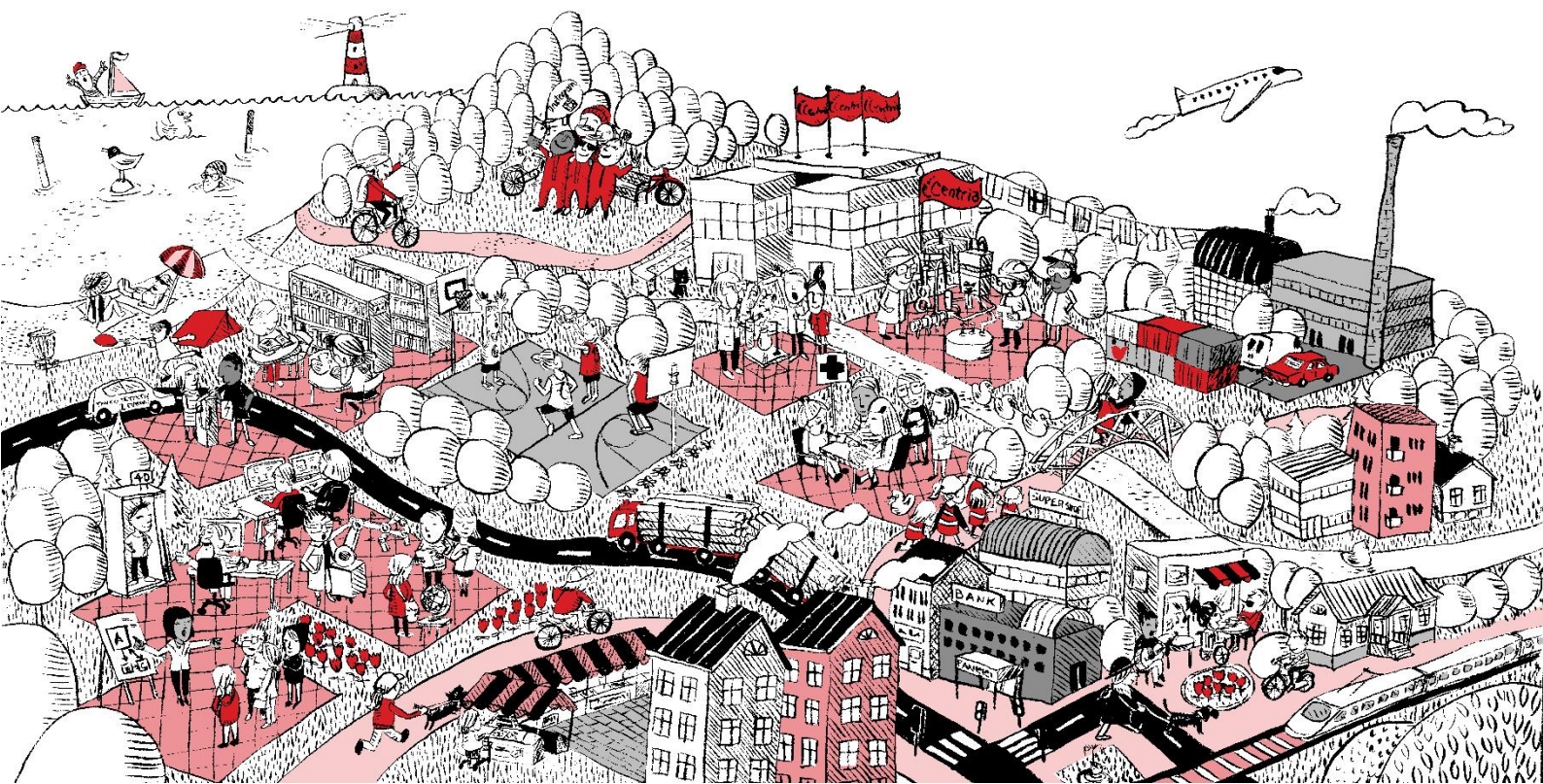Yisong Zheng

CE-ZR SOLID SOLUTION CATALYST: A NEW CATALYST FOR HYDROGEN PRODUCTION FROM METHANOL STEAM REFORMING

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• **ABSTRACT**

Centria University of Applied Sciences	Date June 2021	Author Yisong Zheng
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Hydrogen energy is one of the most active substitutes for fuel cell energy. At present, it is a good choice to solve the storage problem by reforming hydrocarbons to produce the H_2 we need on site. There are many ways to produce a large amount of hydrogen in industry. Among the methods of hydrogen production by reforming hydrocarbons, methanol steam reforming has many advantages, such as low reforming temperature and low CO content in reforming gas.

Most research reports show that CO in reforming gas comes from WGS reverse reaction and methanol cracking reaction, while copper-based catalyst has higher selectivity for CO_2 and H_2. At present, copper-based catalysts have been used in methanol steam reforming for hydrogen production, most of which are $CuO / ZnO / Al_2O_3$ catalysts. However, Ce-Zr solid solution catalyst can improve the thermal stability and reduction performance of copper-based catalyst, solve the problem of poor stability of copper-based catalyst, and improve the performance of copper-based catalyst.

In this thesis work, through the introduction of a variety of hydrogen production methods, and the comparison of a variety of hydrogen production methods, the methanol reforming reaction system is highlighted. In addition, Ce-Zr solid solution was prepared by sol-gel method, and $CuO / Ce_{0.8}Zr_{0.2}O_2$ catalysts with different Cu content were prepared by impregnation method. The catalysts were characterized by H_2-TPR, BET and XRD. The influence of Cu content on the structure and properties of $CuO / Ce_{0.8}Zr_{0.2}O_2$ catalysts was discussed. It is expected to prepare $CuO / Ce_{0.8}Zr_{0.2}O_2$ catalyst with high activity and high stability. Finally, the prospect and challenge of cerium zirconium solid solution catalyst for methanol steam reforming for hydrogen production were prospected.

Key words
catalyst, Ce-Zr solid solution, hydrogen, methanol steam reforming

CONCEPT DEFINITIONS

List of abbreviations

Al_2O_3	Aluminum oxide
AWEs	Alkaline electrolyzed water
BET	The famous bet equation
CeO_2	Cerium dioxide
$Ce(NO_3)_3 \cdot 3H_2O$	Cerium nitrate
$Ce_{0.8}Zr_{0.2}O_2$	Nano cerium zirconium solid solution
CH_4	Methane
CH_3COOH	Acetic acid
$C_6H_{12}O_6$	Glucose
CH_3OH	Methanol
CO	Carbon monoxide
CO_2	Carbon dioxide
Cu	Copper
Cu-Ce-Zr	Copper-Cerium-Zirconium
$Cu(NO_3)_2 \cdot 3H_2O$	Cupric nitrate trihydrate
CuO	Cupric oxide
H_2	Hydrogen
H_2-TPR	Automatic gas adsorption analyzer
HNO_3	Nitric acid
LPG	Liquefied petroleum gas
MSR	Methanol steam reforming
$NH_3 \cdot H_2O$	Ammonia water
Pd-Zn	Palladium-Zinc
PEMWEs	Water electrolysis by polymer proton exchange membrane
PSA	Pressure swing adsorption
SOEC	High temperature oxide electrolyzed water
TOF	Turnover frequency
WGS	Water–Gas Shift
XRD	X-ray diffraction
Zn-Cr	Zinc-Chromium
ZnO	Zinc oxide
$Zr(NO_3)_4 \cdot 5H_2O$	Zirconium nitrate pentahydrate
ZrO_2	Zirconia

Symbols

F_R	Reforming tail gas flow under standard conditions (ml / min)
F	Feed rate set by pump (ml / min)
ρ_{mix}	Mixing density of methanol aqueous solution (g / ml)
w	Molar ratio of methanol to water
m_{cat}	Mass of catalyst (kg)
C_{CO}	The volume mole concentration of CO in reforming tail gas
C_{CO2}	The volume mole concentration of CO_2 in reforming tail gas
C_{H2}	The volume mole concentration of H_2 in reforming tail gas
A_1	Specific surface area
A_2	Specific surface area of copper
V_1	pore volume
V_2	hydrogen production rate
λ	Incident wavelength
T	reaction temperature

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1 INTRODUCTION

Methanol steam reforming is the reaction with the highest hydrogen content in methanol hydrogen production process, so the study of this reaction is very attractive. Hydrogen production from methanol steam reforming is a rapidly developed hydrogen production method in recent decades, which has the advantages of convenient operation, easy access to raw materials, mild reaction conditions and less by-products. Due to the addition of water, the reaction by product content is reduced, but there are still some technical problems in the application of methanol steam reforming hydrogen production: methanol steam reforming hydrogen production is a strong endothermic reaction, which needs a lot of heat from the external environment. The reaction volume is limited by heat mass transfer and the dynamic response of the reaction is slow. Copper-based catalysts have been used in some areas to achieve good results in methanol steam reforming. (Ye, W., Guo, X. & Ma, T.. 2021.)

The process uses methanol and desalinated water from convenient sources as raw materials, at 220 °C to 280 °C, catalyzed by a special catalyst into conversion gas composed mainly of hydrogen and carbon dioxide. Copper-based catalysts show excellent activity in methanol reforming for hydrogen production, but how to prolong the service life of copper-based catalysts is still one of the problems to be solved (Nuzhdin, A.L., Bukhtiyarova, M., Bulavchenko, O. & Bukhtiyarova, G.A. 2020). Exploring how to improve the thermal stability of copper-based catalysts and reduce the carbon deposition of catalysts is an important challenge to solve this problem.

In addition, the catalysts containing CeO_2 and ZrO_2 have higher H_2 selectivity and lower CO selectivity than the traditional Cu supported catalysts. (Liao, M., Guo, C., Guo, W., Hu, T., Xie, J., Gao, P. & Xiao, H. 2021.) CeO_2 can improve the thermal stability and reduction performance of copper-based catalyst, solve the problem of poor stability of copper-based catalyst and improve the performance of copper-based catalyst.

2 HYDROGEN PRODUCTION METHODS

Since hydrogen appears to be a potential solution for a carbon free society, its production plays a key role in showing how well it meets the standards of environmentally sound and sustainable development. Of course, hydrogen can be produced from many sources, such as water, hydrocarbon fuels, biomass, hydrogen sulfide, borohydride and hydrogen containing chemical elements. Because hydrogen cannot exist as a single element anywhere, it needs to be separated from the above sources, and energy is needed to achieve this separation. The energy forms driving the hydrogen production process can be divided into four categories: thermal energy, electric energy, light energy and biochemical energy. These kinds of energy can be obtained from primary energy (fossil, nuclear, and renewable) or from recovered energy through various paths. (Kannah, R.Y., Kavitha, S., Preethi, Karthikeyan, O.P., Kumar, G., Dai-Viet, N.V. & Banu, J.R. 2020.)

At present, it is a good choice to solve the storage problem by reforming hydrocarbons and producing H_2 in situ. At the present time, about 80 percent of the world energy demand is met by fossil hydrocarbons-coal, petroleum and natural gas (Davis 1990). There are many ways to produce hydrogen in industry, and the traditional method of hydrogen production from electrolytic water is one of them. However, it is a challenging problem to reduce CO content in reforming gas to 10ppm. Among the methods of hydrogen production by hydrocarbon reforming, methanol steam reforming (MSR) has attracted extensive attention in recent years due to its advantages of low reforming temperature and low CO content in reforming gas. (Kannash et al. 2020.)

2.1 Electrolysis of water to produce hydrogen

At present, hydrogen in the market mainly comes from steam reforming of fossil fuels and by-product hydrogen, while hydrogen production from electrolytic water has the characteristics of carbon free, environmental protection and flexibility, which has gradually attracted attention. Hydrogen production by water electrolysis is a convenient method. When a direct current is applied to an electrolytic cell filled with electrolyte, water molecules undergo an electrochemical reaction on the electrode and decompose into hydrogen and oxygen. (Lu, S., Zhao, B., Chen, M., Wang, L., Fu, X. & Luo, J. 2020.)

Hydrogen production from electrolytic water is believed to be the starting point for many people to understand the way of hydrogen production. This is a kind of "reverse process" in which water is used as raw material and hydrogen reacts with oxygen to produce water. Therefore, as long as a certain form of energy is provided, water can be decomposed, and the purity of hydrogen is very high. The efficiency of hydrogen produced by electrolysis of water can reach 75% - 85%. (Lu et al. 2020.) Although this technology has the advantages of simple process and no pollution, but the power consumption is huge, so its application is limited. Moreover, because the conductivity will limit the electrolyte, a relatively low working current density is required. Although the principle is very simple and easy to understand, the power consumption of large-scale production of H_2 is extremely huge. Every 4.5 ~ 5.5 kW/h of electricity consumed can only produce 1 cubic meter of H_2, so it has great limitations at present. (Paidar, M., Fateev, V. & Bouzek, K. 2016.)

Traditional electrolyzed water for hydrogen production mainly includes alkaline electrolyzed water (AWEs), polymer proton exchange membrane electrolyzed water (PEMWEs) and high temperature oxide electrolyzed water (SOEC). Take AWEs as an example to illustrate that AWEs is a commercialized hydrogen production technology from electrolytic water. (Paidar et al. 2016.) However, AWEs cannot operate under high voltage, narrow load range, poor flexibility, and cannot support high current operation (generally about 400mA/cm^2) (Grigoriev, S., Bessarabov, D., Fateev, V. & Millet, P. 2020).

