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Original Research

Research on Emission Reduction Properties of Cerium Zirconium Composite Oxides on PM and NO_X of Diesel Engines

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Abstract

This paper studies the emission reduction properties of carbon smoke particles (PM) and nitrogen oxides (NO_X) using cerium zirconium composite oxides. Firstly, the cerium-zirconium composite oxides catalysts were prepared and analyzed by XRD, SEM, ICP and BET. Then the exhaust catalytic treatment experiment was carried out on the self-built Changchai CZ2102 diesel engine test bed. The exhaust temperature of diesel engine was raised to 500ºC by using temperature programmed technology to simulate the exhaust condition of Marine diesel engine to ensure the experimental data is more accurate. Finally, lanthanum was added into the cerium zirconium composite oxide to modify the catalyst to improve its catalytic performance. The exhaust treatment experiment was carried out again, and the experimental data were compared and analyzed Studies show that cerium zirconium composite oxides of NO_X and PM are with high catalytic efficiency which can be further improved after adding lanthanum elements. Therefore, this diesel engine post-treatment technology has a great development prospect.

Keywords: catalyst, catalytic efficiency, lanthanum, pollution

Introduction

Pollution has become a problem on a global scale and poses a significant risk in terms of human health and natural ecosystems. There are more and more studies on environmental pollution by scholars at home and abroad.

Mehmet Cetin et al. [1] studied the effect of indoor plants on indoor CO_2 concentrations under certain light conditions. Five indoor plants were placed in a glass-walled compartment to measure carbon dioxide levels. The glass compartments used in the study were positioned to provide an illuminated environment while protecting against direct sunlight. The plants were placed in a confined space with a glass wall of approximately 0.5 m^3 (0.7 m x 0.7 m x 1 m) in volume. The CO_2 measuring device in the compartment is arranged to measure CO_2 every 5 minutes. The study found that all plants reduced their carbon dioxide levels to some extent during the day.

The aim of this study of Aydin Turkyilmaz et al. [2] was to determine the variation of heavy metal concentrations with traffic density in some landscape plants sampled in areas with different traffic densities.

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The results showed that different plant species and traffic density had different concentrations of heavy metals.

In the study of Elif Bozdogan Sert et al. [3], the aim was to find out the metals that were accumulated in rosemary leaves and stems and the rosemary leaves. The leaves and the stems were to be used as a biomonitors to reveal the rate of metal pollution along the highway. Their findings concluded that the rosemary could have a decent capacity to accumulate Al, Cd, Cr, Cu, Fe, Mn, Pb, and Zn in both leaves and stem. Therefore rosemary officinalis is a great tool in determining the amount of traffic-related pollution in urban areas.

Hakan Sevik et al. [4] considered edible landscaping posed a considerable risk. Heavy metal accumulation in plants grown in urban centers could reach to high levels, and consuming these plants would allow these heavy metals a direct access into the human body and wreak havoc to the public health.

Hakan Sevik et al. [5] think the use of tree rings as biological monitors is one of the most effective ways to measure changes in heavy metal concentrations in the atmosphere. Perennial plants in their country form annual rings, and by measuring the concentration of heavy metals in these annual rings, the information about the change of heavy metal concentration in this region could be gotten.

Mehmet Cetin et al. [6] think measuring regional and temporal changes of air pollution by scientific studies will guide the determination of the precautions to avoid negative effects of air pollution on people's health. The purpose of this study is to evaluate the air quality based on CO_2 amount and amount of particulate matter in 6 different dimensions, and to determine the change in sound level on a regional basis depending on the time of day and the season in different areas of Bursa city center. The results of their study show that the effect of season on noise and CO_2 was statistically insignificant.

Mehmet Cetin [7] thinks the indoor amount of CO_2 is over 1000 ppm, which in turn, could directly affect the performances of the candidates directly via headache, dizziness, fatigue, and a loss of concentration. In this study, changes in the indoor amount of CO_2 in some central exam were examined, and certain evaluations were made. The findings of the present study indicate that the threshold value is usually exceeded within 10 minutes, following the start of exams, and when indoor CO_2 amounts are higher than 1500 ppm, which is considered in most exams as the limit of harm to health, and circulating air in the hallways and keeping the doors of exam halls open throughout the exam period are not adequate for keeping the indoor CO_2 amounts below 1000 ppm. Air circulation is a must in exam halls to ensure healthy exam environments.

Mehmet Cetin et al. [8] studied the effects of cave air quality on visitors' health. It measures the amount of carbon dioxide and particulate matter. The results showed that carbon dioxide levels increased rapidly from the entrance to the cave. This result can be interpreted to mean that indoor air quality may change when visitors visit, and some health problems may arise, especially due to the effects of increased carbon dioxide levels. As a result, this change may cause some headaches, dizziness, throat and nose irritation, sneezing, coughing, and tears.

