



## Research Paper

Research of DPF regeneration with NO<sub>x</sub>-PM coupled chemical reactionPenghao Jiao<sup>a,b</sup>, Zhijun Li<sup>a,\*</sup>, Boxi Shen<sup>a</sup>, Wen Zhang<sup>a,b</sup>, Xiangjin Kong<sup>a</sup>, Rui Jiang<sup>a</sup><sup>a</sup> State Key Laboratory of Engines, Tianjin University, Tianjin 300072, China<sup>b</sup> Tianjin Electronic Information College, Tianjin 300350, China

## HIGHLIGHTS

- A NO<sub>x</sub>-PM coupled chemical reaction mechanism containing N<sub>2</sub>O reaction for DPF regeneration is improved.
- Two key coefficient in NO<sub>x</sub>-PM reaction are defined and analyzed, which have a major impact on DPF regeneration.
- During the reaction process of NO<sub>x</sub>-PM, N<sub>2</sub>O and CO are important intermediate products affecting DPF regeneration efficiency.

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## ABSTRACT

Diesel engine exhaust gas flows through the DOC upstream of the DPF system. In this process, NO contained in NO<sub>x</sub> is oxidized into NO<sub>2</sub> and then enters DPF. The presence of NO<sub>2</sub> can greatly reduce the light-off critical temperature of soot particles, so that the soot particles captured by DPF will conduct a certain amount of continuous passive regeneration at a lower temperature. However, there is the complex coupling reaction relationship between NO<sub>x</sub> and PM contained in the DPF, not only the reaction between the particulates and NO<sub>x</sub>, but also a series of reaction between CO and NO<sub>x</sub>. And except NO and NO<sub>2</sub> of NO<sub>x</sub> in diesel engine exhaust which are recognized and studied widely, there is a small amount of N<sub>2</sub>O generated as the intermediate product in the entire reaction process of DPF generation. The oxidation ability of NO<sub>2</sub>, NO, and N<sub>2</sub>O contained in NO<sub>x</sub> are different, and the change of diesel engine exhaust composition also affects the quantity and proportion of them. These factors have a close relationship with the removal of soot particulate, in other words, the regeneration of DPF. This paper builds the NO<sub>x</sub>-PM reaction mechanism in DPF, and studies the chemical reaction process between NO<sub>x</sub> and PM under different inlet conditions. This paper defines the coefficient  $\alpha$ , which is used to characterize the ratio of NO<sub>2</sub> in diesel engine exhaust at the DPF inlet accounting for the total amount of NO<sub>x</sub>. The results show that when  $\alpha$  is between 0.7 and 0.8, the good regeneration removal effect of soot particulates under the premise of not worsening NO<sub>x</sub> removal efficiency is achieved. The molar ratio of NO<sub>x</sub> at the DPF inlet and carbon in the PM is defined as  $\beta$ . When  $\beta \approx 1$ , NO<sub>x</sub> removal efficiency is the maximum. When  $\beta \geq 8$ , the soot particulates can complete continuous passive regeneration totally only by relying on the mutual reaction of DPF internal reactants in this condition. Investigation results show that N<sub>2</sub>O and CO are important intermediate products during the reaction process of NO<sub>x</sub>-PM.

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## 1. Introduction

In the former DPF research, NO<sub>2</sub> oxidability was considered better than O<sub>2</sub>, and the existence of NO<sub>2</sub> can greatly reduce the light-off critical temperature of soot particulates. As shown in Fig. 1 [1–3], the existence of NO<sub>2</sub> can reduce the oxidation temperature of soot particulates from 450–550 °C to 200–300 °C (reacting with O<sub>2</sub>), improves the burning rate of soot particulates, and enables the DPF to conduct part passive regeneration at the lower

diesel engine exhaust gas temperature. It is generally recognized that the oxidation process of soot particulates in DPF has the reactions as shown in Formula (1) [4–13].



As shown in Formula (1), the three reactions can describe the oxidation process of soot particulates by NO<sub>2</sub> and O<sub>2</sub> in DPF, but also it has certain limitation and imperfection. This is because there is a small amount of N<sub>2</sub>O contained in the NO<sub>x</sub> from diesel engine exhaust, besides the NO and NO<sub>2</sub>. N<sub>2</sub>O is a potent

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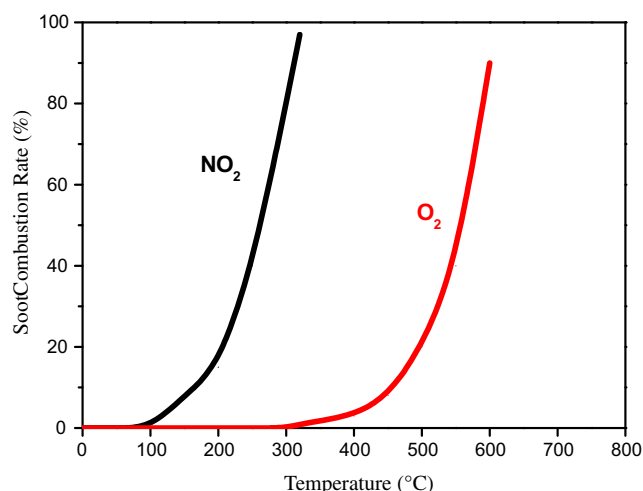


Fig. 1. The combustion temperature of soot.

greenhouse gas, and it stays a long time in the atmosphere and can be transferred into the stratosphere. Meanwhile,  $N_2O$  is one of substances causing ozone layer depletion. Although with very low atmosphere concentration,  $N_2O$  is a greenhouse gas which is 310 times more potent than carbon dioxide [14]. Its warming effect on the global climate will become significant in the future, so the increase of  $N_2O$  concentration has attracted great attention of scientists. In addition,  $N_2O$  not only exists in diesel engine exhaust, but also exists in the reaction process of  $NO_x$  and soot particulates as an important intermediate product. So the reaction process involving  $N_2O$  should be considered for advanced research.

Meanwhile the DPF filter wall is coated with a layer of the noble metal catalyst for improving the renewable efficiency of soot particulates. The principle of this approach is mainly to drive the soot particulates in Formula (1) to react with  $NO_2$  to generate  $NO$  to be oxidized to  $NO_2$  continuously, thus making it react with soot particulates continuously, and improving the regeneration efficiency of soot particulates. In the DPF coated with the catalyst, the reaction process of  $NO_x$  and soot particulates is more complicated than the original reaction process in DPF, and the oxidation path of soot particulates is more complex with more intermediate products, but meanwhile the regeneration efficiency of soot particulates is higher, and a certain amount of diesel engine  $NO_x$  also can be removed.

Worldwide, scholars have done a lot of research on the removal of  $NO_x$  and particulate emissions from diesel engine exhaust [15–18]. Some of them have made a deep study of the reaction mechanism between the  $NO_x$  and the particles. When Schejbal et al. [19] studied the reaction mechanism in the catalytic DPF, they added the reaction of the soot particulates with  $NO$  and the reaction of  $CO$  with  $NO$ . When Artioli et al. [20] studied the storage-reduction of diesel engine  $NO_x$ , they also studied the coupling reaction of  $NO$  and  $NO_2$  with soot particulates. Cho [21] reported that  $CO-N_2O$  reaction plays an important role during  $NO$  reduction by  $CO$ . Su et al. [22] did a more detailed study of the  $CO-N_2O$  reaction, found that removing  $CO$  out of the reaction system, the oxygen generated via the dissociation of adsorbed  $N_2O$ . To the aftertreatment system, reactions in upstream  $DOC + DPF$  also have influences to the downstream  $SCR$  [23,24]. Dual fuel mode significantly decreases the  $NO_x$ , carbon dioxide ( $CO_2$ ) and  $PM$  emissions. However, the hydrocarbon ( $HC$ ) and carbon monoxide ( $CO$ ) emissions may increase by several times or even more than 100 times in comparison to normal diesel combustion [25]. Müller et al. [26] investigated the oxidation of soot particulate in the presence of  $NO_2$  and found that an increased surface

functionalization with oxygen groups and a subsequent decomposition thereof are the main reasons for acceleration of the soot oxidation by  $NO_2$  in the low temperature region (250–400 °C). Bogdanic et al. [27] developed a DPF Model and investigated model extensions as well as further development regarding soot monitoring during regeneration. Lee et al. [28] predicted the thermal behavior of the monolith during regeneration and the conversion efficiency of  $NO_2$  from  $NO$  with an integrated exhaust system of a diesel oxidation catalyst ( $DOC$ ) and DPF by one-channel numerical simulation. The results indicate that the case of the volume ratio of ' $DOC/DPF = 1.5$ ' within the same diameter of both monoliths produced close to the maximum conversion efficiency and oxidation rate of  $PM$ .

