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A Review of Research on the Enhancement of the Low-Temperature Activity of Automotive Three-Way Catalysts

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Abstract. With the continuous implementation of the dual carbon strategy, the motor vehicle emission control standards keep tightening, and the treatment of the exhaust pollutants during the cold start stage of gasoline vehicles has become a key research topic in the catalysis field. The three-way catalyst (Three-Way Catalyst, TWC), as the core component of the gasoline vehicle exhaust purification, has insufficient catalytic activity at low temperature and low pollutant conversion efficiency under cold start conditions, which has hindered the further upgrade of emission regulations. This paper reviews the internal causes of the deterioration of the three-way catalyst low temperature performance, covering several problems such as the adsorption poisoning on the surface of precious metals, the insufficient oxygen migration capability of the oxygen storage material at low temperature and the competitive adsorption of water vapor. Around three directions, namely the modification of precious metal active components, the modification of the oxygen storage support and the regulation of the metal-support interface interaction, the research progress of the existing modification methods is summarized, with emphasis on the application potential of single atom catalysis, high entropy oxide oxygen storage materials and electrically heated catalytic integration technology in low temperature three-way catalysis. Based on the existing research results, the practical gap between the laboratory conditions and the industrial application is compared, and future research directions such as the development of aging resistant multifunctional catalysts and the computational catalysis assisted material screening are prospected.

Keywords: Three-way catalyst, low-temperature activity, cold start, oxygen storage material, single atom catalysis, high entropy oxide

1. Introduction

1.1. Research background and national strategy

Under the guidance of the strategic goals of "carbon peaking" and "carbon neutrality", mobile source pollution prevention and control has become an indispensable part of atmospheric pollution control work. Motor vehicle exhaust is an important source of urban atmospheric pollutants, and the exhaust control effect directly affects public health, and is also related to the process of the regional ecological environment quality improvement [1]. Gasoline vehicles account for a relatively high

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proportion of the total number of motor vehicles, and whether pollutants in the exhaust such as carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO_x) can be effectively purified is of great significance for urban air quality compliance and the implementation of the dual carbon goals.

The three-way catalyst is the mainstream technical means for the purification of the gasoline vehicle exhaust at the present stage, and in the theoretical air-fuel ratio environment it can complete the catalytic conversion of the three pollutants CO, HC and NO_x at the same time [2]. After more than forty years of technical iteration, the overall technical system of the three-way catalyst has become mature. However, facing the increasingly strict emission regulations and the practical needs of low carbon development, the shortcoming of the catalyst low temperature activity has been continuously prominent, and has become the key technical problem limiting the further improvement of the exhaust purification capability.

1.2. Exhaust emission standards and the cold start bottleneck

The motor vehicle emission regulations of China have been updated step by step from China I to China VI, and the pollutant emission limits continue to tighten [3]. The regulatory requirements keep rising, and the industry also puts forward higher standards for the pollutant emission control under low temperature conditions. Existing relevant studies have proved that, within the standard test cycle, the cold start process is the main source of the HC and CO emissions [4].

The cold start stage refers to the operating period after the vehicle is ignited, when the catalyst bed temperature has not yet reached the light-off temperature (generally about 250 ℃). In this stage, the conversion efficiency of the three-way catalyst for CO, HC and NO_x often fails to reach 30%, and a large amount of unpurified pollutants is discharged directly into the atmosphere [5]. The thermal efficiency of the modern internal combustion engine keeps rising and the overall exhaust temperature of the engine shows a downward trend, which further amplifies the negative impact brought by the cold start emissions. The research of Bartley et al. [6] mentions that the high efficiency internal combustion engine causes a reduction of the exhaust temperature, and the catalyst stays below the light-off temperature for a long time; the traditional close-coupled catalysts and the optimization schemes such as reducing the thermal mass have found it difficult to meet the technical requirements of the future emission regulations.

