogen production by methanol steam reforming. *International Journal of Hydrogen Energy* 2019; 44(14): 7252–7261. doi: 10.1016/j.ijhydene.2019.01.254
78. Tajrishi OZ, Taghizadeh M, Kiadehi AD. Methanol steam reforming in a microchannel reactor by Zn-, Ce- and Zr-modified mesoporous Cu/SBA-15 nanocatalyst. *International Journal of Hydrogen Energy* 2018; 43(31): 14103–14120. doi: 10.1016/j.ijhydene.2018.06.035
79. Deshmane VG, Abrokwah RY, Kuila D. Synthesis of stable Cu-MCM-41 nanocatalysts for H_2 production with high selectivity via steam reforming of methanol. *International Journal of Hydrogen Energy* 2015; 40(33): 10439–10452. doi: 10.1016/j.ijhydene.2015.06.084
80. Mohtashami Y, Taghizadeh M. Performance of the ZrO_2 promoted Cu–ZnO catalyst supported on acetic acid-treated MCM-41 in methanol steam reforming. *International Journal of Hydrogen Energy* 2019; 44(12): 5725–5738. doi: 10.1016/j.ijhydene.2019.01.029
81. Sá S, Silva H, Brandão L, et al. Catalysts for methanol steam reforming—A review. *Applied Catalysis B: Environmental* 2010; 99(1–2): 43–57. doi: 10.1016/j.apcatb.2010.06.015
82. Fasanya OO, Al-Hajri R, Ahmed OU, et al. Copper zinc oxide nanocatalysts grown on cordierite substrate for hydrogen production using methanol steam reforming. *International Journal of Hydrogen Energy* 2019; 44(41): 22936–22946. doi: 10.1016/j.ijhydene.2019.06.185
83. Tonelli F, Gorriz O, Tarditi A, et al. Activity and stability of a CuO/CeO_2 catalyst for methanol steam reforming. *International Journal of Hydrogen Energy* 2015; 40(39): 13379–13387. doi: 10.1016/j.ijhydene.2015.08.046
84. Palo DR, Dagle RA, Holladay JD. Methanol steam reforming for hydrogen production. *Chemical Reviews* 2007; 107(10): 3992–4021. doi: 10.1021/cr050198b
85. Kapran AY, Orlyk SM. Hydrogen production in methanol reforming on modified copper-zinc catalysts: A review. *Theoretical and Experimental Chemistry* 2017; 53: 1–16. doi: 10.1007/s11237-017-9495-9
86. Takezawa N, Iwasa N. Steam reforming and dehydrogenation of methanol: Difference in the catalytic functions of copper and group VIII metals. *Catalysis Today* 1997; 36(1): 45–56. doi: 10.1016/S0920-5861(96)00195-2
87. Shishido T, Yamamoto Y, Morioka H, Takehira K. Production of hydrogen from methanol over Cu/ZnO and $Cu/ZnO/Al_2O_3$ catalysts prepared by homogeneous precipitation: Steam reforming and oxidative steam reforming. *Journal of Molecular Catalysis A: Chemical* 2007; 268(1–2): 185–194. doi: 10.1016/j.molcata.2006.12.018
88. Frank B, Jentoft FC, Soerijanto H, et al. Steam reforming of methanol over copper-containing catalysts: Influence of support material on microkinetics. *Journal of Catalysis* 2007; 246(1): 177–192. doi: 10.1016/j.jcat.2006.11.031
89. Hammoud D, Gennequin C, Aboukaïs A, Abi Aad E. Steam reforming of methanol over x% Cu/Zn–Al 400 500 based catalysts for production of hydrogen: Preparation by adopting memory effect of hydrotalcite and behavior evaluation. *International Journal of Hydrogen Energy* 2015; 40(2): 1283–1297. doi: 10.1016/j.ijhydene.2014.09.080