In summary, the coupling reaction of  $NO_x$  with soot particulates and  $CO$  should be considered comprehensively for the complex reaction process in DPF. However, it is obvious that the reactions in Formula (1) are not able to achieve. The purposes of this paper are to improve a relatively complete  $NO_x-PM$  coupling reaction mechanism, to clarify the reaction relationships between  $NO_x$ ,  $N_2O$ ,  $C$ ,  $CO$  and so on, and to study the factors influencing the internal reactions in DPF.

## 2. $NO_x-PM$ reaction mechanism in DPF

$NO$  contained in DPF will be oxidized to  $NO_2$  due to the existence of catalyst in DPF. The reaction mechanism of  $NO_x$  and soot particulates in DPF is obtained by considering the reactions R1–R16, as shown in Table 1 [4–13]. The reaction scheme of  $NO_x$  and soot particulates in DPF is shown in Fig. 2.

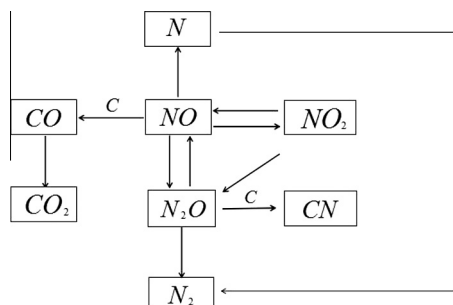
$NO$  is roughly divided into four parts. The first part comes from  $NO_x$  included in diesel engine exhaust, in other words, the remaining  $NO$  which flows through the  $DOC$  but not fully oxidized to  $NO_2$ ; The second part comes from a small amount of  $NO$  formed by the combustion of afterburner combustion improver; The third part comes from the  $NO$  generated in the reaction process of  $NO_2$  and soot particulates; The fourth part comes from the  $NO$  generated from the relevant reaction of  $N_2O$  and other intermediate reactants. The four part is oxidized to  $NO_2$  under the action of catalyst in DPF, and  $NO_2$  continues to participate in the latter reaction. So the reaction R7 should be added to the reaction mechanism. Due to the high activity of  $NO_2$ , there will be a part of  $NO_2$  reduced to  $NO$  and  $O_2$ , considering the reduction reaction of  $NO_2$ , so the reaction R8 will be added to the reaction mechanism.  $N_2O$  is an indispensable part in the whole reaction system and  $N_2O$  will be transformed between  $NO$ ,  $NO_2$ ,  $N_2$  and other components, to participate in the reaction in addition to its existence in diesel engine exhaust. So the reactions R9–R13 are added to the reaction mechanism.  $N_2O$  and  $NO$  have oxidation resistance and they can react with part soot particulates in the presence of catalyst.  $N_2O$  will react with soot particulates to form  $NO$ .  $NO$  will react with soot particulates to form  $CO$  and nitrogen atoms. So the reactions R2 and R3 are added to the reaction mechanism. Under the effect of catalyst,  $CO$  in DPF will participate in mutual reaction between  $NO_x$ , and plays an important role in the whole reaction process. The reduction of  $NO_x$  (including  $NO$ ,  $NO_2$ ,  $N_2O$ ) by  $CO$  will generate  $N_2$  or an important component and reactant of the nitrogen atom, and  $CO$  itself will generate  $CO_2$  when implementing the complete oxidation reaction. So the reactions R4–R6 are added to the reaction mechanism. The reaction of nitrogen atoms association to form  $N_2$  molecule is considered. So the reaction R16 is added to the reaction mechanism. Finally, the three reactions in Formula (1) are reorganized and added to the reaction mechanism as R1, R14 and R15.

After the diesel engine exhaust entering the DPF, the mutual transformation reaction process between  $NO_x$ , reaction process

**Table 1**

The reaction mechanism inside DPF.

No.	Reactions $k_f = AT^b \exp(-E/RT)$	A	b	E	Remarks
R1	$C + NO_2 = CO + NO$	$3.90E+13$	0	177	Reaction mechanism of C and NOx
R2	$C + N_2O = CN + NO$	$4.10E+13$	0	258	
R3	$C + NO = CO + N$	$2.90E+13$	0	322	
R4	$NO_2 + CO = NO + CO_2$	$2.19E+13$	0	29200	Reaction mechanism of CO and NOx
R5	$N_2O + CO = N_2 + CO_2$	$2.70E+13$	0	740	
R6	$NO + CO = N + CO_2$	$1.90E+11$	0	3400	
R7	$NO + O_2 = NO_2 + O$	$1.00E+13$	0	600	Conversion reaction between NOx
R8	$NO_2 + NO_2 = NO + NO + O_2$	$2.00E+12$	0	26825	
R9	$NO_2 + NO = N_2O + O_2$	$1.00E+12$	0	60000	
R10	$N_2O + OH = N_2 + HO_2$	$2.00E+12$	0	40000	
R11	$N_2O + O = N_2 + O_2$	$1.40E+12$	0	10800	
R12	$N_2O + O = NO + NO$	$2.90E+13$	0	23150	
R13	$N_2O + N = N_2 + NO$	$1.00E+13$	0	19870	
R14	$CO + O_2 = CO_2 + O$	$2.50E+12$	0	47800	Reaction mechanism of C, CO and $O_2$
R15	$C + O_2 = CO + O$	$2.00E+13$	0	576	
R16	$N + N = N_2$	$2.90E+10$	0	133	

**Fig. 2.** The reaction scheme of NOx and soot particulates in DPF.**Table 2**

The main parameters of diesel engine ISDe285.

Name	Parameters
Type	Direct injection, L6
Swept volume (L)	6.7
Compression ratio	16.6
Bore (mm)	107
Stroke (mm)	120
Max. rated power	210 kW at 2100 min <sup>-1</sup>
Max. rated torque	970 N m at 1400 min <sup>-1</sup>

between soot particulates and NOx, reaction process between CO and NOx, reaction process between soot particulates and  $O_2$  and the reaction of the mutual combination of nitrogen atoms to form  $N_2$  molecule are detailed in Table 1.

### 3. Experiment

The engine bench test is used to obtain the emission data of the corresponding emissions upstream and downstream of DOC and DPF under different conditions and reaction conditions to verify the correctness of the reaction mechanism and provide the initial input data and comparison basis for the subsequent simulation calculation.

The engine bench test device used in the system is ISDE285 diesel engine and the matching DPF post-processing system of Dongfeng Cummins Co., Ltd. The main technical parameters of diesel engine are shown in Table 2.

DPF matched with Cummins ISDE285 diesel engine uses the diesel particulate trap produced by Anhui Actblue Energy Conser-

**Table 3**

The main structure parameters of DPF.

Name	Parameters
Filter materials	Cordierite
Filter manufacturing plant	NGK (Suzhou) Environmental Ceramics Co., Ltd.
Filter length (mm)	280
Filter diameter (mm)	228
Filter volume (L)	11.42
Hole density (cpsi)	400
In wall thickness (μm)	6.5
Outer wall thickness(μm)	1
Cushion type	Vermiculite
Cushion manufacturing plant	England, Sappho
Cushion thickness (mm)	13.5
Cushion weight (g/m <sup>2</sup> )	2400
Case material	SUS304
Case manufacturing plant	Shanghai Baosteel

vation and Environmental Protection Technology Co., Ltd., and its main structure parameters are shown in Table 3.