The large-scale popularization of the hybrid vehicles further raises the performance threshold of the three-way catalyst (TWC) for the low temperature activity. During the driving process of a traditional fuel vehicle, cold start generally occurs only once. The hybrid model is different, the engine starts and stops frequently following the driving conditions, and the catalyst bed temperature fluctuates greatly. After the engine stops and the fuel is cut off, the catalyst loses the high temperature exhaust heat source, and the bed temperature quickly falls back below the light-off temperature; when the engine starts again, the catalyst needs to be reheated until the light-off state is reached, which is equivalent to repeating the cold start process several times in a single driving cycle. The repeated temperature rise and fall directly increases the time proportion of the catalyst running at low temperature and low efficiency during the whole vehicle operation, and the low temperature emission problem has thus become a major difficulty in the exhaust treatment of the hybrid models.

Frequent cold and hot fluctuations pose a double performance test for the three-way catalyst. On the one hand, the warm-up time of the catalyst is compressed, and it needs a lower light-off temperature and a faster light-off rate, so that after the engine restarts the pollutants can be converted with high efficiency in a short time; on the other hand, the repeated cold and hot shocks

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accelerate the sintering and aging of the active components of the catalyst, making the low temperature catalytic performance even worse. The catalyst formulations and the structural schemes developed for the steady state conditions in the past have found it difficult to adapt to the complex and variable temperature conditions of the hybrid models.

1.3. The main content of this review

Around the core contradiction of the insufficient low temperature activity of the three-way catalyst, this paper carries out the review work from the levels of the catalytic reaction mechanism, the material modification methods and the emerging frontier technologies. First, from three angles of the precious metal adsorption poisoning, the kinetic limitation of the oxygen storage material and the competitive adsorption of the water vapor, the internal mechanism by which the three-way catalytic reaction is constrained under the low temperature condition is analyzed; second, the research status of the traditional modification methods such as the precious metal particle size and valence state regulation, the element doping and morphology optimization of the oxygen storage support and the enhanced metal-support interface interaction is summarized; on this basis, the research progress of the single atom catalysts, the high entropy oxide oxygen storage materials and the electrically heated catalytic integration technology in improving the low temperature activity is introduced; finally, the existing difficulties and challenges of the research at the present stage are summarized, and the future research directions are prospected.

2. Limiting factors of the three-way catalytic reaction at low temperature

The deterioration of the low temperature activity of the three-way catalyst is the result of the superposition of multiple factors. Besides reducing the intrinsic kinetic rate of the catalytic reaction, the low temperature environment also changes the available degree of the active sites, the oxygen species supply capacity and the adsorption behavior of the reactant molecules. Multiple factors act together, and finally the catalyst performance drops significantly.

2.1. Precious metals are easily poisoned at low temperature

The platinum group precious metals (Pt, Pd, Rh) are the core active components of the three-way catalyst, and the number of the active sites on the surface of the precious metals and the degree to which they can be contacted directly determine the overall catalytic reaction rate. In the low temperature working conditions, the CO gas undergoes strong adsorption on the surface of the precious metals, occupying a large number of the active sites, so that the other reactant molecules cannot complete the adsorption and activation. This phenomenon is the CO poisoning [7]. Bäröth et al. [8] carried out systematic experiments on the influence of different hydrocarbons on the cold start performance of the three-way catalyst, and the results show that the unsaturated hydrocarbons such as acetylene strongly inhibit the activity of the Pd-based catalyst even at a very low concentration; 70 ppm acetylene can reduce the CO conversion efficiency by 40%. The fundamental reason for the inhibition is that the unsaturated hydrocarbons have a higher adsorption energy than CO and NO, and occupy the active sites on the surface of the precious metals preferentially. At the same time, CO undergoes strong adsorption on the Rh surface and inhibits the dissociative adsorption process of NO, and the dissociation of NO is the rate determining step of the NO_x reduction reaction, which further depresses the NO_x conversion level in the low temperature environment [9].

