The Study on Series of Copper Catalyst in the Reactor of Dielectric Barrier Discharge to Remove NO_x

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ABSTRACT: Dielectric barrier discharge assisted catalyst can effectively remove NO_x, catalyst plays an important role in the process of reaction. The series of copper catalyst carried by active carbon, ratio of removal NO_x, main productions and catalyst character before and after used have been studied in the reactor of dielectric barrier discharge. The experiment results show that non-thermal plasma can not only activate reagents to bring activated particles and radicals, but also have catalyst activated to improve adsorption and catalytic character. The main production of the chemical reaction is copper nitrate and deposited in activated carbon surface. The NO_x has been reduced by carbon element of activated carbon to come into bring nitrogen under the non-thermal plasma effected condition.

Keywords: Dielectric barrier discharge, Removal of NO_x, Copper oxide catalyst, Active carbon carrier

1 INTRODUCTION

Dielectric barrier discharge is one way to generate non-thermal plasma which can effectively generate electron, ion, living radical and many kinds of excited free particle. Non-thermal plasma with high activity power has a lot of activity atomic oxygen(O) and free radical with intensively oxidation produced by atomic oxygen, which oxidize NO forming NO_2 , so it has specific superiority in removing NO_x from automobile exhaust. Besides, it does not affect automotive engine performance due to simple structure [1,2]. But under normal conditions, reactive oxygen species change as follow: $NO+O \rightarrow NO_2$, $NO_2+O \rightarrow NO+O_2$. That cycle processes consume reactive oxygen species and create oxygen, at the same time, they effect NOx removal and reduce energy efficiency[3] Assisted catalyst, NO is further oxidized into NO_3^- to stop that cycle processes and improve NO_x removal and effectively reduce power consumption of dielectric barrier discharge system. The reason is that compared to potential of plasma, the surface of catalyst is negative potential and cations strike on the surface of catalyst under acceleration of sheathing voltage, which is good to product elution and reaction[4、5]. Therefore studying catalyst plays an important role in dielectric barrier discharge reactor.

The relative concentration of NO_x from automobile exhaust is not high(200 ppm-300 ppm), so that catalyst should have good adsorption and storage properties. NO_x adsorbs on the surface of catalyst to improve the reaction concentration of NO_x. At the same time, catalyst should better fit non-thermal plasma environment and has better reactivity and selectivity[6、7、8]. This paper studies the relation between NO_x removal ratio and copper oxide catalyst, the carrier of which is coal-based activated carbon in dielectric barrier discharge reactor and analyses on the main products and changes between catalyst before and after reaction.

2 EXPERIMENT

2.1 Experimental Medicine and Instruments

Experimental medicine: $ZnCl_2$: breaks bond of hydrocarbon of pulverized coal and improves key hole and gap ratio inside the activated carbon particles to improve specific surface area of catalyst. $CuSO_4 \cdot 5H_2O$: generates copper oxide activated points at high temperature attaching or inlaying to the surface of activated carbon. Carefully chosen pulverized coal: ash is smaller than 6% and particle size is small than 200 mesh. Coal tar: of which adhesive action makes catalyst mold. And other medicine includes citric acid, air steel bottle, NO/N_2 steel bottle and other auxiliary materials.

Instruments: Non-thermal plasma power system, dielectric barrier discharge catalytic reactor, NO_x on-line detection system (NGK and Horiba portable gas analyzer PG-225), scanning electron microscope (SEM), nitrate ion detector (761 Compact 1C Ω Metrohm), muffle furnace.

2.2 Preparation of Catalyst

(1) choosing pulverized coal carefully: select suitable coal type, remove ash, grind and screen.