The whole test bench diagram and schematic diagram of the engineer are as shown in Fig. 3.

By the above the engine bench test, the actual engine-related emission data (Load = 50%, containing DOC and DPF inlet, outlet emission data) is obtained as shown in Table 4.

The boundary condition of DPF reactor, volume  $V = 11.42$  L, was set with test equipment parameters. The initial data is entered according to the emission data of diesel engine emissions at the inlet of DPF front end when the actual working load is equal to 50%, and rotation speed is 1600 r/min. The NOx-PM built above is used to conduct the simulation calculation on the reactants inside DPF, and the simulation results are compared with the test data of diesel engine emissions at the inlet of DPF, to verify the correctness and rationality of the simulation results of the emissions changes in DPF by NOx-PM mechanism, thus taking the reaction mechanism as the theoretical foundation of the subsequent simulation.

Fig. 4A is the comparison diagram of NOx conversion rate between test value and simulation value, and you can see from the figure that the conversion efficiency of NOx within 350–600 s raises fast, reaching the maximum conversion rate after 600 s. The variation trends of simulation value and experiment value are consistent. The NOx maximum conversion rate of the simulation value is 13.1%, slightly higher than 12.9% of the test value. The maximum relative error value is 4.7% at  $t = 550$  s and the error is within the acceptable range. Simulation value matches the test

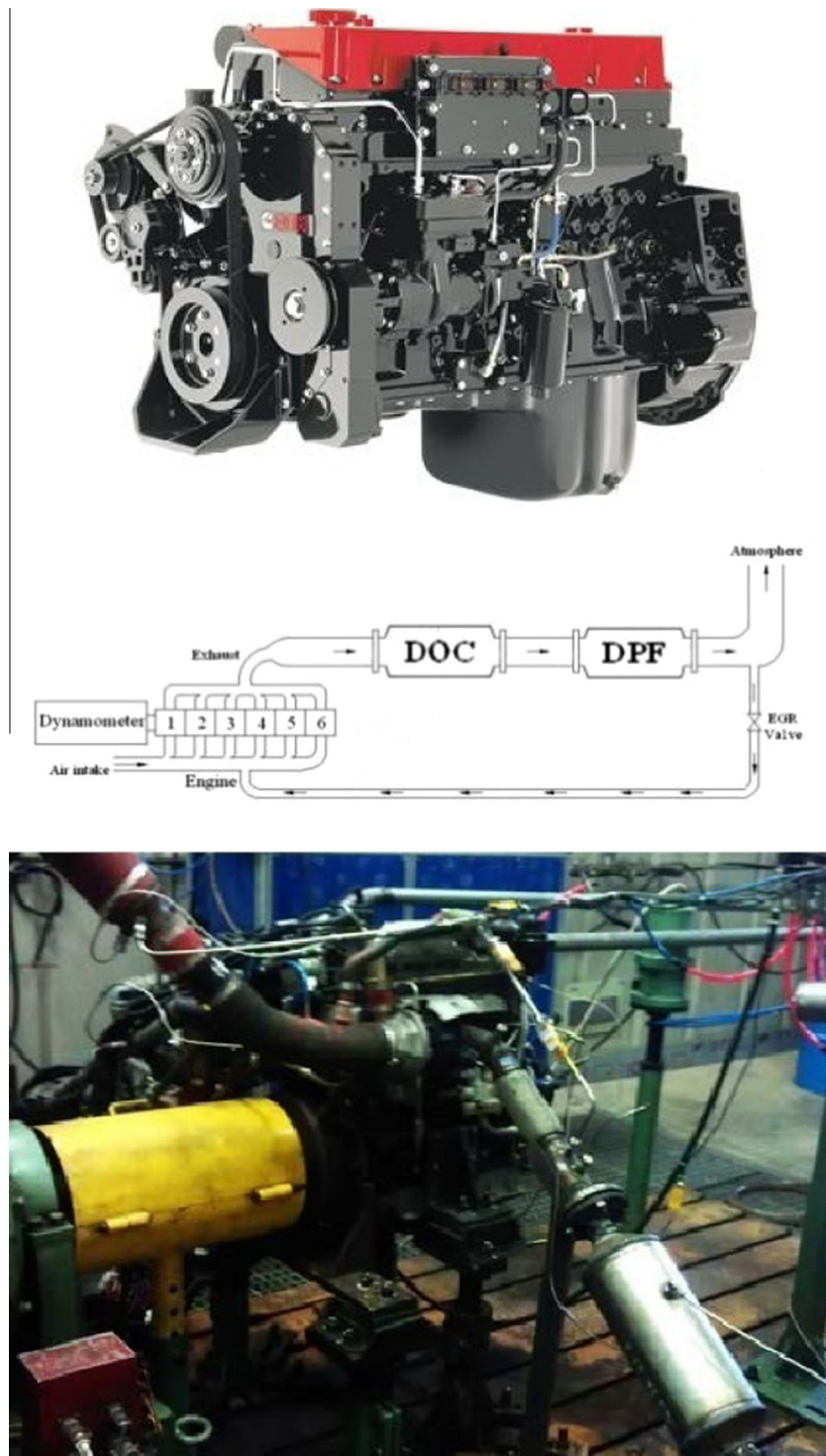


Fig. 3. The test bench diagram and schematic diagram of the engine.

value well, and the mechanism can be used for the subsequent simulation.

Fig. 4B is the comparison diagram of between test value and simulation value of PM quality. It can be seen from the figure that PM is trapped quickly after entering the DPF in the first place, and has been trapped completely within the 600 s. The variation trends of simulation value and experiment value are consistent, of which PM minimum value of the simulation values at the inlet is close to 0, slightly lower than 0.226 of the test values, and the maximum

relative error value is 5.3% at  $t = 400$  s, and the error is within the acceptable range. Simulation value matches the test value well, and the mechanism can be used for the subsequent simulation.

#### 4. Results and discussion

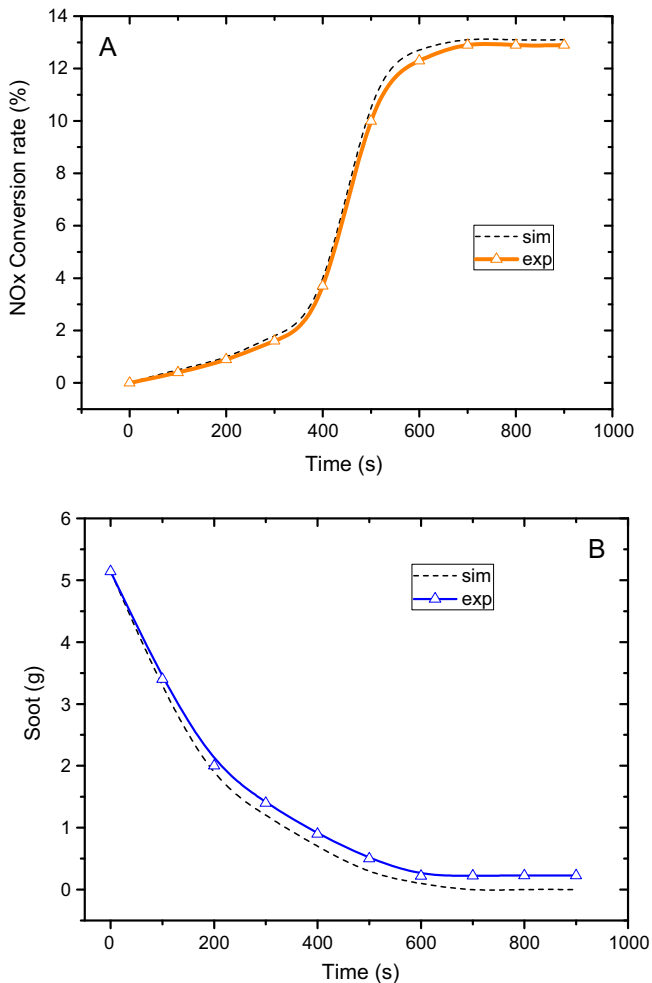
With the NOx-PM reaction mechanism built in this paper, the test value can match with the reactants change trend. And the



**Table 4**

CO HC NOx emission of downstream of DOC and DPF.

