

Study On Adsorption Characteristics Of NO Adsorbed Catalysts At Low Temperature

Boru Zhang^a, Weijun Liu^a, Shuhua Zhang^b, Wenlei Bai^a, Zaibing Hao^a

^aCollege of Mechanical and Automotive Engineering, Shanghai University Of Engineering Science

^bCollege of Chemistry and Chemical Engineering, Shanghai University Of Engineering Science

Corresponding Author: Boru Zhang

ABSTRACT: Ce-Fe-Mn/ACFN low temperature catalysts were prepared by impregnation method, and the catalysts were characterized by thermogravimetric differential calorimetry (TGA). The effects of temperature, oxygen and sulfur dioxide on the adsorption and removal of NO were studied in laboratory. The results show that the optimum temperature for the preparation of the catalyst is about 350 °C, the release of NO from ACFN containing metal oxides is accelerated at above 300 °C and the loss of ACFN is accompanied by the loss of ACFN, and the ability of ACFN to adsorb NO increases by 11% compared with that of ACF. The adsorption efficiency of CMF-ACFN for NO was up to 32%, and the average adsorption efficiency of CMF-ACFN after reduction increased from 34% to 56%.

KEY WORDS: Low temperature denitrification; Sulfur poisoning; ACF; NSR

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I. INTRODUCTION

With the acceleration of industrialization and economic integration in the world and the rapid development of the national economy, the demand for heavy trucks is becoming more and more urgent. The percentage of heavy trucks in the truck market has rapidly increased from 4% in 2009 to 70% in 2009. The number reached more than 880,000 units [1-2]. Diesel engines have higher thermal efficiency and output power than gasoline engines, making them the primary choice for heavy-duty trucks. In Europe and the United States, diesel engines are widely used in various types of vehicles, and heavy-duty vehicles are basically diesel engines. The output of China's diesel engines is also growing rapidly. From 1,584,600 units in 2006 to the end of 2012, the total annual output of China's diesel engines reached 2,692,200 units [3]. The dramatic increase in heavy-duty vehicles is also becoming more and more serious for environmental pollution.

Unlike gasoline engines, diesel engines use compressed gas technology, which has a high air-fuel ratio. Although the high air-fuel ratio controls CO and HC emissions, the displacement of NO_x and PM is significantly increased. When the road is crowded and the internal combustion engine is in a low-temperature working environment for a long time, the NO_x emits a lot. At this time, due to the low temperature, the catalyst can not effectively treat the NO_x emitted by the engine. The NO_x emission of the diesel engine at low temperature is not very high. Effective feasibility measures [4-7].

As a high-efficiency adsorbent for preventing environmental pollution and gas purification, activated carbon fiber not only occupies a major position in the treatment of fixed exhaust emissions, but more scientists have recently explored whether it can be applied to the reduction of mobile pollution sources such as automobiles and ships.

Compared with alumina, activated carbon fiber has great advantages as a catalyst carrier. ACF is a fiber with a diameter of 10-30 μm. It has a high specific surface area, and there is no large pore in ACF, only a small number of transition pores. The micro pores exist on the surface of the fiber, and the adsorbed material does not need to pass through large pores, transition pores, and small pores in sequence, and thus has good adsorption performance [8-9].

The purpose of this thesis is to study an adsorption catalyst with activated carbon fiber as carrier and manganese oxide, cerium oxide and ferric oxide as catalytic active agents. The catalyst was characterized by thermogravimetric differential thermal analyzer. The effects of temperature, oxygen, sulfur dioxide, etc. on the adsorption and removal of NO by the catalyst were studied by means of laboratory gas distribution.

