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Review

Advances in Enhancing the Stability of Cu-Based Catalysts for Methanol Reforming

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Abstract: The advent of fuel cells has led to a series of studies on hydrogen production. As an excellent hydrogen carrier, methanol can be used for reforming to produce hydrogen. Copper-based catalysts have been widely used in methanol reforming due to their high catalytic activity and low-cost preparation. However, copper-based catalysts have been subjected to poor stability due to spontaneous combustion, sintering, and deactivation. Thus, the research on the optimization of copper-based catalysts is of great significance. This review analyzes several major factors that affect the stability of copper-based catalysts, and then comments on the progress made in recent years to improve the catalytic stability through various methods, such as developing preparation methods, adding promoters, and optimizing supports. A large number of studies have shown that sintering and carbon deposition are the main reasons for the deactivation of copper-based catalysts. It was found that the catalysts prepared by the modified impregnation method exhibit higher catalytic activity and stability. For the promoters and supports, it was also found that the doping of metal oxides such as MgO and bimetallic oxides such as CeO_2-ZrO_2 as the support could present better catalytic performance for the methanol reforming reaction. It is of great significance to discover some new materials, such as copper-based spinel oxide, with a sustained-release catalytic mechanism for enhancing the stability of Cu-based catalysts. However, the interaction mechanism between the metal and the support is not fully understood, and the research of some new material copper-based catalysts in methanol reforming has not been fully studied. These are the problems to be solved in the future.

Keywords: hydrogen production; methanol reforming; Cu-based catalysts; stability

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1. Introduction

With the booming economy, energy consumption and harmful gas emissions have increased sharply [1–3], and the decline of fossil fuels has become a major obstacle to sustainable development. With the needs of global sustainable development, we urgently need some new fuels. Hydrogen is a well-known clean energy carrier, and fuel cells can convert the chemical energy in fuel hydrogen and oxidant oxygen into electricity (sustainable energy). Hydrogen can come from many sources [4,5], for example, photolysis of water for hydrogen production [6–8], traditional fossil fuel hydrogen production [9,10], biomass hydrogen production [11–13], and hydrogen production from water electrolysis [14,15]. In recent years, more and more studies have been conducted on methanol steam reforming. Methanol reforming produces hydrogen with low CO selectivity and high hydrogen selectivity, and has little effect on the electrode toxicity of proton exchange membrane fuel cells [16]. Moreover, methanol steam reforming does not require the vaporization step in hydrogen production, which can bring good economic benefits [17,18]. Liquid methanol (CH_3OH) is a perfect hydrogen carrier that is more facile to transport than hydrogen gas [19–21]. There are many ways to produce methanol, such as the synthesis gas to methanol and the direct oxidation of methane to methanol [22]. However, many scientists have called for "green methanol" from renewable hydrogen and CO_2 hydrogenation [23]. There are also many ways to synthesize methanol from renewable energy such as biomass, wind power, and solar energy. For example, many works have reported methanol synthesis directly from photo/electronic catalytic CO_2 reduction in water [24]. It is very useful for the industry and our society to produce methanol from renewable energy using CO_2 as a raw material. In addition, when the captured CO_2 source is biomass, it is called bio-methanol [25]. This means that methanol could also be obtained through thermochemical and biochemical conversion of biomass gasification and electrolysis [26]. Gautam et al. have provided an excellent review on the current trends and future perspective of bio-methanol as a renewable fuel from waste biomass [26]. Bio-fuels (e.g., bio-methanol, bio-ethanol, biodiesel) would be a significant alternative fuel for the future. Compared with other fossil fuels, methanol with a low carbon atom and high hydrogen-to-carbon ratio can significantly reduce the occurrence of side reactions [27–29].

There are four typical ways to produce hydrogen from methanol: methanol decomposition (MD) [30–32], partial oxidation of methanol (POM) [33–35], steam reforming of methanol (SRM) [9,36], and oxidative steam reforming of methanol (OSRM) [37–39]. Methanol reforming can produce a large amount of hydrogen, which is one of the important reasons why it is widely studied by researchers [40–42]. SRM also contains two side reactions, which are methanol decomposition and water gas shift reactions [43].

The catalyst is the key factor that affects the hydrogen production efficiency of methanol reforming. The deactivation of the catalyst can easily reduce the yield of hydrogen and the lifetime of the catalyst. Noble metals have high catalytic activity and stability, but the cost is too high, limiting their large-scale application [44–46]. Copper-based catalysts have low cost and excellent catalytic activity, and they are good candidates for methanol reforming for hydrogen production process [19,20,27]. For example, CuO-ZnO-Al_2O_3 catalysts are often used in methanol reforming to produce hydrogen, and their performance is also very good [47,48]. Bagherzadeh et al. investigated the effect of adding ZrO_2-CeO_2 to CuO-ZnO-Al_2O_3 catalysts, and found that the selectivity for H_2 was high and the selectivity for CO was low [49]. Mohtashami et al. introduced ZrO_2 to a Cu/ZnO catalyst and studied its MSR (Methanol Steam Reforming) performance, and the methanol conversion reached up to 97.8% with the selectivity for H_2 of 99% [48]. However, Cu-based catalysts suffer thermal instabilities [50], such as spontaneous combustion, sintering, and deactivation [22,51,52]. The reports have shown that when the temperature is higher than 300 °C, the copper particles in the copper-based catalyst are easy to sinter [53]. There is also a by-product methyl formate produced in methanol reforming that promotes catalyst deactivation through pyrolysis [22]. Thus, how to improve their stability is an important and meaningful topic.

In addition to the factors of the copper-based catalyst itself, the methanol reforming hydrogen production reactor also has a great influence on the stability of the catalyst, for example, methanol steam reforming is a strong endothermic reaction, which requires the reactor temperature not to be too high [54]. Moreover, the production of the reactor is relatively complicated, and requires relatively complex technology and high cost With the development of technology, the design of the reactor can become simpler and simpler, and the more likely it is that a reactor that makes the catalyst more stable can be created. It has been reported in the literature that the reactors used for hydrogen production from methanol reforming are mainly packed bed reactors [55]. However, this kind of reactor requires high temperature, which is its disadvantage, so other reactors have been studied in recent years, such as membrane reactors [56,57] and microporous reactors [58,59]. Moreover, in recent years, many researchers have made great efforts in the design of methanol reforming reactors and have achieved good results; for example, Mironova et al. designed a flow reactor with a Pd-Cu membrane in which methanol steam reforming can achieve a high hydrogen yield compared to conventional reactors [60], while Wang et al. designed a rib-type microreactor for methanol steam reforming and found that the conversion rate of methanol reached 99.4% [59]. With the development of science and technology, 3D printing technology is also used to design catalysts [61]; this technology can design a reactor suitable for catalysts. Moreover, other technologies, such as plasma-assisted reactors and solar-powered MSR reactors [55,62] or the novel solar triple-line photothermal chemical energy and heat storage medium reactor proposed by Du et al. can effectively prevent the deactivation of the catalyst and achieve the stability of the reaction [62].

To improve the stability of copper-based catalysts, we should understand the various reasons for the deactivation of copper-based catalysts. This review discusses several factors that affect the stability of copper-based catalysts, and then summarizes some strategies made by researchers in optimizing the stability of copper-based catalysts in recent years, such as improving preparation methods and supports, adding promoters, and designing novel Cu-based catalytic materials. This will have certain significance for the optimization of copper-based catalysts.

2. Deactivation Analysis of Copper-Based Catalysts

Many factors affect the stability of copper-based catalysts, and the deactivation mechanisms are also different. The study of the deactivation mechanism is of great significance for optimizing copper-based catalysts. Researchers have employed various characterization methods, such as Raman, X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photon spectroscopy (XPS), and thermogravimetric (TG) to characterize the catalyst and the cause of catalyst deactivation.

According to the continuous efforts of researchers, the main factors that affect the deactivation of copper-based catalysts are summarized as follows: (1) The interaction of the active metal and support forms an alloy, which leads to the deactivation [63,64]. Then, the alloying process reduces the adsorption of relevant reactants. For example, Cheng et al. investigated the reasons for the deactivation of Cu/ZnO, and found that Zn dissolves into the Cu lattice, resulting in the deactivation of the catalyst [64]. (2) Carbon deposition also deactivates Cu-based catalysts. Researchers typically use TG to analyze the carbon deposition of catalysts. For instance, Li et al. analyzed the carbon deposition over a Cu/SAC catalyst and P-modified Cu/SAC catalyst after use in methanol reforming by TG [65]. They found that carbon deposition mainly occurred at 150–350 °C, and carbon deposits were about 4%, which was deactivated after 24 h. (3) The other obvious deactivation reason is the sintering and agglomeration of copper nanoparticles (NPs). When the dispersion of copper particles is high, the catalyst has more active sites, but the Cu NPs are sintered and aggregated under a high-temperature reaction for a long-term stability test. Yao et al. reported a Cu/ZrO_2 catalyst containing ZrO_2 with better copper dispersion and greatly improved stability [66]. On the contrary, the aggregation of copper particles reduces the active sites, resulting in reduced catalyst activity. Researchers usually analyze the dispersion of Cu-based catalysts by XRD, N_2O pulse titration, TEM, and H_2 temperature-programmed reduction (H_2-TPR) [67]. The factors that affect the sintering and aggregation of copper particles are also different. In general, the larger the specific surface area of the catalyst, the less likely the copper nanoparticles are to aggregate [68]. When the active metal–support interaction is weak, the catalyst is more easily sintered [69]; (4) the catalyst poisoning by foreign substances also leads to deactivation. For example, some elements such as chlorides and sulfur can cause catalyst poisoning [70,71]. They usually occupy the acidic sites of the catalyst, leading to catalyst deactivation [72–74].