	Engine speed (rpm)	CO (ppm)	HC (ppm)	NOx (ppm)	PM (g)
DOC inlet	1300	704.71	70.783	817.85	6.69
	1600	122.98	65.437	1090.5	6.04
	1900	44.975	50.906	1203.7	3.556
DOC outlet (DPF inlet)	1300	46.5	12.377	800.45	5.688
	1600	7.2	12.263	1084.2	5.141
	1900	4.3	12.597	1198.4	3.023
DPF outlet	1300	39	10.377	719.4	0.299
	1600	5.8	10.263	941.7	0.226
	1900	3.5	10.597	1073.8	0.108



**Fig. 4.** (a) Comparing of the simulating results and experimental values on the conversion rate of NOx. (b) Comparing of the simulating results and experimental values on PM mass change between the front and end of DPF.

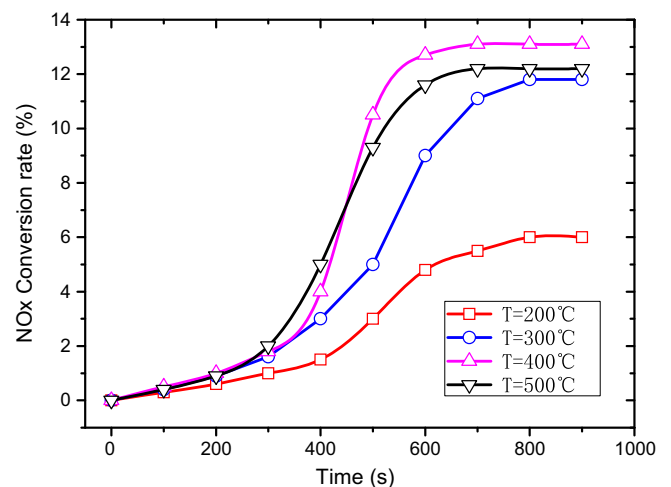
reaction result of the NOx and soot particulates can be described accurately. The reaction mechanism can be also used to study the change rule of initial reactants and intermediate products in DPF. In addition, adding the related reaction mechanism and numerical simulation can greatly reduce the corresponding test dose in the research process of the NOx-PM coupling reaction in DPF, save the test cost, and can further study the influence factors of reaction process, and explore the changes of the intermediate products and its role in the reaction process.

This paper uses the Perfect Stirred Reactor model to simulate NOx-PM response. Let DPF reactor volume  $V = 11.42$  L, the engine Load = 50%, engine speed  $n = 1600$  r/min, DPF inlet NOx =

1090 ppm (including NO = 1000 ppm, NO<sub>2</sub> = 90 ppm), exhaust gas flow  $Q = 125$  g/s, the reaction time  $t = 15$  min, the trapped PM quality is 5 g in DPF during the period, and the simulated calculation is implemented on the reaction process between NOx and PM based on the initial condition above, to study the influencing factors of the reaction process.

#### 4.1. The influence of the exhaust temperature on NOx PM reaction

Fig. 5 is the change trend comparison diagram of NOx conversion rate over time under different exhaust temperature at the DPF inlet. The figure shows that when exhaust temperature is  $T = 200$  °C at the DPF inlet, and the light-off critical temperature of the soot particulates hasn't been reached, due to the lower initial temperature. In other words, there are few soot particulates involving the reaction with NOx, so the maximum conversion rate of NOx is very low in the late reaction, only around 6%, and the time of reaching saturation is very long. As the exhaust temperature at the DPF inlet rises, NOx conversion rate increases obviously, and the time of reaching saturation also gradually shortens, and NOx conversion rate reaches the highest value 13.1% when the exhaust temperature at the DPF inlet is  $T = 400$  °C. DPF inlet temperature continues to rise, although the curve slope of NOx conversion rate at  $T = 500$  °C is higher than that at  $T = 400$  °C between 400 and 550 s, and the final conversion rate of NOx is lower than that at  $T = 400$  °C. There are two reasons for this situation: First, the higher exhaust temperature at the DPF inlet inhibits the reduction removal reaction of NOx making the range of related reversible reaction increase toward the direction of the NOx; Second, with the increase of the exhaust temperature at the DPF inlet, the proportion of the soot particulates and oxygen reaction increases at



**Fig. 5.** Change of The conversion rate of NOx with time.

above 450 °C, resulting in the decrease of soot particulates reacting with NO<sub>x</sub> synergistically, thus reducing the NO<sub>x</sub> removal efficiency at high temperature. Thus it can be seen that as the exhaust temperature at the DPF inlet rises, and the NO<sub>x</sub> conversion rate first increases and then decreases. The temperature ranges from increasing to decreasing should be between 400 and 500 °C, and higher exhaust temperature inhibits the NO<sub>x</sub> conversion efficiency, causing more NO<sub>x</sub> emissions.

Fig. 6 is the change trend comparison diagram of PM quality in DPF over time under different exhaust temperature at the DPF inlet. The figure shows that when exhaust temperature at the DPF inlet is  $T = 200$  °C, although there is NO<sub>x</sub> in the exhaust and NO<sub>x</sub> can significantly reduce the light-off critical temperature of soot particulates. The light-off critical temperature of the soot particulates hasn't been reached, due to the lower initial temperature, so PM quality in DPF doesn't significantly reduce and slightly decreases only within the scope of  $T = 400$ – $600$  s until it reaches equilibrium. There is still more than 80% of soot particulates not oxidized after the reaction ends. As the exhaust temperature at the DPF inlet rises, PM reaches its light-off critical temperature under the action of NO<sub>x</sub>, so PM is oxidized at a ferocious rate and quality has been dramatically reduced compared with the situation at  $T = 200$  °C. When the exhaust temperature at the DPF inlet is  $T = 500$  °C, P is oxidized and 90% P is removed under the combined action of NO<sub>x</sub> and oxygen at the end of the reaction. Thus it can be seen that as the exhaust temperature at the DPF inlet rises, oxidation rate and removal efficiency of soot particulates trapped by DPF continuously rises.

#### 4.2. The influence of different ratio relations between NO<sub>2</sub> and NO on the NO<sub>x</sub>-PM reaction

After the NO<sub>x</sub> in diesel engine exhaust flows through the DOC, the ratio relation between NO and NO<sub>2</sub> in the NO<sub>x</sub> after entering DPF has changed, because some NO is oxidized to NO<sub>2</sub>. In order to facilitate the study, the ratio of NO<sub>2</sub> accounting for the total amount of NO<sub>x</sub> in diesel engine exhaust at the DPF inlet is defined as  $\alpha$ , indicated as Formula (2).

$$\alpha = \frac{V_{\text{NO}_2}}{V_{\text{NO}_x}} \quad (0.1 \leq \alpha < 1) \quad (2)$$

There into,  $V_{\text{NO}_2}$  represents the content of NO<sub>2</sub> in the NO<sub>x</sub>,  $V_{\text{NO}_x}$  represents the total NO<sub>x</sub>,  $\alpha$  is the dimensionless number, representing the ratio of NO<sub>2</sub> accounting for the total amount of NO<sub>x</sub>