(2) preparing solution: $ZnCl_2$ is confected to 10% solution by adding deionized water, and pulverized coal treated by some special technologies is added into that solution and stirred uniformly; $CuSO_4 \cdot 5H_2O$ is confected to 6% solution by adding deionized water, then add citric acid

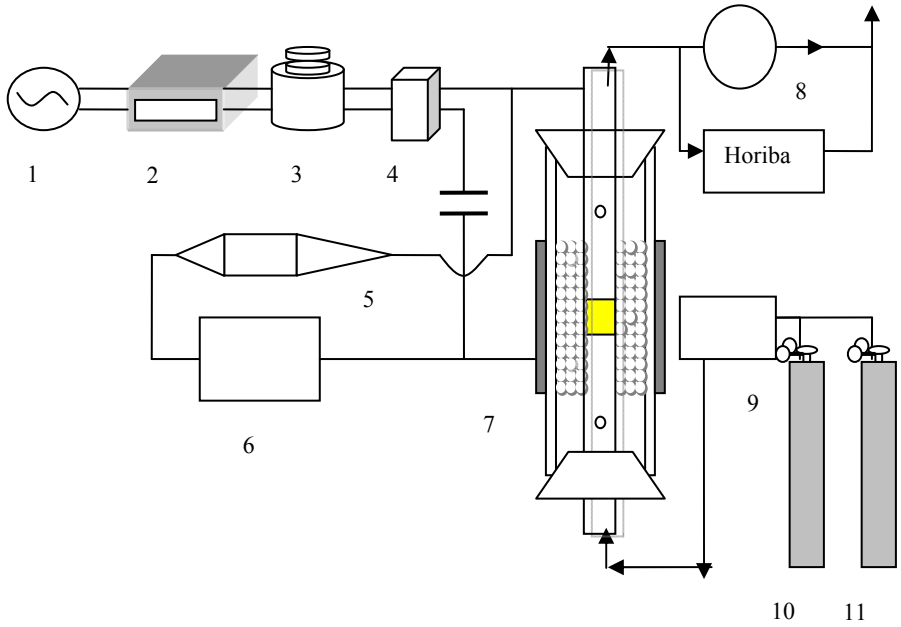
and other auxiliary materials into that solution and stirred uniformly. Place for 24 h.

(3) Granulation: pulverized coal is added into coal tar and stirred uniformly, then suppress it in a mould to compress forming.

(4) Heating activation: catalyst particles naturally dry for 24 h, then put them in muffle furnace and heat at the temperature of 200 ℃ to dry finalization completely, and heat activation at the temperature of 600 ℃.

2.3 Experimental Method

Experimental schema is shown as Fig. 1.



1. Power Supply; 2. Power Meter; 3. Transformer; 4. Naon; 5. Attenuation Problem; 6.Oscilloscope; 7. Reactor of dielectric barrier discharge assisted catalyst; 8. NO_x online analysis of NGK; 9. Mass flow controller; 10.Air cylinder; 11. NO Gas Cylinder.

Fig. 1 Experimental schema

Fill reactor with catalyst and marbles which have the same volume with the catalyst, then inlet simulation gas. Under the difference of input voltage, the concentration of NO, NO_x of outlet gas is on-line tested with NGK and HORIBA. Changes between catalyst before and after reaction is tested by SEM, besides, the concentration of NO_3^- is tested with nitrate ion detector.