However, with the development of society, electricity can be provided by a variety of primary energy, including fossil fuel, nuclear energy, solar energy, water energy, wind energy and ocean energy. And nuclear energy, water energy and ocean energy are rich in resources and can be used for a long time, and are still in the development stage. (Lu et al. 2020.) With the development of the times and the progress of technology, solar energy has caught people's attention. Through the conversion of solar energy to produce H_2, and with the continuous enhancement of people's ability to convert solar energy, the cost of producing H_2 becomes lower and lower. Although there have been many breakthroughs in scientific research technology at home and abroad, there is still room for development. (Paidar et al. 2016.)

2.2 Biological hydrogen production

Bio hydrogen production refers to hydrogen production from biomass by gasification and microbial catalytic dehydrogenation. The idea of biological hydrogen production was first put forward by Lewis in 1966. Its research and development mainly focus on the photolysis and fermentation of green algae, cyanobacteria and photosynthetic bacteria. In 1970s, the worldwide energy crisis broke out, and the feasibility study of biological hydrogen production was highly valued. (Akhlaghi, N. & Najafpour-Darzi, G. 2020.)

Biological hydrogen production has the advantages of energy saving, clean, abundant raw materials, mild reaction conditions, energy consumption and no consumption of mineral resources. There are many kinds of biological hydrogen production methods, so far, the commonly used methods are photosynthetic hydrogen production, fermentation bacteria hydrogen production, photosynthetic and fermentation bacteria mixed culture hydrogen production, various biological hydrogen production methods have different characteristics. In general, biological hydrogen production technology is not yet fully mature, and needs to be further studied before large-scale application. All kinds of biological hydrogen production methods have their own unique advantages, but also have some shortcomings. So far, they cannot achieve large-scale production of hydrogen to meet the needs of the world. However, with the progress of the times, biological hydrogen production will also make significant progress. (Akhlaghi, N. & Najafpour-Darzi, G. 2020.)

2.2.1 Direct biological photolysis for hydrogen production

Photoautotrophic organisms such as green algae and cyanobacteria can use carbon dioxide, water and solar energy to synthesize organic materials for energy storage. (Akhlaghi, N. & Najafpour-Darzi, G. 2020.) However, in the absence of oxygen, they can also use light energy, catalyzed by hydrogenase, to photolysis water and produce hydrogen:

$$4H_2O + \text{light energy} \rightarrow 4H_2 + 2O_2. \qquad\qquad (2.1)$$
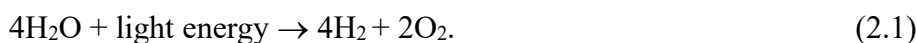
The direct photolysis of water is coupled with photosynthesis, and the reduction force, electron and driving force are mainly from photosynthesis. The principle of this technology is simple, but the O_2 produced by the photosynthesis system in direct photolysis will inhibit the activity of hydrogenase, resulting in a very short hydrogen production time. (Akhlaghi, N. & Najafpour-Darzi, G. 2020.) The

advantages of this technology are low reforming temperature, high hydrogen content and low CO content in the product.

2.2.2 Indirect biological photolysis for hydrogen production

The oxygen produced by photosynthesis of green algae and cyanobacteria will inhibit the catalytic activity of hydrogenase, so it cannot continuously carry out high activity direct biological photolysis of aquatic hydrogen. In order to understand the inhibition of oxygen removal, indirect biological photolysis of aquatic hydrogen can be used to artificially obtain an oxygen free environment. The reaction formula is as follows:

$$12H_2O + \text{light energy} \rightarrow 12H_2O + 6O_2. \tag{2.2}$$
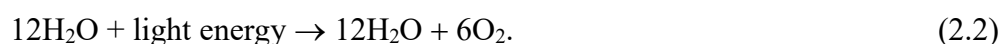
The method improves the sensitivity of hydrogen to oxygen in the product by separating hydrogen and oxygen produced in the reaction. The principle of this method is that CO_2 is fixed in carbohydrates while O_2 is generated, and H_2 is generated by anaerobic dark fermentation. The biggest advantage of this method is that hydrogen can be produced from water. (Akhlaghi, N. & Najafpour-Darzi, G. 2020.)

2.2.3 Hydrogen production by photofermentation

Some photosynthetic bacteria can use inorganic or organic substances in nature as proton and electron donors to produce hydrogen under the catalysis of hydrogenase. (Pandey, A. & Sinha, P.. 2021.) Taking organic acetic acid as an example, the reaction mechanism is as follows:

$$C_2H_4O_2 + 2H_2O + \text{light energy} \rightarrow 4H_2 + 2CO_2. \tag{2.3}$$
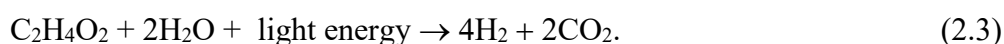
Since this kind of reaction is similar to fermentation process under anaerobic conditions, this kind of hydrogen production method is called photofermentation. Although the substrate utilization and energy conversion efficiency of this process are not ideal, it has a good development prospect because it can be combined with the treatment of organic wastewater in factories. (Pandey, A. & Sinha, P.. 2021.)

2.3 Hydrogen production from fossil fuels

Reforming of fossil fuel to produce hydrogen is the most widely used hydrogen production technology at present. There are three kinds of hydrogen production methods: steam reforming, partial oxidation and autothermal reaction. (Cormos, C. 2011.) At present, the most common hydrogen production method of fossil fuel is using oil, natural gas and coal as raw materials. Among them, the hydrogen production technology using natural gas (mainly composed of methane) as raw material has relatively small impact on the environment, and the development is the most mature. According to statistics, about 40% of the world's hydrogen is obtained by natural gas hydrogen production technology. (Muradov, N. 2017.)

According to the report of the white paper on hydrogen energy and fuel cell transportation solutions, the technology of hydrogen production from fossil fuels is the most mature and the cost is the lowest, and the cost of hydrogen production from power grid and electrolyzed water is the highest. Over the past decade, energy demand has grown at an annual rate of 1.2%, while the share of fossil fuel production has remained around 75%. (Cormos, C. 2011.)

At present, the global hydrogen production mainly depends on the process of extracting hydrogen from fossil fuel raw materials. About 96% of hydrogen is generated directly from fossil fuels, and about 4% of hydrogen is generated indirectly through fossil fuel power generation. (Muradov, N. 2017.) According to the analysis, there are mainly several reasons: The hydrogen production mode based on fossil fuels is large-scale and mature in technology. Coal, oil and natural gas have been transported maturely, and the storage scheme can meet the industrial demand. In addition, the price of grid power is high, the scale of hydrogen production by electrolysis is generally small, and the overall cost of hydrogen is high. Therefore, it is mainly used in the application scenarios where there is a certain demand for hydrogen, the scale is small, it is difficult to obtain hydrogen resources by transportation, and there is no other alternative, such as hydrogen cooling unit, gem processing. (Cormos, C. 2011.)

2.3.1   Hydrogen production from coal

At present, hydrogen production from coal (coal gasification) plays a leading role in domestic hydrogen production. Hydrogen production from coal is a process in which coal reacts with oxygen first, then reacts with water to obtain gaseous products with hydrogen and carbon monoxide as the main components. (Xia, D., Xiatong, Y., Su, X. & Zhao, W. 2020.) After desulfurization and

purification, carbon monoxide continues to react with water vapor to generate more hydrogen gas. Finally, hydrogen product with certain purity is obtained through separation and purification. The process of hydrogen production from coal gasification generally includes coal gasification, gas purification, carbon monoxide conversion and hydrogen purification. The core technology of hydrogen production from coal is to convert coal into gaseous products through different gasification technologies, and then to high purity hydrogen through low temperature methanol washing and other separation processes. (Wojtaszek, M. & Wasielewski, R. 2021.) The reaction equation is:

$$C + H_2O \rightarrow CO + H_2 - Q. \tag{2.3}$$

$$CO + H_2O \rightarrow CO_2 + H_2 + Q. \tag{2.4}$$

The total reaction equation is:

$$C + 2H_2O \rightarrow CO_2 + 2H_2 - Q. \tag{2.5}$$
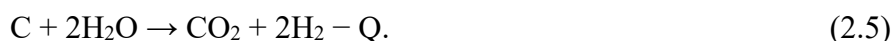
Compared with the traditional hydrogen production process of hydrocarbon steam conversion used in petrochemical industry, the domestic coal hydrogen production process has the advantages of low raw material cost and large-scale unit, but the disadvantages are large equipment investment and immature technology. (Wojtaszek, M. & Wasielewski, R. 2021.)

As the main component of coal, carbon is the traditional principle of hydrogen production from coal. Carbon can replace hydrogen in water to produce H_2 and CO_2, so as to produce hydrogen. (Xia et al. 2020.) There are two main methods to produce hydrogen gas from coal: one is coal coking (or high temperature retorting), the other is coal gasification. There are two main methods to produce hydrogen gas from coal: one is coal coking (or high temperature retorting), the other is coal gasification. Coking refers to the production of coke from coal at 900 - 1000 ℃ under the condition of isolated air, and the by-product is coke oven gas. The coke oven gas contains 55-60% hydrogen (volume), 23-27% methane and 6-8% carbon monoxide. Each ton of coal can produce 300-350m_3 of gas, which can be used as city gas and raw material for hydrogen production. China started research and development in the 1960s. At present, industrial production units have been built to produce feed gas for ammonia synthesis and methanol synthesis. Its gas composition is 35-36% (volume) of hydrogen, 44-51% of carbon monoxide, 13-18% of carbon dioxide and 0.1% of methane. There are a large number of small and medium-sized ammonia plants in China, all of which use coal as raw material to produce hydrogen

gas after gasification. This is a method of obtaining hydrogen source with Chinese characteristics. The equipment cost accounts for the main part of the investment. Therefore, hydrogen production from traditional gas is suitable for large-scale hydrogen users above 10000 m^3/h, and is generally used in ammonia and methanol production. (Wojtaszek, M. & Wasielewski, R. 2021.)

At present, according to the different specific coal consumption, the carbon emissions of hydrogen production routes from coal in the domestic market vary greatly, so the carbon emissions of coal chemical industry should be treated rationally (Li, J. & Cheng, W. 2020). First of all, as a coal rich country, China has been making continuous progress on the technical road of clean and efficient utilization of coal, and many of the coal gasification technologies are in the leading position in the world. In this way, the utilization rate of coal can be improved to the extreme. Second, the purity of carbon dioxide produced by coal hydrogen production can reach more than 98%, saving the cost of carbon capture section. As the most abundant carbon resource in the world, CO_2 should be transformed into high value-added carbon dioxide products or chemicals through the idea of CO resource utilization, so as to obtain economic benefits. (Wojtaszek, M. & Wasielewski, R. 2021.)

2.3.2 Hydrogen production from natural gas

Natural gas is one of the main energy sources and plays an important role in the global energy pattern. Natural gas reforming is one of the most studied reactions in heterogeneous catalysis, because it is directly related to key industrial processes such as methanol or ammonia synthesis (Roger, A. & Parkhomenko, K. 2020). As a traditional hydrogen production industry from natural gas, steam reforming of natural gas has been used since the early 19th century. Through continuous process improvement, not only the quality of catalyst has been enhanced, but also breakthroughs have been made in process design, process conditions selection, equipment type and layout improvement. (Korotkikh O. & Farrauto R. 2000.)

Compared with coal hydrogen production, natural gas hydrogen production has the advantages of high yield, low cost and less greenhouse gas emissions. The essence of hydrogen production from natural gas is to replace hydrogen in water with carbon in methane. (Chehade, A.M., Daher, E., Assaf, J., Riachi, B. & Hamd, W. 2020.) Carbon acts as a chemical reagent and provides heat for replacement reaction. Most of the hydrogen produced comes from water and a small part comes from natural gas itself. In order to prevent carbon evolution reaction in the conversion process, excessive water vapor

should be added in the reaction process. Its advantages are mature technology, low cost and high hydrogen conversion rate. However, the application of natural gas as chemical raw materials is strictly limited. (Korotkikh O. & Farrauto R. 2000.)

The method is to produce hydrogen by reaction with steam in the presence of catalyst. The reaction was carried out at 800 - 820 ℃. The content of hydrogen in the gas produced by this method can reach 74% (volume). Most large-scale ammonia methanol plants use natural gas as raw material to catalyze steam conversion to produce hydrogen. China has carried out a lot of effective research work in this field, and has built a large number of industrial production facilities. In China, the intermittent steam reforming process of natural gas has been developed to produce raw materials for small ammonia plants. This process does not require the use of Superalloy reformer and has low investment cost. The production cost mainly depends on the source of raw materials, and the application of this method is limited due to the uneven distribution of natural gas tamping cloth in China. The equipment investment of hydrogen production from natural gas is relatively high, which is not suitable for small-scale hydrogen users (Ishimoto, Y., Voldsund, M., Nekså, P., Roussanaly, S., Berstad, D., & Gardarsdottir, S. 2020).