3. Method for Avoiding Deactivation of Cu-Based Catalysts

As depicted above, we know what causes the catalyst to deactivate; thus, we can optimize the catalyst through various methods, such as by optimizing the preparation method, adding promoters, changing the support, and exploring new catalysts. An excellent catalyst should be a combination of activity, selectivity, and stability; thus, it is significant to optimize the catalyst based on the comprehensive consideration.

3.1. Improving Preparation Methods

The preparation method affects the copper dispersion, microstructural properties, and surface areas of copper-based catalysts, which determine the catalytic performance, especially the catalytic stability. Herein, we selected the preparation of Cu-ZnO series catalysts as examples. According to the previous literature, there is an interaction between Cu and Zn [20,75], and this interaction is helpful to enhance the catalyst activity. In addition, the preparation method has a great influence on the metal–support interaction. Therefore, optimizing the preparation method is of great significance for the improvement of catalyst activity. There are several traditional preparation methods for the synthesis of methanol reforming catalysts, such as the hydrothermal method, dipping method, co-precipitation method, and sol-gel method [48,76,77]. Sanches et al. prepared a Cu/ZnO catalyst by the co-precipitation method [75], and Liao et al. synthesized a $CuO/ZnO/CeO_2/ZrO_2$ catalyst by the one-step hydrothermal method [78]. A series of CuZn/MCM-41 catalysts were prepared by the co-impregnation method [77] and achieved good results. After the catalyst was operated for 5 h, the methanol conversion rate was stable at 88%, and the H_2 selectivity was 91%. The effects of synthesis methods on the catalyst were also compared. By comparing the performance of catalysts synthesized by one-pot hydrothermal synthesis, co-impregnation, continuous impregnation, and copper impregnation in MSR, it was found that the catalyst synthesized by the co-impregnation method had the best activity.

Mohtashami et al. also compared the effects of three different methods, namely sol-gel, conventional impregnation, and modified impregnation, on Cu/ZnO catalysts [48]. The results showed that the catalyst prepared by the improved impregnation method exhibited better catalytic activity and stability. The methanol conversion and H_2 selectivity were as high as 97.8% and 99.0%, respectively, while the CO selectivity was 0.4% at 300 °C. The activity of the catalyst was still stable after 40 h of operation. Catalysts prepared by traditional preparation methods have some defects, such as an uneven surface, poor contact between the two metals, and uncontrolled particle morphology with agglomeration [79,80]. Therefore, there is a need to improve the traditional synthesis method to optimize the performance of the catalyst.

Some reports have also explored novel preparation methods. For example, the Ce-CuZn/CNTs catalyst prepared by microwave-assisted polyols had a better catalytic performance than those prepared by impregnation and coprecipitation [80]. There have also been $CuO/ZnO/Al_2O_3$ catalysts prepared by microwave-assisted solution combustion [76], and the effect of the preparation method was also obvious. As shown in Figure 1, Bagherzadeh et al. used a novel oxalate gel coprecipitation method to prepare $CuO\text{-}ZnO\text{-}Al_2O_3\text{-}ZrO_2\text{-}CeO_2$ nanocatalysts, and found that all samples performed excellently in the methanol reforming reaction [49]. The methanol conversion reached 100% at 240 °C, and the selectivity for H_2 was 75%. Moreover, the methanol conversion remained stable at 100% for 300 h. In addition to the above fresh preparation methods, there are several other novel preparation methods such as the ultrasonic-assisted method and ammonia evaporation method [81]. Ye et al. prepared three $Cu\text{-}ZnO/SiO_2$ catalysts by modified Stöber, sol-gel, and ammonia evaporation methods (Figure 2), which have been applied to methanol synthesis and methanol reforming reactions [81]. They demonstrated that the preparation method influences the location and dispersion of metal species, with the ammonia evaporation method exposing a high concentration of Cu^+ species and suitable $Cu\text{-}ZnO_x$ interaction for MSR. Figure 2d shows the mechanism diagram of the CuZnSi-AEM catalyst used for methanol synthesis and methanol reforming reactions, with the formate as a key intermediate for these two reactions.

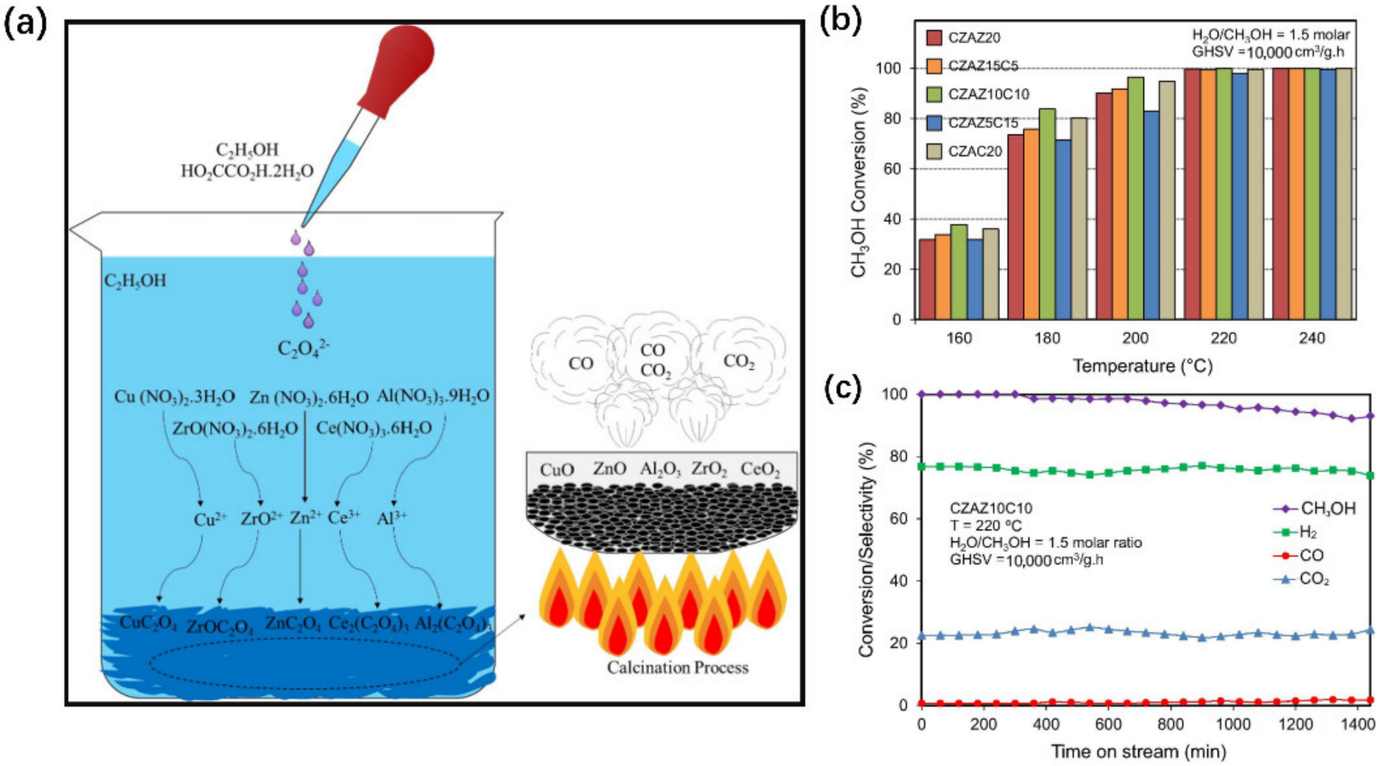

Figure 1. The synthesis of ZrO_2-CeO_2-promoted CuO-ZnO-Al_2O_3 nanocatalyst for methanol-to-hydrogen production: (**a**) Illustration of oxalate gel coprecipitation synthesis method; (**b**) influence of ZrO_2-CeO_2 loading on catalytic performance; and (**c**) runtime performance testing of methanol-to-hydrogen production. Reproduced with permission [49]. Copyright Elsevier, 2017.