Mehmet Cetin et al. [9] think urban parks are very important for the healthy development of a city. The urban parks have many different functions for the city, such as recreation, ecology and land organization. One function is their impact on urban air quality.

In addition to the traffic pollution to the city, the pollution of Marine environment by ships is becoming more and more serious, especially the PM and NO_X emitted by the combustion of Marine diesel engines, which pose a serious threat to the environment and human health. The pollutants from marine diesel engine contain a large amount of NO_X which will stimulate the human lungs, making it more difficult to resist respiratory diseases such as cold.

At present, the common means to reduce the combustion temperature of carbon particles is to reduce the emission of carbon particles by catalytic oxidation reaction with the help of catalytic performance of catalyst. At the same time, most of the research methods to remove NO_X from Marine diesel engines adopt catalytic reduction method, which is to reduce the high-priced state of NO_X to the low-priced state of N and convert it to N_2 to achieve harmless emission. How to remove carbon particles PM and NO_X at the same time has been studied by both domestic and overseas scholars.

Dhal Ganesh Chandra et al. [10] proposed that NO_X and particulate matter are difficult to remove from diesel exhaust. Since engine modification alone cannot reduce NO and soot particulate emissions to allowable levels, post-treatment activities that reduce emissions at the same time should be developed.

Prasad Ram et al. [11] reviewed many types of catalysts that have been studied to control both black carbon particles PM and NO_X. These types of catalysts include platinum group metals (PGM, Pt, Pd, Rh, Ir) based oxides, spinel type oxides, hydrotalcite type oxides, rare earth metal oxides, mixed transient metal oxides, etc.

Zeng Lirong et al. [12] synthesized silver-supported cerium-based catalysts by sol-gel method. The properties of the catalysts were investigated by TG, H_2-TPR, XRD, SEM, TEM, BET and XPS. The results show that Ag nanoparticles are successfully loaded onto the surface of CeO_2, and the relative content of Ag nanoparticles is about 10.22 wt.%, close to the theoretical value (10%).

Li Qian et al. [13] showed that both NO_2 and nitrate contributed greatly to the influence of NO_X on soot combustion activity in cerium doped catalysts. As the doping agent Ce increases, more NO_2 is produced. After the introduction of appropriate amount of Ce, the resulting NO_2 was stored in the form of bridging double-dentate nitrate at Mn-Ce sites, confirming that the reaction activity of NO_2 with soot at Mn and/or Ce sites was higher than that of nitrite or monodentate nitrate. In conclusion, $Mn_{0.5}Mg_{2.5}Ce_{0.1}Al_{0.9}O$ is considered to be the most potential catalyst for soot combustion.

Wang Jianqiang et al. [14] discussed the reaction principle of diesel vehicle oxidation catalytic technology, including the reaction mechanism of CO oxidation, HC oxidation and NO_X oxidation; and reviewed the deactivation mechanism of diesel vehicle oxidation catalyst, including thermal deactivation, chemical deactivation and regeneration mechanism, was reviewed. Finally, they forecasted the development of oxidation catalytic technology for diesel vehicles.

Leandro Fontanetti Nascimento et al. [15] studied the application of solid lanthanum-cerium zinc catalyst in the catalytic regeneration of diesel particulate filter (DPF) for diesel engines. Mixed-oxide CeO_2-ZnO-La_2O_3 (Ce-Zn-La) was synthesized by sol-gel method mediated by lactic acid. The oxide can effectively encase cordierite substrate for the capture and combustion of soot. Thermogravimetric and differential thermal analysis (TGA/DTA) confirmed that the catalyst effectively reduced the oxidation temperature of soot. The Ce-Zn-La ternary mixed oxide catalyst with Ce/Zn/La atomic ratio of 2:1:0.5 has the highest catalytic activity below 390ºC, which promotes the oxidation of soot. This indicates that a large number of oxygen vacancies in the catalyst structure produce oxygen species at low temperature. Raman spectroscopy results show that there are oxygen vacancies and lattice defects in Ce-Zn-La samples, which are the key parameters affecting the stability and REDOX performance of the catalyst.

Nataliia O. Popovych et al. [16] studied effects of CeO_2 and Al_2O_3 on catalytic activities of NO, CO and C_nH_m over Pd/Co_3O_4/cordierite catalysts. The results show that the effect of CeO_2 on the performance of Pd/Co_3O_4/cordierite catalyst is related to the preparation method. The addition of CeO_2 improved the SO_2 resistance of Pd/Co_3O_4/cordierite. In the reaction of CO and C_nH_m with oxygen, the activity of Pd/Co_3O_4/cordierite catalyst decreases due to the formation of $CoAl_2O_4$ by the second support.

Yu Hualiang [17] studied simultaneous catalytic removal of NO_X and PM from diesel engine with copper-iron type catalyst. In this study, the exhaust environment of diesel engine was simulated, programmed temperature reaction technology was adopted and the PM in diesel engine exhaust gas was simulated with carbon black. Composite metal oxides were used as catalysts to make the carbon black and NO_X REDOX each other on the same catalytic bed to realize the simultaneous catalytic removal of pollutants. The relationship between catalyst structure and performance was revealed by using various modern analytical techniques, and the mechanism of simultaneous catalytic removal of carbon black and NO_X was analyzed.