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2.2. Slow oxygen release of the oxygen storage material at low temperature

The ceria-zirconia composite oxide (CeO_2-ZrO_2) is the most widely used oxygen storage material (Oxygen Storage Material, OSM) in the three-way catalyst, and it completes the oxygen storage and release through the Ce^{4+}/Ce^{3+} redox cycle and plays the role of buffering the fluctuation of the air-fuel ratio [10]. But in the low temperature environment below 250 ℃, the generation of the oxygen vacancies and the migration of the bulk phase oxygen inside the ceria-zirconia solid solution are both subject to the kinetic constraint, and the dynamic oxygen storage capacity (Dynamic Oxygen Storage Capacity, DOSC) of the material shows an obvious attenuation [11]. The related study of Ozawa [12] confirms that the oxygen release behavior of the ceria-zirconia solid solution has a significant temperature dependence. Under the low temperature condition, only the oxygen species on the surface of the material participate in the catalytic reaction, and the bulk phase oxygen is affected by the diffusion resistance and is difficult to transfer to the surface to participate in the cycle; after the temperature rises, the subsurface and the bulk phase oxygen are gradually activated, and then the oxygen storage capacity can be fully exerted. This constraint at the kinetic level causes that under the low temperature state the oxygen storage material cannot fully release the oxygen to oxidize CO and HC, and the air-fuel ratio window in which the catalyst can work normally is narrowed accordingly.

2.3. Competitive adsorption of water vapor and impurities

The proportion of the water vapor in the vehicle exhaust is roughly in the range of 10%-15%, and under the low temperature condition the water vapor significantly interferes with the catalytic performance of the catalyst. The water vapor molecules undergo the competitive adsorption with the reactants on the surface of the catalyst and occupy the active sites, and can also combine with the precious metals to generate the hydroxyl species and change the electronic structure of the active center [13].

Besides this, under the low temperature working condition the incompletely burned hydrocarbons are easy to adsorb and accumulate on the surface of the catalyst, forming the carbonaceous deposits and physically covering the active sites. At the initial stage of the cold start, the high boiling point organic substances such as the aromatic hydrocarbons and the ethanol condense on the surface of the catalyst with a relatively low temperature, and then gradually desorb as the overall temperature of the catalyst rises, showing an obvious desorption peak [8]. This condensation-desorption process further causes the active sites to be blocked in the low temperature stage. The sulfur and phosphorus impurities inside the exhaust, although their content is not high, are easier to adsorb and accumulate on the surface of the catalyst in the low temperature environment, bringing the irreversible chemical poisoning damage [6].

3. Core strategies for improving the low temperature activity of three-way catalysts

Aiming at the various low temperature performance constraint mechanisms mentioned above, the researchers have developed a series of catalyst modification methods, mainly around the three lines of the optimization of the precious metal active components, the modification of the oxygen storage support and the regulation of the interface effect, relying on the multi-scale structure design to realize the improvement of the low temperature catalytic performance (Table 1).

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Table 1. Main limiting factors of the low temperature activity of three-way catalysts and the corresponding improvement strategies

Corresponding problem	Treatment measure
Poisoning of precious metals at low temperature	Particle size control
	Dispersion enhancement
	Valence state regulation
	Chemical state optimization
	Application of single-atom catalysts
Slow oxygen storage and release	Element doping
	Oxygen vacancy regulation
	Morphology and pore structure regulation
	High entropy oxide oxygen storage materials
Competitive adsorption of water vapor and impurities	Application of the precious metal-support interface effect
	Electrically heated catalytic integration technology

3.1. Optimization of the active precious metals

3.1.1. Particle size control and dispersion enhancement

The size of the precious metal particles directly determines the level of the catalytic activity. Reducing the particle size of the precious metal particles and improving the dispersion can expose more surface active sites and increase the number of the active centers available for the low temperature reaction [14]. Anderson et al. [15] prepared a precious metal doped alumina aerogel catalyst, which still maintained a high specific surface area of 290~460 m^2/g after 800 ℃ heat treatment; the light-off temperatures of the Pd/Al_2O_3 aerogel for CO and propylene were as low as 190 ℃ and 220 ℃ respectively, and the precious metal loading was only about 10% of that of the traditional catalysts.

