Stability of Cu-Based Catalysts for Methanol Reforming

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The stability of copper-based catalysts is an important property that affects the catalytic efficiency, which determines the service life of the catalytic base in the methanol steam reforming (MSR) reaction, and plays an important role in the sustainable production of hydrogen.

Keywords: Methanol Steam Reforming ; Copper based catalyst ; stability

1. Introduction

With the booming economy, energy consumption and harmful gas emissions have increased sharply[1][2][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][7][8], traditional fossil fuel hydrogen production[9][10], biomass hydrogen production[11][12][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][20][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][28][29].

There are four typical ways to produce hydrogen from methanol: methanol decomposition (MD)[30][31][32], partial oxidation of methanol (POM)[33][34][35], steam reforming of methanol (SRM)[9][36], and oxidative steam reforming of methanol (OSRM)[37][38][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][41][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][45][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].

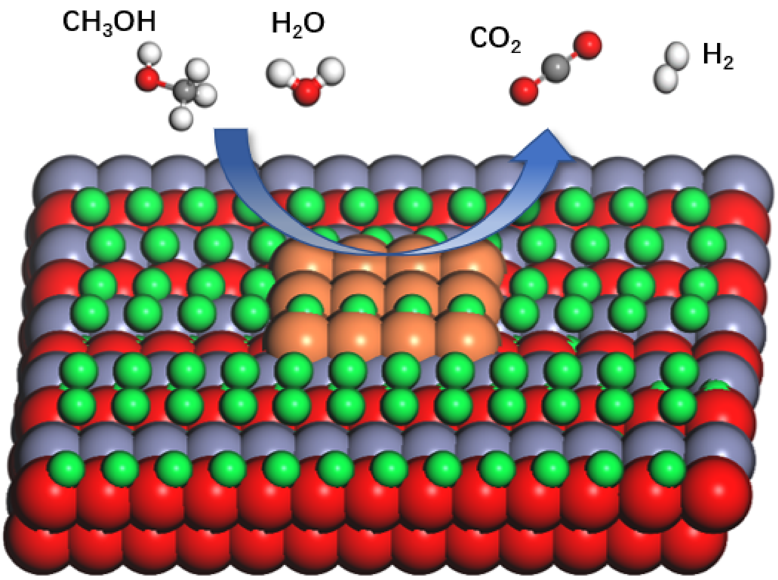

Figure 1. The reaction process of methanol reforming for hydrogen production.

2. Research Progress on Avoiding Deactivation of Copper-Based Catalysts

Improving the stability of copper-based catalysts is of great significance for improving the efficiency of methanol reforming to hydrogen production. However, there are also many difficulties. In the future, researchers should make great efforts in this regard.

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], 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]. Sanches et al. prepared a Cu/ZnO catalyst by the co-precipitation method[63], and Liao et al. synthesized a $CuO/ZnO/CeO_2/ZrO_2$ catalyst by the one-step hydrothermal method[64]. A series of CuZn/MCM-41 catalysts were prepared by the co-impregnation method[65] 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.

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[66], 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[67]. The addition of promoters changes the structural properties of the catalyst. For example, Sanches et al. [63] 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[68]. 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[69]. 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.

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