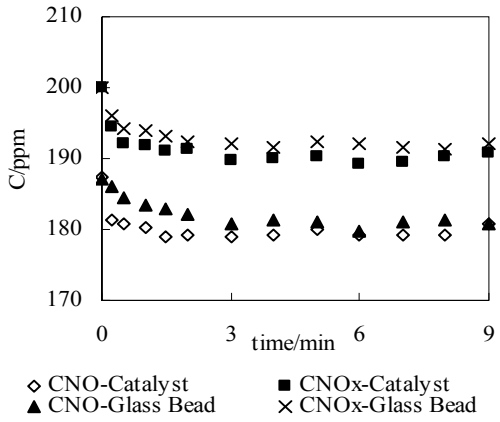
3 RESULT AND DISCUSSION

3.1 The Effect of Dielectric Barrier Discharge on Catalyst Reaction

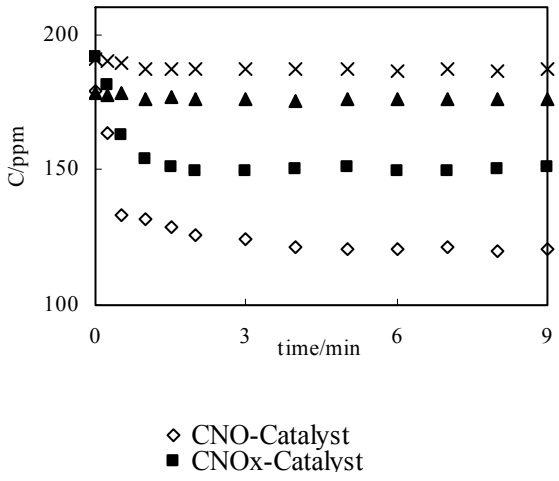
40 g catalyst is filled in the non-thermal plasma fixed bed and under normal condition, simulation gas NO_x the concentration of which is 200 ppm is added into the bed and the inlet gas flow is 4.0 L/min.

Under the same condition, input power of dielectric barrier discharge system are 4 W, 6 W, 8 W, 10 W, 12 W respectively. When catalyst and marbles are filled into reactor respectively, the relation between time and concentration of NO and NO_x of outlet gas is showed as (a), (b), (c), (d), (e) in Fig. 2.

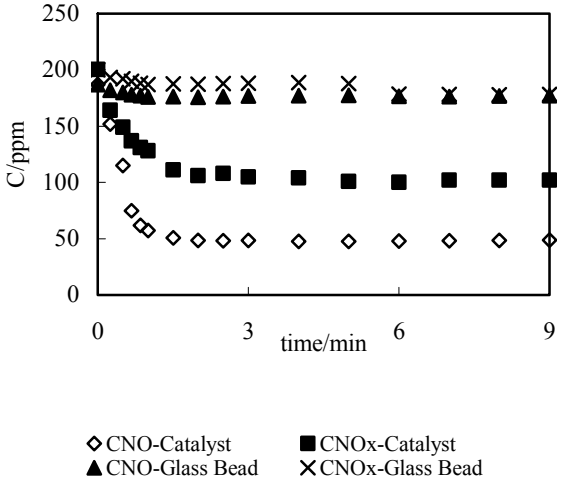
CNO-Catalyst in Fig. 2: when the reactor filled with catalyst, the concentration of NO of reactor outlet gas; C NO_x-Catalyst: when the reactor filled with catalyst, the concentration of NO_x of reactor outlet gas; CNO-Glass Bead: when the reactor filled with marbles, the concentration of NO of reactor outlet gas; CNO_x-Glass Bead: when the reactor filled with marbles, the concentration of NO_x of reactor outlet gas.