Although domestic and foreign scholars have studied the use of catalytic materials to remove soot particles PM and NO_X of diesel engines at the same time, their PM oxidation activity temperature is high, the reduction rate of NO_X is low, and the catalytic materials used are expensive, which fails to meet the requirements of engineering application. Due to the low price and special properties of rare earth materials, the research objective of this paper is to use rare earth materials catalyst to further reduce the oxidation activity temperature of PM and improve the reduction rate of NO_X. The research of this paper has great engineering application value for diesel emission reduction.

Material and Methods

Mechanism of Simultaneous Catalysis of PM and NO_X in Diesel Engines

Removal Reaction Model of Soot Particles PM [18]

$$O_2 + 2^* = 2O^* \tag{1}$$

$$C + 2O^* = CO_2 + 2^* \tag{2}$$

$$C + CO_2 = 2CO \tag{3}$$

$$C + NO_2{}^* = 2CO^* + N_2 \tag{4}$$

$$CO^* + O^* = CO_2 + 2^* \tag{5}$$

Reduction Mechanism of NO [19]

The reduction mechanism of NO is not clear, and there are mainly three explanations as follows.

The first explanation is that after NO is adsorbed on the active site, the NO molecule is decomposed into nitrogen atom and oxygen atom. The nitrogen atom adsorbed on the adjacent active site combines to form nitrogen molecule, while the remaining oxygen atom combines with the activated CO molecule adsorbed on the adjacent active site to form carbon dioxide.

$$CO + \ {}^* = CO^* \tag{6}$$

$$NO + \ {}^* = NO^* \tag{7}$$

$$NO^* + \ {}^* = N^* + O^* \tag{8}$$

$$N^* + N^* = N_2 + 2^* \tag{9}$$

$$N^* + NO^* = N_2 + O^* + \ {}^* \tag{10}$$

$$N^* + NO^* = N_2O + 2^* \tag{11}$$

$$O^* + CO^* = CO_2 + 2^* \quad (12)$$

The second explanation is that NO and CO are adsorbed on the active site, and the intermolecular reaction occurs after activation to generate carbon dioxide and N atoms adsorbed on the active site, and the active N atoms combine in pairs to form nitrogen molecules. The adsorption models for CO and NO are consistent with the adsorption Equations (6) and (7).

$$CO^* + NO^* \rightarrow CO_2 + N^* + \quad ^* \quad (13)$$

$$2N^* \rightarrow N_2 + 2^* \quad (14)$$

The third explanation is that the NO molecule adsorbed at the adjacent active site reacts to generate N_2 and two oxygen atoms adsorbed at the active site, and the oxygen atom in the adsorbed state combines with the CO in the adjacent adsorbed state to generate CO_2. The adsorption models for CO and NO are consistent with the adsorption Equations (6) and (7).

$$2NO^* = N_2 + 2O^* \quad (15)$$

$$2NO^* = N_2O + O^* + \quad ^* \quad (16)$$

$$O^* + CO^* = CO_2 + 2^* \quad (17)$$

Preparation of Cerium-Zirconium Composite Oxide Catalyst Powder

Cerium-zirconium composite oxides were prepared by co-precipitation method. Co-precipitation method [20, 21] is one of the common methods for the preparation of cerium-zirconium composite oxides. It is to add precipitator to a variety of metal salt mixed solution for co-precipitation, and then obtain the final product through filtration, washing, drying, roasting and other processes. For cerium-zirconium composite oxides, water-soluble salts of cerium-zirconium are generally used as rare earth sources. Ammonia water is a common precipitant in co-precipitation method. In general, co-precipitation method is simple, low-cost, low equipment requirements, can be used for large-scale industrial production.

In this experiment, $Ce(NO_3)_3$•$6H_2O$ and $Zr(NO_3)_4$•$5H_2O$ were used as rare earth sources, ammonium bicarbonate was used as precipitator, and hexadecyl trimethyl ammonium bromide was used as surfactant to prepare target powders. Fig. 1 shows the flow chart of preparation of cerium-zirconium composite oxides.

