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Investigation of Adsorption Characteristics and Influencing Factors for Diesel Engine Exhaust Particles

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Abstract: The adsorption process of diesel exhaust particles has a great influence on the particles. A single-cylinder diesel exhaust particle collection system was established to collect particle samples with different adsorption environment conditions, and the adsorption capacity of the samples was analyzed and characterized by an isothermal adsorption test; the change patterns of particle characteristics were investigated by the scanning electron microscope and thermogravimetric analyzer, correlation analysis of the factors influencing the adsorption process was performed. The results show that the particles have adsorption capacity and belong to the type of multilayer adsorption on porous media; the pore diameter is continuously distributed in the range of 8-80 nm with multiple peaks, which is the category of mesoporous and macroporous; the adsorption capacity of the sample particles increase with the increase of engine speed. Compared with the particles at the inlet of the exhaust pipe, the box-counting dimension (D_B) of particles at the outlet increased, the content of water and soluble organic fraction

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(SOF) increased, the activation energy (E) decreased. Among the parameters affecting the adsorption process, the increase of hydrocarbons concentration contribute to the increase of particle adsorption and E reduction; the increase of the average temperature of the exhaust pipe inhibit the increase of the D_B , and the increase of the temperature difference between the inlet and outlet facilitate the adsorption of water and SOF by the particles; the decrease of the adsorption time is one of the main reasons for the slowdown of the increase in D_B ; the average pore diameter had the greatest positive correlation with the amount of variation in the D_B ; the increase in specific surface area and pore volume of the sample particles was the dominant cause of the increase in adsorption capacity as well as the decrease in E.

Keywords: diesel engine; PM; adsorption; micromorphology; oxidation properties; soluble organic fraction

1. Introduction

Diesel exhaust particles are porous media with a large specific surface area and adsorption capacity (Collura et al. 2005). During the exhaust process, the particles are highly susceptible to adsorption of water vapor and gaseous SOF. the adsorption behavior cause changes in the degree of particle agglomeration and components, which affects the regeneration of the DPF (Young et al. 2012). When these organic particles emitted into the atmosphere, the particles suspended in the air continue their adsorption behavior and develop secondary organic aerosols (SOA), making the particles more toxic and affecting human health, visibility and climate change. It is essential to

investigate the adsorption characteristics of diesel exhaust particles and the effect of adsorption behavior on the microscopic characteristics of the particles.

A lot of research work has been conducted at home and abroad on the adsorption capacity of diesel particulates and the factors influencing it. Rothenberg et al. (1985) concluded that diesel particulates are more porous, have larger pore volumes, have a higher adsorption capacity, and the type of adsorption of hydrocarbons by the particulates belongs to class II isothermal adsorption. Y.-H. Song et al. (2002) suggested that adsorbent concentration, temperature, and adsorption time are the main factors affecting the adsorption capacity. Hermosilla et al. (2019) studied the isothermal adsorption process of activated carbon on n-butane. The results showed that an increase in n-butane concentration led to a rapid increase in the adsorption of activated carbon. Rexer et al. (2013) investigated the adsorption characteristics of shale on methane at different temperatures and examined the effect law of temperature on the adsorption of methane by shale. The results indicated that the shale adsorption of methane decreased with the increase of temperature. The increase of adsorbent concentration promotes the increase of adsorption; the increase of temperature has a certain inhibitory effect on physical adsorption; the longer the adsorption time in the adsorption saturation range the greater the adsorption capacity. Furthermore, the adsorption capacity of particulate matter is significantly influenced by the particle pore parameters (B. Dou et al. 2011). Cai et al. (2013) concluded that the larger the specific surface area and pore volume of the particles, the stronger the adsorption capacity. The adsorption capacity of the particles is affected by the adsorbent concentration, temperature, adsorption time,

specific surface area of the particles and pore parameters together.