II. EXPERIMENTAL

2.1 Catalyst preparation

In this experiment, activated carbon supported metal oxide catalyst was prepared by impregnation method. Firstly, ACF was added in deionized water to boil and then modified with 60% nitric acid. Wash to

neutral and dry in oven at 100 °C and set aside in dryer. The catalyst was prepared by isovolumetric impregnation method: the solution of $Mn(NO_3)_2$, $Fe(NO_3)_3$, $Ce(NO_3)_3$ was removed at a certain concentration, and the molar ratio of Fe,Mn,Ce to plasma water was 1. The metal oxide content is 20% of the mass of the catalyst carrier and is configured into impregnation solution. Equal volume impregnation to a certain amount of ACFN. The beaker was sealed with a fresh film, then oscillated in a constant temperature water bath oscillator for 1 hour, then dried at 65 °C, 110 °C for 4 h, and then burned in nitrogen atmosphere at 350 °C for 6 h to prepare the catalyst.

In order to compare the effect of the experiment, three groups of catalysts were set up to test and compare. The first group was ACF, the second group was ACF, modified by nitric acid, and the third group was ACFN, modified activated carbon fiber loaded with CeO_2 , MnO_2 , Fe_2O_3 at the same time. Recorded as CMF-ACFN.

2.2 Calculation of simulated gas composition and airspeed ratio

The simulation of the gas composition in this experiment is mainly based on the composition of the exhaust gas emitted by the diesel engine under idle conditions. Table 1 shows the emission range of pollutants in the exhaust of diesel engines for general vehicles and construction machinery [10].

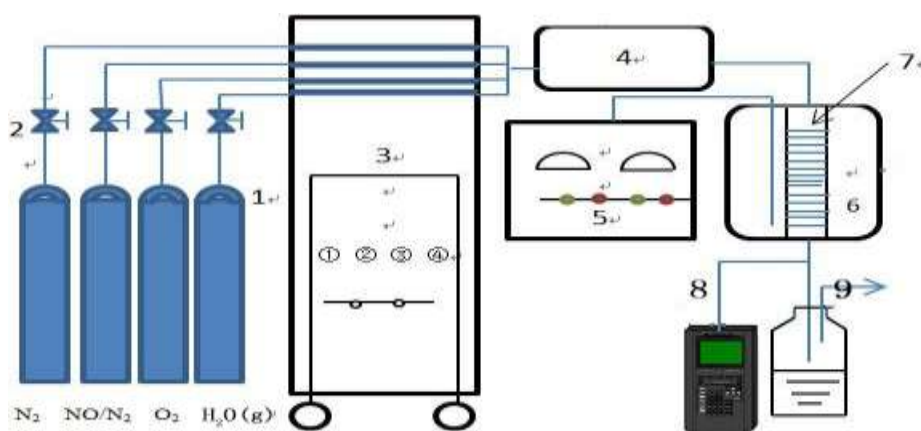
Table 1-1 Composition and temperature of the diesel exhaust

Composition	Unit	Idle condition	Maxoutputcondition
NO _x	ppm	50~200	600~2500
O ₂	Vol%	2~18	2~11
HC	ppm	50~500	<50
CO	ppm	100~450	30~2000
CO ₂	Vol %	2~3.5	12~16
SO ₂	ppm	20~200	20~200
N ₂	Vol %	else	else
Gas temperature	°C	100~200	550~750

In the gas distribution experiment, diesel engine exhaust gas components such as N₂, NO, O₂ and SO₂ are contained in sequence under simulated conditions, and a reductive gas, NH₃, is also included. Suppose there are only nitrogen, oxygen and nitric oxide in the gas in a certain working condition, and it is required that the concentration of NO is 250ppm, the concentration of O₂ is 2.5ppm, and the total volume flow of air intake V is 1000 Nml/min,. According to the difference of the gas content in the cylinder and the error of the instrument, the actual gas distribution is V (NO) = 0.25Nml/min, V (N₂) = 974.75Nml/min, V (O₂) = 25 Nml/min. According to the conditions required by the experiment, the following gas components and their concentration are: C (NH₃)=375ppm, C(SO₂)= 50 ppm, and the actual gas distribution is V (NH₃) = 31.5 Nml/min, V (SO₂) = 62.5 Nml/min.