According to the ratio of monomer oxide calculation, the molar ratio of various chemical compounds (CeO_2):(ZrO_2) of target powder is 7:3, according to the calculation results, the corresponding quality of Ce $(NO_3)_3$•$6H_2O$, Zr $(NO_3)_4$•5 H_2O is taken. To prepare two bottles of the corresponding original solution using deionized water as solvent, a bottle of adding rare earth nitrate and some quantity hexadecyl trimethyl ammonium bromide, the mixture of rare earth cation concentration is 0.5 mol/L, another bottle of ammonium bicarbonate solution concentration is 1 mol/L. The two solutions were magnetically stirred at room temperature to fully dissolve the solute. The pH of NH_4HCO_3 solution is adjusted to about 8.5 by titration with ammonia. At a constant temperature of 70°C, continuous magnetic stirring is carried out. Using ammonium bicarbonate

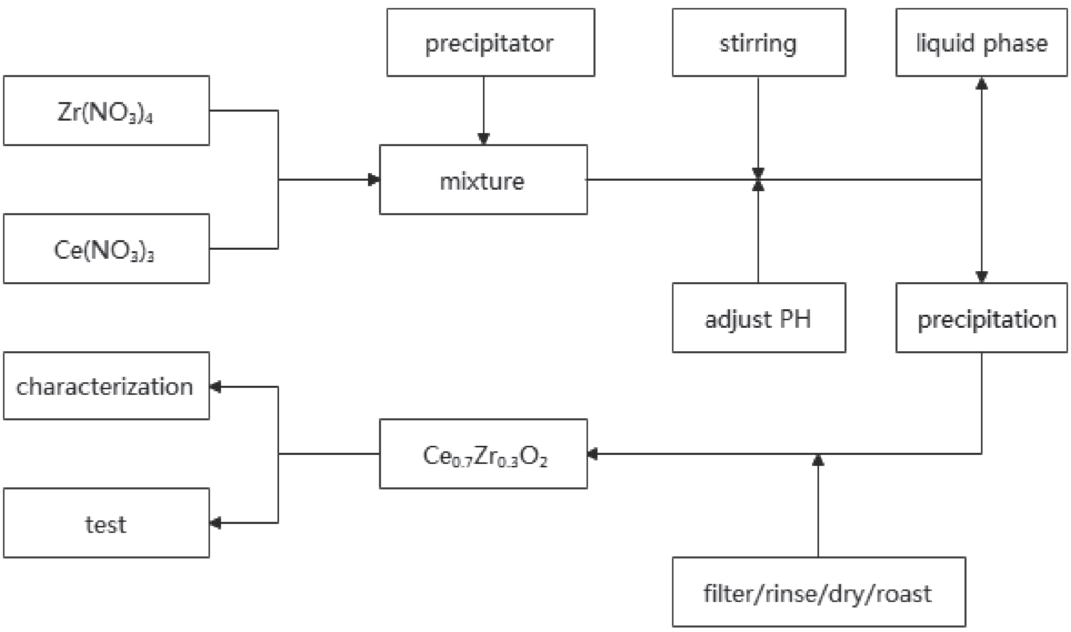

Fig. 1. Preparation flowchart of cerium-zirconium composite oxides.

solution as titrant, the solution is slowly dropped into the rare earth salt solution until the titration was excessive. The pH value of the solution is adjusted to 8-8.5. The reaction temperature is maintained and the magnetic stirring is continued. After a certain time of continuous reaction, the precipitate is filtered. First, the deionized water is rinsed repeatedly, and then the anhydrous ethanol was rinsed. Then the target powder is obtained by drying for 1 hour at the temperature of about 100ºC and roasting for 4 hours at 500ºC in muffle furnace. The theoretical chemical formula of catalyst powder is $Ce_{0.7}Zr_{0.3}O_2$.

Results and Discussion

Characterization of Catalytic Performance of Cerium-Zirconium Composite Oxide Catalyst

X-ray Diffraction Analysis (XRD)

An appropriate amount of cerium-zirconium composite oxide powder is taken into the glass tank of the sample, evenly coated and pressed with a glass cover, and then placed in the X-ray diffractograph for experiment. The X-ray diffraction pattern obtained is shown in Fig. 2.

Four diffraction peaks can be seen from the graph in Fig. 2. The diffraction angles 2θ are respectively 28.34, 32.46, 46.63 and 56.78, and there is a diffraction peak with high intensity at 2θ=28.34. The results showed that the cubic fluorite structure existed in the sample, which was helpful for oxygen storage and release. There is no obvious impurity peak and less impurity in the chromatogram, so the preparation results are relatively successful.

Scanning Electron Microscopy Analysis (SEM)

An appropriate amount of cerium-zirconium composite oxide powder was taken to dry in a drying oven at 60ºC for 1 hour, and then the scanning electron microscope experiment was carried out. The SEM photos are shown in Fig. 3.

It can be observed from the SEM diagram of Ce-Zr composite oxides that the particle size distribution of Ce-Zr composite oxides is not uniform, both small and large particles exist, and the shape of large particles is irregular. Therefore, it can be concluded that the growth of grains is not uniform and a small amount of agglomeration occurs, but the overall distribution of grain size is small. In general, the catalyst powder prepared meets the design requirements.

