CO_2-CH_4 Reforming Based on Nickel-based Catalysts

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Abstract. The current environmental problems are serious in nature. Due to greenhouse impact and a series of chain reactions caused by the massive emission of carbon dioxide (CO_2) into the atmosphere, the ecological environment of the earth has been seriously damaged. The removal and reuse of CO_2 is a current hot topic. The use of two greenhouse gases, CO_2 and methane (CH_4). And these two greenhouse gases can be used to produce different industrial products. However, the CO_2-CH_4 reforming reaction is difficult. The introduction of a catalyst in the reaction can avoid the problems of low conversion rate, long time and high energy consumption. At present, nickel-based catalysts are being greatly concerned in this reaction due to their low cost and high efficiency. Based on this background, this research focuses on four preparation methods for nickel-based catalysts, including deposition precipitation method, reflux impregnation method, solution combustion method and ammonia evaporation method. Three types of nickel-based catalysts, including single metal nickel-based catalysts, bi-metallic nickel-based catalysts, and multi-component nickel-based catalysts, are introduced about their activity performances in the CO_2-CH_4 reforming reaction. To sum up, the introduction of nickel-based catalysts can promote the directional regulation of reaction products, which can be carried out faster, saving energy and reducing consumption, which has very important research significance.

Keywords: CO_2, CH_4, Catalytic Conversion, Nickel-based Catalyst, Activity Performance.

1. Introduction

The main atmospheric greenhouse gases include carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4), fluorocarbons (CFS), and others. Among these gases, CO_2 is one of the main gases causing the greenhouse effect. Over the past century, with the continuous improvement of the population and living standards, the global CO_2 emissions have increased year by year. The concentration has risen sharply from 280 ppm before the industrial revolution to 402 ppm, directly leading to the intensification of the greenhouse effect and the rise of the global average temperature [1]. Therefore, it is urgent to limit the excessive emission of CO_2. Meanwhile, making use of CO_2 as a resource is crucial.

Exploring the catalysis and conversion of CO_2 and using it to prepare some other high value-added chemicals is of great significance for energy saving and emission reduction of greenhouse gases and improving the effective utilization of CO_2 resources. The conversion of CO_2 into valuable chemical raw materials such as formic acid, low-carbon olefins, aromatic hydrocarbons and methanol through catalytic reaction is helpful to alleviate many environmental problems at present. At the same time, it is also helpful for people no longer to rely on fossil energy. This method can reasonably use the CO_2 resources with abundant reserves, low cost and renewable resources to replace some fossil raw materials needed by human beings. To a certain extent, it is conducive to sustainable development. It is a research direction of great significance and an important means to achieve "carbon neutralization". Among them, the CO_2-CH_4 reforming reaction is a utilization of CO_2 catalytic conversion. It can convert two main greenhouse gases (CH_4 and CO_2) into an important chemical raw material, which is synthesis gas (hydrogen and carbon monoxide). It can also be further used to produce liquid fuel

(Fischer Tropsch synthesis) and other chemicals (dimethyl ether, methanol and acetic acid, etc.). Unlike the traditional chemical reaction, the CO_2-CH_4 reforming reaction has the phenomena of low CO_2 conversion, high energy consumption and long conversion time without the help of catalyst. To avoid such problems, the introduction of catalyst has become a new trend, and nickel-based catalyst has become a better choice in the CO_2-CH_4 reforming reaction.

Some researchers proposed a CO_2-CH_4 reforming reaction route to convert general gas into high value-added gas, and preliminarily explored the performance of reforming reaction with nickel, carbon monoxide and other catalysts. Group VIII transition metals Fe, Co, and Ni as well as noble metals like Pt, are primarily used as the active catalyst components in recent decades for the catalysis of the CO_2-CH_4 reforming reaction. Compared with the transition metal active components, the noble metal active components have the advantages of higher activity, more stable, and better resistance to carbon deposition. But it's challenging to develop industrial applications since noble metals are so expensive. For the different transition metals, the results show that the catalytic activity of Ni-based catalyst was higher than that of the Co-and Fe-based catalysts. As a result, a change from noble metal catalyst to transition metal catalyst (mostly Ni-based catalyst) or composite catalyst is an unavoidable trend in the investigation of catalysts for the CO_2-CH_4 reforming reaction to syngas.