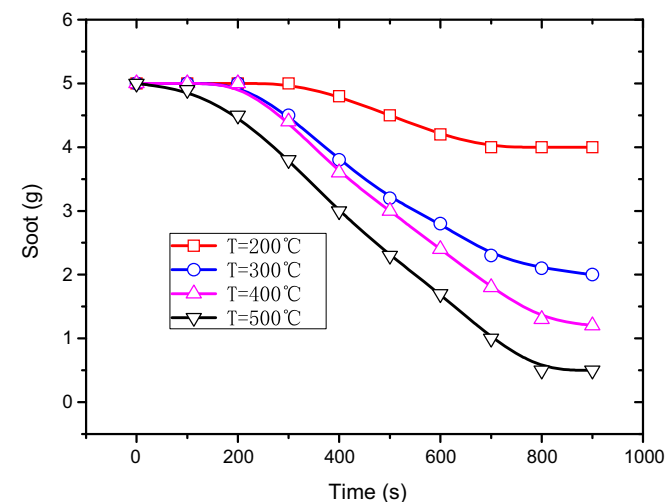


Fig. 6. Change of PM mass with time.

in diesel engine exhaust at the DPF inlet, and its size represents the amount of NO<sub>2</sub> contained in the exhaust gas. The initial content of NO<sub>2</sub> is about 10% of the total amount of NO<sub>x</sub>. Due to the oxidation of DOC, NO will be converted to NO<sub>2</sub>, so the proportion of NO<sub>2</sub> will increase. As a result,  $\alpha$  value should be greater than or equal to 0.1. Reversible reaction exists between NO and NO<sub>2</sub>. DOC is not able to oxidize NO contained in NO<sub>x</sub> into NO<sub>2</sub> completely, that is, the ratio of NO<sub>2</sub> contained in NO<sub>x</sub> cannot be 100%. So  $\alpha$  value range should be greater than or equal to 0.1 and less than 1 (i.e.,  $0.1 \leq \alpha < 1$ ). In addition, the total quantity of NO<sub>x</sub> remains the same when  $\alpha$  changes, that is, the increase and decrease of NO<sub>2</sub> are transformed from NO inside the NO<sub>x</sub>.

Fig. 7A is the variation trend of NO<sub>x</sub> conversion rate over  $\alpha$  when the exhaust temperature at the DPF inlet is  $T = 400$  °C. The figure shows that NO<sub>x</sub> removal efficiency is the highest at  $\alpha = 0.1$ , NO<sub>x</sub> removal efficiency keeps decreasing with the increase of  $\alpha$ , NO<sub>x</sub> removal efficiency reduces to the minimum 1.9% at  $\alpha = 1$  (it is theorized that all NO<sub>2</sub> is converted into NO, but actually it cannot) from 13.1% at  $\alpha = 0.1$ , and decreasing amplitude is more than 85%. Thus it can be seen that NO<sub>x</sub> removal efficiency keeps decreasing with the increase of  $\alpha$ . But it is worth noting that when  $\alpha$  is between 0.7 and 0.8, and NO<sub>x</sub> removal efficiency is on the decline, but declines slowly; NO<sub>x</sub> removal efficiency keeps a rapid decline, and decline rate is very quick beyond the range of 0.7–0.8; NO<sub>x</sub> removal efficiency decreases to 1.9% from 9.5% only within the

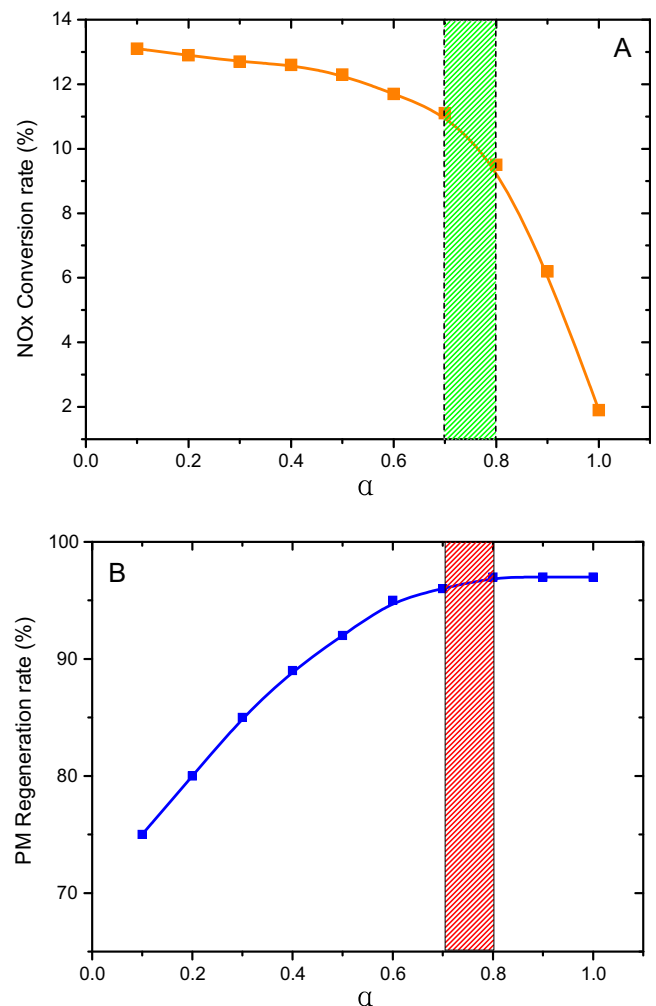


Fig. 7. (a) The regeneration effect of NO<sub>x</sub> with the change trend of  $\alpha$ . (b) The regeneration effect of PM with the change trend of  $\alpha$ .

range of 0.8–1.0, and the ratio of the reduction range accounting for the total reduction range of NO<sub>x</sub> removal efficiency when  $\alpha$  changes from 0.1 to 1.0 is 68%, nearly two thirds.

Fig. 7B is the variation trend of soot particulates regeneration effect over  $\alpha$  when the exhaust temperature at the DPF inlet is  $T = 400^\circ\text{C}$ . As can be seen from the figure that the maximum removal efficiency of soot particulates depending on passive regeneration is around 75% at  $\alpha = 0.1$ ; With the increase of NO<sub>2</sub> ratio at the inlet, in other words, the increase of  $\alpha$  value, the maximum removal efficiency of soot particulates rises rapidly, reaching the maximum about 97% at  $\alpha = 0.8$ , increasing by nearly 30% than that at  $\alpha = 0.1$ . Thus it can be seen that the increase of NO<sub>2</sub> ratio accounting for NO<sub>x</sub> at the inlet can significantly accelerate the oxidation process of soot particulates, and improve its regeneration efficiency. Therefore, we need to take measures inside the DOC of DPF front end such as increasing reaction time, and reaction temperature to convert as much NO as possible into NO<sub>2</sub>, and this has great improvement in improving the subsequent regeneration efficiency of soot particulates in DPF. But combined with the variation trend of NO<sub>x</sub> conversion rate over  $\alpha$  in Fig. 7A, when  $\alpha$  is beyond the range of 0.7–0.8, and NO<sub>x</sub> removal efficiency will worsen; When  $\alpha$  exceeds 0.8, the removal efficiency of soot particulates has reached saturation; after  $\alpha$  continues to be improved, the effect is not obvious. So through comprehensive consideration,  $\alpha$  value is controlled in the range of 0.7–0.8 by controlling the working process of DOC, to achieve the good regeneration removal effect of soot particulates under the premise of not worsening NO<sub>x</sub> removal efficiency.