Inductively Coupled Plasma Spectrometer (ICP)

Table 1 shows the ICP measurement data of (Ce, Zr)O, which represents the actual elements and corresponding contents of the powder, namely the chemical composition of (Ce, Zr)O. According to the analysis of the measured data, the deviation between the actual content of Ce and the design value is great, which is less than the design value. The difference between the actual content of Zr and the design value is small. From the aggregate data, in addition to Ce and Zr, the powder also contains 4.37% of other substances, such impurity elements may be from the rare earth sources, the purity of each reagent used in the test, test equipment and operation methods, which will cause the preparation error. The prepared powder contains less impurities, and the actual content and proportion of Ce and Zr deviated little from the design value, which is within the allowable error range. Therefore, the prepared powder can basically meet the design requirements. The catalyst is defined as $Ce_{0.7}Zr_{0.3}O_2$ according to the design value of the stoichiometric ratio of each component.

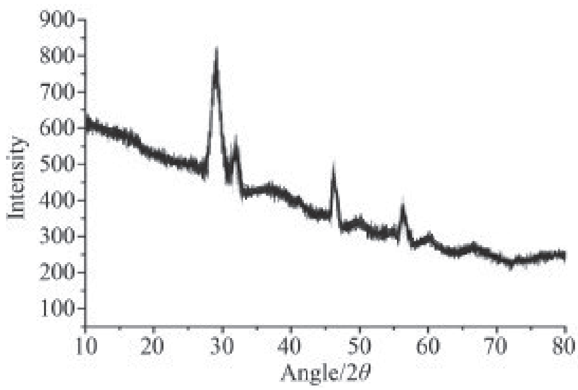

Fig. 2. XRD image of cerium-zirconium composite oxides.

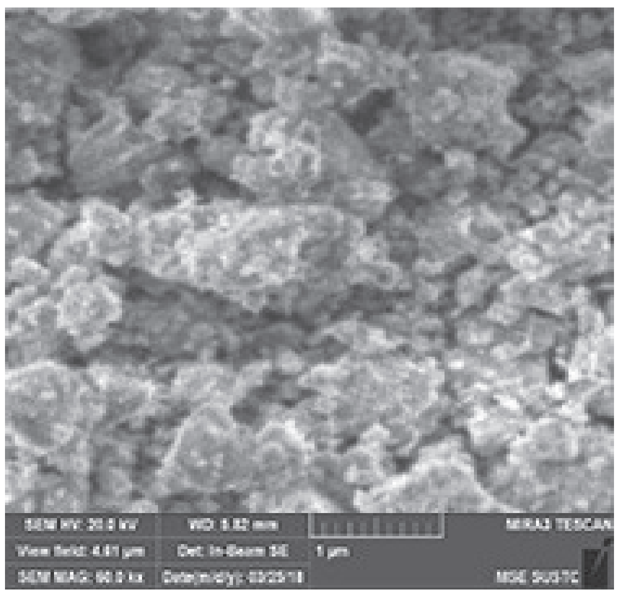

Fig. 3. SEM image of cerium-zirconium composite oxides.

Table 1. Chemical composition quantitative analysis table.

Composition	Test content %	Design content %	Error %
CeO_2	66.78	70	-4.6
ZrO_2	28.63	30	-1.37
$Ce_{0.7}Zr_{0.3}O_2$	95.41	100	-4.37

Table 2. BET testing data.

Specific surface area (m^2/g)	Pore volume (cm^3/g)	Aperture (nm)
41.65	0.0147	3.286

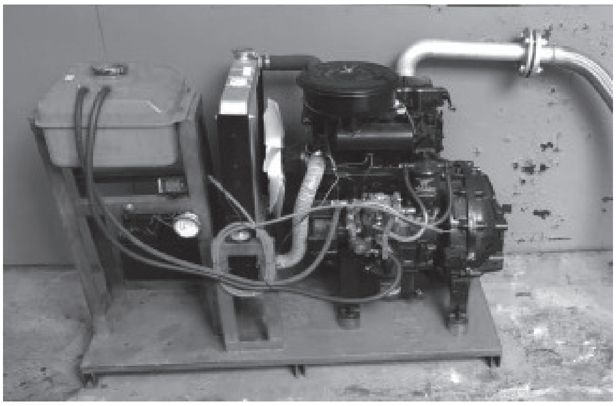

Fig. 4. Changchai CZ2102 diesel engine.

Specific Surface Area Analysis (BET)

After detection and calculation via the specific surface area analyzer, the results that the specific surface area of the sample is 41.65 m^2/g can be concluded, as shown in Table 2. Due to the low precision of the equipment and limited time, the sample particle can only reach the micron level, and its specific surface area is not too high, but the sample particle generally meets the design requirements of this experiment, and the self-made catalyst powder is relatively successful.

Emission Reduction Test of PM and NO_X of Diesel Engine by Ce-Zr Composite Oxide

The diesel engine used in this bench test is produced by Changchai Co. Ltd and its model is CZ2102, as shown in Fig. 4. Its main technical parameters are shown in Table 3. The detection instruments are shown in Table 4.

Table 3. Parameters of Changchai CZ2102 diesel engine.