Adsorption behavior of particles is one of the main ways of exhaust particle surface growth. Many studies have been conducted by domestic and foreign scholars on the evolution of particle characteristics during the exhaust process. XinLing and Zhen (2012) study argued that the exhaust dilution process of diesel engines causes volatile organic compounds to condense and adsorb on the surface of existing particles, and that temperature is an important factor affecting the gas-particle conversion process. Z. Dou et al. (2017) investigated the change in particle size during the exhaust process. The results indicated that as the exhaust length increased and the exhaust temperature decreased, gaseous hydrocarbons and sulfates were adsorbed on the particle surface, leading to an increase in particles in nucleation mode. J. Gao et al. (2018) collected particles at different locations of the exhaust pipe. The results demonstrated that as the temperature of the exhaust pipe decreased, the gas-phase hydrocarbons in the exhaust components would condense and adsorb on the particles that had become nucleated, leading to an increase in the organic content on the surface of the particles; the particles were more agglomerated with each other, and the content of functional groups on the surface of the particles increased and the oxidation activity was enhanced. C. Wang et al. (2020) conducted a study on the variation of particulate SOF mass fraction during the exhaust process. The results showed that the SOF mass fraction of particles increased as the exhaust temperature decreased and volatile organic compounds condensed and adsorbed on the particle surface or in the pores. Z. Wang et al. (2016) concluded that with the exhaust process, the content of H₂O and SOF in the

particles increased and the oxidation activity of the particles increased. Choi et al. (2004) investigated the relationship between the oxidation characteristics of the particles and the content of the adsorbed SOF. The results showed that the SOF adsorbed by the particles increase the oxidation activity of the particles. The adsorption behavior of the particles during the exhaust process leads to changes in the agglomeration degree, components, and oxidation activity of the particles.

In the exhaust process, the adsorption behavior of particles is greatly influenced by the exhaust environment. The adsorption performance and the changes of microscopic characteristics of particles at the inlet and outlet of the exhaust pipe were studied. A 186FA diesel engine particle collection test bench was established, and the particles at the inlet and outlet of the exhaust pipe were collected under different environmental conditions such as HC concentration and temperature in the exhaust pipe and particle adsorption time. The specific surface area and pore diameter distribution analyzer, scanning electron microscope and thermogravimetric analyzer were used to determine the adsorption capacity, specific surface area and pore diameter parameters of the particles. The box-counting dimension, components and activation energy of the particles were investigated, and the effects of different adsorption environment parameters and adsorption performance parameters on the adsorption behavior of the particles were discussed to facilitate the regeneration of DPF as well as provide a theoretical basis for investigating the adsorption behavior of particles in the atmospheric environment.

2. Experimental setup and methodology

2.1. Experimental program and particle collection

The test machine is a 186FA diesel engine with the detailed parameters shown in

Table 1.

Table 1. Test engine specifications

Parameters	Value
Number of cylinders	1
Cylinder diameter /mm	86
Stroke /mm	72
Compression ratio	19
Displacement /L	0.418
Rated speed /r·min ⁻¹	3600
Rated power /kW	6.3
Maximum torque /N·m	20.1
Maximum torque-speed /r·min ⁻¹	2700

To investigate the effects of different adsorbent concentrations, temperature and adsorption time on the adsorption behavior of particles, the length of the test diesel engine exhaust pipe was selected as 3 m. The particles were collected from the diesel engine at 100% load rate of low speed (1500 r·min⁻¹, 2.5kW), maximum torque (2700 r·min⁻¹, 5.7kW) and nominal (3600 r·min⁻¹, 6.3kW), which were coded as samples 1, 2 and 3. The adsorption capacity of the particles at different conditions was measured and characterized. The HC emission was measured during the test, the exhaust temperature at the inlet and outlet of the exhaust pipe was measured, and the environmental

parameters of the adsorption process were obtained as shown in **Table 2**.

Table 2. Environmental parameters of the adsorption process

Sample	HC	Inlet	Outlet	Temperature	Adsorption
	concentration	temperature	temperature	difference	time /s
	/10 ⁻⁶	/°C	/°C	/°C	
1	338	223	110	113	0.82
2	362	324	173	151	0.59
3	425	379	257	122	0.44

To satisfy the different requirements for particle morphology and component analysis, two particle collection methodologies were used as shown in **Fig.1**. A wire mesh filter in series with the exhaust pipe was used to collect particles at the inlet and outlet of the exhaust pipe for isothermal adsorption tests and thermogravimetric analysis without increasing the exhaust back pressure; a sampling tube with an electric vacuum pump and a Teflon filter membrane was used to collect particles at the inlet and outlet of the exhaust pipe in parallel with the exhaust pipe for microscopic morphology analysis.