Natural gas steam reforming technology is relatively mature, the main process includes: natural gas pretreatment, CO water vapor shift, pressure swing adsorption purification. Endothermic reaction is the main reaction of the hydrogen production process, and the raw materials for hydrogen production are water and natural gas. Among them, natural gas is not only fuel but also reactant raw material. Among all kinds of natural gas hydrogen production technologies, the traditional methane steam reforming is the most economical method. However, the hydrogen production process needs to absorb a lot of heat, resulting in high energy consumption and emission of CO_2 (Bhandari, R., Trudewind, C. & Zapp, P. 2014) The main chemical reactions are as follows:

$$CH_4 + H_2O \rightarrow CO + 3H_2. \hspace{3cm} (2.6)$$

$$CO + H_2O \rightarrow CO_2 + H_2. \hspace{3cm} (2.7)$$

$$CH_4 + 2H_2O \rightarrow CH_2 + 4H_2. \hspace{3cm} (2.8)$$

The reaction condition of hydrogen production by this method is that the catalyst catalyzes the combination reaction of natural gas and water vapor at 79 - 810℃. Under this condition, the content of

H_2 can reach 69% of the gas structure. However, the utilization rate of raw materials in this process is relatively low: for example, in the conversion reaction of CO and water, the conversion rate of CO is only 40%, while in the conversion reaction of CH_4 and water vapor, the conversion rate is about 78% (Huang T. J. & Wang S. W. 1986).

The essence of hydrogen production from natural gas is to replace hydrogen in water with carbon in methane, and then successively absorb N_2, CO, CH_4 and CO_2 by pressure swing adsorption (PSA) after heat exchange, condensation and steam / water separation. At present, the technology of natural gas as raw material for hydrogen production is relatively mature, but the energy consumption and production cost are high, and the equipment investment is large. (Chehade et al. 2020.)

2.3.3   Hydrogen production from methanol

Chemical recycling of carbon dioxide to produce renewable fuels and materials, mainly methanol, provides a powerful choice to solve the two problems of global climate change and fossil fuel depletion (Goeppert, A., Czaun, M., Jones, J., Prakash, G.K. & Olah, G.2014). Compared with coal and natural gas, methanol is rich in raw materials and easier to store and transport, so it has been rapidly promoted in recent decades. Methanol itself is an excellent fuel for internal combustion engines, fuel cells and stoves, and dimethyl ether, the dehydrated product of methanol, is a substitute for diesel and LPG. In addition, methanol can be converted into ethylene, propylene and most of the petrochemical products currently obtained from fossil fuels. (Mahendra K. Awasthi, Rohit K. Rai, Silke Behrens & Sanjay K. Singh 2020.) With the continuous improvement of methanol hydrogen production process and catalyst, the scale of methanol hydrogen production is expanding, and the cost of hydrogen production is also decreasing, which has become the preferred scheme for small and medium-sized hydrogen production. Methanol is rich in raw materials for hydrogen production, which makes it easier to store and transport; the reaction temperature of hydrogen production is low, and the separation is simple. The disadvantage is that methanol is a secondary energy product with high raw material cost. The scale of hydrogen production is suitable for small-scale hydrogen production. (Awasthi, M.K., Rai, R., Behrens, S. & Singh, S. 2021.)

Compared with the traditional hydrogen production methods, methanol reforming has the following three advantages. The first point the sources of hydrogen production raw materials are wide and the price is low. As a common chemical raw material, methanol can be produced from fossil resources and

biomass (all organic matter formed by photosynthesis of green plants directly or indirectly). In addition, the utilization rate of hydrogen is high and the utilization rate of methanol is high. The molecular formula of methanol is CH_3OH, which has high hydrogen content, high energy density and high hydrogen yield. Finally, the hydrogen production unit is simple, and methanol is easy to store and transport, so it can be made into assembled or mobile methanol hydrogen production unit. In recent decades, hydrogen production from methanol has shown a wide application prospect. (Mahendra et al. 2020.)

2.3.4   Hydrogen production from gasoline reforming

As the raw material of hydrogen production for fuel cell, gasoline has attracted great attention at home and abroad. Although developed countries in the world have invested a lot of manpower and material resources to study the process of hydrogen production from Gasoline Oxidation and reforming, the research on the reaction kinetics of hydrogen production from Gasoline Oxidation and reforming has not been reported. Because gasoline is a mixture of alkanes, cycloalkanes, olefins and aromatics, it is of great significance to select the appropriate hydrocarbon to study the kinetics of gasoline (Chen, Y., Xu, H., Jin, X. & Xiong, G. 2006).

The existing perfect infrastructure can be used to produce hydrogen by reforming gasoline. Gasoline contains different types of hydrocarbons, including alkanes, cycloalkanes, olefins and aromatics. Gasoline also contains many sulfur compounds and a small quantity of additives, sometimes even oxidants and ethanol. When aromatic compounds are not considered, the hydrocarbon components of gasoline have similar reforming performance, and oxidation additives are helpful to improve the reforming reaction. In addition, the process of liquid hydrocarbon oxidation reforming is more complex than that of gaseous methane oxidation reforming. (Kassel L.S. 1971.) From the study of coal to syngas (Martin H. 1976), it can be predicted that the final product of oxidation reforming of hydrocarbons in gasoline does not contain other hydrocarbon components except methane. If the reaction time is long enough, the CO, CO_2, H_2 and H_2O in the reaction product will reach equilibrium according to CO shift reaction (Allen D. W., Gerhard E. R. & Likins M. R. 1972).

The results show that the reaction rate of all alkanes is faster than that of methane, and the reaction rate of different hydrocarbons is different. Therefore, it is of great significance to select suitable hydrocarbons instead of gasoline to study the kinetics of hydrogen production by oxidative reforming. At the present time, there are still many technical problems in gasoline reforming. (Kassel L.S. 1971.)

2.4 Comparison of hydrogen production methods

Presently, hydrogen is produced by steam reforming of natural gas and other hydrocarbons requiring high energy input (Kapdan, I., & Kargı, F. 2006). The petrochemical industry with large demand for H_2 generally adopts technologies such as light oil steam conversion, natural gas steam conversion or coal hydrogen production, while the fine chemical industry, pharmaceutical electronics industry with small demand for H_2 generally adopts methanol cracking or electrolytic water to produce H_2. (Lu et al. 2020.)

It can be seen from various hydrogen production methods that methanol autothermal oxygen production, gasoline reforming hydrogen production and biological hydrogen production are not available for industrialization at present. In terms of production scale, the natural gas steam conversion process is extremely suitable for large-scale production. In terms of production cost, although the technology of water electrolysis is relatively mature, it consumes a lot of energy. From the composition of cracking gas, the raw materials of methanol cracking process are easy to obtain, the process and operation are simple, but the technology maturity is not very perfect, and methanol decomposition for hydrogen production is not suitable for fuel cells. Therefore, the suitable hydrogen source for fuel cell will be selected in the hydrogen production from water gas, natural gas conversion and methanol steam reforming. (Nazarova, G., Ivashkina, E., Ivanchina, E., Oreshina, A. & Vymyatnin, E.K. 2021.)

For hydrogen production from coal and natural gas, it is necessary to comprehensively evaluate the cost of coal and natural gas and carbon emission cost. Under the current condition of low carbon tax, the cost of hydrogen production from coal will be lower than that from natural gas. Under the background of high carbon tax cost in the future, in areas with abundant natural gas reserves and low raw material price, hydrogen production from natural gas can have a good performance. The technology of hydrogen production from natural gas is perfect and suitable for mass production, but it has high risk and high requirements for operation level. (Uyar T S & Besikcy D 2017.) As methanol is a secondary energy, it is not recommended to use methanol to produce hydrogen under normal circumstances. However, methanol is a liquid chemical product, which is convenient for storage and transportation. Therefore, it can be flexibly applied to small-scale hydrogen production in areas with small hydrogen demand but high natural gas and coal prices. As the cost of hydrogen production from

industrial electricity is much higher than that from fossil energy, it is generally not recommended. However, the water electrolysis device is simple and less investment. (Nazarova et al. 2021.)

3 HYDROGEN PRODUCTION REACTION SYSTEM WITH METHANOL REFORMING

Methanol is a very important organic chemical raw material. At present, the output of methanol in the world has exceeded $2.5*10^7$ t/a. It is the third largest chemical product after the synthesis of ammonia and ethylene. Hydrogen can be produced by cracking methanol. There are three main ways to produce hydrogen from methanol: steam reforming of methanol, cracking of methanol and partial oxidation of methanol. In recent years, with the progress of science and technology, hydrogen production by methanol electrolysis and hydrogen production by ultrasonic decomposition of methanol aqueous solution as two new hydrogen production methods gradually come into people's view. (Gurau, V., Ogunleke, A. & Strickland, F.. 2020.)

With the development of fuel cell electric vehicles, it is urgent to study the methanol reforming system for hydrogen production. Methanol hydrogen production is characterized by low investment, high degree of automation and easy adjustment of production capacity, which is especially suitable for small and medium-sized hydrogenation users. Among them, methanol partial oxidation reforming method is less used in industry because the content of CO is more than 10% and the yield of H_2 is very low. (Huang T. J. & Chren S. L. 1988.) In contrast, the CO content of methanol steam reforming method is generally about 1%, and the yield of hydrogen is very high. The principle is that under a certain pressure and temperature, the catalyst, methanol and water are added into the reforming reactor for the following reaction:

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2. \tag{3.1}$$

Methanol steam reforming has the advantages of simple operation, high hydrogen production and low by-product content, which has a great development prospect. No matter in energy consumption or raw materials, or even in the scale and efficiency of hydrogen production, methanol has become the most advantageous methanol hydrogen production technology because of its high-density energy, wide source, easy storage, reliability and safety. (Huang T. J. & Chren S. L. 1988.)

3.1 Hydrogen production from methanol steam catalytic reforming

Methanol steam reforming is a kind of hydrogen production technology developed in the 1980s abroad. A lot of researches have been carried out in Canada, Britain, Australia and other countries. As early as the 1970s, Johnson Matthey used methanol steam reforming to produce hydrogen, but only limited to the production of hydrogen in laboratory reformer, and the removal of CO and CO_2 by metal Pd membrane as some special uses. The high price and limited supply of palladium boundary its application. Steam reforming has the highest hydrogen content in the methanol hydrogen production process. Therefore, the research of steam reforming is attractive. (Turco, M., Bagnasco, G., Costantino, U., Marmottini, F., Montanari, T., Ramis, G. & Busca, G. 2004.)

Steam reforming of methanol to produce hydrogen is the conversion of methanol and water under a certain temperature, pressure and catalyst to produce hydrogen, carbon dioxide and a small amount of carbon monoxide and methane mixture. Methanol steam reforming has the advantages of low reaction temperature and simple separation. The theoretical hydrogen yield per unit mass of methanol is 18.8% (mass fraction), which means that the hydrogen yield is higher than that of hydrogen produced by direct decomposition of methanol, and the content of carbon monoxide in the product is lower. Therefore, the methanol steam reforming technology is mainly used to produce hydrogen. (Jiajia, Z., Zhang, Y., Wu, G., Mao, D., & Lu, G. 2016.)

Methanol and desalted water (water with calcium and magnesium ions removed by ion exchange method) are used as raw materials from the outside. They are mixed in a certain proportion, heated and vaporized, and superheated to reach a certain temperature and pressure, and then enter the methanol high-level tank and desalted water storage tank. Desalted water, as absorption solvent, is sent to purification tower by desalted water pump. After absorbing unreacted methanol in conversion gas, it enters feed liquid storage tank again. (Turco et al. 2004.) Together with methanol from methanol high-level tank, it is pressurized to reaction pressure by feed liquid metering pump and then sent to heat exchanger for preheating. Then it enters gasification superheater to gasify feed methanol water solution and overheat it to the required temperature. Feed gas is in the process of conversion In the reactor, two reactions of gas phase catalytic cracking and conversion are completed under the action of catalyst to generate conversion gas containing CO_2, H_2 and CO. The reaction equation is as follows:

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 - Q. \hspace{3cm} (3.2)$$

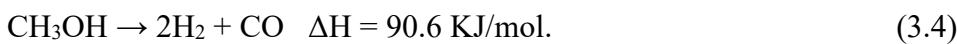$$CO_2 + H_2 \rightarrow CO + H_2O + Q. \hspace{3cm} (3.3)$$
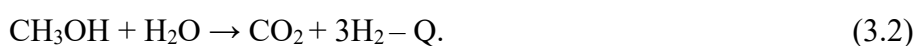
The conversion gas is cooled to about 40 °C by heat exchanger and condenser, and then enters the purification tower to recover unreacted methanol. The gas enters the PSA section to extract hydrogen, and the washing liquid returns to the feed liquid tank for reuse. (Turco et al. 2004.)

Steam reforming of methanol is a rapid developing method for hydrogen production in the recent ten years. It has the advantages of convenient operation, easy availability of raw materials, mild reaction conditions and less by-products. The content of by-products is reduced due to the addition of water. The use of the catalyst in this technology will not affect the effect of hydrogen production, and the hydrogen production performance is high and the cost is low, and the reaction device is very simple, and the H_2 content in the reforming gas can reach about 75%, so this technology is widely used in industry. (Zhou et al. 2016.)