As a result, this research will mainly introduce four common synthetic methods for Ni-based catalysts, including deposition precipitation method, reflux impregnation method, solution combustion method and ammonia evaporation method. And this research will systematically analyze the catalytic performance of the Ni-based catalysts.

2. Preparation of Ni-based catalyst

Other than osmium, noble metal elements (ruthenium, rhodium, iridium, palladium, and platinum) are typically used as the primary active ingredients of the catalyst for CO_2-CH_4 reforming. In terms of activity in CO_2-CH_4 reforming, noble metal catalysts are better than non-noble metal ones. However, precious metal resources are scarce and expensive in actual production, and the problem of recycling should be considered. Therefore, the research on catalysts is mainly focused on non-noble metal catalysts. The development of inexpensive and efficient catalysts for CO_2-CH_4 reforming is receiving increasing attention.

Group VIII metal catalysts have excellent catalytic activity for reforming catalytic reactions and excellent catalytic stability at high temperatures (≥750 ℃) and better resistance to carbon accumulation than other metal catalysts, and are widely used in CO_2-CH_4 reforming. Solymosi et al. pointed out in his study that noble metal Ru catalysts are more catalytically active in CO_2-CH_4 reforming [2]. However, the major drawbacks of the application of such noble metal catalysts in CO_2-CH_4 reforming are that they are comparatively expensive and are rare resources, leading to high costs and reduced cost performance in research and even production, which makes it difficult to achieve their application in the industrial pathway. Therefore, domestic and international research on CO_2-CH_4 reforming catalysis has mainly focused on transition-metal compounds.

Nickel-based catalysts have good catalytic activity for CO_2-CH_4 reforming to syngas. However, the application of these catalysts not only need to consider whether the support is cheap and easy to obtain and the cost is low, but must also fully consider their catalytic activity. When CH_4 and CO_2 are reformed to produce syngas, the catalytic activity of the used catalyst can be affected by the support. Because the support not only serves as a physical support during the actual response, but it also has the potential to influence the active components. Therefore, it is very necessary to develop new and more excellent preparation methods of Ni-based catalysts according to these factors.

To further improve the catalytic activity and stability, researchers have loaded non-precious and precious metals on metal oxides to obtain better redox properties to make more efficient CO_2-CH_4 reforming catalysts. For example, Tomsihige et al. has loaded Ni and Pt on Al_2O_3 and found that the obtained catalyst Pt/Al_2O_3 had catalytic activity which was significantly higher than that of Ni/Al_2O_3 [3]. Different catalyst preparation techniques have unintended impacts on the catalyst's catalytic performance. The creation of nickel-based catalysts can be done in a variety of ways, and this research primarily introduces a few popular ones at this time, namely deposition precipitation method, reflux impregnation method, solution combustion method, and ammonia evaporation method.

2.1. Deposition Precipitation Method

Zhang et al. prepared NiCo/MgO catalysts by the deposition-precipitation method [4]. A certain amount of $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $CO(NH_2)_2$, and MgO were combined in a specific ratio and swirled gradually over the course of two hours at a steady temperature and alkali. The products were extracted and filtered until the filtrate was neutral. Then they would be dried, roasted and cooled. The resulting catalyst was noted as DP catalyst. The deposition precipitation method is a simple way to produce such a catalyst, and the reaction conditions are controlled. Around 88% and 92% of CH_4 and CO_2, as shown in Figure 1, with the use of the prepared Ni-based catalysts, were transformed to new substances, mainly due to the tiny particle size of the active component (which is only 9.7 nm), high dispersion (which can reach 10.4%) and high reduction of the active metal (which improves the catalytic activity). Meanwhile, the stronger interaction between the metal and MgO also makes this catalyst more stable after reduction and prevents catalyst sintering.

