Oxidation of soot promoted by Fe-based spinel catalysts

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Keywords: soot, CDPF, spinel, oxidation, DFT

Abstract

Diesel engine has attracted much attention because of its good power performance, fuel economy, reliability and durability, but the exhaust gas containing soot has significant impact on environment and human health. Catalyzed diesel particulate filter (CDPF) that reduces the activation energy of soot oxidation by catalysts is used to eliminate soot. In this work, MFe₂O₄ spinel (M = Cu, Ni and Co) was synthesized by sol-gel method to catalyze the oxidation of soot. The characterization results of MFe₂O₄ showed that CuFe₂O₄ possessed the smallest average grain size (65.6 nm) and the best redox activity. The activity tests of the catalysts showed that the activity order of the catalyst is CuFe₂O₄ (330 °C) > CoFe₂O₄ (411 °C) > NiFe₂O₄ (464 °C). DFT results showed that soot is more easily adsorbed on the O-terminal surface of CuFe₂O₄ and reacts with oxygen vacancies, resulting in the promotion of soot oxidation by the diffusion of oxygen from the inside to the surface. It also proves that CuFe₂O₄ has the best catalytic effect on soot.

1. Introduction

With the rapid development of the global economy, the demand for energy is increasing, and non-renewable energy such as fossil energy is becoming more and more scarce, which makes the energy crisis increasingly serious. At the same time, the pollution of automobile exhaust has seriously affected people’s normal life. Therefore, how to make efficient use of fuel to improve its combustion efficiency is significant.

Diesel engine has good power performance, fuel economy, reliability and durability, and its exhaust emissions of carbon dioxide and unburned hydrocarbons are very low, so it has attracted much attention for many years [1, 2]. However, the exhaust gas treatment technology of diesel vehicles is not yet mature, and the resulting soot and nitrogen oxides will not only seriously pollute the atmospheric environment, but also cause substantial harm to human health [3, 4]. Therefore, in order to protect the environment, provide human beings with a healthy low-carbon life, and reduce tail gas emissions, it is very necessary to carry out exhaust post-treatment technology.

After years of development, the post-treatment technology of diesel engine soot has formed three branches: diesel oxidation catalyst (DOC), diesel particulate filter (DPF) and particle oxidation converter (POC). DOC technology has excellent performance in the removal of hydrocarbons and CO, but the contents of two components in diesel engine exhaust are very small, and it has little oxidation capacity to soot. POC technology often designs the interior into a wrinkled structure to improve the contact area between soot and active substances and improve the catalytic effect. However, the catalytic efficiency is only 60%, and the unremoved soot will be deposited and block the converter. The catalytic effect of DPF technology is much better than the other two technologies, and it can effectively eliminate more than 90% soot particles in Filter [5, 6]. However, DPF filter will be blocked with the increasing amount of soot accumulated in the filter. In order to achieve the regeneration of the filter, catalyzed diesel particulate filter (CDPF) is necessary. In this technology, high efficiency catalysts are coated on the pore wall of honeycomb structure, and the activation energy of soot
oxidation reaction is reduced through the catalytic selectivity of the catalyst to soot. Since the exhaust
temperature of diesel engine is between 200 °C and 400 °C in the real operating conditions, the ignition
temperature of diesel particles depends on the adsorbed hydrocarbons and usually exceeds 550 °C [7].
Therefore, the key of CDPF technology is to study the efficient and stable catalyst to reduce the soot oxidation
temperature within the engine exhaust temperature range.

The core problem of CDPF catalytic regeneration technology is to improve the soot oxidation activity, soot
adsorption performance, catalyst stability and thermal shock resistance of the catalytic coating [8, 9]. In recent
years, more and more efficient catalysts have been developed for soot oxidation. According to their structure and
composition. They are divided into four categories: precious metal catalysts, metal oxide catalysts, composite
metal oxide catalysts and alkali metal and alkaline earth metal catalysts [10]. Among the catalysts for soot
combustion, the multi-component composite metal spinel catalyst is a kind of catalyst with fixed structure,
although it can be regarded as a mixture of many kinds of single metal oxides, however, there is a synergistic
effect between its single reference oxides, such as structural and electronic modulation, so it avoids the
disadvantages of single metal oxides, retains the advantages of single oxides, and has better catalytic
performance. For spinel (AB₂O₄) oxides, their catalytic properties depend on the properties of ions at An and B
sites. The A site is generally divalent cation and the B site is generally trivalent cation. According to the different
positions occupied by cations, spinel can be divided into positive spinel and inverse spinel structure. Similarly,
the spinel catalyst has a good ability to oxidize soot, and its thermal stability is also very good.