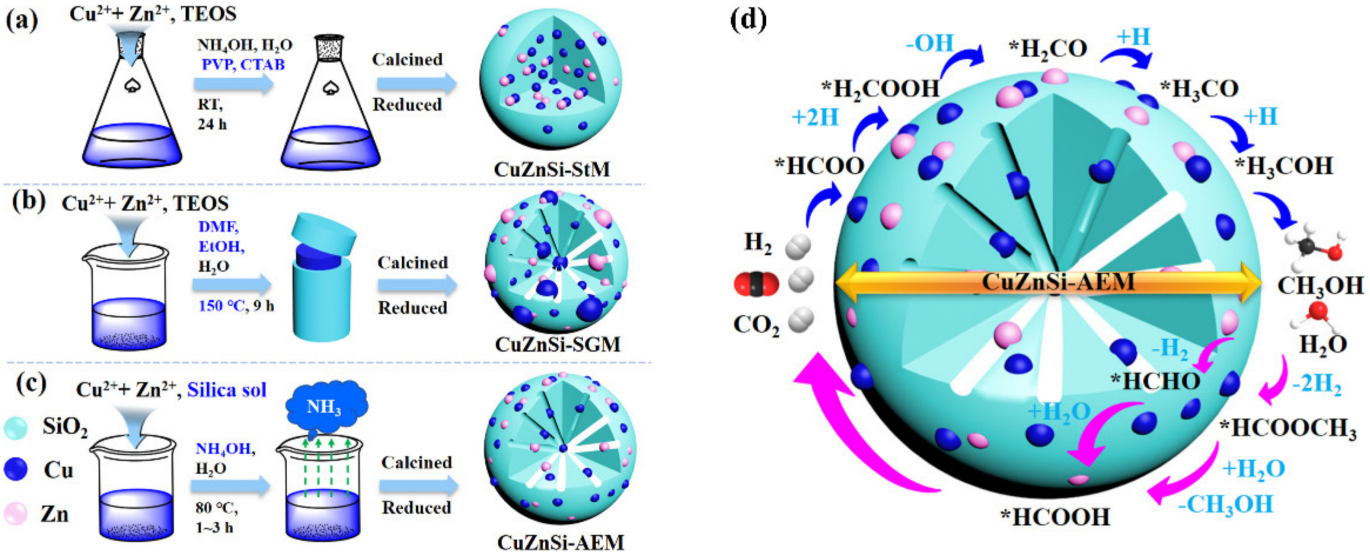

Figure 2. A series of CuZnSi catalysts were reported for CO_2 hydrogenation and methanol reforming reaction: (**a**–**c**) Schematic illustration of the preparation of three CuZnSi catalysts by different methods and (**d**) the mechanism of CuZnSi-AEM catalyst used for methanol synthesis and methanol reforming. Reproduced with permission [81]. Copyright Wiley-VCH, 2021.

In addition to the above-mentioned Cu/ZnO-based systems, the preparation methods of Cu/ZrO_2-based catalysts are also frequently investigated. Supporting copper on ZrO_2

can improve the dispersion and reducibility of active metal copper [41]. It has been reported that Cu/ZrO_2 catalysts can be prepared in various ways, such as co-precipitation of metal salts, copper impregnation on ZrO_2 supports, amorphous aerogel formation, and polymer templating techniques [82]. Ploner et al. prepared a Cu/ZrO_2 catalyst based on a similar procedure of water impregnation, which improved the activity and selectivity of methanol reforming for hydrogen production by changing the copper loading [40]. It was found that the Cu/ZrO_2 catalyst prepared by the fractional precipitation method can improve the activity and stability of the catalyst. The above preparation method affects the ratio of active metal and carrier, which in turn affects the catalyst activity [83]. In addition, some researchers have improved the microstructure of the catalyst. As is shown in Figure 3, Ploner et al. also prepared Cu/ZrO_2 by a sol-gel spontaneous combustion method, and obtained catalysts with a high stability [84]. The Cu/ZrO_2 prepared by this method possessed better stability and activity than the catalyst prepared by impregnation and co-precipitation methods.

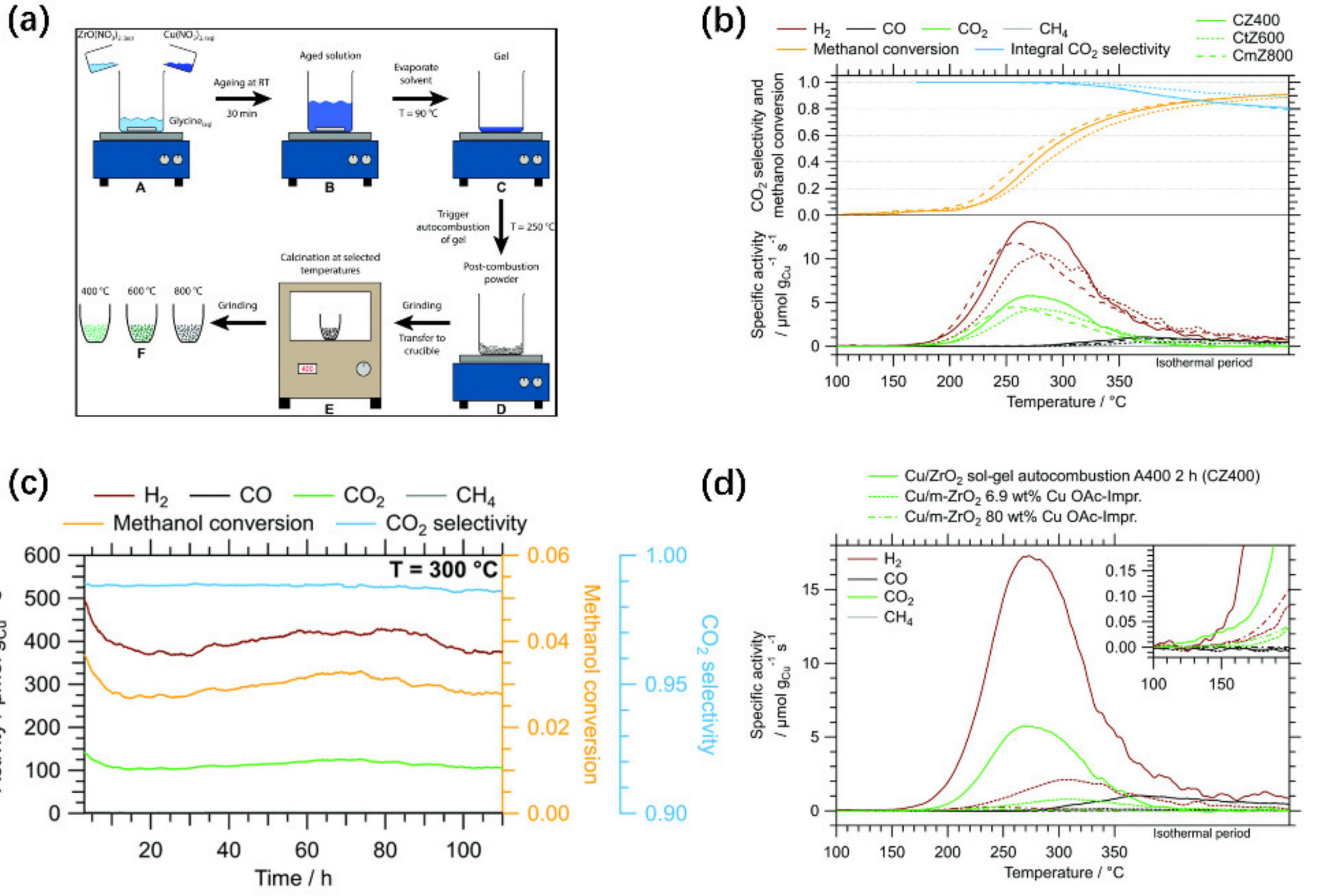

Figure 3. Sol-gel spontaneous combustion synthesis of Cu/ZrO_2 catalyst for methanol steam reforming: (**a**) Schematic diagram of sol-gel spontaneous combustion of three samples; (**b**) methanol steam reforming curves of three samples between 100 °C and 350 °C; (**c**) isothermal long-term methanol steam reforming testing of sample Cu/ZrO_2 at 300 °C; and (**d**) comparison of Cu/ZrO_2 with other catalysts. Reproduced with permission [84]. Copyright Royal Society of Chemistry, 2021.

In the past few years, copper-based spinel catalysts have shown their advantages in many chemical reactions, such as SRM [85], OSRM [86], WGSR [87], and CO oxidation [88]. Researchers have employed Cu-based spinel catalysts for methanol reforming. The active copper of copper-based spinel is gradually released from the spinel bulk phase to the surface, which promotes the stability of the catalyst. As with other Cu-based catalysts, the preparation method also has a great influence on the Cu-based spinel. Parsaee et al. [89]

prepared a Cu-Zn-Ce-Al spinel catalyst by two methods, namely the sol-gel method and homogeneous precipitation method. They explored the effect of temperature on catalyst performance, and found that in all preparation methods, the homogeneous precipitation method is beneficial to improving the methanol conversion rate. Liu et al. explored the effect of different preparation temperatures on the catalytic performance of Cu-Al spinel catalysts, and the catalytic performance was the best when the catalyst preparation temperature was at 950 °C. The source of the raw material for the catalyst preparation also has an effect on the catalyst. Qin et al. explored the effect of three different copper sources on the performance of the catalyst [90]. They compared the performance of catalysts prepared from $Cu(OH)_2$, $(CH_3COO)_2Cu$, and $Cu(NO_3)_2$, and the results showed that the catalyst synthesized from $Cu(OH)_2$ had the best activity and stability in MSR, and the catalyst showed a trend of slow-release catalysis.

Table 1 summarizes the work of some researchers to avoid catalyst deactivation by improving the preparation method in the last three years. From Table 1, we can find that researchers have achieved good results by improving the traditional preparation method. The catalytic performance, especially the stability of the catalyst, has been improved. The problem of carbon deposition has been decreased by developing new preparation methods. However, it would be useful to develop a catalyst with an even better catalytic performance in the future.

Table 1. Copper-based catalysts for MSR prepared by different preparation methods.