Fig. 1. Schematic diagram of the test setup and particle collection

2.2 Characterization methodology

2.2.1 Adsorption performance measurement

As a powdered solid, carbon black is commonly used as a standard sample in adsorption experiments. Printex U is widely used as a substitute for diesel exhaust particles owing to its physicochemical properties are very comparable to those of diesel exhaust particles, and carbon black was selected for adsorption capacity comparison with diesel exhaust particles (Tighe et al. 2016). Nitrogen is chemically stabilized, and pure nitrogen was taken as the adsorbent to research the isothermal adsorption properties of the particles.

A commercial carbon black Printex U from Degussa was employed and a specific surface area and pore diameter distribution analyzer (Make: Quanta chrome, USA, model: NOVA3000e) was applied to investigate the adsorption capacity of carbon black compared with the particulate samples. The specific surface area and pore diameter distribution analyzer employs the principle of the static capacity method of isothermal physical adsorption to determine the adsorption process, the parameters of the instrument are presented in **Table 3**. Under isothermal conditions, nitrogen is introduced into the sample tube under vacuum, and the nitrogen is adsorbed by the sample surface under the action of van der Waals forces, eliciting a pressure drop. The isothermal adsorption curve is determined by calculating the molar mass of the adsorbed gas at the adsorption equilibrium. The particles were degassed before the test to eliminate water vapor as well as soluble organic fraction from the pores of the particles.

Table 3. Specific surface area and pore analyzer parameters of NOVA3000e

Parameter	Value
Gas flow /mL·min ⁻¹	≤100
Measurement repeatability	≤±3%
Measurement range of specific surface area /m ² ·g ⁻¹	0.1~3500
Pore diameter measurement range /nm	2~200
Degassing temperature range /°C	25~450

2.2.2 Characteristics of particle

Particles at the inlet and outlet of the exhaust pipe were analyzed by SEM (Make: JEOL, Japan, model: JSM-7001F). The magnification of the JSM-7001F is 10 to 500,000 times. And the resolution is 1.2nm (30kV), 3.0nm (1kV). Microstructure analysis was performed in combination with MATLAB software, and the magnification of all samples was kept at 35,000×.

The TGA/DSC1 (Make: METTLER-TOLEDO, Switzerland, model: 1100LF) has a high-precision micro-gram electronic balance with a sensitivity of 0.1μg and a maximum load of 1 g. The measuring device is equipped with a temperature sensor with a temperature range of room temperature to 1600°C and an accuracy of ±0.3°C. The injection flow rate of the thermogravimetric analyzer was set to 50 mL·min⁻¹, and the reaction gas used was O₂ and the protective gas was N₂. Before the test, the gas was introduced to discharge the air, and 3 mg of the particulate matter was taken for testing. Thermogravimetric analysis of the particles was performed at a heating rate of 10°C·min⁻¹, and the temperature in the heating furnace was heated from 40°C to 900°C

to obtain a temperature dependence curve of the mass of the particles. The measured accuracy and uncertainty of each instrument are given in **Table 4** (Zhang et al. 2020).

Table 4. Accuracy of measurements and uncertainties

Instruments	Range	Accuracy	Percentage of uncertainties
Thermogravimetric	RT~1600°C	±0.3°C	±0.02%
Analyzer	0~1g	±0.1μg	±0.01%
Electronic precision balance	0~99 kg·h ⁻¹	±0.01 kg·h ⁻¹	±0.2%

2.3 Evaluation index

2.3.1 Adsorption performance

The adsorption between particles and HC substances occurs on the surface of the particles and the pore walls. The specific surface area and pore parameters of the particles affect the adsorption performance of the particles and are the primary indicators for estimating the capacity of the adsorbent (Zhao et al. 2016).