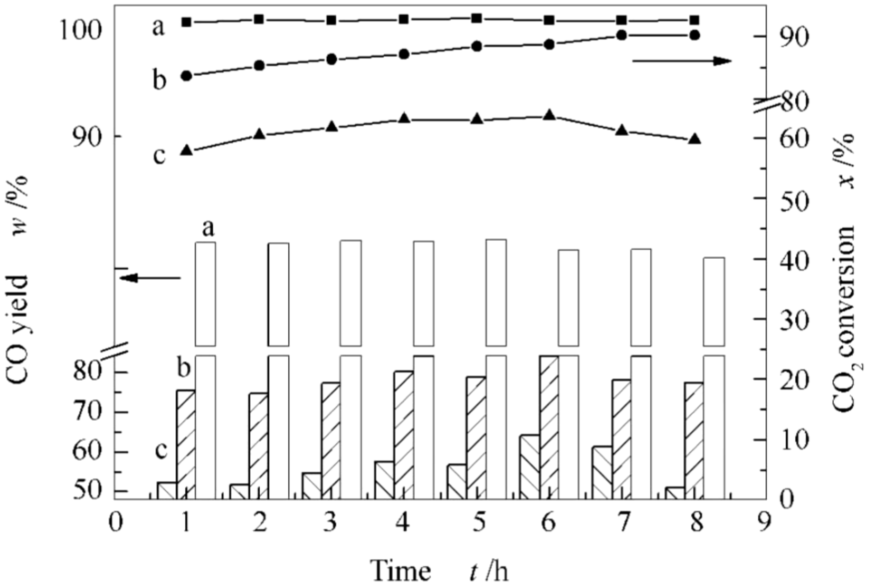


Figure 1. CO_2 conversion and CO yield with the prepared Ni-Co/MgO catalysts [4]

2.2. Reflux Impregnation Method

By mixing a specific quantity of $Ni(NO_3)_2 \cdot 6H_2O$ with γ-Al_2O_3 particles to create a suspension, Tao Ji produced a Ni/-Al_2O_3 catalyst,slowly adding NH_4HCO_3 [5]. The mixture was then stirred until they are dry at room temperature. Lastly, the product will be dried, roasted and cooled. The resulting catalyst was recorded as RI catalyst. In the reflux impregnation method, the process of reflux regulates the particle size, improving the dispersion of metal particles as well [6]. Ammonia can be used to boost CO_2 adsorption and improve metal-carrier interactions while also decreasing the acidity of the carrier [7] and reducing its acidity. In the study of Gai et al. [6], CH_4 and CO_2 conversion could result in up to 86.2% and 87.9% respectively, and the minimum carbon accumulation reached 0.88% with good synergistic performance of the reaction.

2.3. Solution Combustion Method

Mo et al. utilized the technique of solution combustion [8]. In a specific volume of water-ethylene glycol combination (V/V=1), the researchers dissolved Ni $(NO_3)_2 \cdot 6H_2O$ and Al $(NO_3)_3 \cdot 9H_2O$ by stirring vigorously for some time at room temperature. The product was then roasted and cooled after the aging process in a porcelain crucible. The resulting catalyst was noted as SC catalyst.

The nickel-based catalyst produced by the solution combustion approach has a high specific surface area, a multistage pore size distribution, and a potent metal-carrier interaction. The conversion of CH_4 can reach 90%. Meanwhile, the reaction-generated carbon accumulation is filamentous type, less than 10 nm in diameter, it does not cover the catalyst's active sites, and the reaction's only effect on grain size was a 38.59% rise, indicating that the SC catalyst is also more resistant to sintering.

2.4. Ammonia Evaporation Method

A type of nickel-based catalyst (Ni/LIT-aAE) was created by Song et al. with ammonia evaporation method [9]. The researchers gradually added a certain concentration of ammonia to a certain dose of Ni $(NO_3)_2 \cdot 6H_2O$ solution. They then added a certain synthetic carrier named KIT-6, and the mixture was heated in a water bath. After being filtered, washed, dried and calcined, the resulting catalyst was recorded as AE catalyst. The nickel-based catalysts prepared by ammonia evaporation method with high concentration of ammonia water showed about 85% and 90% conversion of CH_4 and CO_2 respectively. The reaction yielded small particles of layered nickel silicate, which could make Ni effectively dispersed, increasing the interaction between Ni and the carrier. The mesoporous carrier gave full play to the domain-limiting effect.