Liu Licheng et al. [16] used the ultrasound assisted membrane diffusion reduction method to prepare the Rh based nanocatalysts, the average particle size of the metal particles is less than 3 nm, and the dispersion can reach 45.3%; the low temperature activity of this catalyst for the CO oxidation and the NO reduction is obviously better than the samples prepared by the ordinary impregnation method. However, the precious metal nanoparticles themselves have poor thermal stability, the particles agglomerate in the high temperature aging process and the number of the active sites decreases, which is still a practical problem to be solved.

3.1.2. Valence state regulation and chemical state optimization

The chemical valence state of the precious metals has an obvious influence on the low temperature catalytic performance. Taking the Pd-based catalyst as an example, the proportion of PdO and the metallic Pd directly changes the reaction path and the reaction rate of the CO oxidation and the NO reduction [17]. Existing studies have confirmed that the PdO species are more favorable for the low temperature CO oxidation reaction, while the metallic Pd is more suitable for the NO dissociative adsorption. By adjusting the pretreatment process and changing the properties of the support, the

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distribution of the Pd oxidation state can be regulated, so that multiple pollutants are converted with high efficiency at the same time under the low temperature conditions.

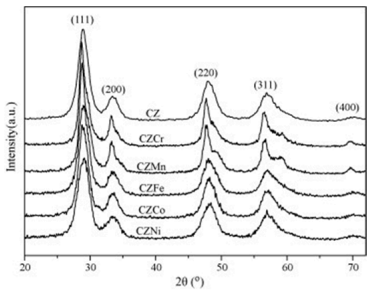
Ichikawa et al. [18] developed a three-way catalyst with a low light-off temperature, adding the Pr compounds to improve the low temperature oxygen storage capacity of the ceria-based materials, and introducing Ba as the thermal stabilizer to inhibit the sintering of the precious metals; after the sample was aged at 1100 ℃, the light-off temperature can be reduced by 90 ℃. This multi-component synergistic regulation idea both ensures that the precious metals maintain a highly dispersed state and adjusts the valence state distribution of the precious metals, taking both the low temperature activity and the thermal stability of the catalyst into account.

3.2. Modification of the oxygen storage support materials

3.2.1. Element doping and oxygen vacancy regulation

Introducing the third and the fourth element into the ceria-zirconia solid solution is an effective way to improve the low temperature oxygen storage performance of the material. The doping of the rare earth elements or the transition metal elements causes the lattice distortion, lowers the formation energy of the oxygen vacancies and promotes the oxygen migration and release under the low temperature condition.

Yang et al. [19] investigated the modification effect of the Nd doping on the CeO_2-ZrO_2 solid solution. After the Nd doping, the oxygen storage capacity and the thermal stability of the material are improved, and the light-off temperatures of the fresh sample for CO, C_3H_6 and NO decrease by 20~30 ℃. Li et al. [20] systematically studied the changes brought to the performance of the $Pd/Ce_{0.67}Zr_{0.33}O_2$ catalyst by the doping of several transition metals Cr, Mn, Fe, Co and Ni; the experiments prove that the Fe and Co doping can generate a ternary Ce-Zr-M-O solid solution with a uniform composition, improve the oxygen migration rate and the oxygen storage capacity, reduce the light-off temperature of the catalyst and at the same time widen the air-fuel ratio window (Figure 1).