The specific surface area, pore diameter and pore volume were selected as the evaluation indexes of the adsorption performance (Ma et al. 2016, 3). The Brunauer-Emmett-Teller (BET) method was used to determine the specific surface area of carbon black and exhaust particles from nitrogen isotherm adsorption data obtained at P/P_0 between 0.05 and 0.35 (Sahbaz et al. 2015), and the expression of the equation is (1)

$$\frac{1}{W\left(\frac{P_0}{P}-1\right)} = \frac{1}{W_m C_1} + \frac{C_1-1}{W_m C_1} \left(\frac{P}{P_0}\right) \quad (1)$$

Where P_0 is the saturated vapor pressure of N₂ at a certain temperature; P is the

N_2 pressure during the test; W is the adsorption amount of N_2 at the relative pressure P/P_0 ; W_m is the saturated adsorption amount of a single molecular layer; C_l is a constant, which is related to the strength of the interaction between the adsorbent and the adsorbent.

The Density-Functional-Theory (DFT) method was employed to analyze the average pore diameter and pore volume parameters of diesel exhaust particles (Bardestani et al. 2019). The formula for DFT is (2)

$$V(P) = \int_{H_{min}}^{H_{max}} J(H) \rho(H, P) dH \quad (2)$$

Where $V(P)$ is the adsorption volume at a relative pressure of P ; $J(H)$ is the pore diameter distribution function from H_{min} to H_{max} ; and $\rho(H, P)$ is the adsorption volume at a relative pressure of P and pore diameter of H .

Combined with isothermal adsorption test data, the pore size distribution of the particles was obtained by solving equation (2) with a fast non-least squares method, and then the average pore diameter and pore volume parameters were calculated.

2.3.2 Characteristics of particle

(1) Box counting dimension

Box counting dimension (D_B) is one of the fractal theories, which characterizes the compactness and density of the particle population structure composed of particles, the higher the dimension, the higher the compactness and density, and quantitatively characterize the agglomeration between particles (Ai et al. 2014). The D_B was calculated using MATLAB based on SEM images (Leistner et al. 2012). Box-counting dimension calculation formula is expressed as (3)

$$D_B = -\lim_{r \rightarrow 0} \frac{\lg N(r)}{\lg(r)} \quad (3)$$

Where D_B is the self-similar fractal dimension of the SEM image; r is the length of a square box; $N(r)$ is the number of boxes required to cover the entire graphics area with a square box with side length r .

(2) Component

In the oxidation process, the starting temperature to 130°C is the evaporation stage of water (H_2O) in the particles; the temperature range from 130°C to 250°C is the rapid evaporation of low boiling point SOF, and 250-500°C is the slow volatilization of high boiling point SOF; 500°C to 850°C is the oxidative decomposition of dry soot (Dry Soot, DS), and the remaining part is the difficult oxidative decomposition of ash (Ash) (Z. Wang et al. 2017). The mass fraction of weight loss in each temperature interval in the weight loss curve (TG) was counted to derive the mass fraction of each component in the particles.

(3) Activation energy

Activation energy is an important parameter in the combustion process. It reflects the degree of combustion and is the minimum energy required for the reactant molecules to reach the activating molecule. The smaller the activation energy, the easier the particles are oxidized and the more likely the chemical reaction occurs (J. Song et al. 2006). The activation energy of the particles was calculated by the Coats-Redfern integration method, and equation (4) was the Coats-Redfern equation (Raj et al. 2013).

$$\ln \left(-\frac{\ln(1-c)}{T^2} \right) = -\frac{E}{RT} + \ln \left(\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right) \quad (4)$$

Where C is the rate of change of mass; R is the molar gas constant; T is the reaction

temperature; E is the activation energy; β is the heating rate.

Due to $E \gg RT$, equation (4) is reduced to equation (5)

$$\ln \left(-\frac{\ln(1-c)}{T^2} \right) = -\frac{E}{R} \cdot \frac{1}{T} + \ln \left(\frac{AR}{\beta E} \right) \quad (5)$$

The latter term in equation (5) was regarded as a constant, and equation (5) was reduced to a one-primary equation (6), where $1/T$ is the independent variable x ; and $\ln(-\ln(1-c)/T^2)$ is the Dependent variable y .

$$y = -ax + b \quad (6)$$

The activation energy of the particles is derived by fitting the TG curve.

