

**Non-thermal Plasma Combined with Modified
Adsorption Catalyst for Removal of NO_x**

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Abstract

Non-thermal plasma assisted catalysis is one effective method to remove NO_x from diesel engine exhaust. Catalysts, such as Al_2O_3 , Cu-ZSM-5, BaY, Pt/ Al_2O_3 , V_2O_5 - WO_3 / TiO_2 have been investigated. Ideal catalysts should show good stability, higher activity or efficiency, low costs, resistance to poisons and easily to be regenerated. The main research of this thesis is to develop low cost catalysts, evaluate their performance and propose plasma catalysis model. Three developed catalysts are based on Sepiolite, Attapulgite clay and coal derived Activated Carbon.

Dielectric barrier discharge reactor is placed in a thermo-tank at 180°C . Preparation of Modified Sepiolite Catalyst (MSC) includes three critical steps as acid washing, surface modification and then surface activation. For NO_x removal, their reactivities are in the following order: plasma with MSC, MSC, plasma with MSC without acid washing and only soaking $\text{Cu}(\text{NO}_3)_2$ and calcination, plasma with SOP, and then plasma process along.

The rare earth Ce is used to prepare the Modified Attapulgite Clay Catalyst (MACC). The calcination temperature shows a significant influence on the NO and NO_x removal rates. Optimal temperature is around $400 - 600^\circ\text{C}$.

The Coal-based Activated Carbon Catalyst (CACC) is used to remove NO_x with NTP. The NO_3^- ions can be detected in the leaching solution with the used CACC. The order of removal efficiency is: plasma with catalyst > Plasma with glass bead > only catalyst > only plasma.

In terms of the NO_x removal rates at the same condition, it is found that the Coal-based activated carbon gives the best performance in contrast with the modified sepiolite catalyst, modified attapulgite clay catalyst.

Electrical characteristics of a packed bed reactor have been simulated by using a simplified model. Effect of the pellet size can be predicated in terms of the input discharge power.

According to present experimental results, it is anticipated that the proposed active carbon has a great potential for industrial application. The catalyst is very cost effective and it can be easily regenerated. Its practical applications, however, need to be further investigated with exhaust gases.

Keywords: Dielectric Barrier Discharge, NO_x removal, plasma catalysis, exhaust gas cleaning, chemical catalysis.

1. Introduction

1.1 Objective of the research

With the rapid development of human society, the environment protection has been paid attention by the human being. However, the automobile exhaust has gradually become the one of main pollution source in the urban air, and the pollutants from exhaust gas are nitrogen oxides (NO_x), hydrocarbon fuel (HC), black carbon, oil mist, and etc. People's life and health was seriously affected. Therefore, how to effectively control the exhaust pollution has become an important problem for the science and technology workers.

For the automobile exhaust gas, the concentrations of NO_x , HC, and CO are 100 – 3000 mg/m^3 , 500 -1000 mg/m^3 and 1- 2%, respectively [1-3]. Specially, nitrogen oxides has a great harm to the environment, NO is easy to form photochemical smog under the sun, which is also harmful to human respiratory system. Meanwhile, NO can destroy atmospheric ozone and form acid rain [4-5]. In order to control the NO_x pollution from automobile exhaust, this thesis focuses on non-thermal plasma combined with modified adsorption catalyst to remove NO_x .

1.2 State of the art of three-way catalyst for NO_x removal

Three-way catalyst (TWC) [6-8] is considered to be an ideal choice for NO_x removal, since it can directly decompose nitrogen oxides into nitrogen and oxygen under thermodynamics conditions. The critical issue is to find a suitable catalyst to improve

reaction rate [9-16]. Three-way catalytic converter is recognized as one of main technologies to control automobile exhaust emitting. The three-way catalytic converter is composed of the three-way catalyst packed into the stainless steel shell and the buildup installed in the exhaust pipe of automobile. The three-way catalyst is made of cordierite or ceramic honeycomb carrier and loaded on activated alumina and cerium oxide, and then impregnated with palladium (Pd), platinum (Pt), rhodium (Rh) three kinds of noble metals, traditionally. As a result of the large surface area of the catalyst carrier, when the exhaust passes through the three-way catalytic converter, the components of HC, CO, and NO_x and other pollutants will be changed into N₂, H₂O and CO₂ and other un-harmful or lowly harmful components by the oxidation-reduction reaction [17]. For the lack of precious metal resources, nowadays many investigators have tried to make cheap and effective TWC with non-precious metals, rare earth and composite materials.

