

Review on Anti-Coking and Anti-Sintering Modification Strategies of Nickel-Based Catalysts and Their Industrial Application Potential

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Abstract: Nickel-based catalysts have important application value in many fields such as methane dry reforming (DRM), hydrofining, and water electrolysis for hydrogen production due to their abundant reserves, low cost, and excellent catalytic activity. However, under high-temperature reaction conditions, nickel-based catalysts are prone to carbon deposition and nickel particle sintering/agglomeration, leading to the loss of active sites and the decline of catalytic performance, which seriously restricts their industrial popularization. This paper systematically combs the formation mechanisms of carbon deposition and sintering of nickel-based catalysts and their synergistic deactivation effect, elaborates on the mainstream anti-coking and anti-sintering modification strategies such as carrier modification, active component modification, promoter doping, preparation process optimization, and composite modification, and deeply analyzes the action principle, advantages and limitations of various strategies. On this basis, the performance differences and applicable scenarios of different modification strategies are compared and evaluated, and the future development trend of modification technology is prospected, providing theoretical support and practical reference for the modification research and development, performance optimization and industrial application of nickel-based catalysts.

Keywords: Nickel-based Catalysts; Anti-Coking; Anti-sintering; Modification Strategies; Catalytic Deactivation; Performance Evaluation.

1. Introduction

With the increasing urgency of global energy structure transformation and environmental protection needs, catalytic technology, as the core support for energy conversion, pollutant treatment, and fine chemical synthesis, has attracted wide attention. Nickel-based catalysts occupy an important position in many catalytic reactions such as methane dry reforming for syngas production, CO₂ methanation, heavy oil hydrofining, water electrolysis for hydrogen production, and biomass tar reforming due to their excellent catalytic activity, good compatibility, and low cost, becoming one of the research hotspots in the field of industrial catalysis. Among them, methane dry reforming reaction, as an efficient carbon capture and utilization technology, can convert two major greenhouse gases (CH₄ and CO₂) into high-value-added syngas, which not only alleviates the greenhouse effect but also realizes resource recycling, and nickel-based catalysts are one of the most promising catalytic systems for this reaction[1].

Despite their significant advantages, nickel-based catalysts face severe challenges in long-term stability in practical industrial applications. Most catalytic reactions (such as DRM reaction) need to be carried out under high-temperature conditions above 700°C. In this process, carbon species are easily generated on the catalyst surface due to side reactions such as methane cracking and CO disproportionation, forming carbon deposition and covering active sites; at the same time, high temperature will drive nickel particles to migrate, fuse and grow, namely sintering phenomenon, leading to the decrease of catalyst specific surface area and the sharp reduction of active site quantity, and finally causing irreversible deactivation of the catalyst[2]. Carbon deposition

and sintering have become the two core bottlenecks restricting the industrial application of nickel-based catalysts. Therefore, carrying out research on anti-coking and anti-sintering modification of nickel-based catalysts, optimizing their catalytic stability and service life, is of great practical significance and industrial value for promoting the industrial upgrading of catalytic technology and helping to achieve the "double carbon" goal[3].

In recent years, domestic attention to the research on modification of nickel-based catalysts has continued to increase. Many universities and research institutions have carried out a lot of research work around localization substitution and new modification technology research and development, forming research results with Chinese characteristics. The research focus is concentrated on carrier surface modification, rare earth element co-modification, MOFs-derived nano-nickel-based catalyst preparation and other fields[4]. The surface properties of carriers are changed by introducing specific functional groups or ions, the catalytic performance is optimized by using the synergistic effect of rare earth elements, and the uniform dispersion of nickel particles is realized by virtue of the structural advantages of MOFs precursors. In addition, domestic research also focuses on the combination of theoretical calculation and experimental research, using density functional theory (DFT) and other methods to deeply explore the modification mechanism, providing theoretical guidance for catalyst design. However, on the whole, there are still deficiencies in domestic research: the mechanism of some modification technologies is not fully clear, the engineering application capacity of high-end modified catalysts needs to be improved, and there is still a certain gap with the international advanced level.