3 Results and discussion

3.1 Characterization of particle adsorption capacity

Fig. 2 shows the isothermal adsorption and desorption curves of nitrogen gas by carbon black and three groups of sample particles. From **Fig. 2**, it is observed that both carbon black and exhaust particles have adsorption capacity. In the region of relative pressure from 0 to 0.8, the adsorption of nitrogen by both carbon black and particles increases with the increase of relative pressure, and the adsorption increases sharply after the relative pressure exceeds 0.8. From the shape of the adsorption isotherm, the trend of nitrogen adsorption by carbon black and sample particles classified as type II isotherm adsorption, which is the case of adsorption in multiple layers of porous media, similar to the findings of (Fang et al. 2008). The sharp increase in adsorption at relative pressures approaching 1 is primarily attributed to the capillary condensation of nitrogen within the pores of the particles. The adsorption isotherm of the sample does not coincide with the desorption isotherm, and a significant hysteresis of the desorption

isotherm is noticed throughout the measurement range, forming a clear hysteresis loop. The above observations indicate the existence of shape inversion within the pore, i.e., the width of the pore at the depth of the material grain is larger than that at the edge (Kisiela 2016). According to Kelvin's theory, the emergence of a hysteresis loop indicates that the adsorption and desorption of particles are irreversible. Under the same conditions, the adsorption of nitrogen by sample particles 1, 2 and 3 gradually increased, indicating an increase in the adsorption capacity of the samples. The adsorption capacity of particles increases with the increase of diesel engine speed at the same load rate.

Fig. 2. Nitrogen adsorption/desorption isotherms of carbon black and sample particles

Fig. 3 presents the pore diameter distribution curves of carbon black and sample particles obtained by the DFT method. It is shown in **Fig. 3** that the pore diameters of both carbon black and diesel sample particles show a multi-peaked continuous distribution, with pore diameters distributed between 8 and 80 nm. According to the classification of pore diameter, pore diameter less than 2nm belongs to microporous, pore diameter between 2~50nm belongs to medium pore, and pore diameter more than 50nm belongs to the large pore. It is expected that the pore diameters of the samples

belong to the mesopore and macropore categories, and no micropores are present.

Fig. 3. Particle pore diameter distribution

Table 5 presents the specific surface area and pore volume parameters of carbon black and exhaust particles. **Table 5** reveals that the diesel exhaust particles have a large specific surface area and pore volume similar to carbon black. The specific surface area of sample particles 1, 2 and 3 gradually increased, the average pore radius decreased, and the pore volume increased. This attributed to the fact that the air combustion under lower speed conditions is relatively small, the combustion duration and diffusion combustion period of the diesel engine is longer, which facilitates the nucleation and surface growth of the basic carbon particles in the cylinder, and the pores between the generated particles are more compact. With the increase of diesel engine speed, the temperature and pressure in the cylinder increase, the airflow movement is intensified, and the oxidation degree of the particles generated by in-cylinder combustion increases, resulting in more complex pore structure and increased specific surface area of the particles.

The specific surface area contains the particle surface area and the pore wall area, the larger the specific surface area, the greater the chance of contact between the

particles and the adsorbent in the exhaust process, the easier it is for the adsorbent molecules to adhere to the surface of the particles, and the greater the adsorption capacity of the particles. The smaller the pore diameter, the greater the force between the particle pore surface and the adsorbent molecules, the stronger the adsorption capacity of the particles on the material. The pore volume increases, the surface within the particle pores increases, the more adsorbent molecules were accommodated on the surface and within the pores, the stronger the adsorption capacity. This shows that the adsorption capacity of sample particles 1, 2 and 3 gradually increases.