Entry	Catalyst	Preparation	Conv.$_{CH3OH}$/%	Select.$_{H2}$/%	T/°C	Coke Formation/%	Lifetime/h	Ref.
1	Cu-ZnO-ZrO_2/MCM-41	Modified impregnation method	97.8	99.0	300	3.11	60	[48]
2	Cu-ZnO-ZrO_2/MCM-41	Sol-gel	96.3	98.8	300	3.89	40	[48]
3	Cu-ZnO-ZrO_2/MCM-41	Conventional impregnation	94.0	98.5	300	4.69	20	[48]
4	CuO/ZnO/CeO_2/ZrO_2	One step hydrothermal process	99.8	-	330	2.2	30	[78]
5	Ni-Cu/Al_2O_4	Green template-free method	>99.0	42.17	300	<1.0	30	[91]

3.2. Doping Promoters

Adding promoters to copper-based catalysts is also an effective way to optimize catalysts. Promoters can improve the dispersion of copper particles or stabilize the support metals. Promoters can also alloy the active metal with the support metal [63,64]. Different auxiliaries have different effects on the same catalyst, and the same auxiliaries have different effects on different catalysts. We introduce the effect of adding promoters on optimizing catalysts below.

The Cu/ZnO catalyst is one of the most common catalysts in the methanol reforming process. It has been reported that the stability of copper-based catalysts is closely related to ZnO, and there is a certain interaction between metallic copper and ZnO which has a great influence on the catalyst activity [92,93]. In order to improve catalyst stability and activity, researchers have added various promoters. For instance, Pu et al. added Sc_2O_3 to Cu/ZnO and found that it has good stability and activity in methanol reforming for hydrogen production [92], in which Sc^{3+} increases the copper dispersion and enhances the intermetallic interaction. A similar effect makes it suitable to add Mg to Cu/ZnO/Al_2O_3, which enhances the catalyst activity by enhancing the Cu-ZnO interaction and increasing the Cu dispersion [94]. The addition of promoters changes the structural properties of the catalyst. For example, Sanches et al. [75] added ZrO_2 to Cu/ZnO, and found that ZrO_2 clusters in the catalyst could reduce the formation of CO. The addition of ZrO_2 induces microstrains in the Cu and ZnO lattices and promotes the formation of CuO, and CuO is easily reduced. Mohtashami et al. found that ZrO_2 can reduce CuO size and increase

CuO dispersion [48]. Some researchers have also worked to prevent catalyst sintering. The addition of ZrO_2 to Cu/ZnO by Huang et al. improved catalyst durability [95]. Different promoters have different effects on the same catalyst. To reduce carbon deposition, Lorenzut et al. introduced Ni and Co into Cu/ZnO/Al_2O_3, and the carbon deposition was also improved due to the alloying of Ni with Cu [96]. For the traditional Cu/ZnO catalyst, the biggest problem is its durability. ZrO_2 is a good promoter and we need to find more useful promoters.

In addition to ZnO, there are some other supports for copper-based catalysts. It is also common to use SiO_2 as a support because SiO_2 is inert in MSR. Bossola et al. found In-promoted Cu/SiO_2 catalysts with high H_2 selectivity [97], which was attributed to the addition of In improving the electronic properties of Cu and making water easier to activate (Figure 4). Al_2O_3 can effectively improve the dispersion of copper particles; thus, it is often used as a catalyst carrier [98], Li et al. [99] added MgO to Cu/Al_2O_3 and found that MgO could reduce CO formation and increase H_2 selectivity (Figure 5). The interaction between Cu and MgO can avoid the sintering of copper particles, thereby increasing the stability of the catalyst. H_2 selectivity up to 99.3% and CO selectivity as low as 0.15% was achieved in all samples. The copper particle size is almost unchanged after 10 cycles of reaction, which increases the stability of the catalyst. Cu-MgO/Al_2O_3 is a bimetallic catalyst, and intermetallic interactions play an important role in improving catalyst activity. Therefore, it is suggested to explore more bimetallic catalysts. MgO can adsorb methanol and is often used in copper-based catalysts, which improves the efficiency of methanol steam reforming [100]. It is a good idea to improve methanol steam reforming by enhancing the adsorption of reactants, and more adsorbents could be explored in the future. To prevent catalyst poisoning caused by alkaline earth metals and heavy metals occupying the acidic sites of the support, doping CeO_2 into the catalyst can alleviate catalyst poisoning because CeO_2 has the ability to trap heavy metals [74,101].

Table 2 indicates some representative works to improve the catalyst deactivation problem by doping different promoters. From Table 2, we can find that the dispersion of active species has a great influence on the stability of the catalyst, and the doping of MgO can greatly increase the dispersion of active species, thereby improving the stability of the catalyst. In addition to oxides, pure metal doping has also achieved good results. For example, the doping of In can make the active species dispersion reach up to 56.4%. However, the interaction of dopant species and active ingredients is still unclear, which is a problem that needs to be solved in the future, and this will provide ideas for finding better additives.

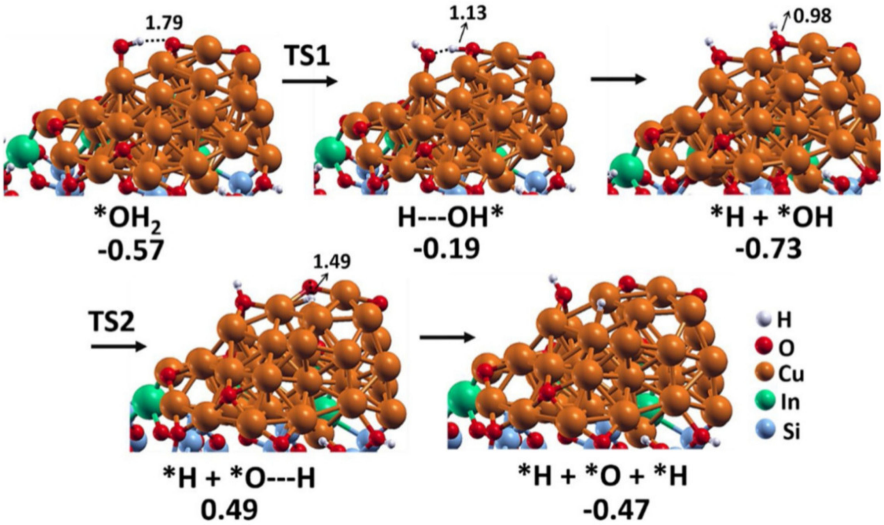

Figure 4. The complete reaction path for the dissociation of H_2O to *H + *O [97]. Copyright Elsevier, 2021.