(a)

Sample	Average pore diameter (nm)	S_{BET}(m^2/g)	Crystallite size (nm)	Lattice parameter (nm)
CZ	20.87	122.0	7.9	0.5407
CZCr	21.54	110.4	9.1	0.5389
CZMn	20.98	124.9	8.5	0.5377
CZFe	22.83	121.0	7.6	0.5336
CZCo	23.86	110.5	7.4	0.5356
CZNi	19.38	154.8	7.8	0.5386

(b)

Figure 1. (a) XRD characterization results of the transition metal doped material (b) analysis of the lattice parameters, the grain size and the effective working surface area of the catalyst [20]

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Yuan et al. [21] synthesized the four-component rare earth oxygen storage material $Ce_{0.45}Zr_{0.45}La_{0.05}Y_{0.05}O_x$, and even after 1050 ℃ high temperature aging the oxygen storage capacity can still reach 284.3 μmol/g and the cubic crystal phase structure remains intact; the catalyst prepared with this material as the support can meet all the requirements of the Euro III emission standard.

3.2.2. Morphology and pore structure regulation

The morphology of the support and the pore structure directly affect the diffusion and the mass transfer of the reactant molecules, and at the same time they relate to the exposure of the active sites. Preparing the oxygen storage materials with the characteristics of the large specific surface area and the mesoporous structure can improve the diffusion conditions of the reactants under the low temperature working condition and raise the actual utilization rate of the active sites [22].

Chang et al. [23] developed the $Al_2O_3/CeO_2/ZrO_2$ composite oxide. Compared with the traditional ceria-zirconia solid solution, this material has a higher low temperature oxygen storage capacity and a better thermal stability performance; the low temperature three-way catalyst developed on the basis of this material shows an obvious drop of the light-off temperature on the vehicles with a relatively low exhaust temperature. Adjusting the grain size and modifying the pore structure can, under the premise of guaranteeing the thermal stability, raise the number of the surface active sites as much as possible, so as to improve the low temperature catalytic performance.

3.3. Utilization of the precious metal-support interface effect

The interface region formed by the contact of the precious metals and the oxygen storage support belongs to the highly active sites of the three-way catalytic reaction; the strong metal-support interaction (Strong Metal-Support Interaction, SMSI) generated at the interface position can accelerate the oxygen transfer and the activation process, and plays a decisive role in the low temperature catalytic activity [24].

Golunski et al. [25] carried out a systematic study on the origin of the low temperature three-way activity of the Pt/CeO_2 catalysts. The reducing atmosphere induces the strong metal-support interaction, and part of the reduced ceria migrates and wraps onto the surface of the platinum particles, generating a ceria-based thin layer with a strong reducibility. Although this thin layer covers part of the original active sites of the platinum, it generates a batch of new active sites that can work at the low temperature, and the support material itself also participates in the catalytic reaction. This study updates the original cognition and also provides a new idea for regulating the interface effect.

The subsequent experiments of Shen et al. [26] further confirmed that the interface formed by Pd and the ceria-zirconia oxide can accelerate the oxygen spillover and the reverse spillover processes and significantly improve the dynamic oxygen storage capacity of the material. The oxygen species at the Pd-(Ce,Zr) O_x interface position have a higher reaction activity, and the CO oxidation reaction follows the two-step reaction mechanism of the oxygen migration-adsorption. Adjusting the distribution ratio of the precious metals on the two supports of the oxygen storage material and the alumina can increase the number of the interface sites and simultaneously improve the low temperature oxygen storage performance and the three-way catalytic effect.

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4. Frontier materials and technologies for low temperature three-way catalysis

With the rapid development of the catalytic science and the material technology, a series of emerging materials and technologies provide the new possibilities for breaking through the low temperature activity bottleneck of the three-way catalyst. The frontier directions such as the single atom catalysis, the high entropy oxide and the electrically heated integration show the great application potential from three dimensions, namely the atomic level active site design, the development of the new oxygen storage materials and the external field assisted heating.

4.1. Application of single atom catalysts

The single atom catalyst (SingleAtom Catalyst, SAC) highly disperses and fixes the precious metals on the surface of the support in the form of the isolated single atoms. The atomic utilization of the precious metals is close to 100%, which provides a new path for reducing the precious metal dosage and improving the low temperature catalytic activity [27].