Table 5. Specific surface area and pore parameters of carbon black and sample particles

Samples	Specific surface area $/\text{m}^2 \cdot \text{g}^{-1}$	Average pore diameter /nm	Pore volume $/\text{mL} \cdot \text{g}^{-1}$
Carbon Black	78.003	13.845	0.099
1	65.408	14.483	0.093
2	78.562	13.236	0.113
3	101.885	10.736	0.152

The adsorption capacity of the adsorbent also depends on its morphological structure (Tang 2020). **Fig. 4** shows the SEM images of the sample particles. Be observed as shown in **Fig. 4**, the diesel exhaust particle agglomerates have certain pore space inside and on the surface with a sponge-like structure. The structure formed by the accumulation between the particles is relatively loose, and the pore structure is complex and irregular. Besides, the basic carbon particles that build up the particles are

composed of multiple layers of graphene, and there are certain gaps between the graphene layers (Pahalagedara et al. 2012). Water vapor and gaseous SOF are absorbed easily on the surface and in the pores.

It also is seen from Figure 4 that with the increase of diesel engine speed, the basic carbon particles of the sample particles have a smaller particle size, looser structure, more complex pore structure and finer pores. This is explained by the fact that under lower speed conditions, the in-cylinder temperature and pressure are relatively low, and the particles are less oxidized during the whole combustion process, and the basic carbon particles are larger. With the increase of diesel engine speed, the reaction time of fuel in the combustion chamber decreases, and the chance of oxidation and growth for particles in the high temperature oxygen-rich area inside the cylinder decreases (Di, Cheung, and Huang 2010), resulting in the reduction of basic carbon particle size and the lower degree of agglomeration between particles. This result also substantiates the specific surface area and pore volume parameters of the particles obtained by nitrogen adsorption.

Fig. 4. SEM diagrams of particles

3.2 Adsorption behavior on characteristics of particle

The D_B of the three groups of sample particles at the outlet and inlet of the exhaust pipe was calculated from the SEM images of the particles (Z. Wang et al. 2019). Based

on the thermogravimetric curves, the mass fraction of H₂O, SOF and the variation of E on the particles at the inlet and outlet of the exhaust pipe were calculated. The variation of the characteristics for the three groups of sample particles is shown in **Fig. 5**.

As is seen in **Fig. 5**, the DB of sample particles 1, 2 and 3 at the exhaust outlet increased by 0.0379, 0.0381 and 0.0274, respectively, compared to the particles at the exhaust inlet, which indicates that the particle gap was gradually filled by adsorbate as the particles in the exhaust adsorbed the exhaust fraction. The surface viscosity of the particles increases (Liu et al. 2020), the number of surface particles increases, and the box-counting dimension increases. With the adsorption of moisture and SOF in the exhaust pipe, the moisture and SOF mass fractions in the particles increased significantly from the inlet to the outlet of the exhaust pipe. The increases in moisture mass fraction of sample particles 1, 2 and 3 were 0.99%, 1.24% and 1.32%, respectively, and the increases in SOF mass fraction were 4.84%, 9.12% and 10.52%, respectively. The activation energy of the particles at the outlet of the exhaust pipe was reduced significantly and the oxidation activity of the particles increased compared to that at the inlet of the exhaust pipe. The activation energy reductions of samples 1, 2 and 3 were 34.77 kJ·mol⁻¹, 38.88 kJ·mol⁻¹ and 47.43 kJ·mol⁻¹, respectively. With the adsorption of SOF by the particles in the exhaust, the SOF mass fraction in the particles increases, and the heat volatilization of SOF will reduce the activation energy of the oxidation reaction of the particles (Meng et al. 2019). During the oxidation warming process, the free SOF in the particles will be oxidized at lower temperatures (Ji et al. 2020), while the non-free fraction of SOF (e.g., organic carbon components such as hydroxyl and

carboxyl functional groups in the adsorption layer) will be burnt in concert with carbon soot at higher temperatures, enabling rapid and complex combustion of the particles and degrading the energy required for the oxidation reaction (Li et al. 2019).