Among the spinel oxides, CuFe₂O₄ has the best catalytic effect, and the maximum soot conversion
temperature is 400 °C in 0.5% NO and 5% O₂ atmosphere [11]. Zhang et al [12] studied the catalytic effect of
ACO₃O₄ on soot, among which ZnCoO₃ had the best oxidation effect on soot (T₅₀ = 569 °C). The substitution
of Co site leads to the change of Co³⁺/(Co²⁺+Co³⁺) ratio and oxygen mobility in spinel structure. The interaction
between Zn and Co leads to larger surface area, higher concentration of surface active Co³⁺ and
more chemisorbed oxygen. Zawadzki et al [13] prepared mesoporous cobalt-alumina spinel CoAl₂O₄, with high
specific surface area by microwave-assisted saccharothermic method and studied its catalytic combustion ability
for soot in the atmosphere where NO₂ and O₂ coexisted. The results show that due to the high chemisorption
capacity of NOₓ on the spinel surface and its ability to quickly oxidize NO to NO₂, the soot oxidation rate of
CoAl₂O₄ spinel is similar to that of the reference Pt/Al₂O₃ catalyst, and reaches the maximum soot combustion
rate around 475 °C. Liu et al [14] prepared Mn₁₋ₓAgₓCo₂O₄ spinel catalyst by sol-gel method, which showed
excellent catalytic performance (T₅₀ = 325 °C) under the condition of loose contact with soot. The high activity
of the catalyst was due to the synergism of chemisorbed oxygen (O²⁻, O⁻) and metallic silver.

In this paper, iron-based spinel catalysts were selected as the target. Firstly, MFe₂O₄ (M = Cu, Ni and Co)
spinel catalysts with different A-site metals were synthesized, and the best iron-based catalysts were obtained by
comparing the performance of iron-based spinel catalysts. The catalytic performance of the catalyst for soot in
air was studied by temperature programmed experiment. The materials were characterized by XRD, Raman,
SEM and H₂-TPR. In addition, we use density functional theory (DFT) to explore the mechanism of catalysis
from the perspective of quantum chemistry calculation.

2. Experiment

2.1. Preparation of catalyst

For spinel MFe₂O₄ (M = Cu, Ni and Co), take CuFe₂O₄ spinel as an example. 0.01 mol Cu(NO₃)₂·3H₂O and
0.02 mol Fe(NO₃)₃·9H₂O were dissolved in 100 ml deionized water to obtain a mixed solution. The mixed
solution was placed in an ultrasonic processor for 20 min to disperse the ions evenly. Then 0.3 M citric acid
solution was slowly added to the mixed solution to form a transparent solution. The molar ratio of all metal
nitrate ions to citric acid is 1:1. Viscous gel is obtained by vigorous stirring in a water bath at 80 °C. The resulting
gel is dried overnight in an oven at 100 °C for 12 h to remove residual water. The prepared xerogel was heated
from 20 °C to 800 °C in N₂ with a heating rate of 10 °C min⁻¹, and the spinel structure was obtained by
calcination at 800 °C for 3 h. Finally, the catalysts were cooled to room temperature in nitrogen atmosphere. The
prepared samples were ground into powder and screened with a sieve of 80–100 mesh.

2.2. Material characterization

The powder x-ray diffraction (XRD) of the sample is carried out in Bruker-AXS-D8. The instrument uses a
copper target with a wavelength of 0.154 nm, an operating voltage of 40 kV and a working current of 40 mA.
After the sample is loaded, the scanning speed is set at 1°/min, the scanning time is 1 s/step, and the scanning is
carried out at a 2θ angle of 10°–80°.
In the formula, $E_{slab}$, $E_{mole}$ and $E_{mole + slab}$ generated, and $T_{max}$ is the temperature corresponding to the maximum combustion rate.

The thermogravimetric analysis (TG) of the sample was carried out on the thermogravimetric analyzer model NETZSCH STA409C/PC. The test conditions are as follows: the catalyst weighing about 10 mg is placed on the crucible, rising from room temperature to 1000 °C at a heating rate of 5 °C min$^{-1}$ in the nitrogen atmosphere of 50 ml min$^{-1}$, and holding at this temperature for 30 min, then naturally cooled to room temperature.