Item	Parameters
Type	CZ2102
Series	102
Number of cylinders	2
Cylinder diameter × stroke	102mm×118mm
Total emissions	1.928L
Air intake form	Naturally aspirated
Cylinder arrangement	Inline
Injection way	Direct injection
Cooling way	Water cooled
Maximum output power	29kw
Rated speed	2800rpm
Net weight	215kg
Emission standards	Country 2 / Euro 2
Diesel engine size	550×580×730mm
Maximum horsepower	40 horsepower

Emission reduction experiment proceeded in a standard atmospheric pressure and 16ºC experiment environment, the engine was started and stable for a period of time, the program temperature controller was used to automatically control heating and cooling process, and could be achieved with temperature rise rate of 1-10ºC/min, the flue gas temperature would be heated to 500ºC, then the main composition content of diesel engine exhaust pollutants could be detected (the test data are shown in Table 5). Table 5 shows the composition content of exhaust pollutants before catalysis. After adding the catalyst, PM and NO_X content was measured at an interval of 5 minutes, and the data were recorded and plotted as a curve, as shown in Fig. 5, Fig. 6, Fig. 7, and Fig. 8.

It can be seen from Fig. 5 and 6 of PM content that the catalytic oxidation of PM started at about 200ºC, and PM content reached the lowest level at about 450ºC, and then the PM content gradually increased again. This indicates that the self-made catalyst has poor high temperature resistance, which leads to local agglomeration and sintering, and results in reduced catalytic activity.

Table 4. Testing instrument.

Instrument name	Type	Range	Manufacturer
NOx detector	DSA2000-NOx	0-1000ppm	Qingdao Dasen environmental protection equipment Co., LTD
Multi-gas detector	PV606	0-5%VOL	Hunan Rike Instrument Co. Ltd

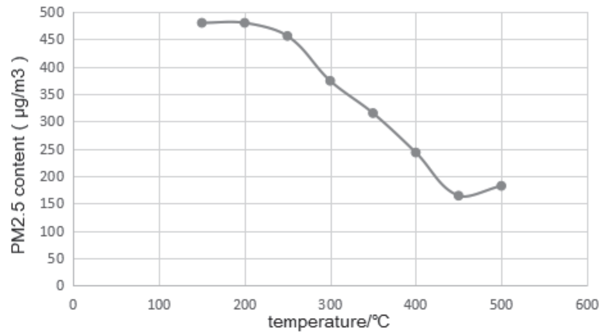

Fig. 5. The variation curve of PM2.5 content after the catalytic.

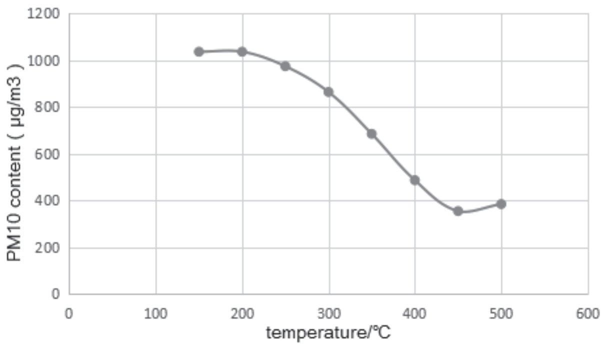

Fig. 6. The variation curve of PM10 content after the catalytic.

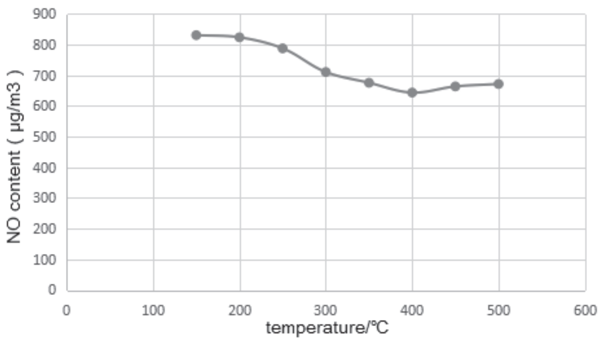

Fig. 7. The variation curve of NO content after the catalytic.

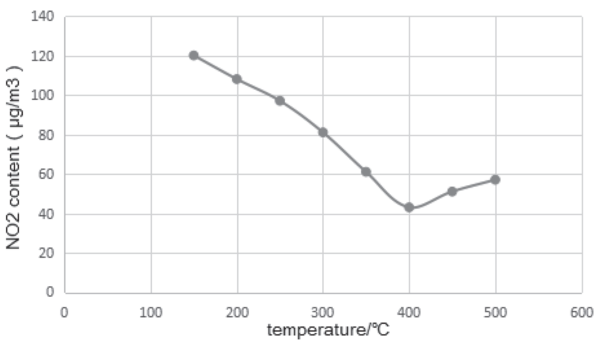

Fig. 8. The variation curve of NO_2 content after the catalytic.