2. Formation Mechanisms of Carbon Deposition and Sintering of Nickel-Based Catalysts

(1) Formation Mechanism of Carbon Deposition

Carbon deposition is one of the common deactivation reasons of nickel-based catalysts in high-temperature catalytic reactions. Its formation process is closely related to reaction type, reaction conditions and catalyst surface properties, mainly originating from the deposition and accumulation of carbon species generated by side reactions such as methane cracking[5], CO disproportionation and unsaturated hydrocarbon polymerization on the catalyst surface. The formation path of carbon deposition varies at different reaction temperatures: under high-temperature conditions, carbon deposition is mainly generated by methane cracking reaction ($\text{CH}_4 \rightarrow \text{C(s)} + 2\text{H}_2$); under low-temperature conditions, CO disproportionation reaction ($2\text{CO} \rightarrow \text{C(s)} + \text{CO}_2$) and the reaction between CO and H_2 ($\text{CO} + \text{H}_2 \rightarrow \text{C(s)} + \text{H}_2\text{O}$) are the main paths for carbon deposition. In addition, the higher the content of unsaturated hydrocarbons in the reaction system, the more serious the carbon deposition phenomenon, and the cracking of methane and other small hydrocarbons will also aggravate the carbon deposition[6].

According to the formation temperature and structural characteristics, carbon deposition can be mainly divided into three types: C_i type (473~673K) is high-activity amorphous carbon and coated carbon, which can react with water vapor to generate CO and H_2 under catalytic action, and has little impact on catalyst activity. C_{ii} type (573~773K) is polymerized carbonaceous substances (such as graphite and aromatic compounds), which are precursors of carbon deposition, with low reaction activity, cannot react with water vapor, and are easy to wrap catalyst active sites leading to deactivation. C_{iii} type (above 773K) is whisker carbon (filamentous carbon), with poor adsorption and low activity, but it grows outward from catalyst particles and has little impact on catalyst activity. Among them, C_{ii} type carbon deposition is the main carbon species leading to the deactivation of nickel-based catalysts, and its generation amount is closely related to nickel particle size, reaction temperature, metal-support interaction and reactant composition[7].

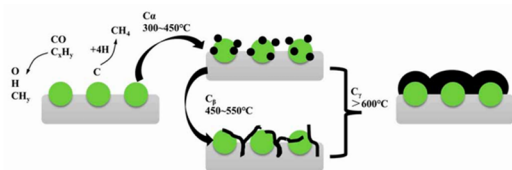


Figure 1. Formation, accumulation and transformation of carbon on metal-based catalysts

(2) Formation Mechanism of Sintering

The sintering of nickel-based catalysts mainly occurs under high-temperature reaction conditions, which is a process of migration, fusion and growth of nickel particles driven by thermodynamics, mainly divided into two types: Ostwald ripening and particle agglomeration[8]. In the Ostwald ripening mechanism, small-sized nickel particles are easy to dissolve in the carrier surface or reaction atmosphere due to their high surface energy, and deposit on the surface of large-sized nickel particles through diffusion, leading to the disappearance of small particles and the growth of large particles; in the particle agglomeration mechanism, the

surface atoms of nickel particles become more active at high temperature, and adjacent nickel particles collide and fuse through surface diffusion to form larger-sized agglomerates, resulting in the decrease of catalyst specific surface area and the reduction of active site quantity.