The surface microstructure of the sample was observed by using the desktop scanning electron microscope (SEM) of (COXEM) EM-30 Plus made by Kusam Company of South Korea. Gold was sprayed for two minutes during sample preparation to enhance the conductivity of the sample, and the working voltage was 20 KV.

The temperature programmed reduction (H$_2$-TPR) of the catalyst was tested on TPDPO 1100, and the H$_2$ signal was detected by thermal conductivity detector (TCD). During each operation, the 100 mg sample was put in, heated to 200 °C at 10 °C min$^{-1}$ in high purity nitrogen of 60 ml min$^{-1}$ and kept at a constant temperature for one hour, and the adsorbed physical gas was removed by pretreatment. Then the temperature is lowered to 20 °C, and the reduction curve of the sample is obtained at a heating rate of 10 °C min$^{-1}$ from 20 °C to 1000 °C in a mixture of nitrogen and hydrogen containing 10% H$_2$.

**2.3. Activity test of catalyst**

The activities of the catalysts were evaluated by temperature programmed oxidation (TPO). According to the mass ratio of soot to catalyst, the soot particles of 10 mg and the catalyst of 200 mg were weighed, and the mixture was grinded for 5 min to obtain a close contact. In each experiment, the mixed sample is loaded into the middle of a quartz tube with an inner diameter of 16 mm, a length of 500 mm and covered with quartz cotton, and then the entire reaction vessel is placed in a programmable tube furnace. In each experiment, the mixed sample is loaded into the middle of a quartz tube with an inner diameter of 500 mm and covered with quartz cotton. Before the reaction, the air should be ventilated for a period of time to remove the components in the air. Then in the air atmosphere, the heating rate is 5 °C min$^{-1}$ from room temperature to 800 °C, and then naturally reduced to room temperature. The resulting gas components first passed through the condensation tube to remove the possible liquid substance, then through the drying tube to remove moisture, and finally analyzed by the gas analyzer (Gasboard-3100). The concentration of CO$_2$ was measured by NDIR non-spectroscopic infrared method. The carbon oxide concentration produced during soot combustion is selected as the index to evaluate the catalytic performance. The initial combustion temperature ($T_{ig}$) of soot is the temperature when CO$_2$ is added, and $T_{max}$ is the temperature corresponding to the maximum combustion rate.

**2.4. DFT calculation**

The calculation method is based on spin-polarized density functional theory. The generalized gradient approximation (GGA) function parameterized by Perdew, Burke and Ernzerhof (PBE) is used to explain the three-dimensional correlation orbitals of Cu and Fe atoms, because GGA can accurately give the structure and electronic properties of spinel. The k points of Monkhorst-Pack grid are used to provide grid parameters, 4 x 4 x 4 k points are used for volume relaxation, and 4 x 4 x 1 k points are used for surface optimization and C adsorption. In all calculations, the electronic wave function is expanded in the plane wave base, using the standard convergent formula 10$^{-5}$ eV of crystal structure and electronic structure with a cutoff energy of 450 ev. In all calculations, the electronic wave function is expanded in the plane wave base. In order to correctly describe the nuclear electrons, the pseudo potential generated by the projection enhanced wave (PAW) method is used. The calculation is done in a so-called super cell, which contains a vacuum of 12Å, which is large enough to avoid the interaction between plates copied in three-dimensional space.

The free molecule (carbon) is added to the plate model, and the adsorption energy ($E_{ads}$) of carbon on the end face of spinel is calculated by equation (1).

$$E_{ads} = E_{(mole+slab)} - E_{mole} + E_{slab}$$

In the formula, $E_{slab}$, $E_{mole}$ and $E_{mole + slab}$ represent the oxygen surface or Fe at the oxygen end, the surface energy at the M end, the energy of the free molecule (carbon) and the total energy with a molecular plate, respectively. For the obtained results, there may be positive and negative numbers, in which the negative number represents the adsorption energy, and the higher the value, the greater the adsorption energy.
3. Results and discussion

3.1. Characterization of catalyst

The crystal phase composition of MFe$_2$O$_4$ (M = Cu, Ni and Co) catalysts was analyzed by XRD, and the results are shown in figure 1. The spectra of NiFe$_2$O$_4$, CoFe$_2$O$_4$ and CuFe$_2$O$_4$ match well with the characteristic peaks of standard XRD spectra (ICDD PDF:74-2081), (ICDD PDF:22-1086) and (ICDD PDF:34-0425). These narrow and strong peaks well confirm the cubic structure and crystallinity of spinel [15]. However, the impure phase of copper oxide was found in the diffraction peak of copper-iron spinel, which is due to the fact that copper oxide can appear in the samples whose calcination temperature is below 900 °C [16, 17]. The calcination temperature of the catalyst prepared in this paper is 850 °C, so it is possible to produce impure copper oxide. The average grain size of the catalyst obtained by Scheler’s formula, as shown in table 1. CuFe$_2$O$_4$ has the smallest grain size of 65.6 nm, followed by CoFe$_2$O$_4$ of 83 nm. The blunt peaks have smaller grain sizes, so NiFe$_2$O$_4$ with sharp peak has the largest grain size of more than 100 nm [18].