Based on the four catalyst preparation methods above, the deposition-precipitation method is simple, where the reaction conditions are mild and easy to control, as well as the great stability in the catalytic reaction. The products made by such routine have efficiently high conversion of CH_4 and production of H_2. The application of additives can effectively prevent the sintering of active components. The deposition-precipitation method is an effective method for the preparation of highly active non-precious metal-loaded catalysts to perform the CO_2-CH_4 reforming.

3. Activity performance of different kinds of nickel-based catalysts

3.1. Monometallic nickel-based catalysts

Nickel-based catalysts have always been the research hotspot of scholars at home and abroad. As a result, Ni-Al_2O_3, as the most common single-metal catalyst, has been studied. The catalyst with Ni as the main catalyst and γ-Al_2O_3 as the carrier has excellent activity and stability (lifetime>120hr), and shows excellent anti-coking performance.

The catalytic performance of catalysts is somewhat influenced by various preparation techniques. As an illustration, Mo et al. synthesized the Ni-Al_2O_3 catalyst by using the solution combustion method [8]. Through experimental characterization, the results show that the prepared catalyst has a larger specific surface area, and a wide pore size distribution. The catalyst's 210-h stability test reveals that the sample prepared by solution combustion method with an 8wt% Ni content maintains a CH_4 conversion rate of nearly 90% while deactivating at a rate of only 0.035%/h. And Figure 2 shows the CO_2 and CH_4 conversion under different experimental conditions. This might be because during the calcination through impregnation, the active components' high fluidity causes them to block some pores. The findings of the TG and TPH of the catalyst after the reaction demonstrate that the coke produced by the reaction is filamentous carbon, where the active sites of the catalyst are not affected. But a significant amount of coke will result in a rapid decrease in reaction activity due to an increase in bed pressure drop.