Table 5. Content of exhaust pollutants before catalysis.

Composition	PM2.5	PM10	NO	NO_2
Testing data	480 μg/m³	1035 μg/m³	830 ppm	120 ppm

It can be seen from the curves 7 and 8 of NO_X content that NO_X content is the lowest when the temperature is about 400ºC, and the trend is similar to the changing curve of PM content. The results show that NO_X and PM in diesel exhaust can be REDOX at the same time under the action of Ce-Zr composite oxide catalyst. Therefore, if the catalyst is modified to improve its catalytic performance, the NO_X and PM can be treated at the same time more effectively, and the emission can be reduced to the convention limit requirements.

After the exhaust was heated to 500ºC and the diesel engine was kept running steadily for 15 minutes, PM and NO_X contents were measured three times, and the average value was taken to reduce the error. The composition content of exhaust pollutants after catalysis is shown in Table 6.

According to the above experimental data, cerium-zirconium composite oxide has a good catalytic effect on soot particles, and the catalytic efficiency of PM2.5 and PM10 can reach 62%, while the reduction rates of NO and NO_2 are only 19.2% and 52.5% respectively. It is further demonstrated that the soot particles have a REDOX reaction with nitrogen oxides under the action of the catalyst, and part of the soot particles are oxidized through the combustion reaction with oxygen, but in a non-catalytic environment, PM the light-off temperature about 500ºC, fully show that the cerium zirconium composite oxide effectively reduces the light-off temperature of PM.

Emission Reduction test of PM and NO_X in Diesel Engine by Ce-Zirconium Composite Oxide Mixed with La

The rare earth metal lanthanum can refine the grain size and inhibit the growth of grain size, so that the powder has a high specific surface area and a small particle size distribution, and the inhibiting effect at high temperature can reduce the sintering of cerium zirconium and improve the thermal aging resistance of the catalyst. The addition of La enhances the migration of lattice oxygen and promotes oxygen storage. The addition of La enhances the NO_X adsorption capacity of cerium zirconium composite oxide, improves the catalytic activity of the catalyst, and reduces the ignition temperature and the maximum activity temperature of PM. $La_{0.05}Ce_{0.65}Zr_{0.3}O_2$ is produced by adding lanthanum to the $Ce_{0.7}Zr_{0.3}O_2$ composite oxide, and the experimental steps of emission reduction are the same as before. The test data are shown in Fig. 9, 10, 11 and 12.

As can be seen from the variation curves of PM content in Fig. 9 and 10, the reduction of PM

Table 6. Content of exhaust pollutants after catalysis.

Catalyst	Composition	1	2	3	Average value	PM Oxidation rate	NOx reduction rate
$Ce_{0.7}Zr_{0.3}O_2$	PM2.5	177 μg/m^3	182 μg/m^3	186 μg/m^3	182 μg/m^3	62.1%	
	PM10	378 μg/m^3	391 μg/m^3	384 μg/m^3	384 μg/m^3	62.9%	
	NO	668 ppm	671 ppm	674 ppm	671 ppm		19.2%
	NO_2	56 ppm	54 ppm	61 ppm	57 ppm		52.5%

in the exhaust increased after La incorporation, and the oxidation rate also accelerated compared with that before modification. Compared with before modification, the performance of the catalyst did not decrease after 450ºC, and the PM content continued to decrease, indicating that the refinement of grain size and improvement of grain distribution reduced the local agglomeration sintering of the catalyst, thus improving the high temperature resistance of the catalyst.

As can be seen from Fig. 11 and 12 of NO_X content change, the catalyst modified by adding La has improved the NO_X emission reduction effect as PM. The decrement of NO_X in the exhaust increased and the oxidation rate was also accelerated compared with that before modification. After 400ºC, the content of NO decreased to 700 μg/m^3 and the content of NO_2 decreased to 60 μg/m^3 without rebound. The results show that the addition of lanthanum not only effectively improves the physical and chemical properties of Ce-Zr composite oxides, but also obviously enhances their catalytic performance.

After the exhaust was heated to 500ºC and the diesel engine was kept running steadily for 15 minutes, PM and NO_X contents were measured three times, and the average value was taken to reduce the error. Table 7 shows the composition content of exhaust pollutants after catalysis.

According to the above experimental data, the catalytic effect of Ce-Zr composite oxide on soot particles was significantly improved after lanthanum was added, and the oxidation rates of PM2.5 and PM10 were increased by 9.4% and 10% respectively, reaching more than 71.5%, which indicated that the modified catalyst also reduced the ignition temperature of PM. The reduction rates of NO and NO_2 are also increased by 4.1% and 7.8% respectively. The results showed that

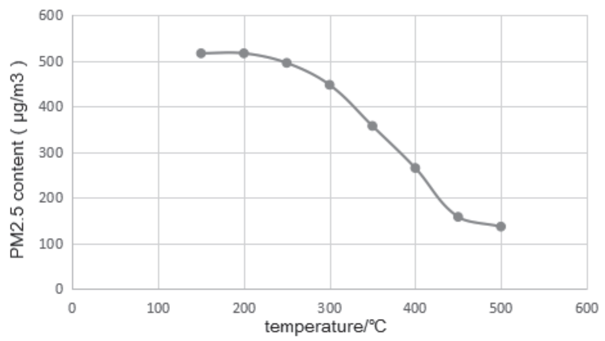

Fig. 9. The variation curve of PM2.5 content after the catalytic.