#### 4.3. The influence of ratio relations between NO<sub>x</sub> and PM on the NO<sub>x</sub>-PM reaction

Due to the coupling reaction between NO<sub>x</sub> and PM in the DPF, the ratio relation between NO<sub>x</sub> and PM is closely related to the reaction between them and their removal efficiency. To simplify the calculation and be convenient to study, the ratio between the number of moles of NO<sub>x</sub> in the chemical reaction process between the two in the diesel engine exhaust at the DPF inlet and the number of moles of carbon in the PM is defined as  $\beta$ , indicated as Formula (3).

$$\beta = \frac{C_{\text{NO}_x}}{C_{\text{PM}}} \quad (3)$$

Thereinto,  $C_{\text{NO}_x}$  represents the number of moles of NO<sub>x</sub>,  $C_{\text{PM}}$  represents the number of moles of carbon in the soot particulates, and  $\beta$  is the dimensionless number, representing the molar ratio of carbon of NO<sub>x</sub> and DPF in diesel engine exhaust at the inlet.  $\beta < 1$  means excessive soot particulates in the exhaust, and  $\beta > 1$  means excessive NO<sub>x</sub> in the exhaust. Due to the increase of EGR rate in the diesel engine exhaust gas recirculation system, NO<sub>x</sub> in diesel engine exhaust can be reduced, and the PM in the exhaust will rise, so the EGR system can be used to adjust the relationship between NO<sub>x</sub> and PM values, in other words, adjusting the  $\beta$  value. According to the research conclusion of the influence of different ratio relations between NO<sub>2</sub> and NO on the NO<sub>x</sub>-PM reaction,  $\alpha$  value is controlled in the range of 0.7–0.8 to achieve the good regeneration removal effect of soot particulates under the premise of not worsening NO<sub>x</sub> removal efficiency, so the research is conducted on this section at  $\alpha = 0.7$ .

Fig. 8A is the variation trend of NO<sub>x</sub> conversion ratio over  $\beta$  when the exhaust temperature at the DPF inlet is  $T = 400^\circ\text{C}$ ,  $\alpha = 0.7$ . The figure shows that when  $\beta < 1$ , there is excessive PM, less NO<sub>x</sub> relative content, and NO<sub>x</sub> removal efficiency has little change; When  $\beta > 1$ , there is excessive NO<sub>x</sub> relative to the PM, and its conversion efficiency gradually reduces with the increase

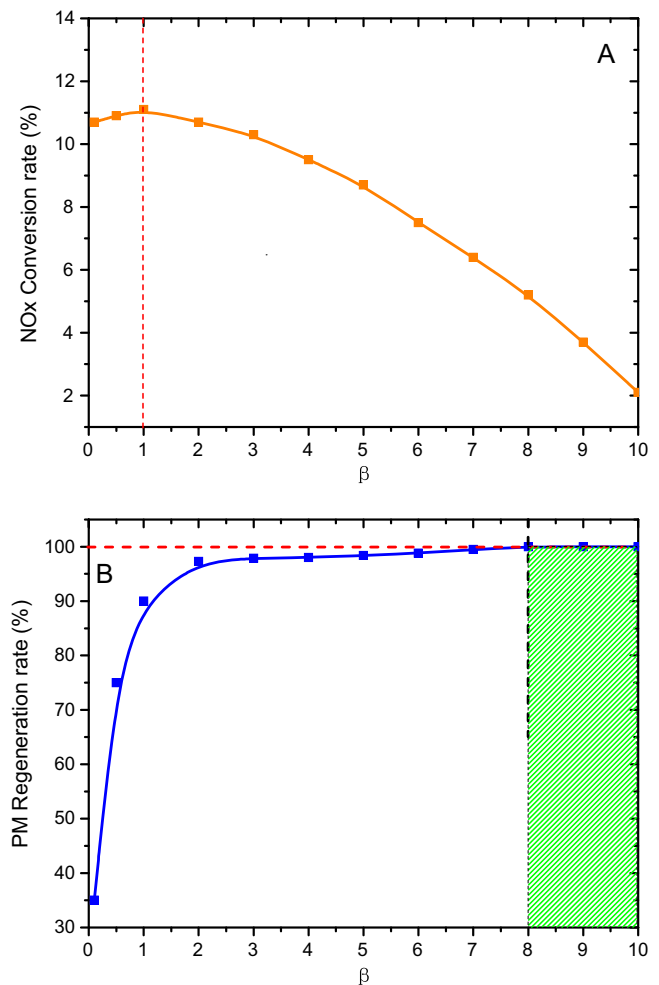


Fig. 8. (a) The regeneration effect of NO<sub>x</sub> with the change trend of  $\beta$ . (b) The regeneration effect of PM with the change trend of  $\beta$ .

of  $\beta$ . Thus it can be seen when  $\beta = 1$  or so, NO<sub>x</sub> removal efficiency is the maximum, and the molar ratio between NO<sub>x</sub> and PM is 1:1.

Fig. 8B is the variation trend of PM conversion ratio over  $\beta$  when the exhaust temperature at the DPF inlet is  $T = 400^\circ\text{C}$ , and  $\alpha = 0.7$ . The figure shows that when  $\beta < 1$  there is excessive PM, and less NO<sub>x</sub> relative content. The PM lacks sufficient NO<sub>x</sub> to react with it, so the removal efficiency is low; when  $\beta = 0.1$ , PM removal efficiency is only about 35%. With the increase of  $\beta$ , the removal efficiency of soot particulates increases rapidly, and it has exceeded 95% when  $\beta = 2$ . When  $\beta \geq 8$ , the removal efficiency of soot particulates is close to reach 100%. It means that the soot particulates can complete 100% passive regeneration continuously only by relying on the mutual reaction of DPF internal reactants in this condition. But it is important to note that when  $\beta \geq 8$ , there is excessive NO<sub>x</sub>, with lower removal efficiency, and the working condition corresponding to the engine is the continuous heavy load working condition, and this condition is kept continuously rarely in the actual operation of the small and medium-sized motor vehicles equipped with DPF, so the ideally continuously and completely passive regeneration may not be realized perfectly, but also NO<sub>x</sub> emissions should be taken into account and the corresponding active regeneration methods are supplemented.

The introduction of  $\alpha$  and  $\beta$  is of great importance in studying the influencing effect of the ratio relationship between NO<sub>x</sub>, and between soot particulates and NO<sub>x</sub> on the diesel engine exhaust emissions and DPF removal efficiency.

The change of  $\alpha$  factor (namely, the ratio value of  $\text{NO}_2$  accounting for  $\text{NO}_x$ ) can be adjusted by the diesel engine aftertreatment device DOC, the change of  $\beta$  factor (namely, the ratio value of  $\text{NO}_x$  and soot particulates) can be adjusted by using the diesel engine aftertreatment device EGR, both are the controllable factors produced on the basis of reaction mechanism simulation calculation, flexible adjustment can be carried out by using the diesel engine aftertreatment control strategy, and both influence the diesel engine exhaust emissions and the working efficiency of the DPF.

#### 4.4. Oxidation comparison of $\text{NO}$ , $\text{NO}_2$ , $\text{N}_2\text{O}$ and the influence of their reaction with $\text{NO}_x$ on $\text{CO-PM}$ reaction

In addition to the  $\text{NO}_x$  ( $\text{NO}$ ,  $\text{NO}_2$ , etc.) in diesel engine exhaust nitrogen oxide, there is a certain amount of  $\text{N}_2\text{O}$ , and it plays an important role in the reaction process of  $\text{NO}_x\text{-PM}$ . When soot particulates mixing with  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_2$  with the equal ratio, Fig. 9 shows the variation trend of soot particulates quality after soot particulates in DPF are oxidized by the equal quantity of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_2$  over the exhaust temperature at the DPF inlet, thus comparing the oxidation capacity of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_2$  on PM to some extent. The figure shows that the oxidation capacity of  $\text{O}_2$  on soot particulates is the least, the light-off critical temperature on the soot particulates is above  $400^\circ\text{C}$ , some soot particulates will be oxidized between  $450$  and  $500^\circ\text{C}$ , and the oxidation rate of soot particulates is less than  $50\%$  after the reaction. The oxidation capacity of  $\text{NO}$  is slightly better than  $\text{O}_2$ , reaching the light-off critical temperature at  $300^\circ\text{C}$ , and the final oxidation rate of the soot particulates is higher than that of  $\text{O}_2$ . The oxidation capacity of  $\text{N}_2\text{O}$  and  $\text{NO}_2$  has their own characteristics.  $\text{NO}_2$  can make the soot particulates have lower light-off critical temperature ( $<250^\circ\text{C}$ ), and will oxidize the soot particulates within the temperature range of  $200$ – $450^\circ\text{C}$ , and the oxidation rate is higher. The light-off critical temperature of soot particulates by the  $\text{N}_2\text{O}$  is slightly higher than that by the  $\text{NO}_2$ , at about  $250^\circ\text{C}$ , but it can oxidize the soot particulates within a very narrow temperature range of  $200$ – $400^\circ\text{C}$ , but its oxidation efficiency on soot particulates is the highest in four oxidizing gases. Although the final oxidation efficiency of  $\text{NO}_2$  on soot particulates is inferior to that of  $\text{N}_2\text{O}$ , and there is less  $\text{NO}_2$  in the actual engine exhaust, its existence can further reduce the critical temperature of soot particulates, to make soot particulates regenerate faster at lower temperatures.