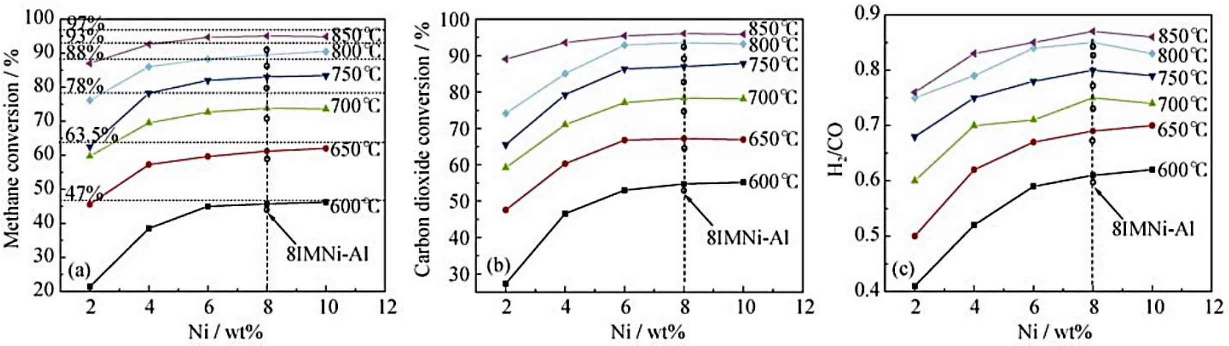


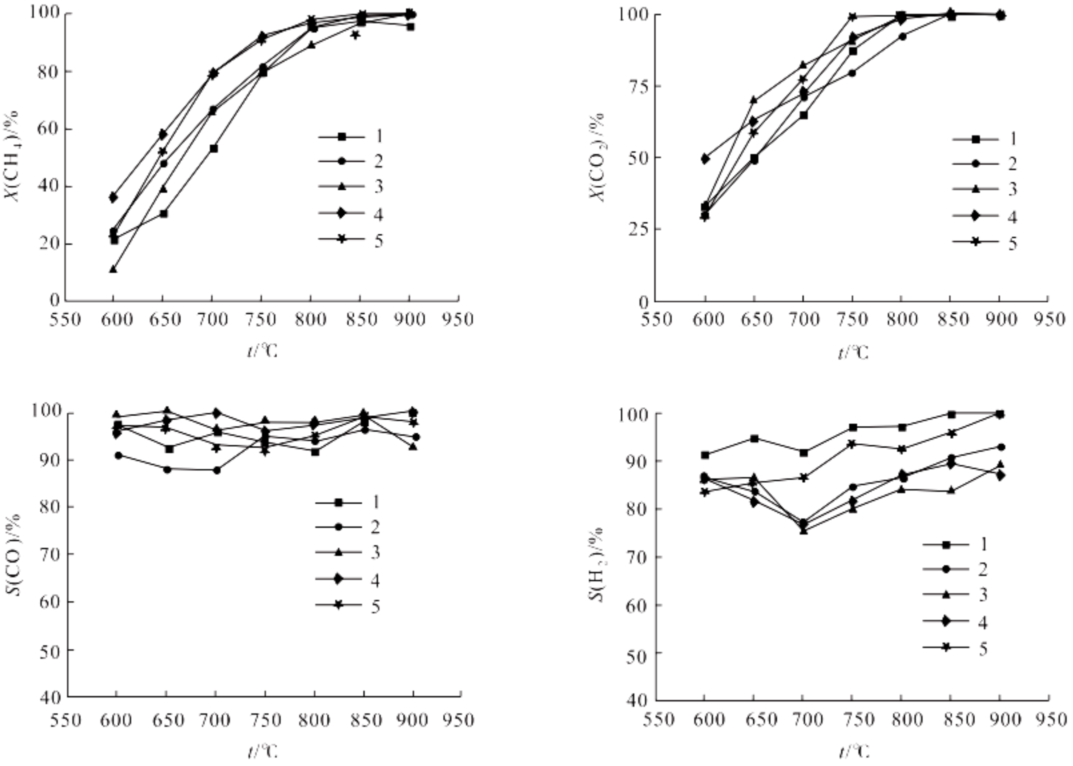
Figure 2. CO_2 and CH_4 conversion over the prepared catalysts [8]

3.2. Bimetallic nickel-based catalysts

Bimetallic catalysts differ from monometallic catalysts in their unique features and high catalytic performance because of their tunable physicochemical properties, electronic interactions, and geometric effects between the two metals. For example, because of the similar lattice parameters of NiO, CoO and MgO, they can form solid solutions, to obtain the active metal with high dispersion following reduction and a robust contact between the active metal and the carrier.

With the same active metal mass fraction, the NiCo/MgO catalyst's reducibility, particle size, dispersion, and specific surface area will differ depending on the preparation method, which will in turn affect how well it performs in the CO_2-CH_4 reforming reaction. Zhang et al. prepared different NiCo/MgO catalysts by four different preparation methods [4]. The results showed that compared with the co-precipitation method, the deposition-precipitation method can provide the complete hydrolysis and precipitation of the active components Ni^{2+} and Co^{2+} during the preparation process. A good alkaline environment not only makes the particle nucleation and growth rate faster, but also avoids local supersaturation. The prepared catalyst has good reducibility, excellent antifouling carbon qualities are the result of the material's small particle size, good Ni/Co dispersion, and large surface area. The CH_4 and CO_2 conversions for the CO_2-CH_4 reforming remained at 88% and 92% on the DP catalyst, which were close to the thermodynamic equilibrium conversions at 800℃. However, the H_2 yields were roughly 10% and 43%. The CO yield is superior to that of the CP and CI catalysts by about 13% and 42%, respectively, and the stability is improved. The DP catalyst has a significant interface between Ni/Co and MgO at the same time, which contributes to its good stability after reduction and its capacity to successfully halt the sintering of the active component Ni/Co. This interaction can be used to improve the stability of the catalyst. As a result, the deposition precipitation method is an efficient technique for creating catalysts supported by non-precious metals that are extremely active.

By using the impregnation approach, Ye et al. created a variety of Ni-Cu-Mo/Al_2O_3 catalysts with various nickel-molybdenum mass ratios [11]. The outcomes demonstrated that the catalysts performed best at 800°C, and had the optimum catalytic activity when their Ni/Mo mass ratio was 0.75. As shown in Figure 3, CH_4 and CO_2 converted at rates of 97.7% and 99.1%, respectively, whereas CO and H_2 had selectivity of 94.4% and 92.1%, respectively, under reaction conditions of 800°C and 182 mL/(gmin) space velocity. The performance of the catalyst can be enhanced by the addition of Mo promoter and increasing the dispersion of Ni on the surface of catalyst [12]. By forming additional active sites on the carrier's surface and enhancing the dispersion of Ni, the addition of Cu additions can further speed up the adsorption, dissociation, and insertion of CO_2 [13-15] and increase the rate of CO_2 conversion.