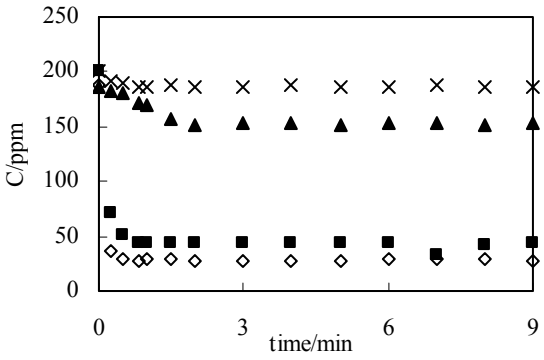
(a) input power 4 W



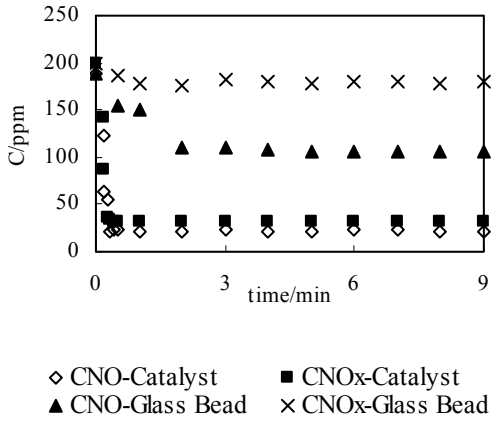
(b) input power 6 W



(c) input power 8 W



(d) input power 10 W



(e) input power 12 W

Fig. 2 The relation between time and concentration of NO and NO_x under the difference condition of 4 W (a), 6 W(b), 8 W(c), 10 W(d), 12 W(e) input power plasma combined with catalyst

(a), (b), (c), (d), (e) in Fig. 2 indicate that (1) the concentration of NO and NO_x of reactor outlet gas decreases with the increasing of input power. The reason is that non-thermal plasma density and the concentration of active oxygen atom increase with the increasing of input power, which oxides NO forming NO_x. (2)The concentration of NO and NO_x of outlet gas comes to a steady state in short tine. That indicates that the effect of non-thermal plasma on chemical reaction is rapid.

Reacting for 9 min, components of outlet gas come to steady state fully. Removal ratio is calculated with the concentrate of NO and NO_x under reaction equilibrium condition. Fig. 3 shows the relation between removal ratio and input power:

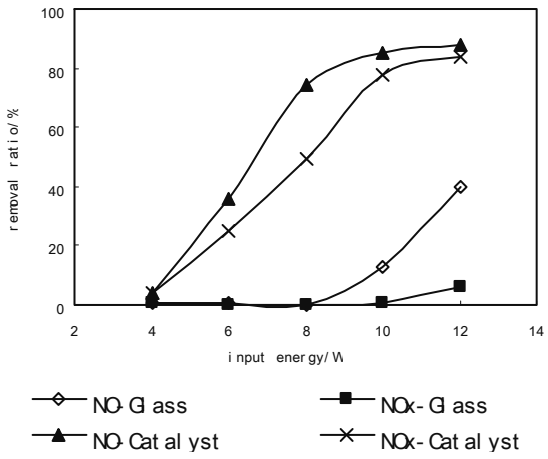


Fig. 3 when chemical reaction reached balances the relation between removal ratio of NO, NO_x and input energy with the catalyst volume the same as glass bead volume condition

Fig. 3 indicates that under the same condition, with the increasing of input power. (1) When the catalyst exists, removal ratio of NO and NO_x is bigger than glass bead exists. The reason is that catalyst not only reduces initial activation energy of catalyst, but also adsorbs and store NO and NO_x. (2) Catalyst improves removal ratio of NO and NO_x; but when the glass bead exist, NO removal ratio increases with the increasing of input power, but NO_x removal ratio changes little. That indicates that catalyst not only accelerates reaction that NO is oxidized to NO, but also improves reaction NO_2 is further oxidized, which stops cyclic reaction that reactive oxygen species combine with itself and create oxygen in the state of non-thermal plasma.

3.2 Catalyst SEM Analysis

Under normal condition, 40 g catalyst is filled into reactor, volume flow of inlet gas 4l/min, the concentration of NO_x 200ppm, input power of dielectric barrier discharge reactor 10.0w. Changes of catalyst surface structure are shown as Figs. 5 and 6, and Table 1 shows composition of catalyst before and after reaction.