2.3 Test equipment and procedures

Simulate the exhaust gas composition of the diesel engine under low temperature conditions, and test the denitration efficiency of the catalyst in a fixed reaction vessel. The test reaction device is shown in Figure 1. The inner diameter of the reactor was 2.5 cm, the experimental gas space velocity was 10 000 h⁻¹, the total gas flow rate was 1000 mL·min⁻¹, and the total mass of the catalyst was 1.02 g.



1-Gas cylinder 2-Pressure reducing valve 3-Gas flow pressure control cabinet 4-Gas mixing chamber
5-Intelligent temperature controller6- Program-controlled muffle furnace 7- Quartz tube 8- Flue gas analyzer 9- Tail gas absorption device

Fig.1 Schematic diagram of experiment system device

The results are as follows:

- (1) the well weighing catalyst is placed in the quartz tube, and the nitrogen is applied to sweep the other gases in the reaction system for 5 min.
- (2) according to the purpose of the experiment, select the intake air composition and adjust the mass flow rate from the mass Flowmeter knob to the required mass flow rate;
- (3) each gas enters each pipeline after decompression by high pressure cylinder pressure reducing valve, opens the valve in front of the Flowmeter, opens the mass Flowmeter control switch, and when the gas flows through the Mass Flowmeter, The mass Flowmeter controls the inlet flow rate of each gas into the initial set flow rate;
- (4) after entering the mixing chamber and mixing homogeneously, each gas enters the reactor, and the gas flows through the catalyst area to carry on the reaction;
- (5) the treated mixture gas flows out of the reaction tube through the outlet of the air, and then the sample analysis and tail gas post-treatment are carried out, and then discharged into the atmosphere;
- (6) after one group of experiments, in order to ensure the accuracy of the next group of experiments, the whole system was swept by N₂ for 5 min.

III. RESULTS AND DISCUSSIONS

3.1 preparation and characterization of catalysts

The nitrate corresponding to various metal oxides of ACF, before and after modification by nitric acid was put into thermogravimetric differential calorimeter (TGA) in turn, and the heating rate of 5 °C/ min was heated from 100°C to 600°C. The mass change rate was observed and the results were as follows:

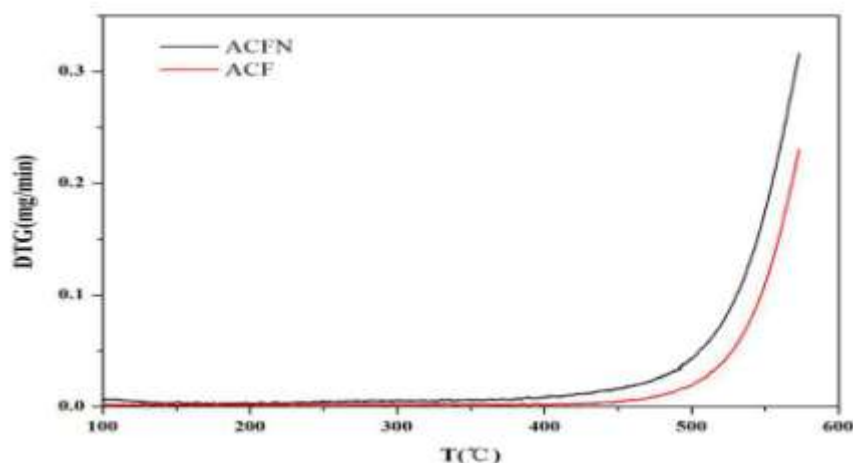


Fig.2 Comparison of quality change rates between ACF and ACFN

The combustion weight loss temperature of ACFN is about 300 °C, which is about 100 °C earlier than that of ACF. This is because the HNO₃ treatment of polyacrylonitrile based activated carbon fiber is carried out in an air atmosphere, which results in the surface of ACF being deeply oxidized. Oxygen groups were formed on the surface of activated carbon fiber, the reaction points were increased, the oxidation reaction was easy, and the proper oxygen content was also helpful to improve the reaction activity of ACF and increase the denitrification rate.