After the diesel engine exhaust flows through the DOC,  $\text{CO}$  emissions have been reduced to a very low level, but  $\text{CO}$  is an important intermediate product in the reaction process of the soot

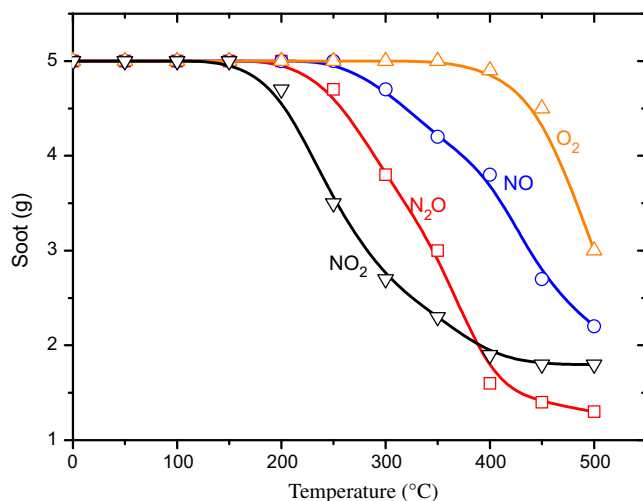


Fig. 9. Comparison of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{O}_2$  on PM oxidation capacity.

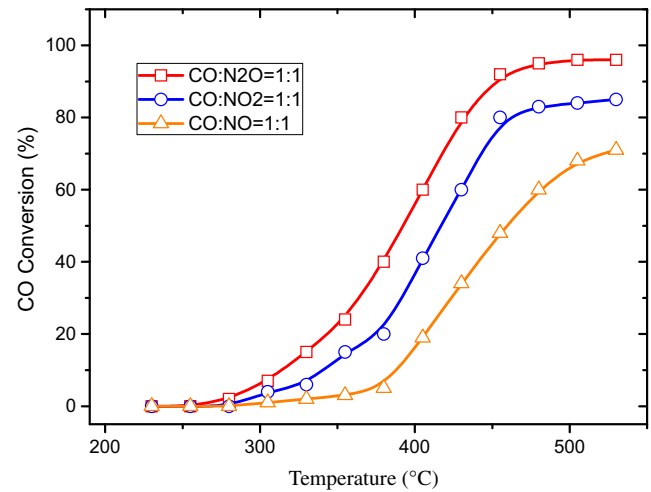


Fig. 10. Influence of the proportion of  $\text{CO}$  and nitrogen oxides on  $\text{CO}$  conversion rate (1:1).

particulates in DPF with nitrogen and oxygen. It can continue to react with other antioxidants and eventually generates  $\text{CO}_2$ , but also can indirectly promote the conversion reaction between  $\text{NO}_x$ .

Fig. 10 is the variation trend of  $\text{CO}$  conversion rate when the ratio of  $\text{CO}$  and  $\text{NO}_x$  is 1:1. The figure shows that under the condition of the mixed reaction of equal  $\text{CO}$  with  $\text{N}_2\text{O}$ , the light-off critical temperature of  $\text{CO}$  is the minimum compared with other two kinds of nitrogen oxides, and it begins to react at around  $270^\circ\text{C}$ , with the highest removal efficiency, and the lowest temperature when saturated. It is thus clear that the  $\text{CO}$  removal effect by  $\text{N}_2\text{O}$  is higher than that by  $\text{NO}_2$  and  $\text{NO}$ . It is proved that the existence of  $\text{N}_2\text{O}$  can make the reaction of  $\text{CO}$  and  $\text{NO}_x$  earlier and faster. Combined with the related reaction mechanism in Table 1, the reaction rate of  $\text{N}_2\text{O}$  with  $\text{CO}$  is faster and the activation energy required is lower, so the oxidation of  $\text{CO}$  can be promoted preferably by  $\text{N}_2\text{O}$ .

Fig. 11 is the variation trend of  $\text{CO}$  conversion rate when the ratio of  $\text{CO}$  and  $\text{NO}_x$  is 2:1. The figure shows that compared with the situation that the ratio of  $\text{CO}$  and  $\text{NO}_x$  is 1:1, the light-off critical temperature of  $\text{CO}$  by three kinds of  $\text{NO}_x$  rises,  $\text{N}_2\text{O}$  which has the highest reaction priority with  $\text{CO}$  makes the light-off critical temperature of  $\text{CO}$  reach about  $370^\circ\text{C}$ , the temperature when sat-

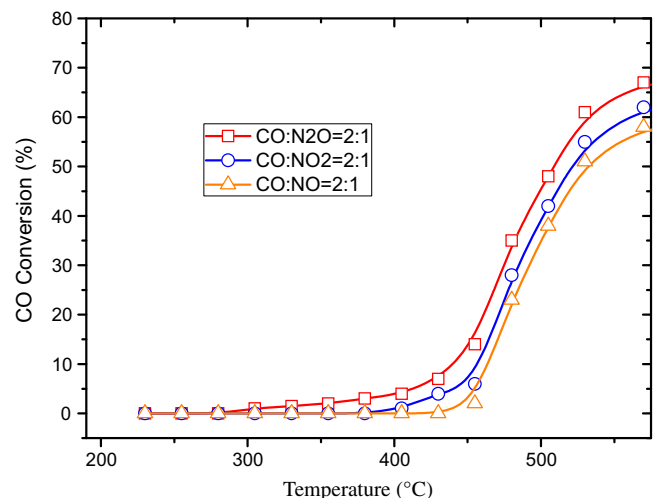


Fig. 11. Influence of the proportion of  $\text{CO}$  and nitrogen oxides on  $\text{CO}$  conversion rate (2:1).



urated is also significantly higher than that when the ratio is 1:1, and the final removal efficiency significantly decreases. When the ratio of CO and N<sub>2</sub>O is 2:1, the maximum removal efficiency on CO is about 68%, lower than that of 71% when the mixing ratio of CO and NO is 1:1. Thus it can be seen that the influence of the ratio relationship between CO and NO<sub>x</sub> is greater than that between CO and different reactants in the reaction process of CO with NO<sub>x</sub>. So increasing the ratio of NO<sub>x</sub> in the reactants appropriately contributes to improving the removal efficiency of CO, and promoting the full reaction of CO with NO<sub>x</sub>.

## 5. Conclusions

In this paper, N<sub>2</sub>O reactions were studied to improve the NO<sub>x</sub>-PM mechanism. The reactions are supplement to the existing theory. Based on the improved mechanism, the chemical reaction process between NO<sub>x</sub> and PM is studied in different inlet conditions. Research results show that the most suitable DPF inlet temperature should probably be between 400 and 500 °C. In this temperature window, the removal efficiency of soot particulates could be higher and should not restrain the NO<sub>x</sub> removal efficiency because of higher temperature.

Coefficient  $\alpha$  is defined, which is used to characterize the ratio of NO<sub>2</sub> in diesel engine exhaust at the DPF inlet accounting for the total amount of NO<sub>x</sub>. The results show that when  $\alpha$  is between 0.7 and 0.8, the good removal effect of soot particulates is achieved under the premise of not worsening NO<sub>x</sub> removal efficiency. The molar ratio of NO<sub>x</sub> at the DPF inlet and carbon in the PM is defined as  $\beta$ . When  $\beta \approx 1$ , NO<sub>x</sub> removal efficiency is probably the maximum. When  $\beta \geq 8$ , the soot particulates could completely continuous passive regeneration totally only relying on the mutual reaction of DPF internal reactants in this condition.