Table 1. Grain size of alkali metal doped CuFe$_2$O$_4$.

| Catalyst  | Grain size (nm) |
|-----------|-----------------|
| CuFe$_2$O$_4$ | 65.6           |
| CoFe$_2$O$_4$ | 83.0           |
| NiFe$_2$O$_4$ | >100           |

3.1.1. Raman spectral analysis

The Raman spectra at room temperature are shown in figure 2, where the analytical wavelengths are selected between 100 and 1000 cm$^{-1}$. CuFe$_2$O$_4$, CoFe$_2$O$_4$ and NiFe$_2$O$_4$ are all anti-cubic spinel structures with space groups of Fd-3m. The lattice vibrations in Fd-3m structures are analyzed by group theory, and five vibrational modes of Raman active phonons are predicted, that is, $\Gamma$(AB$_2$O$_4$)$=A_{1g}+E_g+3T_{2g}$ [19, 20]. From the figure, it is observed that CuFe$_2$O$_4$ has four Raman peaks, which are located around 164, 461, 554 and 678 cm$^{-1}$, respectively. The peaks of these four positions correspond to the Raman vibration modes of T$^{1}_{2g}$, E$_g$, T$^{2}_{2g}$, T$^{3}_{2g}$ and A$_{1g}$ of CuFe$_2$O$_4$, respectively [21]. The bands observed on CoFe$_2$O$_4$ appear at 294, 473 and 684 cm$^{-1}$ are classified as E$_g$, T$^{3}_{2g}$ and A$_{1g}$ vibration modes [22]. The peaks of NiFe$_2$O$_4$ at 201, 325, 483, 568 and 694 cm$^{-1}$ point to the Raman vibration modes of T$^{1}_{2g}$, E$_g$, T$^{2}_{2g}$, T$^{3}_{2g}$ and A$_{1g}$, respectively. Taking NiFe$_2$O$_4$ as an example, the vibration of T$^{3}_{2g}$ mode near 201 cm$^{-1}$ corresponds to the translational motion of tetrahedron, and the vibration of T$^{3}_{2g}$ mode near 483 cm$^{-1}$ belongs to the asymmetric stretching of oxygen of Ni–O in octahedral sublattice. The
vibration of the \( T_{2g} \) mode at 568 cm\(^{-1} \) corresponds to the asymmetric bending of the oxygen of the Ni–O bond, while the \( E_g \) mode around 325 cm\(^{-1} \) is caused by the symmetrical bending of the oxygen atom relative to the metal ion, and the \( A_{1g} \) mode near the 694 cm\(^{-1} \) can be attributed to the stretching of the oxygen atom to the metal ion at the tetrahedral position \([23, 24]\). These five characteristic vibration modes show that the catalyst obviously forms the spinel structure of Fd-3m, which is consistent with the results of XRD. The Raman peaks of the three catalysts are slightly different, which is due to the distribution of different cations and the effect of crystal size.

3.1.2. SEM morphology analysis

Figure 3 shows the SEM image of the calcined MFe\(_2\)O\(_4\) catalyst under 850 °C. The uniform external morphology, size and shape of spinel can be seen from the figure. This is because in the preparation of the catalyst, we use citric acid as the complexing agent of nitrate precursor, which contains a lot of organic matter. In the process of roasting, the decomposition products of organic matter and the gas released by nitrate decomposition will quickly expand and overflow from the inside of the sample, thus forming fluffy and porous uneven pores \([25, 26]\). These voids can well increase the specific surface area of the catalyst, and according to the point of view proposed by Selvan \textit{et al} \([27]\), these voids will form better interparticle connectivity, thus promoting the improvement of the overall material performance. In addition, it can be found from figure 3(b) that the hole size of CuFe\(_2\)O\(_4\) is about 300–500 nm, which is much smaller than that of CoFe\(_2\)O\(_4\) and NiFe\(_2\)O\(_4\). Most of the soot particles are spherical with a diameter of 10–50 nm, so the spinel catalyst has a good contact area with soot particles, which can improve the efficiency of catalytic oxidation of soot particles.