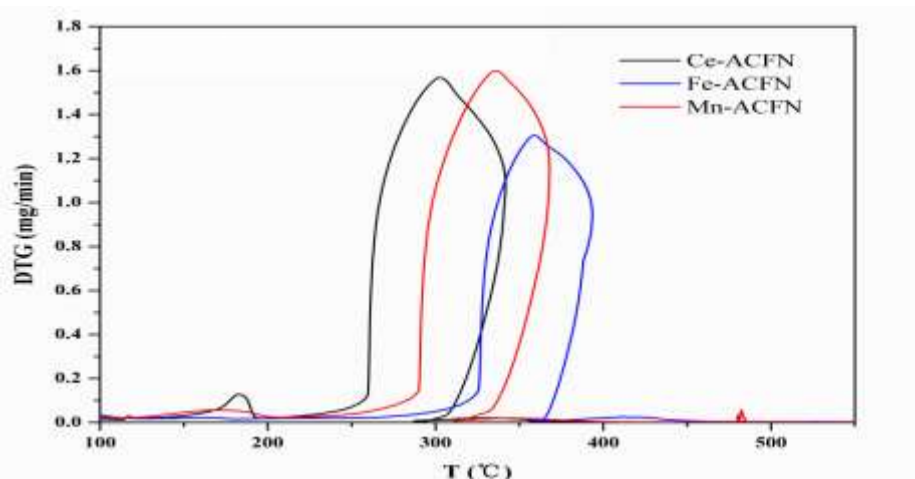


Fig.3 Three nitrate TG curves

Obviously, the decomposition temperature of the three kinds of nitrate is about 300 °C, and cerium nitrate also has a very small removal peak at about 170 °C. The main products of the removal of the three kinds of nitrates are NO and O₂ at the stage of high mass change rate. The remaining products are metal oxides corresponding to three nitrates. According to the rate distribution above, the prepared CMF-ACFN was heated in a tube furnace at 250 °C, 300 °C and 350 °C for 6 h, and the obtained products were thermogravized in N₂ environment. The curves were shown below:

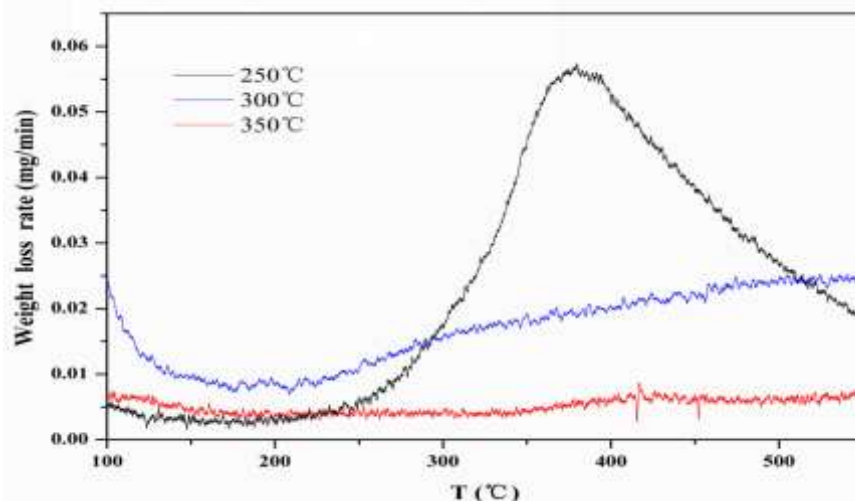


Fig.4 CMF-ACFN Curve after different temperature treatment

Compared with Fig.3, the highest removal rate in Fig.4 is no more than 0.06 mg / min, compared with 1.6 mg / min in fig. 3, the mass change tends to be constant, and at 350 °C, the mass change rate is less than 0.01 mg / min, and there is no obvious change in the rate. All the nitrates in the catalyst are transformed into metal oxides and there is no NO and O₂, so the mass change rate curve is smooth.