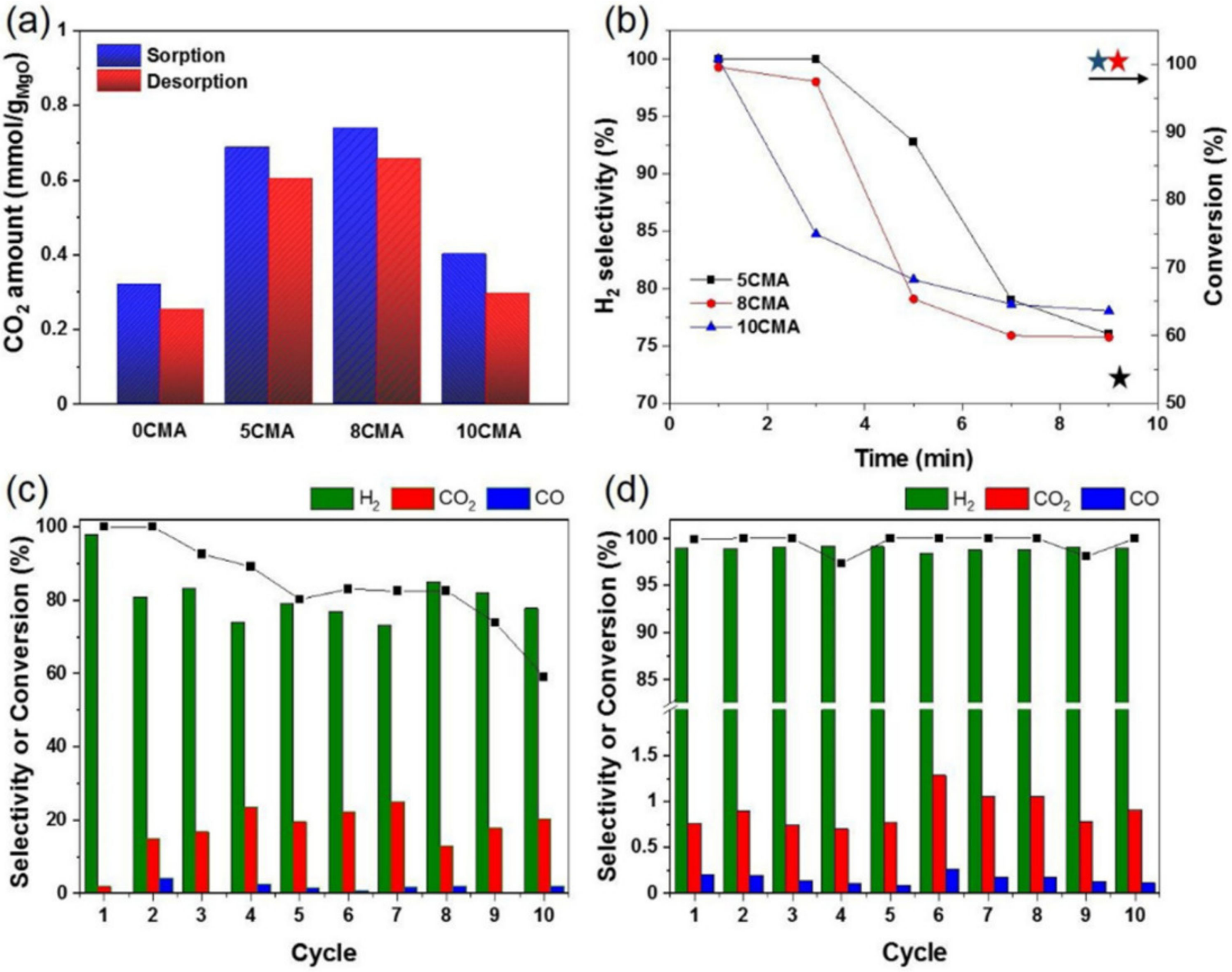

Figure 5. Cu-MgO/Al_2O_3 bifunctional catalyst for methanol steam reforming: (**a**) The level of CO_2 adsorption and desorption of different catalysts. (**b**) methanol conversion and H_2 selectivity in MSR over time for different samples. (**c**) catalytic performance of 8 wt% Cu/Al_2O_3 and 0 wt% Cu-MgO/Al_2O_3 mechanical mixture within 10 cycles. (**d**) catalytic performance of the 8 wt% Cu-MgO/Al_2O_3 catalyst within 10 cycles. Reproduced with permission [99]. Copyright Elsevier, 2020.

Table 2. Copper-based catalysts doped with different promoters for MSR.

Entry	Catalyst	Dopant Species	Conv.$_{CH3OH}$/%	Select.$_{H2}$/%	T/°C	Dispersion/%	Lifetime/h	Ref.
1	Cu/Sc_2O_3-ZnO	Sc_2O_3	95.0	-	220–600	6.9	16	[92]
2	Cu-Al spinel oxide	MgO	96.5	96.5	255	-	450	[102]
3	CuZn/CNTs	Ce.Zr	94.2	98.2	300	18	48	[80]
4	Cu-MgO/Al_2O_3	MgO	~100	99.3	220	62	30	[99]
5	Cu/SiO_2	In	57.1	~100	260	56.4	18	[97]
6	CuFeMg/Al_2O_3	FeO_x	85	97.8	250	24.1	100	[103]

3.3. Optimizing Supports

As an important component of the catalyst, the influence of the support on the activity and stability of the catalyst cannot be ignored. Catalyst supports can affect the dispersion and size of active metals and can also enhance catalyst activity and stability by interacting with active metals [104]. The various catalyst supports proposed in the Section 3.2 (such as ZnO, SiO_2, Al_2O_3, and CeO_2) play different roles. Loading copper on different oxides has different effects; for example, as a common carrier for copper-based catalysts, ZrO_2 is often studied in the synthesis of excellent catalyst materials [105,106]. A study found that ZrO_2 in the catalyst can increase the dispersion of copper particles and the reducibility of the catalyst. Furthermore, CeO_2 can increase the oxygen storage capacity [107]. Some researchers explored the adsorption and hydrogenation of CO_2 to produce methanol [108]. They found that the two supports (CeO_2 and ZrO_2) have different effects on the catalyst. CeO_2 can generate more oxygen vacancies on the catalyst and ZrO_2 can increase the dispersion of copper particles. Therefore, it is also important to revise the supports and thus optimize the catalyst.

To prevent the deactivation of copper-based catalysts, some workers have studied the original supports. As a common support, ZrO_2 is often used to support copper-based catalysts. The influence of two crystal structures of ZrO_2, namely monoclinic m-ZrO_2 and tetragonal t-ZrO_2, has been investigated, and it was found that the m-ZrO_2 supported Cu catalyst was highly selective for CO_2 (Figure 6) [109]. The CO_2 selectivity never dropped below 90% in 160 h, and there was still an upward trend. Bagherzadeh et al. [49] investigate how the amount of support affects the catalyst. They found that with the increase of CeO_2 and the decrease of ZrO_2, the catalytic performance could be better. Through the stability test of the catalyst, it was found that the selectivity of CO, CO_2, and H_2 remained stable for 1440 min. Some researchers doped ZrO_2 with Ce to support copper metal catalysts [29]. They found that the catalysts showed good catalytic performance in MSR, showing, for example, high hydrogen selectivity and good stability. At high temperatures, the hydrogen selectivity of the Ce-added catalyst was not lower than 99.8%, and there was no obvious deactivation after 90 h of operation.

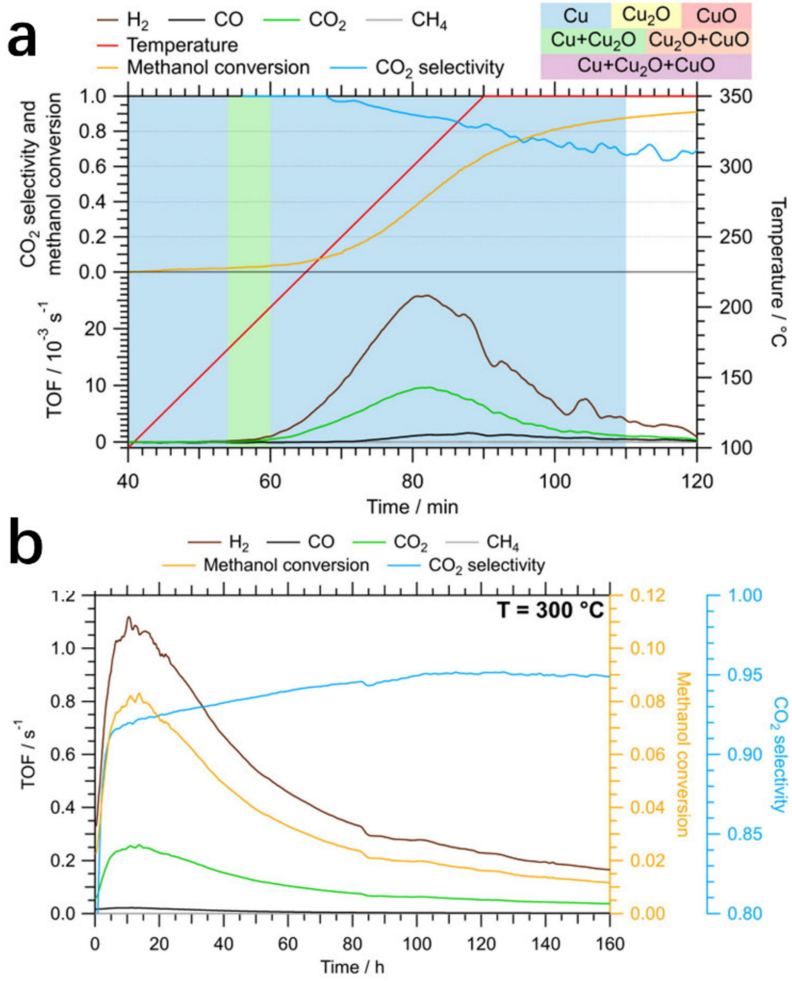

Figure 6. Methanol steam reforming catalyzed by Cu/ZrO_2 catalyst: (**a**) Methanol steam reforming curves of m-ZrO_2 supported catalysts between 100 °C and 350 °C. (**b**) methanol steam reforming curves of catalysts at long time. Reproduced with permission [109]. Copyright Elsevier, 2020.

Since CeO_2 has many oxygen vacancies and these oxygen vacancies are important to enhance the catalyst activity, CeO_2 is often used as a support for the preparation of copper-based catalysts [110–112]. The morphology and structure of the CeO_2 support can affect the crystal plane of the catalyst, thereby affecting the oxygen storage capacity of CeO_2 and thus the performance of the catalyst. Therefore, it is very important to study the effect of supports with different morphologies and structures on catalysts to prevent catalyst deactivation. Some researchers compared the catalytic performance of three different structures of CeO_2, namely nanorods, nanoparticles, and sponges, and their CeO_2 with a nanorod morphology showed better catalytic performance than the other two structures of CeO_2 [113]. They found that the nanorod-shaped CeO_2-supported copper-based catalyst had the smallest copper size of 23.2 nm, and the highest copper dispersion of 16.01%, which indicates that the catalyst had the best anti-sintering ability. Some researchers have also treated the catalyst support. For example, Mohtashami et al. treated MCM-41 with acetic acid [48]. After the treatment, the metal particles of the Cu/ZnO supported by the support were smaller in size and higher in dispersion, which showed good performance and better catalytic stability in methanol reforming for hydrogen production.

In addition to the optimization of traditional supports, some researchers have also explored some new catalyst supports. He et al. prepared a new catalyst precursor, namely ZnAl-LDHs, on γ-Al_2O_3 to support copper, and they found that the CH_3OH conversion rate could reach up to 99.98% [114]. Generally, when the temperature is above 300 °C, Cu-based catalysts are easy to deactivate, while the Cu/γ-Al@MMO catalyst does not decrease the methanol conversion rate when the temperature is higher than 300 °C. This suggests that the carrier can protect the copper from sintering. Khani et al. prepared a new type of sponge-like ceramic support. The support contains Zn, La, and Al. These elements have different effects on methanol reforming for hydrogen production. They found that compared with γ-Al_2O_3, these carrier-supported catalysts have lower reduction temperatures and larger pore sizes [115]. Through the thermal stability test of the carrier, after heat treatment at 1000 °C for 12 h, the surface area of γ-Al_2O_3 decreased by 91%, while the prepared new carrier only decreased by 8%, which greatly improved the stability of the catalyst. This reminds us that in order to explore multifunctional vehicles, we should know the role of each element and then combine them.