Qiao et al. [28] formally proposed the concept of the single atom catalysis in 2011 and prepared the Pt_1/FeO_x single atom catalyst, which showed the outstanding activity and stability for the CO oxidation reaction. Since then, the single atom catalysis has been widely applied in the research related to the three-way catalysis. Khivantsev et al. [9] prepared the atomically dispersed Rh/CeO_2 catalyst, in which the NO can be completely converted under 120 ℃ and the turnover frequency (TOF) can reach 330 h^{-1}; under the condition that the water vapor exists in the system, the low temperature activity is further improved and the NO conversion can already be observed at 50 ℃. Such atomically dispersed Rh sites can reduce the use of the precious metals, and with their special electronic structure and coordination environment they can also realize the low temperature reaction characteristics that the traditional nanoparticle catalysts do not have.

Peterson et al. [29] realized the stable dispersion of the Pd single atoms on the γAl_2O_3 support commonly used in the industry. The sample can undergo the CO oxidation at 40 ℃, and the performance can be recovered after the treatment in the 700 ℃ air atmosphere; the lanthanum co-doping means can stabilize the single atom Pd species and improve the resistance to the thermal aging. The research of Zhao et al. [30] shows that the Pt single atom catalyst supported on the high entropy oxide relies on the strong interaction brought by the PtOM chemical bond, shows an excellent hydrothermal aging stability, and the long-term reaction time of the CO oxidation exceeds 540 h, which has the potential to move toward the practical application.

However, the use of the single atom catalysts in the three-way catalytic systems still faces many practical difficulties. Under the high temperature reduction condition the single atom sites are easy to agglomerate, the evolution law of the activity under the complex exhaust conditions is not yet clear, and the comprehensive efficiency of the catalyst in converting multiple pollutants at the same time still needs deeper exploration.

4.2. High entropy oxide oxygen storage materials

The high entropy oxide (High Entropy Oxide, HEO) generally contains five or more metal elements, and the metal components are in the equimolar or near equimolar ratio and form the single phase solid solution. The high configurational entropy gives the material the unique structural stability, the physical and chemical properties have a large adjustable space, and it has received the wide attention in the catalysis field [31].

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Riley et al. [32] prepared the ceria based high entropy oxide catalyst, introducing the multiple metal components of Al, Fe, La, Mn and Zr. Without adding the precious metals it already has a certain CO oxidation catalytic ability. In the high temperature environment the material still maintains the fluorite single phase structure, and the specific surface area reaches 138 m^2/g, which is better than most of the high entropy oxides prepared by the conventional processes. The test results show that the transition metal cations are mainly responsible for improving the catalytic activity and the rare earth cations guarantee the thermal stability of the material; the multi-component synergistic design can balance the catalytic performance and the structural stability.

Zhang et al. [33] combined the theoretical calculation with the experimental verification and confirmed that the configurational entropy can regulate the concentration of the oxygen vacancies inside the oxide. The number of the oxygen vacancies in the five-element high entropy oxide is significantly higher than that in the uni-element and the binary oxide, and the reduction temperature of the transition metal ions decreases overall. The material itself carries the high concentration of the oxygen vacancies, which makes the high entropy oxide have the potential to become the low temperature oxygen storage material with the excellent performance. Huang et al. [34] found through the observation with the spherical aberration electron microscope that there are a large number of the oxygen vacancies on the surface of the high entropy oxide particles, whether in the oxidizing or the reducing atmosphere; at the same time the dynamic structural reconstruction can occur on the surface, which is also an important internal cause of its outstanding catalytic performance. Albedwawi et al. [35] mentioned in the review literature that the high entropy oxide has the high oxygen migration rate, the rich oxygen vacancies and the good dispersion degree of the metal components, and its performance in the thermal catalysis, the electrocatalysis and the photocatalysis is better than that of the traditional oxide. Using the high entropy oxide as the oxygen storage component of the three-way catalyst is expected to alleviate the insufficient oxygen migration kinetics of the traditional ceria-zirconia solid solution at the low temperature.