It is obvious that the mass change rate of untreated samples varies significantly in the range of 250 °C to 350 °C because of the large amount of gas generated during heating. In contrast, the mass change rate of the samples after high temperature treatment is flat and near zero. It shows that in the catalyst system, nitrate has almost been transformed into corresponding metal oxides, and the preparation of the catalyst has been completed.

3.2 characterization of mass change of catalyst before and after adsorption

In the experiment, two kinds of catalysts, ACFN and CFM-ACFN, which were saturated to adsorb NO under anaerobic condition, were analyzed by TG. The experimental conditions were as follows: the heating rate of 10 °C / min was heated to 600 °C under the action of nitrogen shielded gas, and the results were as shown in fig. 5:

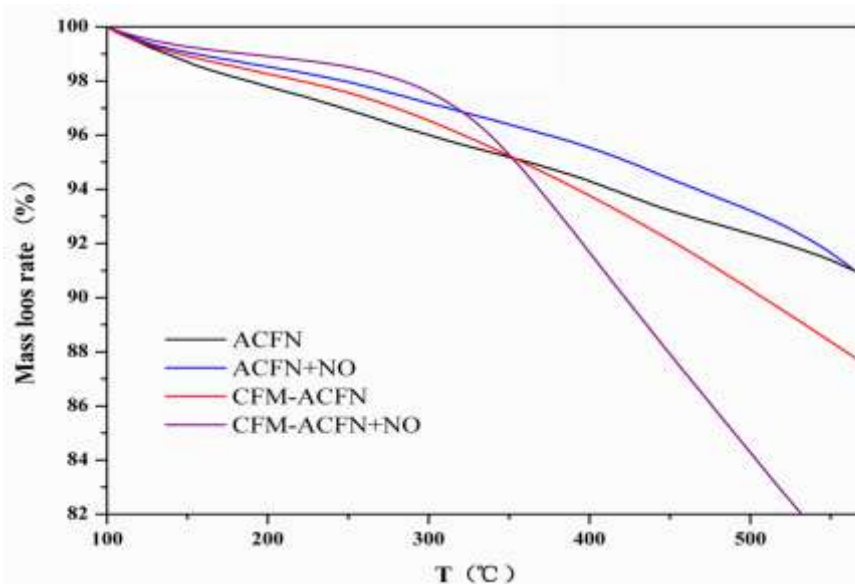


Fig.5 Mass fraction temperature diagram before and after ACFN/CMF-ACFN adsorption

Thermogravimetric differential thermogravimetry (TGA) was used to study the change of catalyst mass with temperature before and after the adsorption of ACFN and CMF-ACFN under the condition of pure N₂ respectively. It is obvious that after the adsorption of ACFN, there is no catalytic conversion of metal oxides. The release rate of NO is relatively slow, and the mass change is significant relative to that before adsorption at about 570 °C. However, due to the increase of adsorption activity sites, CMF-ACFN adsorbed more NO, and the Mn group had catalytic reduction of NO at lower temperature. Therefore, at lower temperature, NO_x was adsorbed. The mass change of CMF-ACFN was more significant and accompanied by the decomposition of ACFN itself, which resulted in the change of CMF-ACFN fraction of adsorbed NO at more than 350 °C than that of CMF-ACFN before adsorption.

3.3 characterization of adsorption properties of different catalysts

In the experiment, the NO gas was injected into the pure N₂ environment, and the NO concentration of the three catalysts was observed when they were adsorbed within 1 h. The percentage was calculated by subtracting the detected concentration from the inlet gas concentration, and the results were as follows:

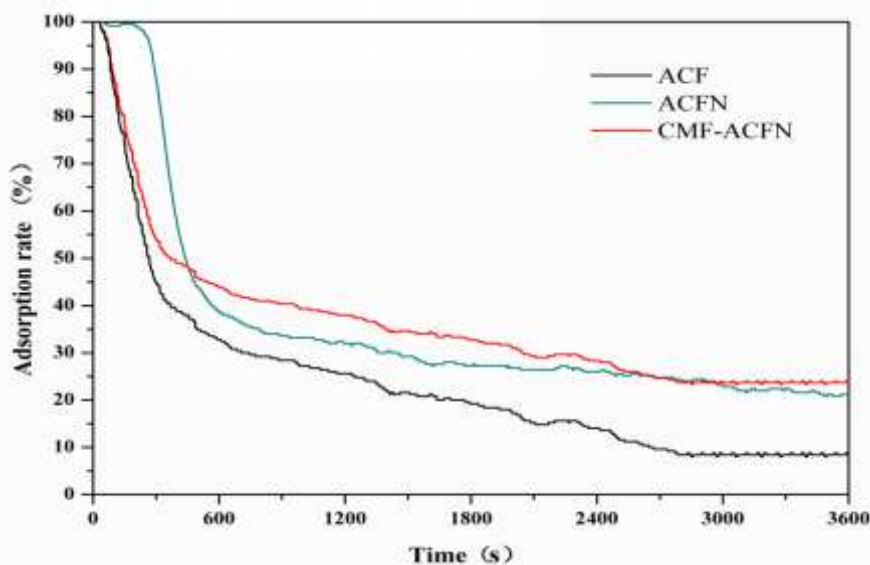


Fig. 6 adsorption efficiency of NO at 300 °C for different catalysts

From figure 6, it can be seen that the adsorption ability of activated carbon fiber modified by nitric acid has been improved significantly, the average adsorption capacity has increased from 15% to 26%, and the adsorption efficiency has been increased by 11%. Over time, the adsorption efficiency of the three adsorbents reached equilibrium at about 2700s, and the adsorption capacity of CMF-ACFN impregnated with metal oxides was slightly larger than that of ACFN. Activated carbon fiber (ACF) has two main forms of physical adsorption and chemical adsorption for NO. The physical adsorption of NO_x gas by activated carbon fiber mainly depends on its pore structure. When carbon fiber adsorbed, adsorption state Different states are presented according to the relationship between pore size and molecular size [11].

The chemisorption of NO_x gas by activated carbon fiber mainly occurs on the surface of activated carbon. NO is oxidized with O₂ on the surface of ACFN to form a NO polymer (NO-O-NO₂), which is then transformed into NO₂. The surface active oxidation sites of activated carbon fiber modified by nitric acid increased, so its chemisorption capacity of NO was improved.

3.4 Characterization of adsorption properties of CMF-ACFN at different temperatures

In the experiment, the NO gas was injected into the pure N₂ environment, and the NO concentration in the exhaust gas was observed when the CMF-ACFN catalyst adsorbed at different temperatures within 1 h. The percentage of the NO concentration was calculated by subtracting the detected concentration from the input gas concentration. The following results were obtained:

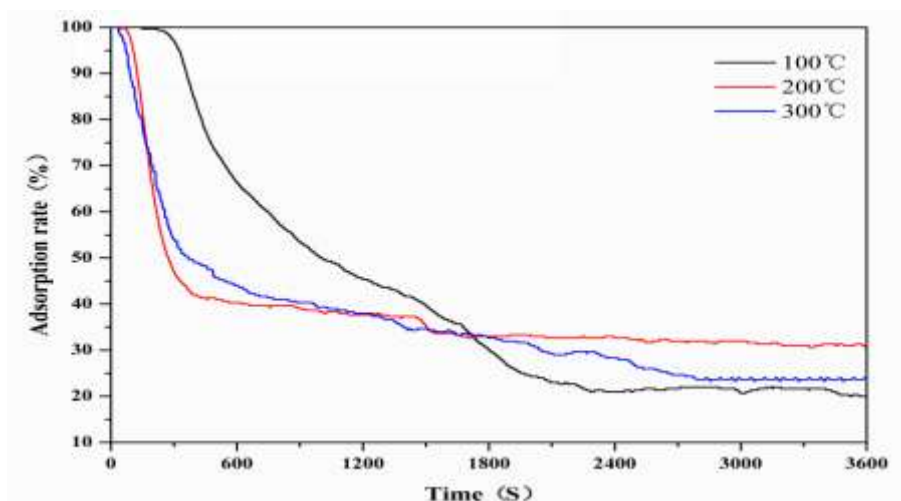
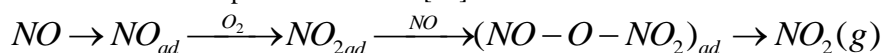