Fig. 5. Adsorption behavior on characteristics of samples

3.3 Correlation analysis of adsorption process influencing factors

To initially determine the correlation between the influencing factors of the adsorption process such as HC concentration, temperature, adsorption time, specific surface area and pore volume, and the variation of characteristics in particles. The increase of box-counting dimension (ΔD_B) of the particles from the inlet to outlet, the increase of water (ΔH_2O) and SOF (ΔSOF), and the decrease of activation energy (ΔE) were adopted as the dependent variables of the adsorption process. The factors affecting the adsorption process (including adsorption environment parameters and adsorption performance parameters) were considered as independent variables, and the parameters

of the independent variables of the adsorption process are shown in **Table 6**. Pearson correlation analysis was performed on the independent and dependent variables.

Table 6. Parameter table of independent variables in the adsorption process

Serial number	Variable Name	Source
A	HC concentration	I. Adsorption
B	Average temperature	environment
C	The temperature difference of adsorption process	parameters
D	Adsorption time	
E	Specific surface area	II. Adsorption
F	Average pore diameter	performance
G	Pore volume	parameters

The correlation heat map of various adsorption process influencing factors on the amount of change in particle characteristics is shown in **Fig.6**.

As is shown from **Fig.6**, ΔD_B is negatively correlated with the exhaust pipe temperature and HC concentration, and positively correlated with the adsorption time. The increase of the average temperature in the exhaust pipe is not conducive to the condensation and adsorption of moisture and SOF on the particle surface and in the pores. The ΔD_B increases with the increase of the adsorption time, probably owing to the significant decrease of the adsorption time resulted in a lower chance of aggregation of the particles by collision in the exhaust pipe. The specific surface area and pore volume were negatively correlated with ΔD_B , the average pore diameter was positively correlated with ΔD_B , and the decrease of average pore diameter was the primary reason

for the decrease of ΔD_B .

The correlation coefficients of the factors influencing the adsorption process were comparable for ΔH_2O and ΔSOF . The correlation between HC concentration and ΔH_2O and ΔSOF was found high, indicating that the adsorption of water and SOF by the sample particles increased with the increase of HC concentration in the adsorption environment. The temperature difference of the adsorption process is positively correlated with ΔH_2O and ΔSOF , demonstrating that the decrease in temperature contributes to the condensation and adsorption of water and SOF on the particle surface. The highest negative correlation between adsorption time and ΔH_2O and ΔSOF indicates that the decrease in adsorption time in this study did not constrain the increase in water and SOF adsorption by the sample particles, which may be explained by the increase in the adsorption capacity of the sample particles 1, 2 and 3 themselves. Among the pore structure parameters, specific surface area and pore volume were positively correlated with ΔH_2O and ΔSOF with high correlation; the average pore diameter was negatively correlated with ΔH_2O and ΔSOF , and similar findings were found by Chen et al. (2018). As the specific surface area and pore volume of the particles increase, the adsorption capacity of the particles increases with the amount of adsorption accommodated in the pores of the particles (Gu et al. 2019). Accordingly, the ΔH_2O and ΔSOF of the sample particles 1, 2 and 3 gradually increase.

The correlation between each independent variable and ΔE remained the same with ΔH_2O , which due to the increase of SOF content is a dominant factor contributing to the decrease of activation energy. As seen in **Fig. 6**, the HC concentration has a

substantial positive correlation to ΔE . As the HC concentration increases, the adsorption of SOF by sample particles 1, 2, and 3 increases, which contributes to the increase in ΔE of the particles at the inlet and outlet of the exhaust pipe. The adsorption time and ΔE have a large negative correlation, and the specific surface area and pore volume have a significant positive correlation on ΔE , indicating that the increase of specific surface area and pore volume has an essential contribution to the reduction of activation energy. Sharma et al. (2012) suggested that particulate matter with a high specific surface area is more susceptible to oxidation. The increase in specific surface area and pore volume enhances the probability of oxygen contact with the particles during the oxidation process, in consequence of the reduction in the energy required for the oxidation reaction. Besides, the specific surface area and pore volume of the particles will increase after the burning of SOF on the surface and in the pores during oxidation (Y. Gao et al. 2019). With the increase in specific surface area and pore volume, the increase in ΔE of sample particles 1, 2, and 3 at the inlet and outlet of the exhaust pipe.