1-w(Ni/Mo) =0.15;2-w(Ni/Mo) =0.30;3-w(Ni/Mo) =0.45;4-w(Ni/Mo) =0.60;5-w(Ni/Mo) =0.75

Figure 3. Activity of catalysts at different Ni/Mo mass ratio [11]

3.3. Multi-component catalysts

Song et al. synthesized a Ni/LIT-aAE catalyst by using ammonia evaporation method and found that layered nickel silicate can be formed by ammonia evaporation method, which promotes Ni highly dispersed in mesoporous channels and effectively prevents carbon deposition [9]. The catalyst samples prepared with ammonia water with a concentration of 28% and 20% have excellent catalytic activity and anti-carbon deposition ability. And there is hardly any carbon deposition at 700°C, where the conversion rates for CH_4 and CO_2 are roughly 5% and 91%, respectively. When the ammonia content (10%) has been reached excessive layered nickel, silicate is formed to destroy the pore structure, and severe carbon deposition occurs after the reaction. The traditional impregnation method causes many Ni particles to agglomerate and accumulate on the outer surface of the support, there is also serious carbon deposition.

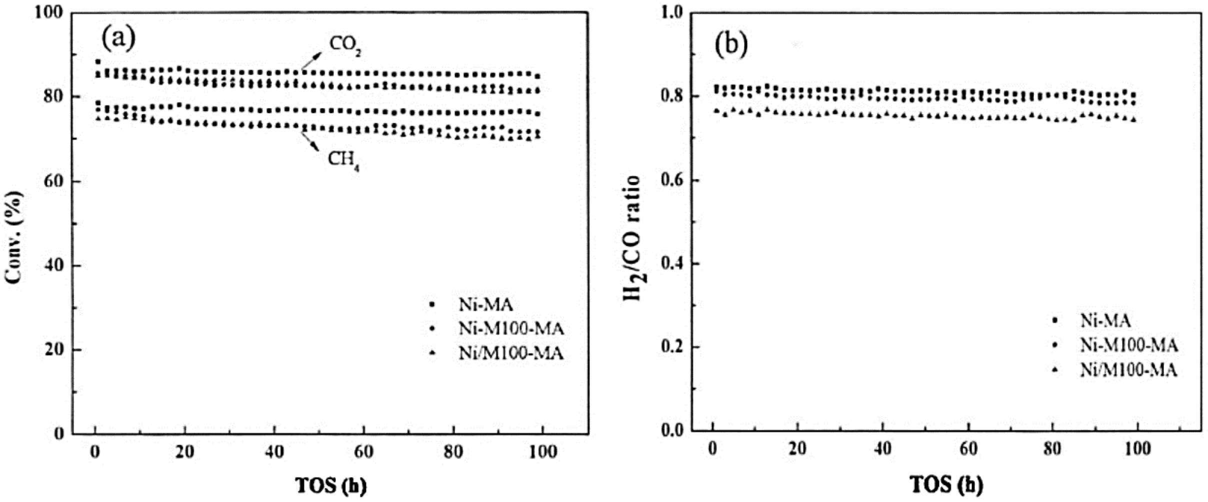


Figure 4. Analyzing the effects of catalysts on CH_4 and CO_2 conversion [16]