It should also be seen that the multi-component design of the high entropy oxide brings the difficulties at the level of the engineering application. The simultaneous synthesis process of the multiple components is complex, and the cost of the raw materials is higher than that of the traditional ceria-zirconia material; in the large scale batch preparation, the phenomenon of the uneven element distribution is easy to appear, and the performance reproducibility under the mass production condition needs to be further optimized. But as a new generation of the oxygen storage material that breaks through the traditional oxide design idea, its intrinsic performance advantage is very prominent, and the preparation process still needs to be continuously optimized.

4.3. Electrically heated catalytic integration technology

From the point of view of the system engineering, relying on the external energy input to accelerate the temperature rise of the catalyst is the direct technical solution to the cold start emission problem. The electrically heated catalyst (Electrically Heated Catalyst, EHC) uses the onboard power supply to generate the heat through the energization, and raises the catalyst bed temperature above the light-off temperature in a short time [36].

Whittenberger et al. [37] developed a resistive heating metal substrate converter, which relies on the traditional 12 V onboard electrical system and can heat the catalyst to the 350 ℃ light-off temperature within 30 s; combined with the secondary air injection technology, the reduction of the HC and CO emissions in the cold start stage can exceed 50%. As the electrification level of the whole vehicle keeps rising, the onboard power supply capability is enhanced, creating the favorable conditions for the large scale implementation of the electrically heated catalysts. Hamedi et al. [38]

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carried out a comparative experiment, adopting the intermittent heating strategy with the pulse width of 30 s and comparing it with the continuous heating mode, and the conversion efficiencies of CO and THC are improved by 34% and 31% respectively, with the energy utilization efficiency obviously improved. Duan Lishuang et al. [39] carried out the experiments on the diesel engine bench, where the electrically heated catalyst can shorten the time for the exhaust temperature after the DOC to reach 138 ℃ by 767 s; under the cold start low load condition, the total conversion efficiencies of CO and HC are improved by 92.8% and 50.8% respectively.

Ning et al. [40] proposed the Bangbang and active disturbance rejection composite control strategy, realizing the precise temperature regulation in the preheating and the post heating stages of the electrically heated catalyst and providing the algorithmic support for the system optimization. Velmurugan et al. [41] built the simulation analysis framework, providing the tool for the development and the evaluation of the cold start control strategy of the whole vehicle equipped with the electrically heated three-way catalyst. The electrification level of the hybrid vehicles keeps rising, and the electrically heated catalytic integration technology is expected to become an important technical route to solve the cold start emission.

5. Conclusion and prospects

A large number of the results have been accumulated in the research on the enhancement of the low temperature activity of the three-way catalyst, but there is still an obvious gap between the excellent performance obtained under the laboratory simulated conditions and the real running conditions of the vehicles [42, 43].

The first is the performance degradation caused by the high temperature aging. During the actual running of the vehicle, the catalyst repeatedly experiences the alternating action of the high temperature environment and the oxidizing and reducing atmosphere. The aging phenomena such as the sintering and the growth of the precious metal particles, the crystal phase transition of the oxygen storage material and the collapse of the pore structure are hard to avoid, and directly cause the low temperature catalytic activity to keep deteriorating.

The second is the poisoning failure caused by the complex exhaust components. The real exhaust contains the impurities such as the sulfur, the phosphorus and the lead, and the ash generated by the combustion of the lubricating oil gradually accumulates on the surface of the catalyst, bringing the chemical poisoning damage; the poisoning effect is further aggravated in the low temperature environment. Most of the laboratory evaluations use the simulated reaction gases with the simple components, and it is difficult to reproduce the poisoning and the degradation process under the real working condition.

Besides this, the engineering problems such as the catalyst preparation cost, the feasibility of the large-scale production process and the matching between the catalyst and the vehicle control system also restrict the implementation of the new technologies. The frontier materials such as the single atom catalysts and the high entropy oxides are still at the stage of the laboratory research at present, and there is still a considerable gap to the industrial application.

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