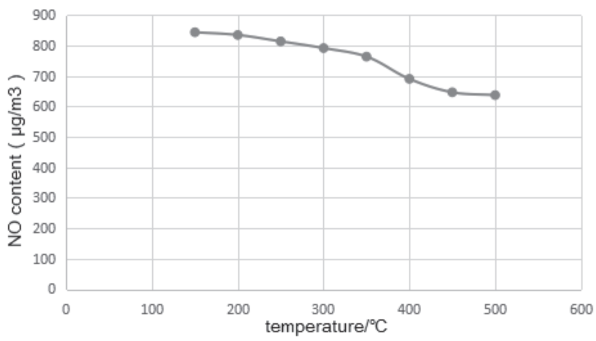

Fig. 11. The variation curve of NO content after the catalytic.

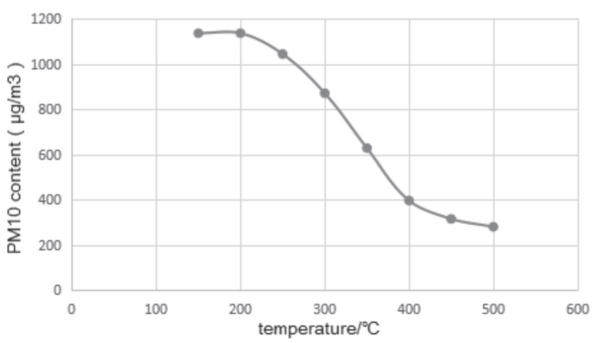

Fig. 10. The variation curve of PM10 content after the catalytic.

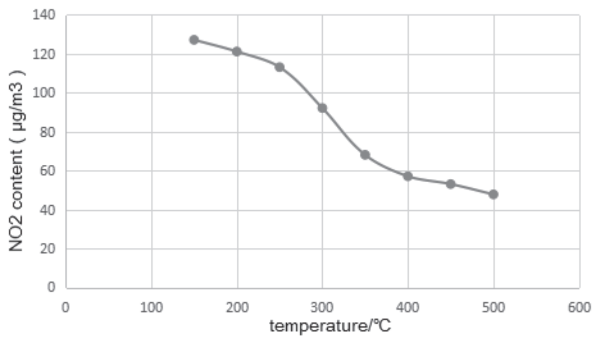

Fig. 12. The variation curve of NO_2 content after the catalytic.

Table 7. Content of exhaust pollutants after catalysis.

Catalyst	Composition	1	2	3	Average value	PM Oxidation rate	NOx reduction rate
$La_{0.05}Ce_{0.65}Zr_{0.3}O_2$	PM2.5	136 μg/m^3	142 μg/m^3	132 μg/m^3	136.7 μg/m^3	71.5%	
	PM10	272 μg/m^3	289 μg/m^3	280 μg/m^3	280.3 μg/m^3	72.9%	
	NO	648 ppm	637 ppm	625 ppm	636.7 ppm		23.3%
	NO_2	43 ppm	53 ppm	47 ppm	47.7 ppm		60.3%

the addition of lanthanum enhanced the adsorption capacity of the catalyst for NO_X gas, enhanced the migration of lattice oxygen and promoted the oxygen storage capacity.

Conclusions

In this paper, a series of emission reduction studies were done on reducing PM and NO_X in diesel engine exhaust by using the good oxygen storage capacity, good adsorption capacity and excellent catalytic performance of cerium zirconium composite oxides. XRD, SEM, ICP and BET characterization methods were used to detect and analyze the catalyst powder, and some physical and chemical properties of the self-made catalyst were verified, indicating that the preparation was relatively successful. Finally, a diesel engine bench was built and the exhaust emission reduction test was carried out by using cerium-zirconium composite oxide as catalyst. The results show that the Ce-Zr composite oxide can effectively reduce the ignition temperature and oxidation activity temperature of PM, and the catalytic effect on PM2.5 and PM10 particles is better, reaching 62.1% and 62.9%, while the reduction rates of NO and NO_2 are only 19.2% and 52.5% respectively. Modified catalyst by adding lanthanum improved the catalytic performance of Ce-Zr composite oxide and the adsorption capacity of NO_X gas. The oxidation rates of PM2.5 and PM10 were increased to 71.5% and 72.9% respectively, and the reduction rates of NO and NO_2 were increased to 23.3% and 60.3% respectively.

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Conflict of Interest

The authors declare no conflict of interest.

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