Fig. 6. Correlation heat map of the factors influencing the adsorption process and changes in particle characteristics

4. Conclusion

Through the diesel engine bench test, the adsorption capacity of carbon black and diesel exhaust particles was estimated and matched. The microscopic characteristics of the particles at the inlet and outlet of diesel exhaust were measured under different adsorption conditions, the rules of changes in particle morphology and oxidation activity caused by the adsorption behavior were summarized, and the correlation between the factors influencing the adsorption process and the changes in particle characteristics was investigated. The research conclusions are as follows:

(1) Diesel exhaust particles and carbon black have comparable adsorption capacity, and both belong to the type of multi-layer adsorption of porous medium for nitrogen gas, and the pore sizes present a continuous distribution of multi-peaks, which correspond to medium and large holes category. 100% load, the diesel engine speed increased from $1500 \text{ r}\cdot\text{min}^{-1}$ to $3600 \text{ r}\cdot\text{min}^{-1}$, the specific surface area of sample particles 1, 2 and 3 increased, the average pore diameter decreased, the pore volume increased, and the pore structure increased. The contact probability between the particles and the adsorbate increased, the amount of adsorbent that could be accommodated on the particle surface and in the pores increased, and the adsorption capacity was enhanced.

(2) The adsorption behavior changes the physicochemical properties of the particles significantly. Compared with the particles at the inlet of the exhaust pipe, the box-counting dimension of samples 1, 2 and 3 at the outlet of the exhaust pipe increased by 2.03%, 1.98% and 1.42%, respectively; The mass fraction of water in the particles

increased by 0.99%, 1.24% , 1.32%, and the mass fraction of SOF increased by 4.84%, 9.12%, and 10.52%, respectively; the energy of samples 1, 2, and 3 were reduced by 34.77 kJ·mol⁻¹, 38.88 kJ·mol⁻¹, and 47.43 kJ·mol⁻¹, respectively.

(3) The adsorption environment parameters and the adsorption performance parameters of particles have a large influence on the adsorption behavior of particles. With the increase of HC concentration, the adsorption of water and SOF by the particles increased and the reduction of activation energy increased; the increase of exhaust pipe temperature suppressed the reduction of box-counting dimension; the increase of temperature difference between inlet and outlet of exhaust pipe enabled the adsorption of particles to increase; the reduction of box-counting dimension decreased with the decrease of adsorption time. As the specific surface area and pore volume of the sample particles increase, the adsorption of water and SOF by the particles increases and the activation energy decreases to a greater extent.

(4) The analysis of the factors influencing the adsorption process reveals that when the diesel engine particles with large specific surface area and abundant pore structure are emitted into the atmosphere with the exhaust gas, the decrease in ambient temperature will cause particles to inevitably adsorb volatile components from the air. As the suspension time of the particles in the air increases, the harmful substances adsorbed on the surface and in the pores of the particles increase, the viscosity of the surface by particles increases, the degree of aggregation between particles and particles increases, and the detrimental extent of particles to the environment and human body increases.

458

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466

467 **Credit authorship contribution statement**

468 **Zhong Wang:** Conceptualization, Methodology. **Qixia Zhang:** Visualization, Writing-
469 original draft. **Shuai Liu:** Investigation, Validation. **Ruina Li:** Software. **Yan Hua:**
470 Software, Analysis of data. **Zheng Dong:** Supervision.

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475

476 **Data Availability**

477 All relevant data are within the manuscript and available from the corresponding
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479

480 **Compliance with ethical standards**

Ethical approval

Not applicable.

Consent to participate

All authors have given consent to their contribution.

Consent to publish

All authors have agreed with the content and all have given explicit consent to publish.

Competing interests

The authors declare that they have no conflict of interest.

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642

Figures

Figure 1

Schematic diagram of the test setup and particle collection

Figure 2

Nitrogen adsorption/desorption isotherms of carbon black and sample particles

Figure 3

Particle pore diameter distribution

Figure 4

SEM diagrams of particles

Figure 5

Adsorption behavior on characteristics of samples

Figure 6

Correlation heat map of the factors influencing the adsorption process and changes in particle characteristics