Han Yunxing designed a catalyst with a double-pore structure in view of the shortcomings of traditional single-pore structure catalysts [16]. The influence of the preparation method of the catalyst and nickel loading on its catalytic and anti-carbon deposition properties was investigated. When the impregnation method’s single-pore and double-pore catalysts were evaluated, it became clear that the double-pore catalyst had better catalytic activity. Figure 4 illustrates that after 100 hours of reaction, the conversion rates for CH_4 and CO_2 were 69.7% and 81.2%, respectively. The bi-porous structure catalyst also has good anti-carbon performance, and the carbon deposition after 100h reaction is 5.8%. This is attributed to the special pore structure of the catalyst, the mesoporous pore is favorable for the dispersion of Ni particles, and the macro-porous pore is favorable for the rapid transport of molecules, enhancing the catalyst's anti-carbon deposition efficacy and catalytic activity. By altering the preparation method, the catalyst is further improved since the impregnation method’s weak metal-support contact force and the reaction at high temperatures ease of causing Ni particle agglomeration, which results in carbon deposition, prevent it from occurring. The results of comparing the double-porous structure catalysts made by the impregnation method and the one-step method revealed that the catalyst made by the one-step method shows excellent catalytic performance such as a higher reduction peak temperature. Figure 5 illustrates the conversion rates of CH_4 and CO_2 after 100 hours of reaction, which are 71.4% and 81.2%, respectively. The catalyst also exhibits a high anti-carbon performance. Only 2.8% of the substance is carbon. This is explained by the fact that the catalyst’s Ni particles are supported on the carrier skeleton, creating a strong metal-support contact force that prevents the Ni particles from clumping together and lowering the production of carbon deposits.

Bi-porous catalysts with a range of Ni concentrations were created in a single process. The findings indicate that as Ni content rises, the surface area and pore volume of the catalyst gradually expand, and the contact between metal and support gradually intensifies. As a result, the catalyst's catalytic activity rises. However, as the catalyst’s carbon deposition and degree of graphitization also rise, its anti-coking performance gradually declines. The catalyst's ability to bind more CO_2 can be achieved by adding the additive Zr, which also helps to regulate the catalyst’s acidity and alkalinity. A little quantity of Zr can also help to boost the stability of the catalyst’s mesoporous structure, which enhances the catalyst's ability to catalyze reactions and prevent coking.

4. Conclusions

In accordance with the “double carbon” aim, the production of valuable industrial goods by the methanation of CO_2 with hydrogen derived from renewable energy sources is seen as an effective and promising technique for carbon capture and use, which is anticipated to achieve carbon recycling. Numerous important developments have been made recently in both nickel-based CO_2 methanation catalysts and the associated reaction processes. As a result, the study on nickel-based catalysts for the CO_2-CH_4 reforming reaction is reviewed in detail in this publication. The significance and status of the research on CO_2 methanation reaction are introduced. The research progress of nickel-based catalysts for CO_2 methanation is presented in four aspects, including advantages, types, preparation methods and activity performance of nickel-based catalysts, including several traditional preparation methods (deposition precipitation, solution combustion, ammonia evaporation and reflux impregnation) followed by their comparison. We summarized the activity performance of monometallic, bimetallic and multi-metallic nickel-based catalysts, the catalytic performance of which is related to the preparation methods and reaction conditions (e.g., reaction temperature and pressure). We present the challenges of the current research and the outlook in such field is given as well.

The research on catalytic reforming of CO_2-CH_4 is of great significance for the realization of CO_2 resource recovery, greenhouse gas consumption and the conversation of resource and energy. However, it is not yet industrially applied due to the unknown mechanism of the reaction process, catalyst sintering, carbon buildup and reaction temperature control. Current researches on CO_2-CH_4

reforming catalysts focus on nickel-based catalysts, which are in favor of excellent catalytic activity and carbon build-up resistance at a lower cost, compared to the precious metal catalysts.

Different catalyst preparation methods influence the results of CO_2-CH_4 catalytic reforming. It is also important to maintain the activity and stability of catalysts at a high level in the heat and inhibit the formation of carbon accumulation. Future research on CO_2-CH_4 catalytic reforming may concentrate on finding more energy-efficient and practical ways to produce catalysts with improved stability, catalytic activity, and resistance to carbon buildup. As the further research of catalysts' active components, additives, carriers, surface structure, acidity and alkalinity, carbon formation and reforming reaction mechanism would continue to improve. The catalyst components should be designed rationally. The reaction conditions should be optimized. The formation of carbon ought to be suppressed. The reforming reaction mechanism could also be revealed as well as the improvement of the catalyst activity, stability and carbon build-up resistance. In the future, the reforming of CH_4 and CO_2 will cover a broad development prospect and wide practical application.

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