The occurrence of sintering is related to many factors, among which reaction temperature is the most critical influencing factor. The higher the temperature, the more intense the atomic movement of nickel particles, and the faster the sintering rate. For example, high-temperature reduction conditions above 800°C are prone to cause rapid deactivation of the catalyst[7, 9]. In addition, the strength of metal-support interaction, catalyst preparation process, reaction time and other factors also affect the sintering rate: the weaker the metal-support interaction, the easier the nickel particles to detach from the carrier surface and migrate and agglomerate[10]; poor dispersion of nickel particles caused by improper preparation process will aggravate the sintering phenomenon; the longer the reaction time, the more obvious the cumulative effect of sintering, and the more significant the decline of catalyst performance.

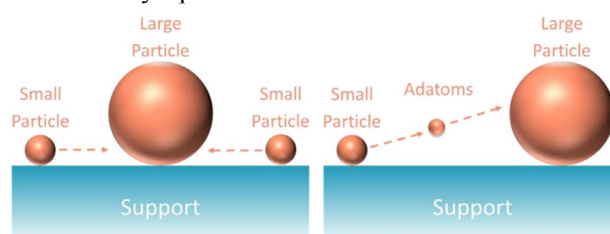


Figure 2. Particle migration and aggregation vs. Ostwald ripening[3]

3. Anti-Coking and Anti-Sintering Modification Strategies of Nickel-Based Catalysts

(1) Carrier Modification Strategy

As an important part of nickel-based catalysts, the carrier not only plays the role of supporting the active component (nickel particles), but also can affect the dispersion of nickel particles and the strength of metal-support interaction by regulating its own structure and properties, thereby improving the anti-coking and anti-sintering performance of the catalyst[11]. The core principle of carrier modification is to select a carrier with high specific surface area, good thermal stability, strong metal-support interaction and appropriate pore structure, and further optimize its performance through modification. Common carriers include Al_2O_3 , SiO_2 , molecular sieves, carbon materials, metal oxides, etc. The modification methods mainly include pore structure regulation, carrier doping modification and carrier surface modification.

Pore structure regulation is to prepare mesoporous, microporous or hierarchical porous carriers by regulating the pore size distribution and specific surface area of the carrier through preparation processes such as template method, hydrothermal synthesis method and sol-gel method. With its reasonable pore size distribution, hierarchical porous carriers can not only provide sufficient loading sites for nickel particles to realize uniform dispersion of nickel particles and inhibit nickel particle agglomeration and sintering, but also promote the diffusion of reactants and products, reduce the deposition of carbon species on the catalyst surface, thus improving both the anti-coking and anti-sintering performance of the catalyst. For example, mesoporous silica

(MCF) carrier can limit nickel particles in mesoporous channels through pore structure regulation, effectively inhibit the growth of nickel particles, and at the same time accelerate the adsorption and diffusion of CO₂ to inhibit carbon deposition[12].

Carrier doping modification is to dope the carrier with non-metallic elements such as N, P, S or rare earth elements such as La, Ce, Sm to regulate the surface acidity and alkalinity, electronic structure and metal-support interaction strength of the carrier[13]. Non-metallic element doping can form defect sites on the carrier surface, enhance the adsorption capacity of the carrier for nickel particles, and improve nickel dispersion; rare earth element doping can use its oxygen storage capacity to promote the oxidation and decomposition of carbon deposition, and at the same time strengthen the metal-support interaction to inhibit nickel particle sintering. For example, when CeO₂ forms a bimetallic oxide carrier with Al₂O₃, La₂O₃, etc., it can increase the specific surface area of the carrier, regulate the pore structure through synergistic effect, and at the same time improve the catalyst activity and stability, change the carbon deposition type and promote the formation of carbon nanotubes[14].

Carrier surface modification is to change the surface properties of the carrier by loading metal oxides, introducing functional groups, etc., regulate the distribution of active sites and electronic structure, enhance the CO₂ adsorption and activation capacity, and inhibit the formation of carbon deposition. For example, modifying the surface of SiO₂ carrier with La₂O₃-Sm₂O₃ composite oxide can increase the basic sites on the carrier surface, promote the adsorption and activation of CO₂, inhibit the side reaction of methane cracking, and reduce carbon deposition; surface acid treatment of Al₂O₃ carrier can increase the surface acid sites, which is conducive to the dispersion and stability of nickel species and improve the anti-sintering performance.