Investigation results show that N<sub>2</sub>O and CO are important intermediate products during the reaction process of NO<sub>x</sub>-PM. N<sub>2</sub>O's existence could further reduce the light-off critical temperature of soot particulates. CO can continue to react with other antioxidants and eventually generates CO<sub>2</sub>, but can also indirectly promote the conversion reaction between NO<sub>x</sub>. The influence of the ratio relationship between CO and NO<sub>x</sub> is probably greater than that between CO and different reactants in the reaction process of CO with NO<sub>x</sub>. Increasing the ratio of NO<sub>x</sub> in the reactants appropriately contributes to improve the removal efficiency of CO, and promote the complete reaction of CO with NO<sub>x</sub>. Understanding of the NO<sub>x</sub>-PM reaction details allows system architecture and control strategies to be optimized for minimal overall diesel emissions.

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## References

- [1] Agus Setiabudi, Michiel Makkee, A. Jacob Moulijn, The role of NO<sub>2</sub> and O<sub>2</sub> in the accelerated combustion of soot in diesel exhaust gases, *Appl. Catal. B* 50 (2004) 185–194.

- [2] C.J. Tighe, M.V. Twigg, A.N. Hayhurst, J.S. Dennis, The kinetics of oxidation of diesel soots by NO<sub>2</sub>, *Combust. Flame* 159 (2012) 77–90.
- [3] B.R. Stanmore, V. Tschamber, J.-F. Brilhac, Oxidation of carbon by NO<sub>x</sub>, with particular reference to NO<sub>2</sub> and N<sub>2</sub>O, *Fuel* 87 (2008) 131–146.
- [4] A.P. Chernukho, A.N. Migun, S.A. Zhdanok, J.C. Rostaing, J. Perrin, Simulation of perfluoromethane decomposition in an atmospheric-pressure microwave discharge, *J. Eng. Phys. Thermophys.* 78 (2) (2005).
- [5] L.A. Graham, S.L. Belisle, P. Rieger, Nitrous oxide emissions from light duty vehicles, *Atmos. Environ.* 43 (12) (2009) 2031–2044.
- [6] MOLEKEL 4.2, P. Flükiger, H.P. Lüthi, S. Portmann, J. Weber, Swiss Center for Scientific Computing, Manno (Switzerland), 2000.
- [7] GOpenMol 3.0, D.L. Bergman, L. Laaksonen, A. Laaksonen, *J. Mol. Graph. Model.* 15 (1997) 301–306.
- [8] L.A. Curtiss, K. Raghavachari, P.C. Redfern, V. Rassolov, J.A. Pople, Gaussian-3 (G3) theory for molecules containing first and second-row atoms, *J. Chem. Phys.* 109 (1998) 7764–7776.
- [9] A.G. Baboul, L.A. Curtiss, P.C. Redfern, K. Raghavachari, Gaussian-3 theory using density functional geometries and zero-point energies, *J. Chem. Phys.* 110 (1999) 7650.
- [10] B.K. Raghavachari, B.B. Stefanov, L.A. Curtiss, Accurate density functional thermochemistry for larger molecules, *Mol. Phys.* 91 (1997) 555–560.
- [11] A. Burcat, B. Ruscic, Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion with Updates from Active Thermochemical Tables, Report ANL 05-20 and TAE 960, September 2005, Electronic Format: <ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics/>.
- [12] R. Notario, O. Castano, J.-L. Abboud, R. Gomperts, L. Frutos, R. Palmeiro, Organic thermochemistry at high ab initio levels. 1. A G2 (MP2) and G2 study of cyclic saturated and unsaturated hydrocarbons (including aromatics), *J. Org. Chem.* 64 (1999) 9011–9014.
- [13] L. Torchin, M. Bordas, J. Robert, Energy partitioning between the equilibrated A and X states of the CN radical formed in the C+ N<sub>2</sub>O reaction, *Appl. Phys. Lett.* 47 (1985) 660–662.
- [14] C.-K. Seo, H. Kim, B. Choi, M.T. Lim, C.-H. Lee, C.-B. Lee, De-NO<sub>x</sub> characteristics of a combined system of LNT and SCR catalysts according to hydrothermal aging and sulfur poisoning, *Catal. Today* 164 (2011) 507–514.
- [15] D. Buono, A. Senatore, M.V. Prati, Particulate filter behaviour of a Diesel engine fueled with biodiesel, *Appl. Therm. Eng.* 49 (2012) 147–153.
- [16] Bin Guan, Reggie Zhan, He Lin, Zhen Huang, Review of state of the art technologies of selective catalytic reduction of NO<sub>x</sub> from diesel engine exhaust, *Appl. Therm. Eng.* 66 (2014) 395–414.
- [17] E. Jiaqiang, Wei Zuo, Junxu Gao, Qingguo Peng, Zhiqing Zhang, Pham Minh Hieu, Effect analysis on pressure drop of the continuous regeneration-diesel particulate filter based on NO<sub>2</sub> assisted regeneration, *Appl. Therm. Eng.* 100 (2016) 356–366.
- [18] Shuzhan Bai, Jiao Tang, Guihua Wang, Guoxiang Li, Soot loading estimation model and passive regeneration characteristics of DPF system for heavy-duty engine, *Appl. Therm. Eng.* 100 (2016) 1292–1298.
- [19] M. Schejbal, J. Štěpánek, M. Marek, P. Kočí, M. Kubíček, Modelling of soot oxidation by NO<sub>2</sub> in various types of diesel particulate filters, *Fuel* 89 (2010) 2365–2375.
- [20] N. Artioli, R. Matarrese, L. Castoldi, L. Lietti, P. Forzatti, Effect of soot on the storage-reduction performances of Pt Ba/Al<sub>2</sub>O<sub>3</sub> LNT catalyst, *Catal. Today* 169 (2011) 36–44.
- [21] B.K. Cho, Mechanistic importance of intermediate N<sub>2</sub>O + CO reaction in overall NO + CO reaction system: I. Kinetic analysis, *J. Catal.* 138 (1) (1992) 255–266.
- [22] Qingyun Su, Yanbin Li, Sheng Wang, Changming Gao, Detailed mechanism for reduction of N<sub>2</sub>O over rhodium by CO in automotive exhaust, *Top. Catal.* 56 (2013) 345–351.
- [23] H. Zhang, J. Wang, Adaptive sliding-mode observer design for a selective catalytic reduction system of ground-vehicle diesel engines, *IEEE/ASME Trans. Mechatron.* 21 (4) (2016) 2027–2038.
- [24] H. Zhang, J. Wang, Y.Y. Wang, Optimal dosing and sizing optimization for a ground-vehicle diesel-engine two-cell selective catalytic reduction system, *IEEE Trans. Veh. Technol.* 65 (6) (2016) 4740–4751.
- [25] L. Wei, G. Peng, A review on natural gas/diesel dual fuel combustion, emissions and performance, *Fuel Process. Technol.* 142 (2016) 264–278.
- [26] J.O. Müller, B. Frank, R.E. Jentoft, et al., The oxidation of soot particulate in the presence of NO<sub>2</sub>, *Catal. Today* 191 (1) (2012) 106–111.
- [27] M. Bogdanić, F. Behrendt, F. Mertins, The influence of a 2-component model on the computed regeneration behaviour of an uncoated diesel particulate filter, *Chem. Eng. Sci.* 63 (2008) 2601–2613.
- [28] S.J. Lee, S.J. Jeong, W.S. Kim, et al., Computational study on the effects of volume ratio of DOC/DPF and catalyst loading on the PM and NO<sub>x</sub> emission control for heavy-duty diesel engines, *Int. J. Automot. Technol.* 9 (6) (2008) 659–670.