3.1.3. \( H_2 \)-TPR reduction performance test

Figure 4 shows the \( H_2 \)-TPR spectrum of the catalyst MFe\(_2\)O\(_4\) (M = Cu, Ni and Co). It can be seen from the diagram that the CuFe\(_2\)O\(_4\) sample has two reduction peaks, namely, the low temperature reduction peak near 301 °C and the high temperature reduction peak near 530 °C. The peak around 301 °C indicates the reduction of CuFe\(_2\)O\(_4\) to Cu and Fe\(_3\)O\(_4\) by hydrogen \([28]\), while the peak around 530 °C indicates the process of further reduction of Fe\(_3\)O\(_4\) to Fe \([29, 30]\). In the spectra of CoFe\(_2\)O\(_4\) and NiFe\(_2\)O\(_4\), only a large high temperature reduction peak was observed between 500 °C ~ 600 °C. This is because the decomposition temperature of CoFe\(_2\)O\(_4\) and NiFe\(_2\)O\(_4\) is relatively high, and their decomposition into Co/Ni coincides with the peaks of Fe\(_3\)O\(_4\) and Fe\(_2\)O\(_3\) gradually reduced to Fe\(_3\)O\(_4\), FeO and Fe, so there is a large peak on the spectrum. It is worth noting that CuFe\(_2\)O\(_4\) will be directly reduced to Cu and Fe\(_3\)O\(_4\), at the lower 301 °C. For CoFe\(_2\)O\(_4\) and NiFe\(_2\)O\(_4\), the reduction peaks of Fe\(_3\)O\(_4\) and Co/Ni shift to the high temperature region, which is about more 200 °C than that of CuFe\(_2\)O\(_4\). The lower reduction temperature means that the redox performance of CuFe\(_2\)O\(_4\) is better, which also shows that the ability of soot oxidation of CuFe\(_2\)O\(_4\) is better than that of the other two catalysts.
Figure 3. SEM topography with different magnifications (a) CuFe$_2$O$_4$: 5000×, (b) CuFe$_2$O$_4$: 10000×, (c) CoFe$_2$O$_4$: 5000×, (d) CoFe$_2$O$_4$: 10000×, (e) NiFe$_2$O$_4$: 5000×, (f) NiFe$_2$O$_4$: 10000×.

Figure 4. H$_2$-TPR diagram of different catalysts.
3.2. Evaluation of TPO activity of catalysts

Figure 5 shows the TPO results of MFe$_2$O$_4$ spinel catalyst under the condition of close contact. The oxidation temperature of soot is listed in Table 2. It can be seen from the figure that in the absence of catalyst, the $T_{ig}$ is 510 $^\circ$C, and the $T_{max}$ is about 680 $^\circ$C. The exhaust temperature of diesel engine exhaust is 200 $^\circ$C–400 $^\circ$C, so it is necessary to study high efficiency catalyst to reduce the soot combustion temperature. Compared with CuFe$_2$O$_4$, CoFe$_2$O$_4$ and NiFe$_2$O$_4$, CuFe$_2$O$_4$ has the best catalytic effect, which can oxidize soot around 330 $^\circ$C, followed by NiFe$_2$O$_4$, begins to be oxidized in 411 $^\circ$C, CoFe$_2$O$_4$ has the worst catalytic performance and begins to be oxidized in 464 $^\circ$C. If $T_{max}$ is used as the standard to evaluate the catalyst, the $T_{max}$ of CuFe$_2$O$_4$ is about higher than that without catalyst.

On the one hand, the excellent catalytic oxidation ability of CuFe$_2$O$_4$ may be due to its strong redox ability (seen in figure 4). The stronger the redox ability, the easier the soot is oxidized in the low temperature region. On the other hand, it may be due to smaller grain size and specific surface area.

The comparison between the iron spinel CuFe$_2$O$_4$ catalyst with the best soot catalytic performance and the existing literature is shown in Table 3. First of all, compared with a series of cobalt spinel catalysts NiCo$_2$O$_4$, ZnCo$_2$O$_4$ and CuCo$_2$O$_4$ without the participation of nitrogen oxides, the catalytic performance of CuFe$_2$O$_4$ is 130 $^\circ$C and 79 $^\circ$C lower than that of the best ZnCo$_2$O$_4$ on $T_{ig}$ and $T_{max}$, respectively. This shows that CuFe$_2$O$_4$ has excellent catalytic performance in air atmosphere, but after adding certain nitrogen oxides to the catalyst, the soot catalytic temperature of CoCr$_2$O$_4$ and BaAl$_2$O$_4$ is lower than that of CuFe$_2$O$_4$ by tens of degrees Celsius, and the performance improvement is not much, so CuFe$_2$O$_4$ still has a certain advantage in soot catalytic performance.