The advantages of the carrier modification strategy are simple operation, low cost, significant improvement of catalyst stability, and adaptation to various catalytic reaction scenarios; its limitations are that some modified carriers (such as some mesoporous carriers) have insufficient thermal stability, which are prone to pore structure collapse in high-temperature reactions, and single carrier modification is difficult to achieve a significant improvement in both anti-coking and anti-sintering performance, so it needs to be used in combination with other modification strategies[15].

(2) Active Component Modification Strategy

The size, dispersion and electronic structure of the active component (nickel particles) are the core factors affecting the anti-coking and anti-sintering performance of nickel-based catalysts. The active component modification strategy mainly optimizes its catalytic performance and reduces the occurrence of carbon deposition and sintering by regulating the size, dispersion and electronic structure of nickel particles, mainly including three methods: nickel particle size regulation, bimetallic/multimetallic alloying modification and active component dispersion optimization.

Nickel particle size regulation is to prepare nano-sized nickel particles by optimizing the preparation process, increase the specific surface area and the number of active sites of nickel particles, and reduce the risk of carbon deposition and sintering. Studies have shown that the smaller the nickel particle size, the better the dispersion, the more surface active sites, the higher the catalytic activity, and small-sized nickel particles are not easy to agglomerate and

sinter, and can inhibit the formation and deposition of carbon deposition precursors. Common size regulation methods include MOFs-derived method, impregnation method, co-precipitation method, etc. Among them, MOFs-derived method, by virtue of the porous structure of its precursor and uniformly dispersed metal sites, can prepare nano-nickel particles with uniform size and excellent dispersion, effectively improving the anti-coking and anti-sintering performance of the catalyst, and is currently a research hotspot in active component size regulation[16].

Bimetallic alloying modification is to form alloys with nickel by introducing metals such as Co, Fe, Cu, Pt, Rh, and use the synergistic effect between metals to regulate the electronic structure and surface properties of nickel, enhance the anti-sintering ability and anti-coking performance. For example, Ni-Co alloy can form a solid solution structure, which can not only promote the reduction of nickel species, increase the number of active sites, but also improve the CO₂ dissociation ability and inhibit carbon deposition, but Co doping is prone to oxidize nickel particles and reduce catalytic activity; Ni-La alloy can promote the formation of nickel silicate, strengthen the metal-support interaction, improve the reducibility of nickel particles, increase surface basic sites, and facilitate carbon deposition removal. The key of alloying modification is to select appropriate alloy elements and proportions to achieve the synergistic improvement of catalytic activity, anti-coking performance and anti-sintering performance[17].

Active component dispersion optimization is to improve the dispersion of nickel particles on the carrier surface by adding dispersants, optimizing calcination temperature and reduction conditions, etc., reduce nickel particle agglomeration, and thus inhibit sintering and carbon deposition. For example, adding dispersants such as citric acid and ethylene glycol can inhibit the aggregation of nickel particles during preparation and improve dispersion; optimizing calcination temperature and reduction conditions can avoid the growth of nickel particles during preparation, and at the same time strengthen the metal-support interaction and reduce particle agglomeration during the reaction. H₂-TPR, XPS and other characterization results show that the better the dispersion of nickel particles, the stronger the anti-sintering and anti-coking performance of the catalyst, and the more excellent the catalytic stability[18].

(3) Promoter Doping Modification Strategy

Promoter doping is a simple and efficient modification strategy. By adding a small amount of promoters (usually metal oxides, alkali metals, alkaline earth metals, etc.) to nickel-based catalysts, the surface properties, electronic structure and active site distribution of the catalyst are regulated by the interaction between the promoter and nickel active components and the carrier, thereby improving the anti-coking and anti-sintering performance. According to the action mechanism, promoters can be divided into three types: structural promoters, electronic promoters and catalytic promoters, and their selection needs to be combined with the catalytic reaction type and catalyst performance requirements.