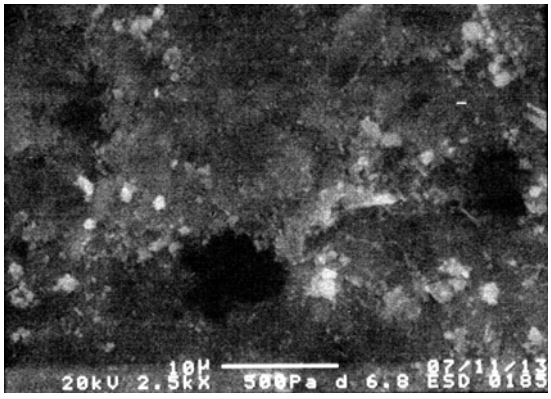


Fig. 4 the new catalyst surface photo

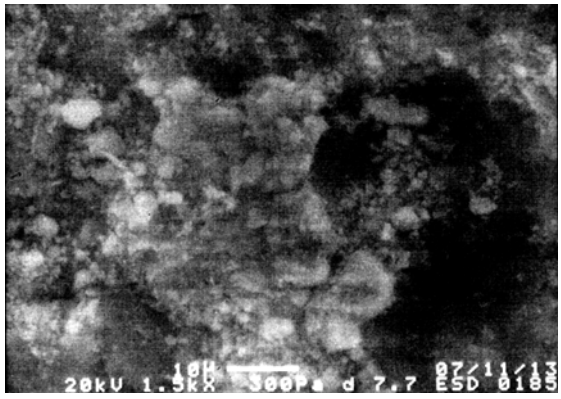


Fig. 5 the used catalyst surface photo

Fig. 6 the new catalyst element analyze

Table 1 the new and used catalyst surface elements analysis

Element	NEW Catalyst		USED Catalyst	
	Weight concentration/%	Molar concentration/%	Weight concentration/%	Molar concentration/%
C	16.90	34.79	30.00	51.46
O	26.59	41.08	26.21	33.76
Al	4.59	4.20	1.79	1.36
Cu	25.60	9.96	20.03	6.50
Zn	26.33	9.96	21.97	6.93
	100.0	100.0	100.0	100.0

Figs. 4 and 5 and Table 1 indicate: (1) Because of abundant surface holes of catalyst, coal-based activated carbon carrier can provide bigger surface area, which can effectively adsorb and concentrate NO and NO_x of simulation gas, and it is good to NO_x removal. (2) The surface of new catalyst is relatively smooth; and the surface of used catalyst has many fine particles. Molar concentration of copper decreased to 6.50% from 9.96% and molar concentration of Zn decreased to 6.93% from 9.96% using catalyst. It indicates that new substance is formed with catalyst assisted non-thermal plasma.

2 g used catalyst particles are immersed in 20 ml deionized water of which PH value is 6.2 for 12 h. Test NO_3^- of leaching solution with nitrate ion detector. Therefore, judge that intermediate reaction is as follow:

$$CuO + NO_x \rightarrow Cu(NO_3)_2$$

$$ZnO + NO_x \rightarrow Zn(NO_3)_2$$

Knowing from the above experimental phenomena and analysis data, NO_2 can be further oxidized into NO_3^- , adopted copper oxide catalyst, the carrier of which is coal-based activated carbon assisted dielectric barrier discharge, under normal condition. Therefore this method is an effective way to remove NO_x.

4 CONCLUSIONS

NO is oxidized into NO_2 and NO_x is reduced significantly and NO_2 is further oxidized into NO_3^-, which stops cyclic reaction that reactive oxygen species combine with itself and create oxygen in the state of non-thermal plasma, adopted copper oxide catalyst, the carrier of which is coal-based activated carbon assisted dielectric barrier discharge. At the same time, nitrogen oxides can be adsorbed and stored on the catalyst, which improves concentration of reactant and reaction rate. Nitrogen oxide removal ratio increases with the increasing of input power of dielectric barrier discharge reactor and this power can effectively generate non-thermal plasma and improve concentration of oxygen species and active species. It also improves adsorption and catalytic activity of catalyst.

ACKNOWLEDGMENTS

Financial support by the International cooperation in science and technology projects in Anhui Province (0808073021) is gratefully acknowledgment.

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