3.2 Hydrogen production from methanol cracking

Hydrogen production from methanol cracking is the direct decomposition reaction of methanol to produce hydrogen. In this process, methanol and desalted water with convenient sources are used as raw materials. At 220 - 280 °C, they are catalytically converted into components on a special catalyst to become the main conversion gas containing hydrogen and carbon dioxide. The principle is as follows. (Zou, H., Pan, T., Shi, Y., Cheng, Y., Wang, L., Zhang, Y. & Li, X. 2020.)

$$CH_3OH \rightarrow 2H_2 + CO \quad \Delta H = 90.6 \text{ KJ/mol.} \tag{3.4}$$

$$CO + H_2O \rightarrow H_2 + CO_2 \quad \Delta H = 41.2 \text{ KJ/mol} \tag{3.5}$$

The H_2 and CO produced by this reaction are cleaner and more effective than methanol and gasoline. They can be directly used in internal combustion engines, and their combustion efficiency is higher than that of liquid methanol and gasoline. (Ruiz-López, E., Caravaca, A., Vernoux, P., Dorado, F. & Lucas-Consuegra, A.. 2020.) At the same time, due to its sufficient combustion, it can effectively reduce the emissions of CO and hydrocarbons. (Zou et al. 2020.)

In addition, it can be calculated from the above formula that the volume fraction of hydrogen product is close to 75%, which is more widely used due to its high hydrogen yield, reasonable energy utilization, simple process control and easy industrial operation. Among them, the reaction (3.4) is the

reverse reaction from syngas to methanol, and the catalysts for methanol synthesis can be used as decomposition catalysts, in which the copper-based catalyst system is the main one. These catalysts show good activity and selectivity for methanol decomposition, and have good elastic deformation when heated. At high temperature, the reaction rate is accelerated and it is easy to decompose into CO and hydrogen. A small amount of dimethyl ether can be observed at low temperature, but hydrocarbons, C_4 or above are hardly observed. (Zou et al. 2020.) Dimethyl ether is formed by dehydration of methanol by Lewis acid center on the surface of Al_2O_3, so the catalyst support Al_2O_3 should be modified to inhibit its formation. However, in some fuel cell electric vehicles, this method has obvious shortcomings: the content of CO in decomposition gas is too high, which is easy to poison the anode Pt electrode of fuel cell. In addition, In the process of the reaction, methanol cannot be fully utilized, and when the reaction pressure is reached, the material will enter the gasification superheater, which is easy to cause overheating in the gasification superheater, and the required temperature cannot be controlled. Under the action of catalyst, the feed gas will generate reforming gas containing CO_2 and CO after catalytic cracking and conversion reaction, thus affecting the hydrogen yield. Because methanol decomposition is an endothermic reaction, if the reaction is used for on-board hydrogen production, additional heating device is needed, and the hydrogen production system is complex, which affects the start-up speed of fuel cell electric vehicles. (Ruiz-López et al. 2020.)

3.3 Hydrogen production from partial oxidation catalytic reforming of methanol

Edwards and others used the "hotspot" patent reactor to study the partial oxidation reforming of methanol. The reaction has the advantages of fast reaction speed, exothermic reaction itself, and the temperature can reach about 450 ℃, which also overcomes the disadvantage of obtaining heat energy from the outside. However, because the reaction is a strong exothermic reaction, it is very likely that the local temperature is too high due to the exothermic speed, resulting in the sintering and carbon deposition of the catalyst and loss of activity. And because the exothermic speed is too fast to control, most of the heat is lost and cannot be fully utilized, so as to reduce the energy utilization rate. The principle is as follows. (Sengodan, S., Lan, R., Humphreys, J., Du, D., Xu, W., Wang, H. & Tao, S. 2018.)

$$CH_3OH + 1/2O_2 \rightarrow 2H_2 + CO_2 \quad \Delta H = -192 \text{ KJ/mol} \qquad (3.6)$$
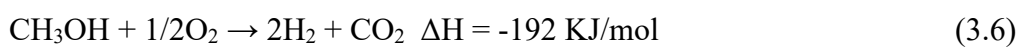
The commercial low temperature methanol synthesis catalyst Cu-Zn / Al_2O_3 shows good catalytic activity for partial oxidation of methanol. (Andache, M., Kharat, A.N. & Rezaei, M. 2020.) The conversion of methanol and the yield of hydrogen are affected by temperature, contact time and the ratio of O_2 / CH_3OH. When the amount of oxygen is less than the reaction quantity, the reaction will occur oxidation and decomposition at the same time. (Sengodan et al. 2018.)
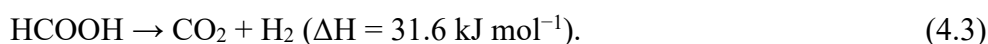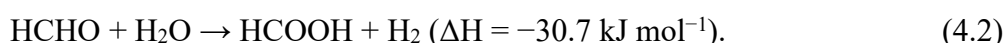
In 1986, Huang and his collaborators first carried out the study of adding oxygen to methanol steam reforming over Cu / Zn Catalyst. (Abdelghany, A.M., Sarhan A.M., Abdel-Latif E. & El-Dossoki, F.I. 2021.) It was found that the addition of oxygen could improve the conversion of methanol. Subsequently, the United States, Germany, Japan and other countries have begun to use partial oxidation of methanol to produce hydrogen instead of steam reforming of methanol to produce hydrogen. The partial oxidation of methanol has many advantages over the steam reforming of methanol. One is that the partial oxidation of methanol is an exothermic reaction using oxygen. When the temperature is close to 500K, the reaction takes place at a fast rate. The other is to use oxygen instead of water vapor as oxidant to make it have higher energy efficiency. The advantages of partial oxidation of methanol to hydrogen are exothermic reaction, fast reaction speed, mild reaction conditions and easy operation and start-up. The disadvantages are that the hydrogen content in the reaction gas is lower than that in steam reforming reaction. Due to the introduction of air oxidation and nitrogen in the air, the hydrogen content in the mixture may be lower than 50%, which is not conducive to the normal operation of fuel cells. The efficiency of the fuel cell is reduced. If the waste heat is not recovered, the thermodynamic efficiency of partial oxidation reforming is low, resulting in a waste of energy. The hydrogen content of fuel cell is 50% - 100%. This method is in the process of research, and there is still a certain distance from industrialization. (Sengodan et al. 2018.)

4 CATALYST OF HYDROGEN PRODUCTION BY METHANOL STEAM REFORMING

So far, there are two kinds of catalysts used in methanol steam reforming in the world, the first is precious metal catalyst, Pd / ZnO is the most commonly used catalyst; the second is non precious metal catalyst, including copper-based catalyst represented by CuO / ZnO / Al_2O_3 catalyst (Andache et al. 2020) and non-copper-based catalyst represented by Zn-Cr catalyst. (Liao et al. 2021.)

Traditionally, hydrogen is produced by methanol steam reforming process in the high temperature range (200 – 350 °C), while Catalyst Assisted hydrogen production from methanol water is more energy-saving due to its operation at low temperature (< 190 °C). In principle, hydrogen production from methanol has mild endothermic property; therefore, appropriate catalyst can activate methanol to produce hydrogen. The experimental evidence shows that in the presence of catalyst, methanol dehydrogenation may follow three continuous paths: first, methanol dehydrogenation to formaldehyde and hydrogen (eqn (4.1)), then formaldehyde dehydrogenation to hydrogen and formic acid (eqn (4.2)) in the presence of water, and finally formic acid dehydrogenation to hydrogen and carbon dioxide (eqn (4.3)). (Awasthi et al. 2021.)

$$CH_3OH \rightarrow HCHO + H_2 \ (\Delta H = 129.8 \text{ kJ mol}^{-1}). \hspace{2cm} (4.1)$$

$$HCHO + H_2O \rightarrow HCOOH + H_2 \ (\Delta H = -30.7 \text{ kJ mol}^{-1}). \hspace{2cm} (4.2)$$

$$HCOOH \rightarrow CO_2 + H_2 \ (\Delta H = 31.6 \text{ kJ mol}^{-1}). \hspace{2cm} (4.3)$$

Using methanol as a potential liquid hydrogen storage material, various catalysts have been explored to produce hydrogen at low temperature while controlling the emission of unnecessary CO and methane. (Awasthi et al. 2021.) At present, the improvement of methanol steam reforming catalyst cannot only reduce the cost of the catalyst, but also improve the effect of carbon monoxide conversion. Heterogeneous catalytic reforming of methanol to produce hydrogen and carbon dioxide has been continuously studied. Different metal based catalysts, such as CuO / ZnO / Al_2O_3, Pd / CeO_2-ZrO_2, Pt_3Ni and Ni–Fe–Mg alloys are used, but most of these catalysts require temperatures and pressures higher than 200 °C (Wan, C., Song, K., Pan, J., Huang, M., Luo, R., Li, D. & Jiang, L. 2020). On the

other hand, commercially viable heterogeneous catalysts for low-temperature hydrogen production are rarely explored. (Pérez-Hernández, R. 2021.) Until recently, Pt / MoC catalysts for methanol hydrogen production were explored, but they are only effective at higher temperatures (150 – 190 °C) and use expensive Pt catalysts. (Jiang, L., Chu, G., Liu, Y., Liu, W., Wen, L. & Luo, Y. 2020.)

At present, the main catalysts for hydrogen production from methanol steam reforming are copper-based granular catalytic materials, among which CuO / ZnO / Al_2O_3 and CuO / CeO_2 granular catalytic materials are the most representative. There are some defects in granular catalytic materials, such as large pressure drop, poor heat transfer and uneven temperature distribution. Especially for the strongly endothermic methanol steam reforming reaction, the granular catalyst has low heat transfer efficiency, resulting in uneven temperature distribution and low mass transfer efficiency, which makes the catalyst less active at high altitude velocity (Wang, Y., Ziyue, H. & Mei, D. 2020).

Compared with the traditional granular catalyst, the overall catalyst has smaller pressure drop and relatively uniform temperature distribution, so it has better application prospects. Liu Na and others prepared cordierite monolithic catalyst for methanol autothermal reforming to hydrogen with cordierite as monolithic catalyst carrier (Jiang et al. 2020), Ce-Zr solid solution oxide as coating and ZnO-Cr_2O_3 as active component, and explored the influence of Zr doping on the catalyst (Mohamed, R., Ismail, A. & Alhaddad, M. 2021). The results showed that the stable operation time of cordierite catalyst coated with Ce-Zr solid solution was increased from 67 h to 120 h, compared with single CeO_2 coating The results show that Ce-Zr solid solution not only has the advantages of CeO_2, but also gives the catalyst better thermal stability, which may be one of the good coatings for methanol steam reforming catalyst. (Pérez-Hernández, R. 2021.)

4.1 Noble metal catalysts

Some of these formulations were more active than a commercial Cu / Zn / Al_2O_3 catalyst, however, the CO_2 selectivities were typically lower. At similar conversions, materials that were highly active were not selective while the less active materials were very selective. Many of the highly active catalysts included noble metals while the highly selective catalysts included base metals. (Setthapun, W., Bej, S.K. & Thompson, L. 2007.)

Pd / ZnO catalyst has good catalytic activity and selectivity. The catalyst has not only the oxide replaceable, but also the stability in the actual operation. But in the methanol oxidation reforming experiment, the activity of Pd-Zn alloy catalyst is easily affected by the size of ZnO carrier and the microcrystalline size of Pd-Zn alloy. (Das, D., Llorca, J., Domínguez, M., Colussi, S., Trovarelli, A. & Gayen, A. 2015.) The reason why Pd-Zn alloy catalyst has high selectivity is because of the interaction between Pd-Zn and ZnO alloy, and the Pd element can promote the production of CO. (Pérez-Hernández, R. 2021.) The selectivity and activity of the catalyst are very important for the oxidation and reforming reaction. Therefore, Pd-Zn alloy needs to be in a high dispersion state to show a good crystal form. (Jiang et al. 2020.)
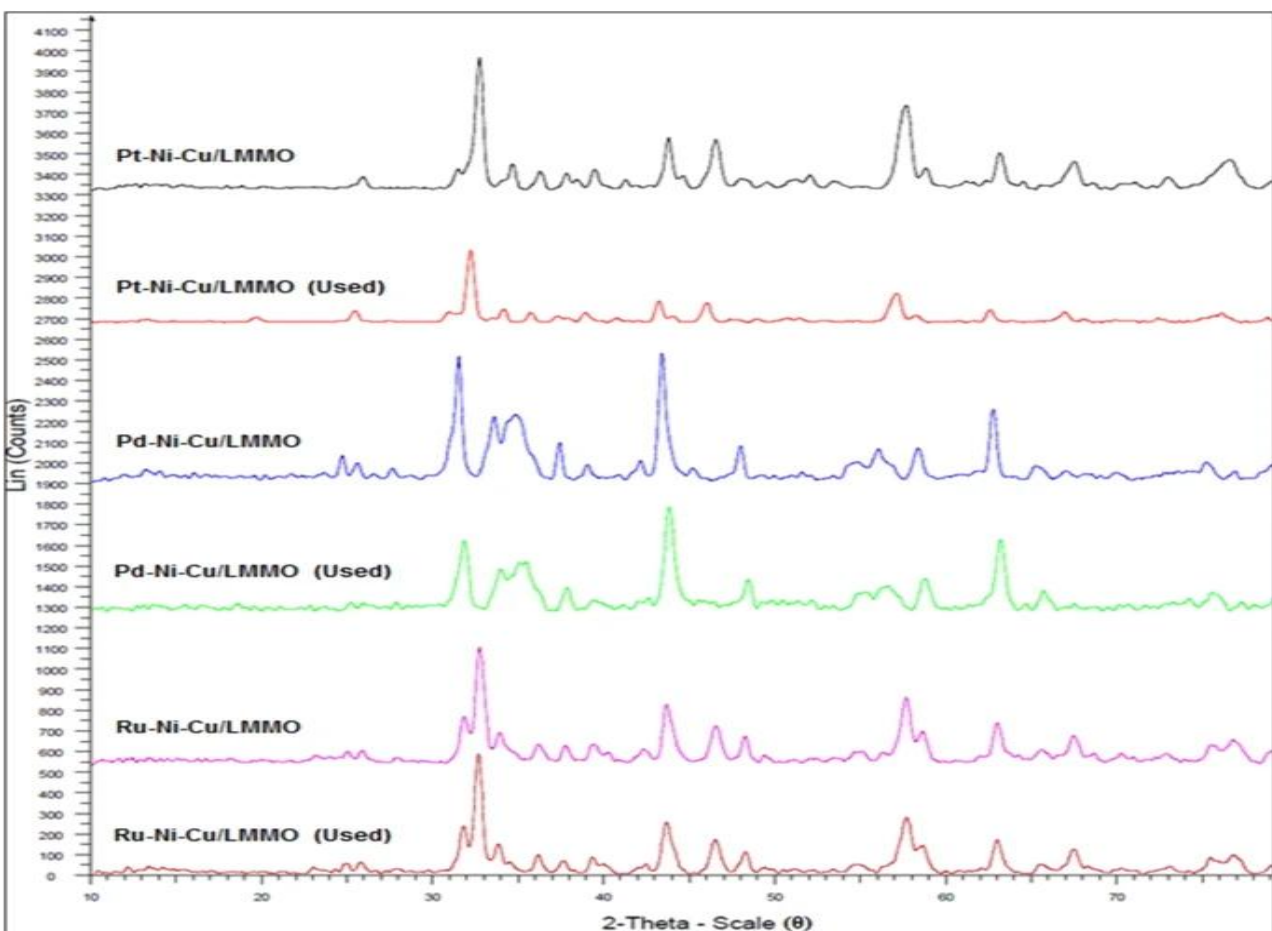