Structural promoters mainly include rare earth metal oxides such as La₂O₃, CeO₂ and Sm₂O₃. Their core role is to inhibit the migration and agglomeration of nickel particles, enhance the anti-sintering ability, and at the same time regulate the surface basic sites of the carrier, promote the adsorption and activation of CO₂, and inhibit carbon deposition. For example, as a structural promoter, CeO₂ can release active oxygen

species during the reaction to oxidize and decompose carbon deposition by virtue of its excellent oxygen storage capacity and oxygen mobility, and at the same time strengthen the metal-support interaction to inhibit nickel particle sintering; La_2O_3 can form stable compounds with the carrier, optimize the catalyst pore structure, improve the dispersion of nickel particles, and reduce carbon deposition[19].

Electronic promoters mainly include alkali metals such as K and Na. Their core role is to regulate the electron density of nickel through electron transfer, change the surface electronic structure of nickel particles, inhibit side reactions such as methane cracking and CO disproportionation, and reduce carbon deposition. Alkali metal promoters can act as electron donors, transfer electrons to nickel particles, reduce the average valence state of nickel, enhance the CO_2 dissociation ability, and at the same time weaken the adsorption strength of carbon species on the surface of nickel particles, promote the desorption of carbon species, thereby reducing carbon deposition accumulation. However, the addition amount of alkali metal promoters needs to be strictly controlled; excessive addition will cover active sites and reduce catalytic activity[20].

Catalytic promoters mainly include alkaline earth metal oxides such as MgO and CaO. They have weak catalytic activity themselves, which can promote the oxidation and decomposition of carbon deposition, realize the "self-cleaning" of the catalyst, and reduce carbon deposition accumulation. For example, MgO can improve the surface alkalinity of the catalyst, promote CO_2 adsorption, and at the same time catalyze the reaction between carbon deposition and CO_2 to generate CO, realizing in-situ removal of carbon deposition, thereby improving the anti-coking performance of the catalyst. In addition, catalytic promoters can also cooperate with structural promoters and electronic promoters to further optimize the comprehensive performance of the catalyst[21].

The advantages of the promoter doping modification strategy are simple operation, low cost, significant modification effect, and flexible adaptation to different types of nickel-based catalysts and catalytic reactions; its limitations are that there is an optimal range for the addition amount of promoters, excessive addition will lead to the decrease of catalytic activity and selectivity, and the effect of single promoter modification is limited, which usually needs to be used in combination with other modification strategies

(4) Preparation Process Optimization Strategy

Preparation process is a key factor affecting the structure, dispersion and metal-support interaction strength of nickel-based catalysts. Optimizing the preparation process can reduce the hidden dangers of carbon deposition and sintering from the source, and improve the stability and catalytic performance of the catalyst. The preparation process optimization strategy mainly includes two types: traditional preparation process improvement and new preparation process application. The core is to realize the uniform dispersion of nickel particles, the optimization of carrier structure and the strengthening of metal-support interaction by regulating preparation parameters and process flow[22].

Traditional preparation processes (such as impregnation method, co-precipitation method, sol-gel method) are the main methods for industrial production of nickel-based catalysts. The focus of optimization is to adjust process parameters to improve catalyst performance. For example, optimizing the impregnation time, impregnation

concentration and calcination temperature of the impregnation method can improve the dispersion of nickel particles on the carrier surface and reduce nickel particle agglomeration; adjusting the precipitation temperature, pH value and precipitant type of the co-precipitation method can control the crystal size and pore structure of the catalyst and enhance the metal-support interaction; optimizing the gelation time, calcination temperature and reduction conditions of the sol-gel method can improve the thermal stability of the catalyst and inhibit high-temperature sintering and carbon deposition[23].