Sintering is the major problem with copper-based catalysts. To reduce the sintering of copper-based catalysts, many researchers have explored mesoporous materials with a high surface area, because such materials can increase the dispersion of active metals, thereby reducing catalyst sintering, for example, MCM-41, KIT-6, and SBA-15 [21,116,117]. Taghizadeh et al. [118] supported KIT-6 on Ce-promoted copper-based catalysts. They found that 3D mesoporous KIT-6 supports could greatly reduce the deactivation rate of copper-based catalysts and reduce the sintering of copper particles. Therefore, in order to reduce the sintering degree of copper-based catalysts, it is a good method to introduce some support materials with large pore sizes.

Table 3 presents the research on the stability of copper-based catalysts with different supports. From Table 3, we can find that ZrO_2-Al_2O_3 has a great influence on the dispersion of copper components, which greatly reduces the deactivation rate of the catalyst and improves the catalytic stability. Some new supports, such as KIT-6, exhibit low Cu dispersion, which also reminds us that it is necessary to find an effective new support.

Table 3. Copper-based catalysts on different supports for MSR.

Entry	Catalyst	Support	Conv.$_{CH3OH}$/%	Select.$_{H2}$/%	T/°C	Dispersion/%	Lifetime/h	Ref.
1	Cu-Zr/AZ	Zeolite-supported	-	90.6	400	-	50	[119]
2	Ce-Cu/KIT-6	KIT-6	~92	99.0	300	9.8	24	[118]
3	CuO/CeO_2	CeO_2	100	-	280	15.33	40	[111]
4	$CuZrAl_X$	ZrO_2-Al_2O_3	96.0	-	270	23.1	30	[105]
5	Cu/$Zn_{1.11}La_{1.26}Al_{0.5}O_{4.27}$	Ceramic support	97	91	300	11.5	12	[115]
6	10% Cu/g-Al@MMO	ZnAl-LDHs/g-Al_2O_3	99.98	97.8	300	14.16	20	[113]

3.4. Emerging Materials and Technologies

3.4.1. Copper-Based Spinel Oxide

To solve the sintering problem of copper-based catalysts, spinel-structured copper-based catalysts have been extensively studied in recent years [43,120,121]. The spinel-structured copper-based catalysts were found to perform in MSR without prereduction [85,122]. Compared to traditional copper-based catalysts, this type of catalyst is more stable. The sustained-release catalytic mechanism is a major reason for maintaining the stability of copper-based spinel catalysts. Slow-release catalysis means that the copper species in the catalyst can be gradually released, and the release rate is not fast; thus, the stability is improved [121,123]. Meanwhile, the unreleased Cu^{2+} can stabilize these released copper species [124]. It can be seen that copper-based spinel oxide catalysts have great potential in the methanol reforming reaction; researchers have also conducted a lot of research on this [125–127]. Figure 7 shows the microstructure of the Cu−Al spinel oxide catalyst and its slow−release catalytic mechanism, we can find that it can be basically not deactivated within 160 h and has excellent stability.

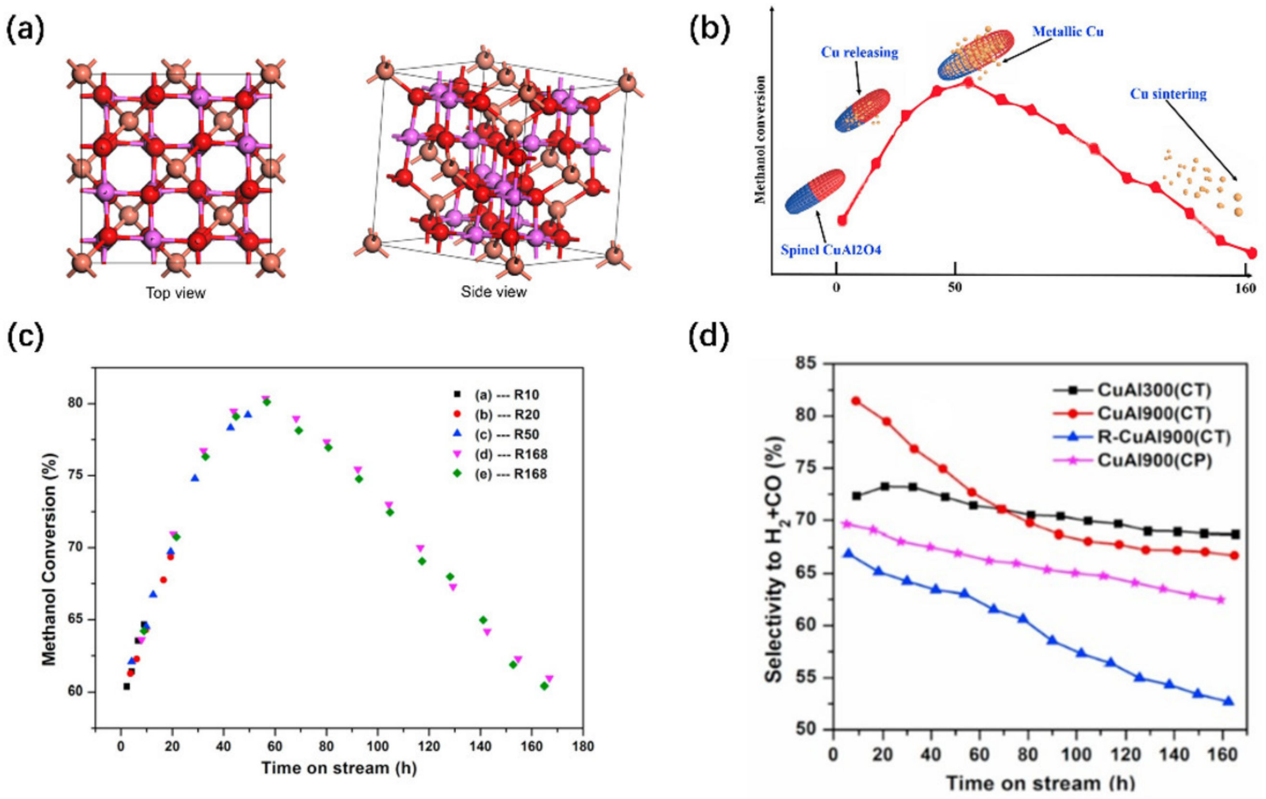

Figure 7. Cu-Al spinel catalyst for hydrogen production from methanol: (**a**) $CuAlO_2$ cell; (**b**) variation of $CuAl_2O_4$ catalytic activity with time; (**c**) catalytic activity of samples prepared at 900 °C as a function of time; and (**d**) variation of catalytic performance of different Cu-Al oxide catalysts with time. Reproduced with permission [43]. Copyright Elsevier, 2018.

In order to study the effect of copper-based spinel oxides on MSR, different copper-based spinel oxides were prepared. Huang et al. explored the catalytic activity of $CuFe_2O_4$, $CuAl_2O_4$, $CuMn_2O_4$, and $CuLa_2O_4$ in MSR [128], and Li et al. explored the catalytic activity of $CuAl_2O_4$, $CuFe_2O_4$, and $CuCr_2O_4$ in MSR [85]; they found that Cu-Al spinel had the best catalytic activity, and various studies have shown that Cu-Al spinel is of great significance [43,85,129]. Researchers have explored the effect of preparation conditions and doping promoters on Cu-Al spinel [89]. For example, after doping Mg into Cu-Al spinel [102,120], the surrounding environment of the copper species changes and the stability is also improved. During catalyst testing, it was found that the Mg-doped catalyst released copper components more slowly and had higher copper dispersion and specific surface area (Figure 8). Others have doped Ni into Cu-Al spinel [121,122], and they found that Ni not only stabilized the released copper species but also inhibited the formation of Cu^{2+}. Our research group studied the doping of Fe, Co, and Ni into $CuAl_2O_4$ and found that Ni and the other two elements are easily doped in different positions, and the charge transfer ability follows the order of Fe > Co > Ni [128]. Through theoretical calculations, our research group also explored the adsorption of high-coverage water molecules on the surface of $CuAl_2O_4$. The study found that the interaction of water molecules on the surface of 110 is stronger. This conclusion is conducive to the development of more effective catalysts [126]. The preparation conditions also have a great influence on the copper-aluminum spinel. The activities of catalysts prepared at different temperatures were studied, and it was found that the preparation temperature of 950 °C had the best activity [124]. Copper-based spinel oxides show a great potential in solving sintering problems, which indicates that they should be further explored.