FIGURE 1. XRD patterns of the noble metal promoted catalysts (fresh and used) (Adapted from Shejale, A.D. & Yadav, G. 2019)

4.2 Non-noble metal catalysts

Copper-based catalysts, especially Cu / ZnO / Al$_2$O$_3$, are commonly used in methanol steam reforming (MSR). (Setthapun at al. 2007.) The Cu / ZnO / Al$_2$O$_3$ catalysts have good low temperature activity

and high hydrogen selectivity for methanol steam reforming. At 250 °C, the highest methanol conversion is 99.4%, and the hydrogen selectivity is 99.9%. The selectivity of Cu / ZnO / Al_2O_3 Catalysts for CO is very low, which makes the mole fraction of CO in the reforming gas less than 0.01%. Compared with the working requirements of fuel cells, they are easy to purify. XRD analysis showed that the diffraction peaks of copper in Cu / ZnO / Al_2O_3 catalyst were obviously broadened and enveloped, and highly dispersed fine copper particles were formed on the surface of the catalyst, which improved the activity and stability of the catalyst. In addition, the composition of catalyst, reaction temperature and activation conditions have great influence on the activity of catalyst (Matus, E., Ismagilov, I., Yashnik, S., Ushakov, V.A., Prosvirin, I., Kerzhentsev, M., & Ismagilov, Z. 2020).

However, these materials have some limitations. For example, copper-based catalysts have limited tolerance to changes in pretreatment conditions and are unstable at high temperatures. These materials are also inactivated when exposed to condensate. Although the addition of Zn, Zr, Cr and Ce promoters can significantly improve the activity of copper-based catalysts, little progress has been made in making these materials more durable. (Setthapun et al. 2007.) However, most of these catalysts have lower CO_2 selectivity than copper-based catalysts. One exception seems to be ZnO supported Pd. These materials are reported to be active and highly selective for carbon dioxide production during MSR. In commercial MSR Cu / ZnO / Al_2O_3 catalyst, the content of ZnO and Cu is relatively high, while the content of Al_2O_3 is relatively low, which leads to the improvement of Cu dispersion and reduction performance by ZnO, thus enhancing the interaction between active component and support. Moreover, the electronic structure of ZnO can be modified by Al_2O_3, which can promote the formation of lattice defects and improve the reduction ability of ZnO. Generally speaking, the addition of Al_2O_3 will increase the specific surface area of the support, so the addition of Al_2O_3 in the coprecipitation catalyst can help to inhibit the sintering and carbon deposition of Cu. (Kim, D., Kim, J. & Jang, Y.. 2019.) However, excessive alumina also promoted the production of HCHO and other by-products. With the increase of alumina content, the MSR activity decreased, which inhibited the reduction of CuO. This is due to the strong interaction between alumina and CuO. (Setthapun et al. 2007.)

The strong reducing atmosphere will lead to the change of catalyst structure, resulting in sintering. Therefore, looking for a substitute for ZnO has aroused considerable interest in recent years. It has been suggested that adding ZrO_2 to Copper-based supported alumina catalyst can improve MSR activity. The addition of ZrO_2 also improves the reducibility and dispersion of Cu, indicating that the effect of ZrO_2 is similar to that of ZnO. CeO_2 improves the thermal stability of copper-based catalyst

and affects the conversion of CO through WGS reaction. In addition, CeO_2 is well-known for its high oxygen storage capacity, which affects the valence state of partially supported CeO_2 metal in the reduction reaction, and produces oxygen vacancies, thus improving the activity. (Liao et al. 2021.)

The deactivation of CuO / ZnO / Al_2O_3 catalyst often occurs in methanol steam reforming. In order to enhance the stability and activity of Copper-based catalysts and resist the growth of Cu sintering, many scientists began to study the preparation of CuO / ZnO / Al_2O_3 catalysts (Matus et al. 2020). The main method is to add promoters such as Zr, Cr and Ce to copper-based catalysts to enhance their catalytic performance. However, the reports on the activity of Cu-Ce-Zr system for MSR are very limited. Ce-Zr oxides with different molar ratios have also been proved to be effective carriers for partial CH_4 oxidation and ethanol reforming. (Liao et al. 2021.)

Adding Zr into the catalyst can stabilize the interaction between Cu^+ and ZnO. In addition, some scientists have been using Zr to process Copper-based catalysts based on CuO / ZnO / Al_2O_3 catalysts. (Abdelghany et al. 2021.) The results show that Cu / Zn / Zr has stronger catalytic activity than Cu / Zn / Al oxides. However, the addition of Zr has little effect on the performance of copper-based catalysts. When the content of Zr reaches 18 wt%, it only has a weak effect on the conversion of methanol and H_2 rate. Compared with Cu / Zn / Al oxide, the TOF value of Cu / Zn / Zr oxide catalyst is higher, which indicates that ZrO_2 is more suitable as carrier than Al_2O_3. (Kim et al. 2019.)

5 EXPERIMENT

As a liquid fuel, methanol has become an ideal fuel for vehicle hydrogen production due to its advantages of high energy density, low carbon content, transportation and storage. The hydrogen production rate and the content of hydrogen and CO in the reaction system of methanol steam reforming should be improved. In particular, the requirement of CO content is more stringent, because CO is easy to cause anode catalyst poisoning. Therefore, the development of catalysts with low temperature, high activity, high hydrogen selectivity and stability has become an important part of methanol steam reforming system. The deactivation of CuO / ZnO / Al_2O_3 catalyst often occurs in methanol steam reforming. (Abdelghany et al. 2021.) The activity of MSR can be improved by adding ZrO_2 to copper-based supported Al_2O_3 catalyst. The addition of ZrO_2 also improves the reducibility and dispersion of Cu, and CeO_2 improves the thermal stability of copper-based catalyst, and affects the conversion of CO through WGS reaction.

Compared with the traditional Cu supported catalysts, the catalysts containing CeO_2 and ZrO_2 have higher H_2 selectivity and lower CO selectivity. CeO_2 can improve the thermal stability and reduction performance of copper-based catalyst, solve the problem of poor stability of copper-based catalyst and improve the performance of copper-based catalyst. In this thesis, the preparation and performance evaluation of the catalyst are mainly carried out through experiments. Ce-Zr solid solution was prepared by sol-gel method, and their activity for methanol steam reforming was investigated. CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalysts with different Cu contents were prepared by impregnation method. (Liao et al. 2021.) The catalysts were characterized by H_2-TPR, BET and XRD. The effects of Cu content on the structure and properties of CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalysts were discussed. It is expected that CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalysts with high activity and high stability will be prepared.

5.1 Safety Measures

Glasses and gloves should be used in the laboratory. The following are the hazards and precautions of chemical reagents. As cerium nitrate is explosive and irritant, it can lead to liver poisoning in high concentration. When the medication meets the combustible fire, it can indorse fire. Explosive mixture

can be formed by mixing with reducing agent, organic matter and inflammable materials (such as sulfur, phosphorus or metal powder). In case of high temperature, it decomposes and releases highly toxic nitrogen oxide gas. During operation, it should be closed to keep local exhaust air, away from fire, heat source, inflammables and combustibles.

Zirconium nitrate can stimulate eyes, skin and mucous membrane. The product is combustion supporting and irritant. In case of skin contact, take off contaminated clothes immediately and rinse skin thoroughly with soapy water and water. In case of eye contact, immediately lift the eyelids, rinse with flowing water or normal saline and seek medical attention. If inhaled carelessly, it should be removed quickly and transferred to fresh air to keep the respiratory tract unobstructed. If you eat it carelessly, drink plenty of warm water immediately, induce vomiting and seek medical attention.

Copper nitrate is irritating to eyes and skin, long-term contact will lead to dermatitis and blood damage, liver damage, nasal mucosa ulcer, nasal septum perforation. In addition, the drug is corrosive and highly irritating, which can cause burns to human body. The operation should be carried out in a closed environment with local ventilation. Storage should be placed in a cool, ventilated warehouse, away from fire, heat sources, packaging and sealing.

Ammonia is very harmful to health. After inhalation, it is irritating to nose, throat and lung, and causes cough and shortness of breath, which may cause laryngeal edema and suffocation; it may also cause pulmonary edema and death. Dangerous characteristics of ammonia water: it is easy to decompose and release ammonia gas, and the higher the temperature is, the faster the decomposition speed is, and it is very easy to cause explosion. If the temperature is too high, the pressure in the container will increase, causing the risk of cracking or explosion.

The following are the precautions for the use of the instrument. Horse boiling furnace is in the first use or after a long period of use must be dried. It should be used in the ambient temperature range of 0 - 40 °C. In order to prevent the jacket from cracking, do not pull out the thermocouple at high temperature. The furnace should be clean and oxide should be removed in time.

5.2 Equipment and reagent

Here are the pharmaceutical reagents needed for the experiment. 5% $NH_3 \cdot H_2O$ solution, 5% HNO_3 solution, $Ce(NO_3)_3 \cdot 3H_2O$, $Zr(NO_3)_4 \cdot 5H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, Deionized water and methanol were used as the reagents required for the experiment.

Here are the experimental equipments needed for the experiment. Electronic analytical balance, muffle furnace, electric blast drying oven, electric stirrer, micro pump, temperature control meter, powder tablet press and gas chromatograph were used as the experimental equipment required for the experiment.

5.3 Catalyst preparation

A mixture of 1.6 mol/L Ce $(NO_3)_3 \cdot 6H_2O$ and 0.4 mol/L Zr $(NO_3)_4 \cdot 5H2O$ was prepared. The mixture of 180 r/min was mixed with 5% $NH_3 \cdot H_2O$ solution at constant temperature water bath at 30 degrees. Until the gel was formed, a 5% HNO_3 solution was added to the gel with the same agitation speed to degum until the gel changed to soliquid. The obtained soliquid was continuously stirred in 30 °C constant temperature water bath for 8 h, and then dried in 120 °C oven for 12 h. The obtained light-yellow solid was roasted in 500 °C muffle furnace for 3 h, and $Ce_{0.8}Zr_{0.2}O_2$ solid powder was obtained after tablet pressing, grinding and 100-200 mesh screening.

CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalyst was prepared by equal volume impregnation. 10 ml of Cu $(NO_3)_2 \cdot 3H_2O$ solution was prepared according to 2%, 5%, 10% and 20% of the total mass of the support. $Ce_{0.8}Zr_{0.2}O_2$ powder was slowly and evenly poured into Cu $(NO_3)_2 \cdot 3H_2O$ solution at 30 °C, stirred for 3 h, left for 2 h, dried in 120 °C oven for 12 h to obtain blue-green solid powder. After calcination for 3 h in 400 °C muffle furnace, the powder was pressed, ground and dried Four kinds of CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalysts, named xCuO / $Ce_{0.8}Zr_{0.2}O_2$ (x = 2%, 5%, 10%, 20%).

5.4 Characterization of catalyst

The element content was determined by Bruker S8 TIGER X-ray fluorescence spectrometer. The phase composition of the sample was determined by Bruker D8 advance X-ray powder diffractometer made in Germany. The test conditions are as follows: Cu K α 1 target, incident wavelength λ = 0.154 nm, tube voltage 40 kV, tube current 40 mA, 20 ° - 80 ° scanning.