Fig. 7 CMF-ACFN adsorption efficiency of NO at different temperatures

It can be seen from the diagram that with the stability of NO content in the system, the adsorption efficiency of NO by CMF-ACFN catalyst is gradually stable, and the efficiency of CMF-ACFN adsorption NO decreases continuously at 100 °C for 0-2400s, and finally remains at about 23%. However, at 200 °C and 300 °C, the CMF-ACFN catalyst was stable at 600s and kept at 34% and 25%, respectively. The physical adsorption of ACFN on NO was mainly dependent on its pore structure. Chemical adsorption mainly occurs on the surface of activated carbon. The reaction path is as follows [12]:



With the increase of temperature, the ability of active site oxidation to store NO increases, but the NO of the physically adsorbed state in ACFN is unstable. When the temperature exceeds 250 °C, it will be released, resulting in the efficiency of NO adsorption of CMF-ACFN being lower than 200 °C.

3.5 comparison of NO reduction with different Catalysts

At the end of the adsorption experiment at 300 °C, the ambient temperature of the catalyst was raised to 350 °C, and the NH₃ was added as the reducing gas. The results of the NO, experiment of removing the adsorbed in the catalyst were shown in the following figure:

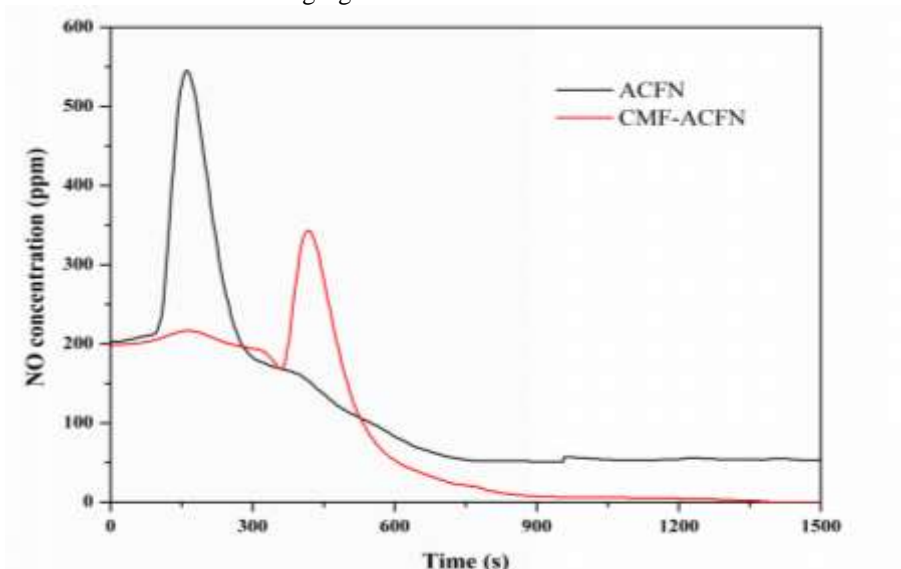


Fig. 8 NO reduction results for different catalysts

At the initial stage of NH₃ entry, the instrument detected a sharp increase in the released NO concentration, due to the effect of high temperature on the ACFN physically adsorbed NO and the competitive adsorption of NH₃ with NO, so at the initial stage of NH₃ entry, A large number of NO, which are physically adsorbed on ACFN, are released. Because CMF-ACFN contains a large number of metal oxides and has more surface active sites, chemisorbed NO has more NO than ACFN. Therefore, the content of NO released at the

early stage of the experiment was relatively low, all of which were about 340ppm. The experiment found that when the processing time, The NO in CMF-ACFN is basically clean when it is larger than 900s, but the NO adsorbed by ACFN can not be completely removed in 1500s due to the absence of metal oxides as catalyst.