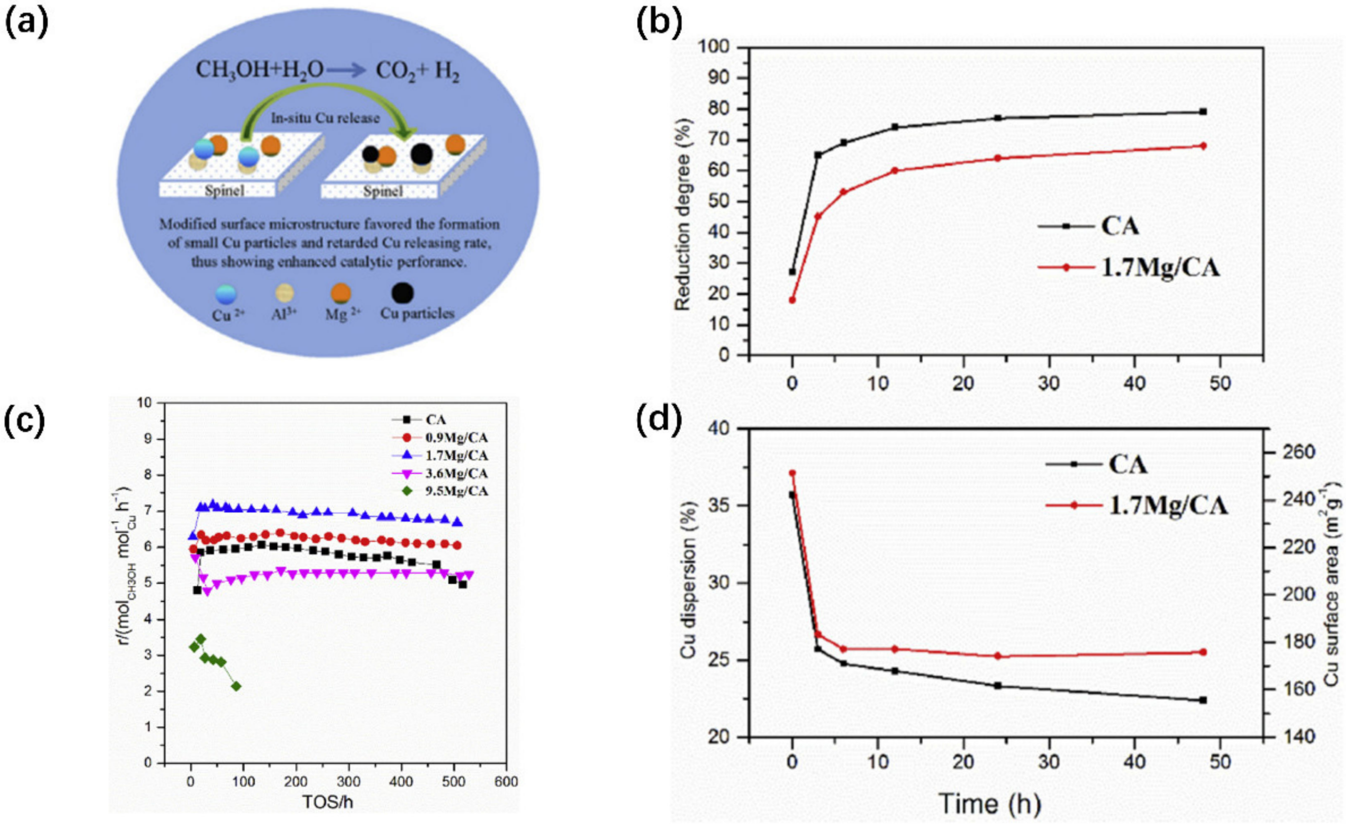

Figure 8. MgO-modified Cu-Al spinel oxide catalyst for methanol steam reforming: (**a**) Reaction process on catalyst; (**b**) the degree of reduction varying with the reduction time; (**c**) stability testing of original samples and Mg-doped catalysts; and (**d**) copper dispersion and surface area versus time. Reproduced with permission [102]. Copyright Elsevier, 2020.

3.4.2. Plasmonic Copper-Based Catalysts

It is well known that the process of methanol reforming for hydrogen production requires high temperatures, and copper-based catalysts are easy to sinter at high temperatures, which greatly reduces the stability of the catalyst. In order to solve this problem, researchers must look for photocatalytic materials. Although photocatalytic methanol reforming for hydrogen production has been studied by many researchers [130–133], these catalytic materials cannot make good use of light energy, and the hydrogen production efficiency is also low. It has been reported that catalysts with plasmonic structures have higher solar energy utilization efficiency, which utilizes solar energy to excite local surface plasmon resonance (LSPR) for synergistic heating, and plasma catalysts have been presented in recent years as an emerging type of catalyst [134–140]. Plasma copper-based catalysts have greater research interest than other metals because of the lower cost of copper. Luo et al. [140] prepared a plasmonic ZnCu alloy catalyst which is solar powered in methanol reforming for hydrogen production and exhibits high hydrogen yield; Figure 9a shows the reaction mechanism of this catalyst. Plasma copper-based catalysts are also frequently studied in other reactions. Copper-based catalysts are often used in methanol synthesis as the reverse reaction of methanol reforming for hydrogen production. A plasma Cu/ZnO catalyst was proposed for methanol synthesis [139], showing an improved activity for methanol synthesis by 54%. Zhou et al. prepared a copper nanoparticle plasmonic photocatalyst for methane dry reforming, and they found that the catalyst can efficiently utilize light energy [138]. Recently, Luo et al. reported a plasmonic Ni-Cu bimetallic catalyst for photocatalytic ethanol dehydrogenation, which exhibited high activity due to the localized surface plasmon resonance mechanism [141]. Plasma catalysts have shown advantages in various photocatalytic reactions, especially in terms of energy saving, which is of great significance for future energy conservation and emission reduction. More plasmonic catalysts should be explored.

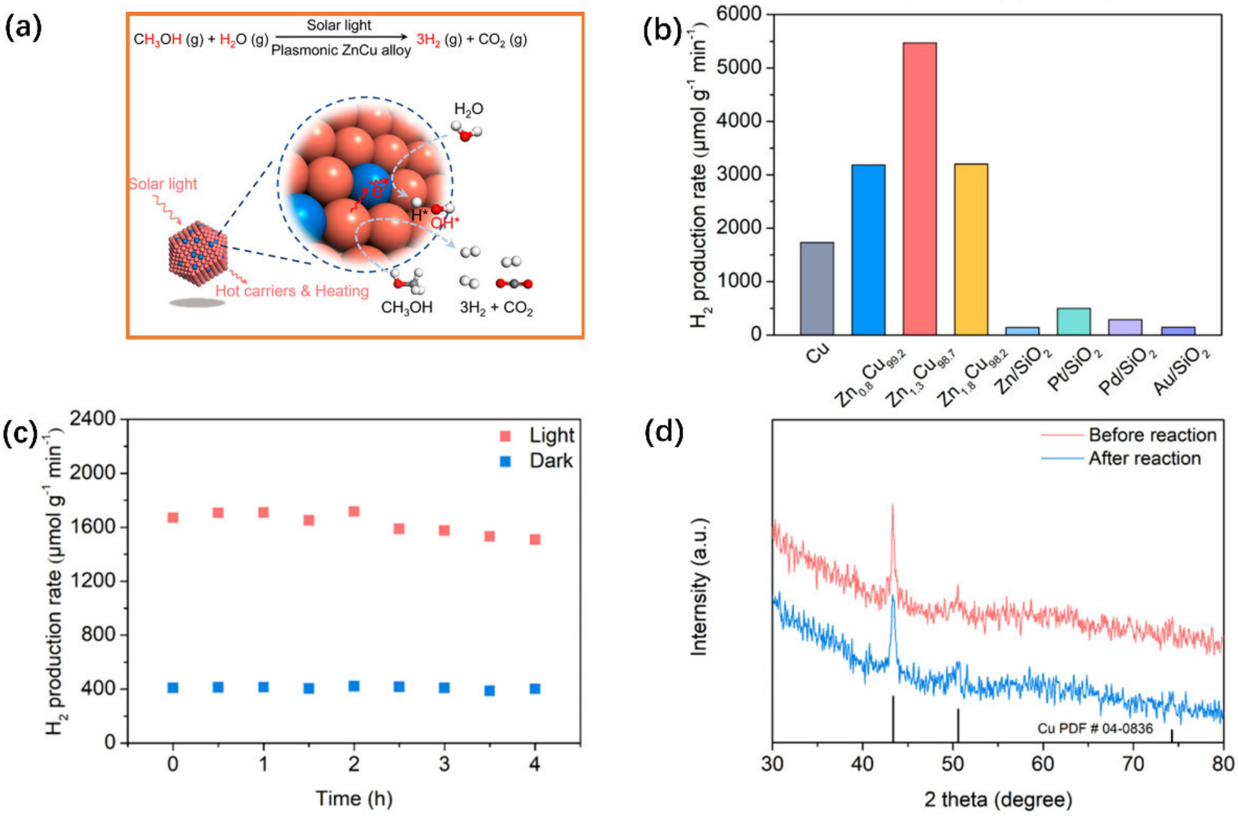

Figure 9. Solar-driven plasma ZnCu alloys for H_2 production: (**a**) Mechanism of plasma ZnCu alloy catalyzed methanol steam reforming reaction; (**b**) methanol steam reforming activity of different catalytic materials; (**c**) stability test of $Zn_{1.3}Cu_{98.7}$ alloy; and (**d**) XRD of $Zn_{1.3}Cu_{98.7}$ catalysts before and after reaction. Reproduced with permission [140]. Copyright American Chemical Society, 2021.