The BET method and BJH method were used to calculate the specific surface area and pore volume, respectively, and then the quantachrome NOVA 2200E physical adsorption instrument was used for detection. The reduction temperature of CuO was determined by the quantachromechemstar dynamic chemisorption apparatus of the United States.

The XRD analysis was performed on a Bruker Xray diffractometer with Cu Kα radiation, λ = 0.154 nm, and 2θ of 3° to 70°, 2°/min. The average particle size of CuO was calculated by the Scherrer equation. The specific surface areas of samples were studied on a Quanta chrome instrument and N_2 adsorption-desorption at -196 ℃. The specific surface area and pore volume were calculated by BET and BJH methods respectively.

The H_2-TPR experiment was tested by the FANTAI instrument. The temperature was programmed from room temperature to 200 ℃ for pretreatment for 1 h. When the temperature was reduced to room temperature, hydrogen and argon mixture (10%H_2-Ar) was added for reduction treatment. The temperature was programmed to 700 ℃ for reduction treatment, and the hydrogen consumption was detected by TCD detector.

The N_2O oxidation experiment was tested by the FANTAI instrument. The sample was pretreated from room temperature to 200 ℃ for 1 hour, and then naturally cooled to room temperature. After pretreatment, the sample needs to be reduced, then oxi-dized, and then reduced. The reduction conditions were heating from room temperature to 400 ℃ for 90 minutes in a 10% H_2-Ar atmosphere, and the oxidation conditions were heating from room temperature to 90 ℃ for 1 hour in a 10% N_2O-Ar atmosphere. Assuming that N_2O only reacts with Cu on the surface to convert to Cu^+.

5.5 Performance evaluation of catalyst

In the laboratory, the performance of the catalyst was evaluated by a self-made fixed bed device. The reactor was made of quartz tube with an inner diameter of 8.5 mm and a catalyst volume of 1 ml. The reaction temperature is controlled by K-type thermocouple, and the content of reforming gas is determined by SP1000.

The specific operation steps are as follows. Take 1 ml of 40-80 mesh catalyst into the quartz tube fixed bed reactor, and check the air tightness of the whole device. 5% H_2-N_2 mixed gas was introduced to adjust the temperature control meter, and the temperature in the reactor was raised to 280 °C at the rate of 2 °C / min for 2 h. Turn off the H_2 gas source, adjust the temperature below the required reaction temperature, and then turn off the N_2 gas source. At this time, use the micro pump to inject the prepared methanol water solution and control the space velocity of methanol gas. The control panel is used to adjust to the required reaction temperature for reaction. The generated gas passes through the condenser and dryer, and then enters the gas chromatography for quantitative analysis. The flow rate of reforming tail gas is obtained by the flowmeter. Adjust the reaction temperature required for the reaction through the control panel again, the content and composition of the generated gas at different reaction temperatures can be measured. Here is the flow chart of experimental unit for hydrogen production from methanol steam reforming.
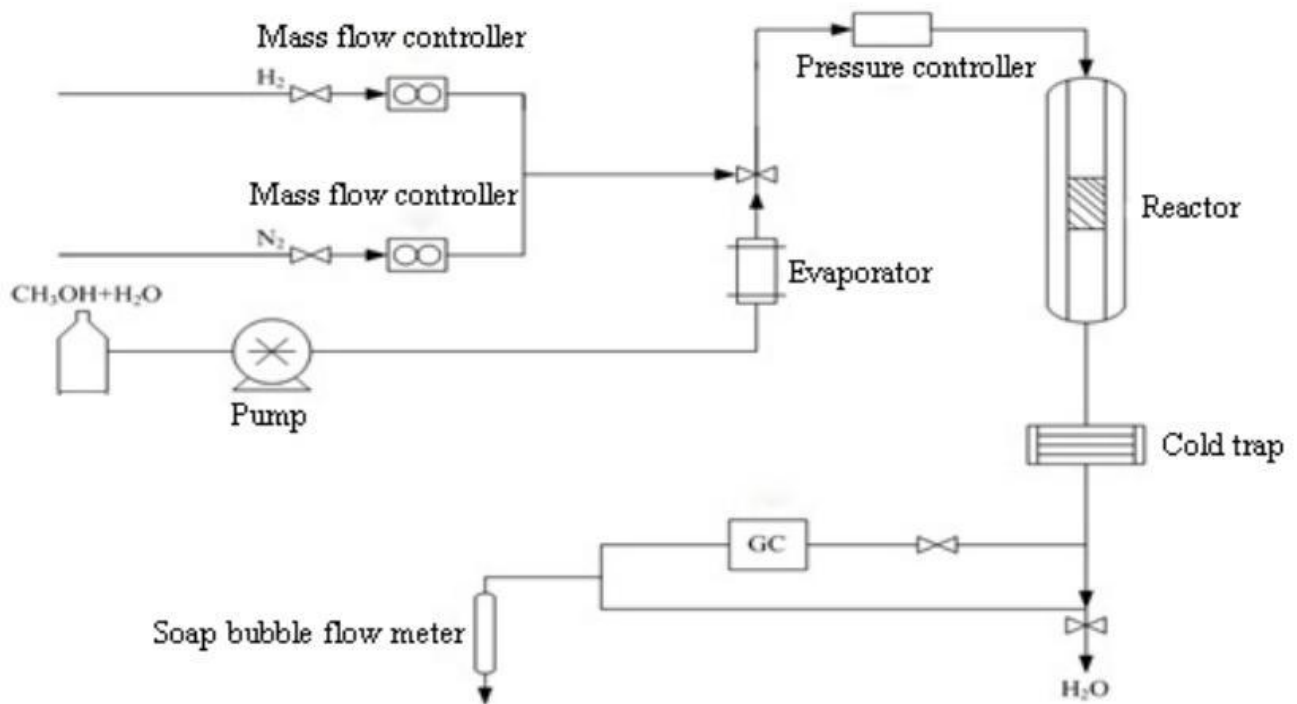
FIGURE 2. Experimental process of methanol steam reforming for hydrogen production

The catalytic performance of the catalyst can be evaluated by methanol conversion, hydrogen production rate and co selectivity. The specific formula is as follows:

Methanol conversion rate: $X(\%) = \dfrac{F_R*(C_{CO}+C_{CO2})*(32+18w)}{(F*\rho*22.4*1000)} * 100\%$

Hydrogen production rate: $Y_{H2}(mL * Kg_{cat}^{-1} * S^{-1}) = \dfrac{F_R*C_{H2}}{60*m_{cat}}$

F_R is the flow rate of reforming tail gas under standard conditions (ml / min). F is the feed rate set by the pump (ml / min). ρ_{Mix} is the mixed density of methanol aqueous solution (g / ml). W is the molar ratio of methanol to water, M_{CAT} is the mass of catalyst (kg). C_{CO}, C_{CO2} and C_{H2} are the volume molar concentrations of CO, CO_2 and H_2 in the reforming tail gas respectively.

6 RESULTS AND DISCUSSIONS

Sol-gel method was used to prepare cerium zirconium sol with Ce $(NO_3)_3$ $6H_2O$ and $2Zr$ $(NO_3)_4$ $5H_2O$ as the raw material for the overall catalyst. Then, two active CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalysts were prepared by impregnating the active component CuO and calcined, and characterized by XRD, SEM, BET and so on. The results show that the CuO / $Ce_{0.8}Zr_{0.2}O_2$ monolithic catalyst with Ce $(NO_3)_3$ $6H_2O$ as cerium source has good catalytic activity and thermal stability. The reason is that the $Ce_{0.8}Zr_{0.2}O_2$ solid solution coating prepared with Ce $(NO_3)_3$ $6H_2O$ as cerium source has uniform distribution on the surface, which increases the loading area of active components, and CuO forms a substance with specific morphology and uniform distribution on the surface of $Ce_{0.8}Zr_{0.2}O_2$ solid solution coating.

The effect of cerium zirconium precursor concentration on the overall catalyst performance was investigated. The catalyst was characterized by XRD, SEM and BET. The results show that when the concentration of Ce $(NO_3)_3$ $6H_2O$ and Zr $(NO_3)_4$ $5H_2O$ are both 1.6 mol / L and the molar ratio is 4 / 1, the overall catalyst CuO / $Ce_{0.8}Zr_{0.2}O_2$ has better catalytic performance. When the reaction temperature is 360 ℃, the molar ratio of water to alcohol is 1.2:1, the space velocity of methanol is 2200 h^{-1}, the conversion of methanol is 91.2%, the content of CO in reforming gas is 5.3%, and the hydrogen production rate of 5% CuO / $Ce_{0.8}Zr_{0.2}O_2$ is 1405 cm^3 kg^{-1} S^{-1} at 360 ℃ (3) the effect of cerium zirconium coating amount on the performance of the overall catalyst for hydrogen production from methanol steam reforming was investigated. The results show that $Ce_{0.8}Zr_{0.2}O_2$ solid solution coating has obvious effect on the catalytic performance. When $Ce_{0.8}Zr_{0.2}O_2$ solid solution coating is thinner, the supported CuO is less and the catalytic activity is poor. When $Ce_{0.8}Zr_{0.2}O_2$ solid solution coating is too thick, obvious pore plugging phenomenon appears, and CuO agglomeration is serious, which affects the catalytic performance.
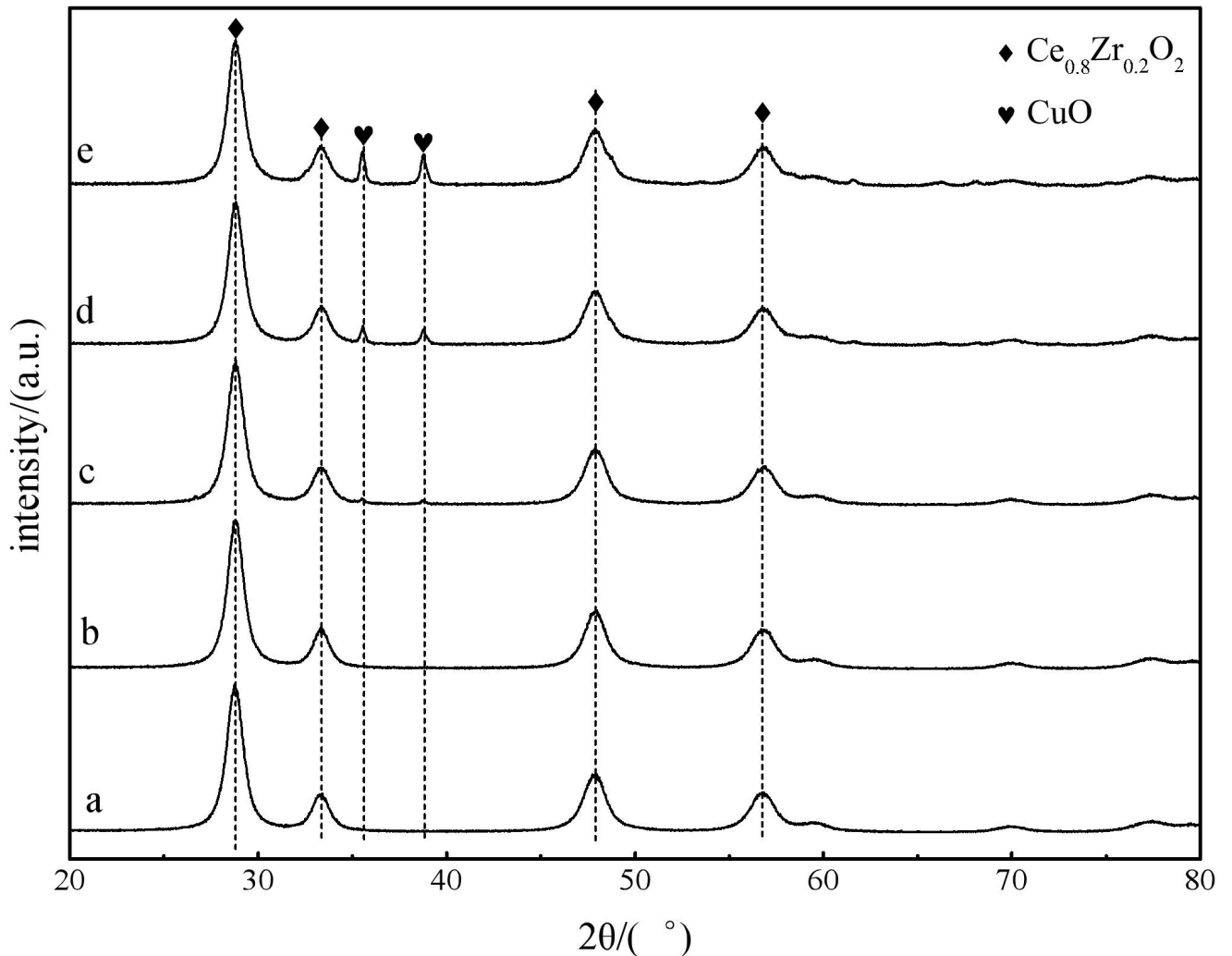
6.1 XRD analysis

FIGURE 3. XRD patterns of $Ce_{0.8}Zr_{0.2}O_2$ catalysts with different Cu contents (a: $Ce_{0.8}Zr_{0.2}O_2$; b: 2%CuO / $Ce_{0.8}Zr_{0.2}O_2$; c: 5%CuO / $Ce_{0.8}Zr_{0.2}O_2$; d: 10%CuO / $Ce_{0.8}Zr_{0.2}O_2$; e:20%CuO / $Ce_{0.8}Zr_{0.2}O_2$)

The XRD patterns show that there is no diffraction peak of ZrO_2, which indicates that cerium zirconium solid solution is well formed. As shown in the figure, the diffraction peaks of CeO_2 shift to 28.5 °, 33.1 °, 47.5 ° and 56.3 ° because the lattice of CeO_2 enters Zr^{4+}, which induces defects in the lattice of CeO_2 and forms CuO / $Ce_{0.8}Zr_{0.2}O_2$ solid solution. Therefore, the characteristic diffraction peaks of CeO_2 shift slightly to high angle. In addition, as for the characteristic diffraction peak of CuO, with the increase of Cu content, the characteristic diffraction peak is stronger and stronger. However, the diffraction peak of CuO does not appear in CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalyst with 2% Cu content, which is due to the low Cu content and high dispersion on the surface of CuO / $Ce_{0.8}Zr_{0.2}O_2$ solid solution.