3.6 Secondary adsorption characterization of different Catalysts

The catalyst which was reduced by NH_3 in 3.4 was placed in quartz tube, and the ambient temperature was controlled at 300 °C. The ability of secondary adsorption of NO on the catalyst after desorption was studied by means of NO. The experimental results are shown in the figure:

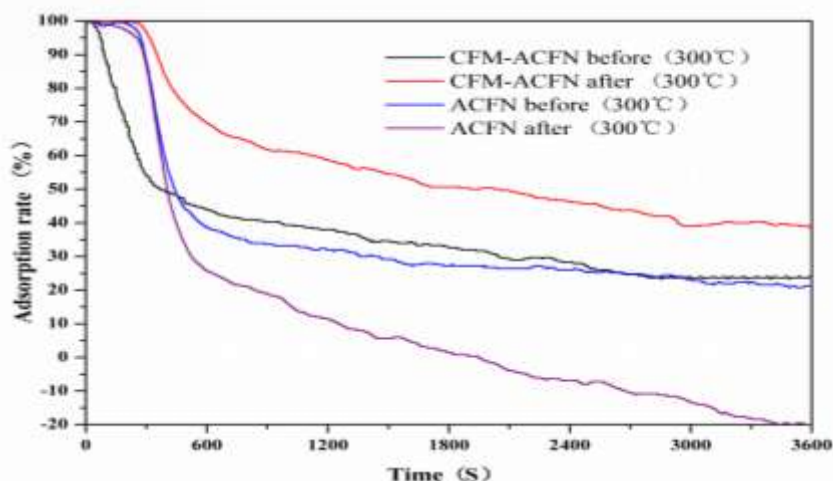


Fig. 9 ACFN/CMF-ACFN desorption NO efficiency at 300 °C

It was found that the ability of ACFN to adsorb NO decreased obviously and lost its adsorption ability when the time exceeded 2000s, and some of the NO which had already been adsorbed were released at the same time, so the adsorption efficiency became negative. This is because after the reduction of ACFN, a large number of chemically active sites are still occupied by NH_3 , which reduces the chemisorption of NO by ACFN. When the percentage of NO in the physically adsorbed state is larger than 2000s, the adsorbed NO of the catalyst is rapidly saturated. The unstable adsorption state of NO is also released from the micropores of ACFN resulting in a negative adsorption capacity of ACFN. And, CMF-ACFN contains metal oxides and can be used as catalyst at 300 °C. The adsorption efficiency of partial NO, is increased from 34% to 56% due to competitive adsorption.

IV. CONCLUSION

In this paper, activated carbon fiber supported metal oxide catalyst was prepared in laboratory, the preparation process was characterized by thermogravimetric differential calorimeter (TGA), and the exhaust gas component of diesel engine at low temperature was simulated. The adsorption efficiency of the catalyst under different gas components is analyzed. The results are as follows:

- (1) the surface oxidation activity of ACF was increased by using nitric acid modified activated carbon fiber, and the ability of ACFN to adsorb NO increased by 11.1% compared with that of ACF.
- (2) Metal oxide impregnated activated carbon fiber mainly increased the chemisorption of NO by activated carbon fiber, so the competitive adsorption of NH_3 would not lead to a large amount of NO release during the reduction of the catalyst. The catalytic reduction efficiency of adsorbed NO was improved.
- (3) the adsorption efficiency of ACFN reduced by NH_3 becomes negative at the second adsorption of NO, while the activated carbon fiber containing metal oxides can use the part of NO, which is adsorbed by NH_3 at the stage of reduction to adsorb NO at the same time. So the average adsorption efficiency increased from 34% to 56%.

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