The application of new preparation processes is an important direction to improve the anti-coking and anti-sintering performance of nickel-based catalysts. In recent years, new processes such as MOFs-derived method, plasma treatment method and atomic layer deposition method have gradually become research hotspots. MOFs-derived method uses MOFs as precursors, and through calcination, reduction and other processes, can prepare nickel-based catalysts with high specific surface area and uniform dispersion. Its porous structure can limit nickel particle agglomeration, and at the same time provide abundant active sites, significantly improving anti-coking and anti-sintering performance; plasma treatment method can bombard the catalyst surface with high-energy particles, remove surface impurities, increase surface defect sites, strengthen metal-support interaction, improve nickel particle dispersion, and reduce carbon deposition; atomic layer deposition method can realize precise loading of nickel particles, control the size and dispersion of nickel particles, and prepare high-performance and high-stability nickel-based catalysts[24].

The advantages of the preparation process optimization strategy are that by adjusting process parameters or adopting new processes, the catalyst performance can be significantly improved without increasing additional costs (or increasing a small amount of costs), and it is suitable for large-scale production needs; its limitations are that the optimization space of traditional preparation processes is limited, and new preparation processes (such as atomic layer deposition method) have problems such as high preparation cost and difficulty in large-scale production, which are difficult to be widely applied[25].

4. Summary and Outlook

This paper systematically combs the formation mechanisms of carbon deposition and sintering of nickel-based catalysts and their synergistic deactivation effect, elaborates on five types of anti-coking and anti-sintering modification strategies including carrier modification, active component modification, promoter doping, preparation process optimization and composite modification, and compares and evaluates the performance differences and applicable scenarios of different modification strategies. The following conclusions are drawn: carbon deposition and sintering are the two core reasons for the high-temperature deactivation of nickel-based catalysts, and they form a vicious circle to accelerate the performance decline of the catalyst; various modification strategies can effectively improve the anti-coking and anti-sintering performance of the catalyst through different action mechanisms, among which carrier modification focuses on inhibiting sintering, promoter doping focuses on inhibiting carbon deposition, active component modification focuses on improving catalytic activity, preparation process optimization focuses on optimizing the

catalyst structure from the source, and composite modification can realize the synergistic improvement of multiple performances.

At present, significant progress has been made in the modification technology of nickel-based catalysts. The action mechanisms of various modification strategies are gradually clear, and the performance of modified catalysts is continuously improved. However, there are still some key problems: the comprehensive performance of a single modification strategy is limited, and it is difficult to meet the requirements of high activity, high anti-coking and high anti-sintering at the same time; the new preparation process has difficulty in large-scale production and high cost; the mechanism of some modification technologies is not fully clear, and the ability of precise modification design is insufficient; the engineering adaptability of modified catalysts needs to be improved, and the compatibility with existing industrial devices is poor.

Aiming at the existing problems of current nickel-based catalyst modification technology and combining with the industry development needs, the future research directions mainly focus on the following four aspects: first, deepen the research on modification mechanism. Combined with DFT calculation, in-situ characterization and other technologies, deeply explore the interaction mechanism between modifiers and nickel active components and carriers, clarify the inhibition mechanism of carbon deposition and sintering, realize the precise design of modification strategies, and improve the modification effect.

Second, develop low-cost and large-scale modification technologies. Develop efficient and cheap modifiers (such as new rare earth composite promoters and non-metallic dopants), optimize new preparation processes (such as MOFs-derived method and plasma treatment method), reduce preparation costs, solve the problem of large-scale production, improve the localization substitution capacity, and promote the industrial popularization of modified catalysts.

Third, strengthen the research on engineering technology. Focus on the molding technology and large-scale preparation technology of modified catalysts, improve their adaptability to existing industrial devices, carry out pilot and industrial side-line experiments, solve the problems of stability and service life in practical applications, and promote the transformation of modification technology from laboratory to industrial application.

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