6.2 Surface properties of catalysts

It can be seen from the following table that the specific surface area of $Ce_{0.8}Zr_{0.2}O_2$ can reach 98.31 m^2 / g without CuO loading, and the specific surface area decreases with the increase of CuO loading. This is caused by CuO entering the pores of Ce-Zr solid solution. In addition, it can be seen from the following table that 5% CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalyst has the largest specific surface area of 5.8 m$^2 \cdot$ g^{-1}, followed by 10% CuO / $Ce_{0.8}Zr_{0.2}O_2$ and 20% CuO / $Ce_{0.8}Zr_{0.2}O_2$, which are 5.6 m$^2 \cdot$ g^{-1} and 5.1 m$^2 \cdot$ g^{-1}, respectively, and the last 2% CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalyst has the smallest specific surface area of 4.8 m$^2 \cdot$ g^{-1}. The reason is that when the Cu loading is low (2% CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalyst), the content of CuO on the surface of the catalyst is less, which is not enough to provide a larger specific surface area of Cu; when the Cu loading is increased to a certain extent (10% CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalyst), Cu will begin to aggregate and grow, which makes the specific surface area of Cu decrease. In addition, it can be seen that the specific surface area of Cu corresponds to the hydrogen production rate. The 5% CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalyst has the largest specific surface area of Cu and the corresponding hydrogen production rate is 1312 cm$^3 \cdot$ kg$^{-1} \cdot$ s^{-1}, which indicates that the specific surface area of Cu is one of the important factors affecting the activity of the catalyst.

TABLE 1. Physical and chemical properties of catalyst and hydrogen production rate of catalyst

catalyzer	A_1/(m$^2 \cdot$g^{-1})	v_1/(cm$^3 \cdot$g^{-1})	A_2/(m$^2 \cdot$g^{-1})	v_2/(cm$^3 \cdot$kg$^{-1} \cdot$s^{-1})
$Ce_{0.8}Zr_{0.2}O_2$	98.3	0.32	--	--
2%CuO/$Ce_{0.8}Zr_{0.2}O_2$	98.3	0.31	4.8	1071
5%CuO/$Ce_{0.8}Zr_{0.2}O_2$	94.6	0.30	5.8	1312
10%CuO/$Ce_{0.8}Zr_{0.2}O_2$	69.5	0.26	5.6	1174
20%CuO/$Ce_{0.8}Zr_{0.2}O_2$	63.2	0.21	5.1	1147

Note: [a]: determined by N_2O experiments; [b]: reaction conditions: temperature 36 °C; water alcohol molar ratio 1.2:1; methanol gas airspeed 2200 h^{-1}.

6.3 H$_2$-TPR analysis
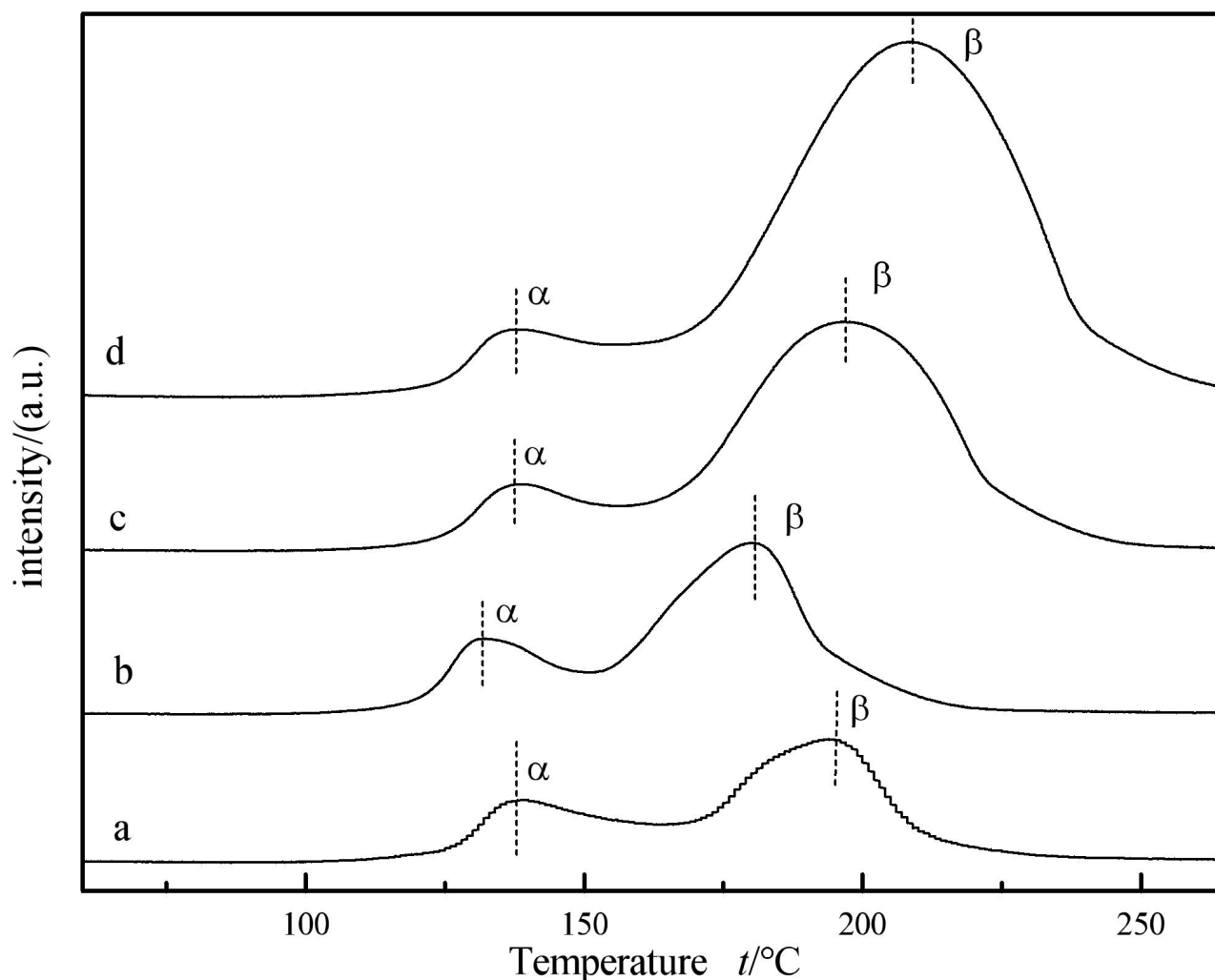
FIGURE 4. H$_2$-TPR spectra of Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalysts with different Cu contents

Note: A: 2% CuO / Ce$_{0.8}$Zr$_{0.2}$O$_2$; B: 5% CuO / Ce$_{0.8}$Zr$_{0.2}$O$_2$; C: 10% CuO / Ce$_{0.8}$Zr$_{0.2}$O$_2$; D: 20% CuO / Ce$_{0.8}$Zr$_{0.2}$O$_2$.

As shown in the figure, the four Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalysts with different Cu contents all have two reduction peaks. The β peak at high temperature is the reduction peak of bulk Cu, and the α peak at low temperature is the reduction peak of surface Cu. The reduction peak temperature of 5% CuO / Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalytic material is lower, which is because the interaction between CuO and Ce$_{0.8}$Zr$_{0.2}$O$_2$ solid solution is stronger, and CuO is easier to be reduced. Therefore, in the figure above, the catalytic activity of 5% CuO / Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalytic material is better. However, for 2% CuO / Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalyst, due to the less Cu content, the total amount of surface copper is less, and the interaction between CuO and Ce$_{0.8}$Zr$_{0.2}$O$_2$ solid solution is weak, so the catalytic performance is not as good as that of 5% CuO / Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalyst. Therefore, the lower the reduction temperature, the stronger the

interaction between the active component and $Ce_{0.8}Zr_{0.2}O_2$ solid solution, and the better the catalytic activity.

6.4 Catalyst performance test

Next, the performance of the catalyst will be tested from three aspects: the relationship between the performance of the catalyst and the reaction temperature, the molar CO content in the reforming tail gas at different reaction temperatures and the hydrogen production rate diagram at different reaction temperatures.

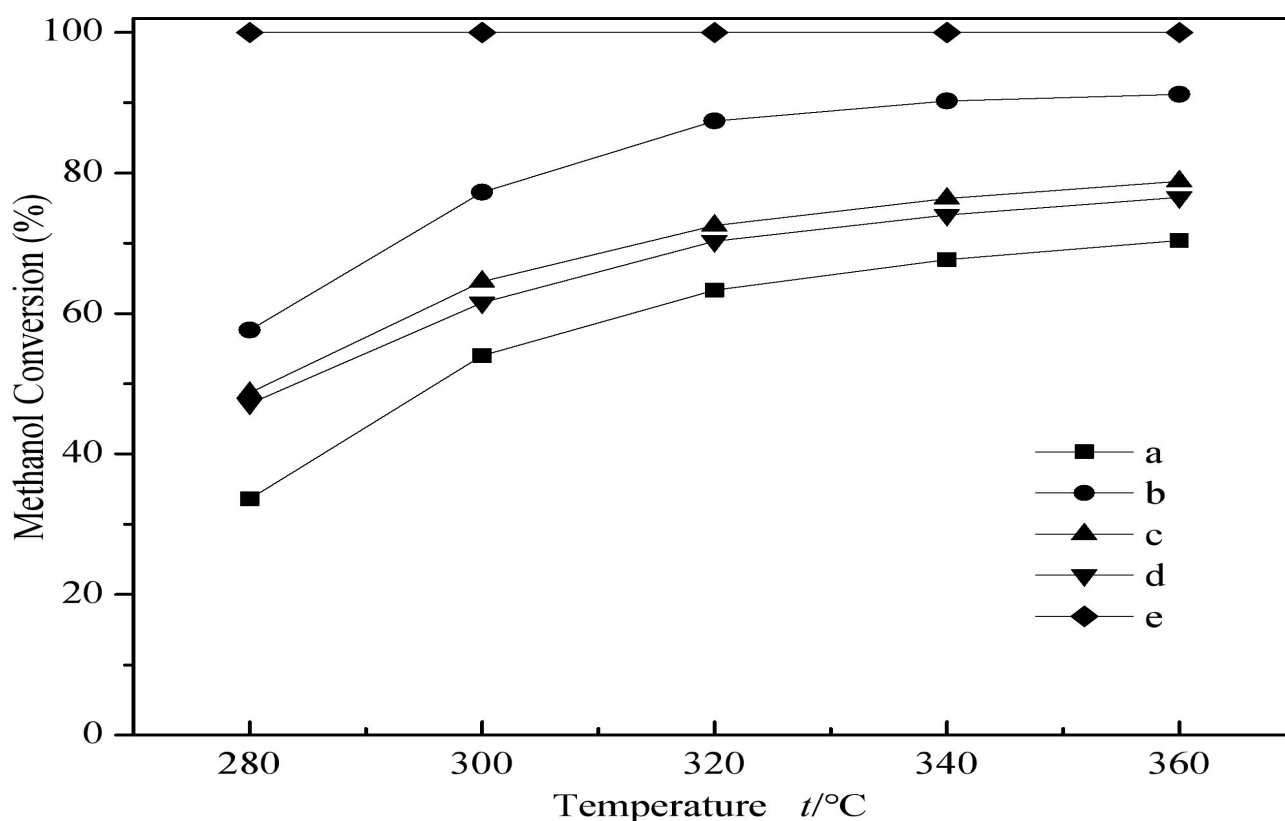### 6.4.1 The relationship between catalyst performance and reaction temperature

FIGURE 5. Relationship between catalyst performance and reaction temperature

Note: a: 2%CuO / $Ce_{0.8}Zr0._2O_2$; b: 5%CuO / $Ce_{0.8}Zr_{0.2}O_2$; c: 10%CuO / $Ce_{0.8}Zr_{0.2}O_2$; d: 20%CuO / $Ce_{0.8}Zr_{0.2}O_2$; e: equil.

However, xCuO / $Ce_{0.8}Zr_{0.2}O_2$ catalyst can remain active at high temperature because the interaction between active component Cu and support in xCuO / $Ce_{0.8}Zr_{0.2}O_2$ catalyst inhibits Cu sintering, so it

can still remain active at high temperature. The reason is that the strong endothermic steam reforming of methanol will affect the increase of reaction temperature, which is conducive to the occurrence of reforming reaction and further improve the methanol conversion.