3.4.3. Metal-Organic Framework-Derived Cu-Based Catalysts

In recent years, the research of metal-organic frameworks (MOFs) has become a popular topic [142,143]. Metal-organic frameworks exhibit a special 3D network structure, and their morphology and properties are relatively easy to change. MOFs have the advantages of rich structural types, low density, and high specific surface areas [144], which are very useful in heterogeneous catalysis [142,145]. For example, metal-organic frameworks such as HKUST-1, ZIF-8, copper-based MOF [Cu(mipt)(H_2O)](H_2O)$_2$,and Cu(BDC) are often studied in heterogeneous catalysis [146–148]. Among them, HKUST-1 is a typical Cu-containing MOF, and MOF-derived copper-based catalysts have also been studied and used in methanol reforming to produce hydrogen. As is shown in Figure 10, Chen et al. prepared MOF-derived CuO-CeO_2 catalysts and used them in methanol reforming for hydrogen production with HKUST-1 as the copper precursor [149]. By the MSR performance tests, they found that the higher the temperature, the higher the methanol conversion of the catalyst, and the rate of deactivation of MOF-derived catalysts was higher than that of conventionally prepared catalysts due to their stronger metal–support interaction and higher copper dispersion, which provides ideas for designing more stable catalysts. Ye et al. also used HKUST-1 as a copper precursor. To prevent the deactivation of copper-based catalysts, they prepared a MOF-derived Cu/SiO_2 catalyst [150]. It was found that this catalyst can easily generate more stable Cu_2O and does not deactivate within 220 h. In addition to using MOFs as a copper precursor, they have also been used to prepare copper-based catalyst supports, and achieved good results. Varmazyari et al. used Cu(BDC) as a catalyst carrier for MSR, and explored the effect of different promoters on the catalyst [151]. Finally, they found that Cu/Ce-Cu(BDC) had the strongest resistance to deactivation and the highest CH_3OH conversion. Carbon deposition was minimal within 32 h, and the researchers believe that MOFs as a catalyst support can improve the dispersion of Cu and strengthen support–metal interaction. This is the same as the conclusion of Chen et al., which shows that MOFs have a great influence on strengthening support-metal interaction and improving the dispersion of Cu particles. These two characteristics are important for enhancing the stability of Cu-based catalysts.

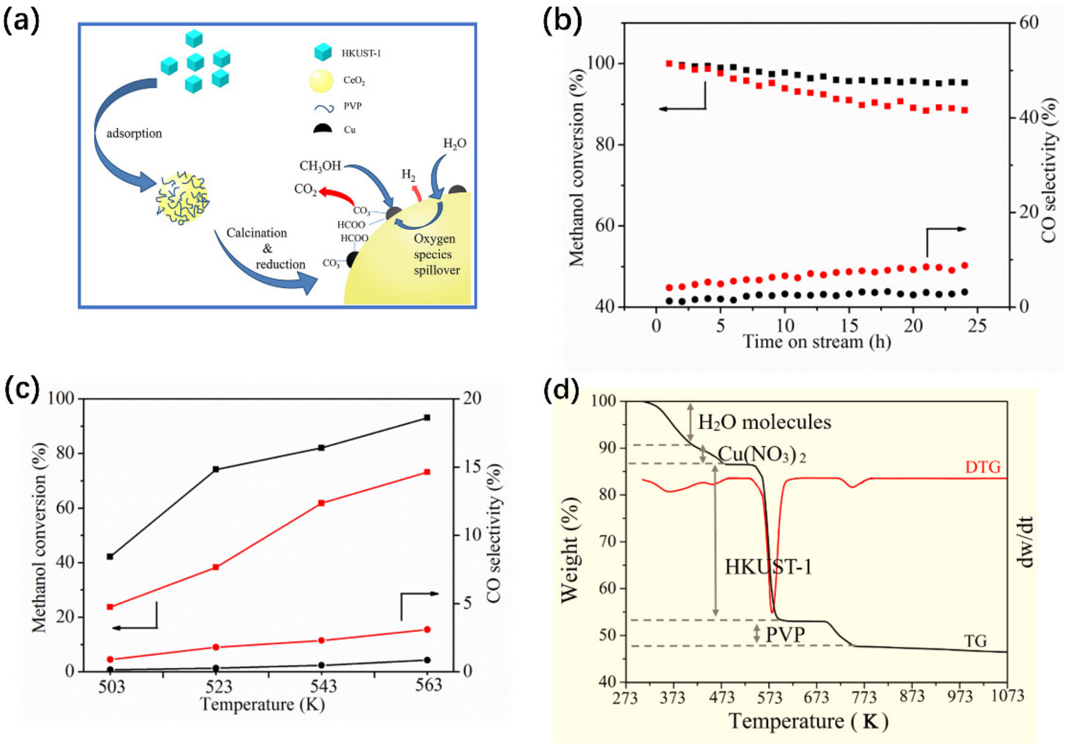

Figure 10. MOF-derived CuO-CeO_2 catalysts for methanol steam reforming: (**a**) Methanol steam reforming reaction mechanism over MOF-derived CuO-CeO_2 catalyst; (**b**) stability testing of CuO-CeO_2 (black dots) and CuO-CeO_2-I (red dots), (square: methanol conversion; circle: CO selectivity); (**c**) catalytic performance of CuO-CeO_2 (black line) and CuO-CeO_2-I (red line) as a function of temperature, (square: methanol conversion; circle: CO selectivity); and (**d**) TG-DTG plots of the HKUST-1-CeO_2 composite, (black line: thermogravimetric curve, red line: differential curve of thermogravimetric curve). Reproduced with permission [149]. Copyright Elsevier, 2020.

Table 4 lists some emerging copper-based catalysts. We found that the catalytic stability of Cu-Al spinel was greatly improved, which was due to its slow-release catalytic mechanism. Although the catalytic activity of MOF-derived catalysts was high, the stability has not been greatly improved. In the future, researchers should pay more attention to the stability of MOF-derived copper-based catalysts.

Table 4. Emerging materials for copper-based catalysts.

Entry	Catalyst	Conv.$_{CH3OH}$/%	Select.$_{H2}$/%	T/°C	Lifetime/h	Ref.
1	$Cu_{1-x}Mg_xAl_3$	96.5	96.5	255	500	[120]
2	Cu-Ni-Al spinel oxides	90.0	—	255	2000	[122]
3	Cu/X-Cu(BDC)	~100	~99	250	32	[151]
4	MOF-derived $CuO-CeO_2$	95.0	97.7	330	30	[149]

4. Conclusions

This review discussed the Cu-based catalysts for MSR, especially with regard to the catalytic stability. First, we summarized several major causes of the deactivation of Cu-based catalysts. Sintering and carbon deposition are the main reasons for the deactivation of Cu-based catalysts. In order to solve the problem of deactivation of copper-based catalysts, this work summarized the progress made by researchers in recent years from three main aspects, including the preparation methods, promoters, and supports. Some researchers have also developed new preparation methods. Although the problem of carbon deposition has been solved and the stability has been improved, the catalytic effect is not good. From the literature we investigated, among all the preparation methods, the catalysts prepared by the modified impregnation method and the one-step hydrothermal method have higher catalytic activity, and for the stability, the modified impregnation method is the best; therefore, the improved impregnation method has a good effect on improving the stability and activity of the catalyst. Different additives and supports have different effects on the stability. For example, Ce has a good oxygen storage capacity, and ZrO_2 can disperse copper particles and reduce the size of copper particles. The dispersion of active species has a great influence on the stability of the catalyst, and doping of some pure metals can achieve very good results, even better than oxide doping. From the literature, the doping of MgO has achieved good results, with the selectivity of hydrogen reaching 99.3% and the conversion rate of methanol being close to 100%. Furthermore, it does not deactivate for 30 h. Among the supports, the copper-based catalysts supported by CeO_2 and ZrO_2 have higher stability and better catalytic activity. With technological innovation, more and more new copper-based catalysts have been developed for the methanol reforming reaction, such as Cu-based spinel oxide, MOF-derived Cu-based catalysts, and plasmonic copper-based catalysts. Among the copper-based catalysts prepared from these emerging materials, copper-aluminum spinel is promising as it remains stable for 2000 h.

Although a lot of research has been done on preventing the deactivation of Cu-based catalysts, there are still many challenges in this field. Firstly, the preparation method could be designed and developed with the idea of green chemistry, which can improve the performance of the catalyst without polluting the environment. Secondly, the microscopic mechanism of many supports and promoters in improving catalytic stability is still unclear. The interaction mechanism between the metal and support is not fully understood. More theoretical calculations could be done to understand them at the atomic and molecular levels. Thirdly, plasmonic and MOF-derived copper-based catalysts have not been fully studied for the methanol reforming reaction, and more efforts could be made in this area in the future. Although the catalytic activity of MOF-derived catalysts is high, the stability has not been greatly improved. In addition, more advanced technologies under mild reaction conditions for methanol reforming could be developed, such as photo-catalytic, plasma-catalytic, and electro-catalytic methanol reforming. This kind of catalyst can efficiently utilize renewable energies such as solar energy and biomass and has great research significance in solving the energy crisis in the future. Through extensive literature reports, it was found that few review articles have focused on the design of reactors for methanol reforming. Thus, the optimization of reaction process conditions and reactor design would also be significant for the stability of Cu-based catalysts.

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