3.3. DFT calculation

MFe$_2$O$_4$ ($M = \text{Cu, Co, Ni}$) with antiferromagnetic arrangement is an important spinel oxide. In the ideal MFe$_2$O$_4$ structure, the tetrahedral hollow region is occupied by Fe atoms, and the octahedral hollow region is occupied by equal M and Fe atoms.
In order to find the ground state of spinel CuFe₂O₄, the unit cell parameters of CuFe₂O₄ bulk structure are comprehensively optimized. The unit optimization of MFe₂O₄ has a certain convergence criterion, that is, the atomic force is $2.0 \times 10^{-3}$ Hartree/Å, the maximum displacement is $5.0 \times 10^{-3}$ Å, and the total energy change is $1.0 \times 10^{-5}$ Hartree. The lattice parameters of the optimized structure are shown in table 4.

In the modeling of surface energy, we consider three cubic spinel planes with low index and the largest spacing between crystal planes, that is, $(100)$, $(110)$, and $(11\bar{1})$ planes. According to Bravais-Friedel-Donnay-Harker theory, they are the most stable planes [34]. According to the previous studies, the surfaces of CuFe₂O₄, CoFe₂O₄ and NiFe₂O₄ have good thermodynamic stability and low catalytic activity [35, 36], which is also the basis of our selection. We have established a model plate in which carbon molecules are adsorbed on the O-end surface, as shown in figure 6.

In addition, the adsorption energy reflects the properties of MFe₂O₄ catalyst, which can be used as the basis for reflecting the comprehensive mechanism of the chemical reaction process of soot molecules (C) and MFe₂O₄. The adsorption energy of soot molecules on the O-terminal surface of MFe₂O₄ is calculated, and the results are shown in table 5. The results show that carbon is more easily adsorbed on the oxygen end surface of CuFe₂O₄, which indicates that the adsorbed carbon can easily interact with the lattice oxygen on the surface of CuFe₂O₄ at high temperature to form oxygen vacancy in COₓ. Due to the appearance of oxygen vacancy, oxygen...
diffuses from the sublayer to the surface, which promotes the oxidation of soot, which proves that CuFe₂O₄ has the best catalytic effect on soot.

4. Conclusion

MFe₂O₄ (M = Cu, Ni and Co) was synthesized to oxidize and remove soot. The activity test of the catalyst showed that CuFe₂O₄ had the best catalytic effect and could oxidize soot around 330 °C. Compared with the soot combustion temperature without catalyst, the initial temperature decreased by 182 °C and the temperature corresponding to the highest CO₂ concentration decreased by 162 °C. The catalysts were characterized by XRD, Raman, SEM and H₂-TPR. XRD results show that the average grain size of CuFe₂O₄ is smaller. Raman results showed that all the catalysts formed spinel structure of Fd-3m. SEM results showed that the decomposition products of organic compounds and gases released by nitrate decomposition formed fluffy and porous non-uniform pores on the spinel surface, which led to the increase of specific surface area. H₂-TPR showed that the redox performance of CuFe₂O₄ was better, and the soot was oxidized more easily in the low temperature region. These characterization results can confirm the better soot oxidation activity of CuFe₂O₄. In addition, the reaction mechanism was explored from the point of view of DFT. The results show that CuFe₂O₄ has a larger adsorption energy for soot and is easier to adsorb soot to promote the reaction between soot and oxygen vacancy on the surface.

Acknowledgments

This work is financially supported by the National Natural Science Foundation of China, China (No.21676148, 42007105), the Fundamental Research Funds for the Central Universities, China (No.30918012202), the Natural Science Foundation of Jiangsu Province (BK20181165) and the 5th Scientific Research Project of '333 High-level Talents Training Project' of Jiangsu Province (BRA2020128).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Table 5. Adsorption energy of carbon on MFe₂O₄ surface.

|        | eV  |
|--------|-----|
| CuFe₂O₄ | −1.46 |
| CoFe₂O₄ | −1.44 |
| NiFe₂O₄ | −1.44 |
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