It can be seen from the above figure that the hydrogen production rate of 5% CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalytic material is relatively high. The hydrogen production rate is 963 cm^3 kg^{-1} S^{-1} under the conditions of 280 °C, water alcohol molar ratio of 1.2:1 and methanol gas space velocity of 2200 h^{-1}. When the reaction temperature rises to 360 °C, the hydrogen production rate is 1312 cm^3 kg^{-1} s^{-1}.

Combined with FIG. 4 and Fig. 5, it can be seen that the 5% CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalyst has larger specific surface area of Cu, lower reduction peak temperature of CuO, stronger interaction between active component CuO and $Ce_{0.8}Zr_{0.2}O_2$ solid solution, so the catalyst has better catalytic activity.

For 2% CuO / $Ce_{0.8}Zr_{0.2}O_2$, 10% CuO / $Ce_{0.8}Zr_{0.2}O_2$ and 20% CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalysts, the interaction strength between Cu and solid solution is similar, but the specific surface area of Cu is different, which leads to different activity of catalysts. In conclusion, the larger the specific surface area of Cu, the lower the reduction temperature of CuO, and the stronger the interaction between CuO and $Ce_{0.8}Zr_{0.2}O_2$ solid solution, the better the catalytic activity of the catalyst.

6.4.2 Molar CO content in reforming tail gas at different reaction temperatures

The reason why the research on CO content in reforming tail gas has attracted the interest of scientists (Zhang L, Pan L W, Ni C J, et al. 2013) is that Pt electrode in proton exchange membrane battery is very sensitive to CO, and CO over 10 ppm will cause poisoning in proton exchange membrane battery. It can be seen from the figure below that the content of CO increases with the increase of temperature. This is because with the increase of temperature, methanol cracking reaction is more likely to occur and a large amount of CO is produced. Moreover, the rise of temperature makes the chemical equilibrium of water vapor shift reaction reverse, thus inhibiting the conversion of CO into CO_2. In addition, it can be seen from the figure that the mole content of CO in 5% CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalyst reforming tail gas is more, which is 5.3%. The second is 10% CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalyst, and the mole content of CO in the reforming tail gas is 4.7%. The second is 20% CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalyst, the mole content of CO in the reforming tail gas is 4.1%; the second is 2% CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalyst, the mole content of CO in the reforming tail gas is the least, which is 1.3%.
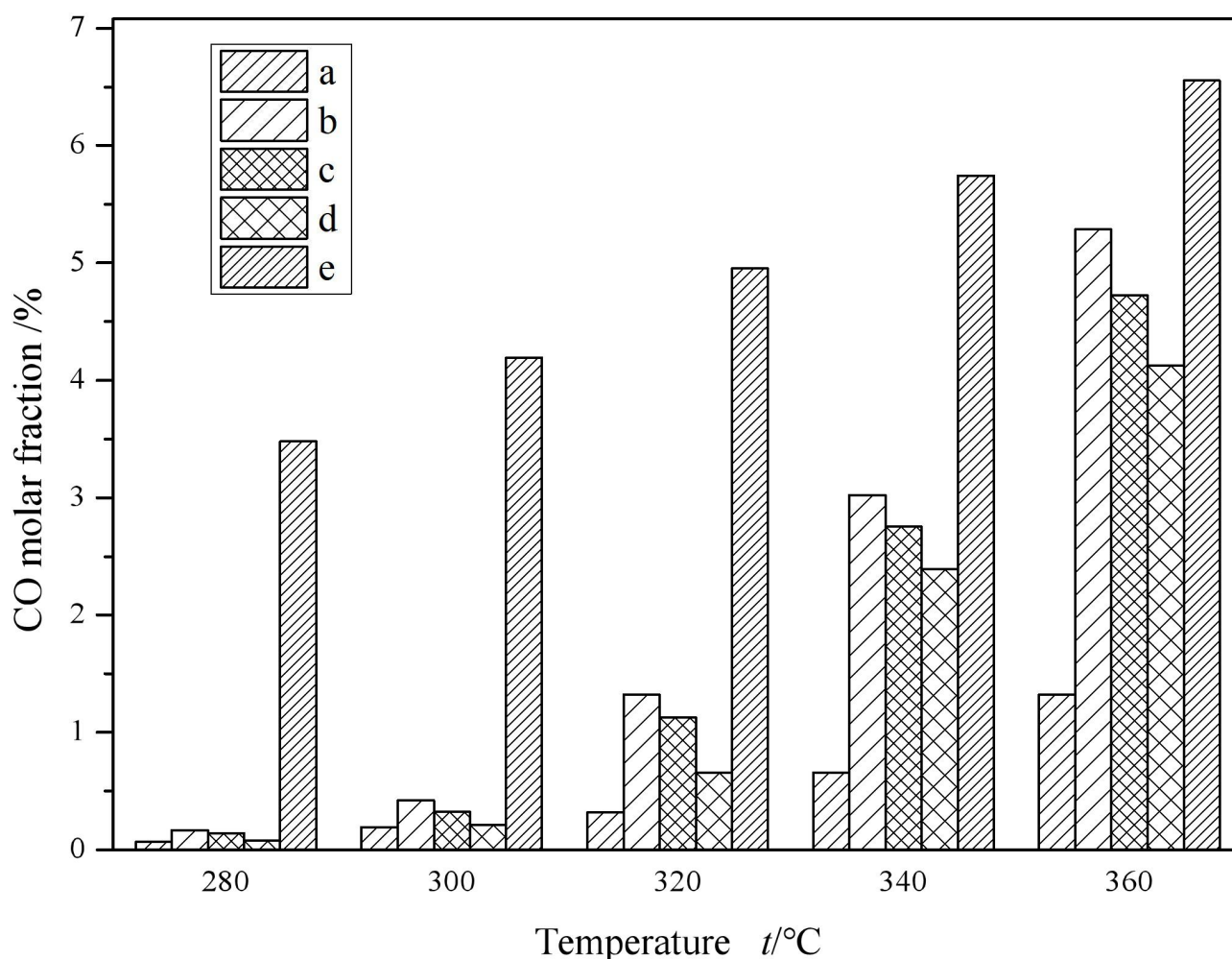
FIGURE 6. Molar CO content in reforming tail gas at different reaction temperatures

Note: A: 2% CuO / $Ce_{0.8}Zr_{0.2}O_2$; B: 5% CuO / $Ce_{0.8}Zr_{0.2}O_2$; C: 10% CuO / $Ce_{0.8}Zr_{0.2}O_2$; D: 20% CuO / $Ce_{0.8}Zr_{0.2}O_2$.

6.4.3 Diagram of hydrogen production rate at different reaction temperatures

As shown in the Figure 8 below, the hydrogen production rate of 5% CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalytic material is relatively high. Under the conditions of 280 °C, water alcohol molar ratio of 1.2:1, and methanol space velocity of 2200 h^{-1}, the hydrogen production rate can reach 963 $cm^3 \cdot kg^{-1} \cdot s^{-1}$, and when the reaction temperature rises to 360 °C, the hydrogen production rate can reach 1312 $cm^3 \cdot kg^{-1} \cdot s^{-1}$. With the increase of temperature, the hydrogen production rate increases 5% CuO / $Ce_{0.8}Zr_{0.2}O_2$ can produce the most hydrogen at 360 °C, and the hydrogen production rate can reach 1405 $cm^3 kg^{-1} s^{-1}$, which indicates that 5% CuO / $Ce_{0.8}Zr_{0.2}O_2$ can provide the basis for the preparation of copper-based

catalysts with high hydrogen production rate (Song, Q., Men, Y., Wang, J., Liu, S., Chai, S., An, W., Wang, K., Li, Y. & Tang, Y. 2020).
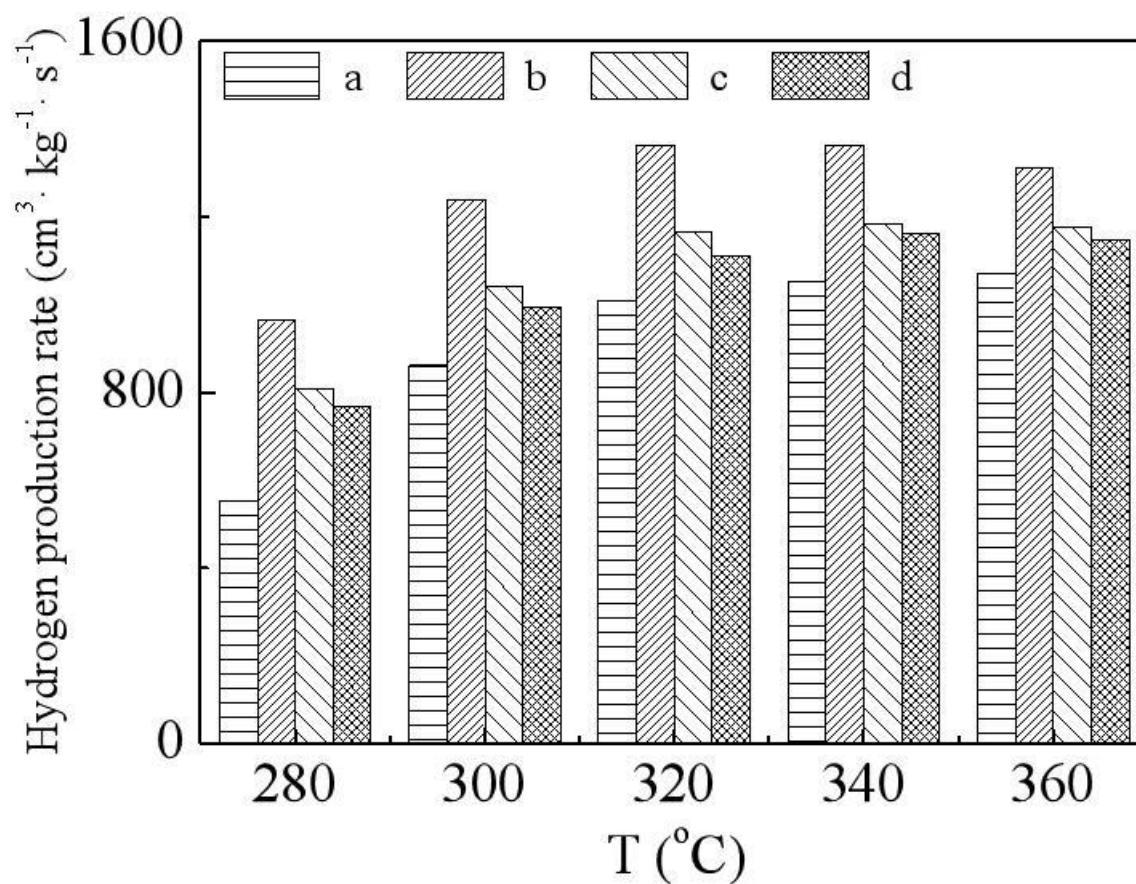

FIGURE 7. Hydrogen production rate diagram at different reaction temperature

Note: A: 2% CuO / $Ce_{0.8}Zr_{0.2}O_2$; B: 5% CuO / $Ce_{0.8}Zr_{0.2}O_2$; C: 10% CuO / $Ce_{0.8}Zr_{0.2}O_2$; D: 20% CuO / $Ce_{0.8}Zr_{0.2}O_2$.

7 CONCLUSIONS

There are many catalytic functions of Copper-based catalysts, especially in hydrogenation catalysis, which have good catalytic performance and great development value. Adding Zr into the catalyst can stabilize the interaction between Cu^+ and ZnO. Copper-based catalysts have been used in steam reforming of CH_3OH to produce hydrogen (MSR), and most of them are CuO / ZnO / Al_2O_3 catalysts. The content of Cu and ZnO in the catalyst is high, while the content of Al_2O_3 is relatively low. ZnO can improve the dispersion and reduction properties of Cu, and enhance the interaction between active components and support. However, the electronic structure of ZnO can be modified by Al_2O_3, which can promote the formation of lattice defects and improve the reduction ability of ZnO. In addition, the catalysts containing CeO_2 and ZrO_2 have higher H_2 selectivity and lower CO selectivity than the traditional Cu supported catalysts. CeO_2 can improve the thermal stability and reduction performance of Copper-based catalyst, solve the problem of poor stability of Copper-based catalyst and improve the performance of Copper-based catalyst.

$Ce_{0.8}Zr_{0.2}O_2$ solid solution was prepared by sol-gel method, and xCuO / $Ce_{0.8}Zr_{0.2}O_2$ catalytic materials with different Cu content were prepared by impregnation method. The effects of Cu content on the structure and catalytic performance were investigated. The results show that Cu content mainly affects the interaction between CuO and support and the specific surface area of Cu. The stronger the interaction between CuO and support and the larger the specific surface area of Cu, the better the catalytic performance of the catalyst. In the 5% CuO / $Ce_{0.8}Zr_{0.2}O_2$ catalyst, the interaction between CuO and $Ce_{0.8}Zr_{0.2}O_2$ solid solution support is strong, and the specific surface area of Cu is high, so it has good catalytic performance. Under the conditions of 360 °C, space velocity 2200 h^{-1}, water alcohol molar ratio 1.2:1, methanol conversion rate reaches 91.2%, and hydrogen production rate reaches 1312 cm^3 kg^{-1} s^{-1}.

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