No matter what are used to make TWC, to ensure the TWC converters work properly it is necessary to meet two conditions: 1) the used of gasoline is unleaded; 2) engine is of closed-loop, and the ratio of air to fuel is 14.7 : 1 [18]. Although the closed-loop system is beneficial to the performance of catalyst, there are still many deficiencies, which can bring the catalyst poisoning, reduce the lifetime and the efficiency of catalytic reduction of NO_x.

The green cars development is fast presently, such as gas or half gas engine, in which the engine uses the nature gas instead of oil fuel, and the components of CO and HC in exhaust gas can be reduced to 87% and 83%, respectively, but the NO_x reduction is relatively smaller. So it is necessary to investigate a new kind of catalyst to remove NO_x from automobile exhaust.

1.3 Overview of the NTP for NO_x removal from exhaust

For the complexity and high concentration of pollutants, problems related to the traditional technologies are low efficiency, secondary pollution, equipment corrosion, process complexity, high cost of investment and operation, and so on. In recent decades, non-thermal plasma technology has been successfully applied to treat solid waste, wastewater, waste gas process and generally drew the people attention in the field of environmental protection.

1.3.1 Concept and types of plasma

Plasma is the fourth phase state of material existence, full of active electrons, charged particles and neutral particles [19]. It can be divided into non-thermal plasma and thermal plasma. When the electron temperature T_e , the ion temperature T_i and the neutral particle temperature T_g is equal, the plasma is in thermodynamic equilibrium state, called the equilibrium plasma or thermal plasma, its temperature is usually above the $5 \times 10^5\text{K}$; when $T_e \gg T_i$, known as Non-Thermal Plasma (NTP), the electron temperature is up to 10^4K or more, while the ion and neutral particle temperature as low as $300 \sim 500 \text{ K}$, non-equilibrium Plasma is called Cold Plasma or Non - Thermal Plasma, which usually generated by gas discharge [20].

1.3.2 Non-thermal plasma generation

Non-thermal Plasma is mainly generated by the gas discharge. According to the mechanism of discharge, the range of gas pressure, character of power source and geometry of the electrode, gas discharge plasma is divided into [21]:

- (1) Glow discharge;
- (2) Corona discharge;
- (3) Dielectric barrier discharge;
- (4) Radio frequency discharge;
- (5) Microwave discharge.

The Corona discharge uses the electrode of very small curvature radius, such as needle-shaped electrode or thin thread electrodes, and the high voltage is in connection with the electrode. Due to the small curvature radius of electrode, the electric field near the electrode is particularly strong, leading to the occurrence of non-uniform discharge, and this is known as corona discharge. For the treatment of air pollutant, the corona discharge is used to remove SO₂, NO_x, VOCs, hydrogen sulfide, and de-colorization from organic dye waste water.

Dielectric barrier discharge (DBD) takes place between two electrodes, and between of them a dielectric barrier is placed. DBD has the advantages characteristics of uniform discharge both in large space and in air pressure [22]. Dielectric barrier discharge can generate a steady discharge and non-spark in a large space, because the accumulated charges on the dielectric barrier induce a reverse electric field. Generally, the structures of DBD reactor can be wire-tube, wire-plate, plate-plate. In terms of frequency, DBD is divided into low-frequency (50 Hz – 100 KHz) and high-frequency (> 100 KHz). The power of DBD is proportional to frequency. The relative dielectric permittivity has two side effects on the non-thermal plasma generator, on the one hand the greater the relative dielectric constant, the larger discharge power got in the gap field; on the other hand, the relative dielectric constant is directly proportional to DBD power. Because the electron

density is high at atmospheric pressure, the DBD is possibility to apply in the large-scale industrial production.

1.3.3 Principle of NTP for gas treatments

The energy transfer in the process of NTP is shown in Figure 1-1 [21]:

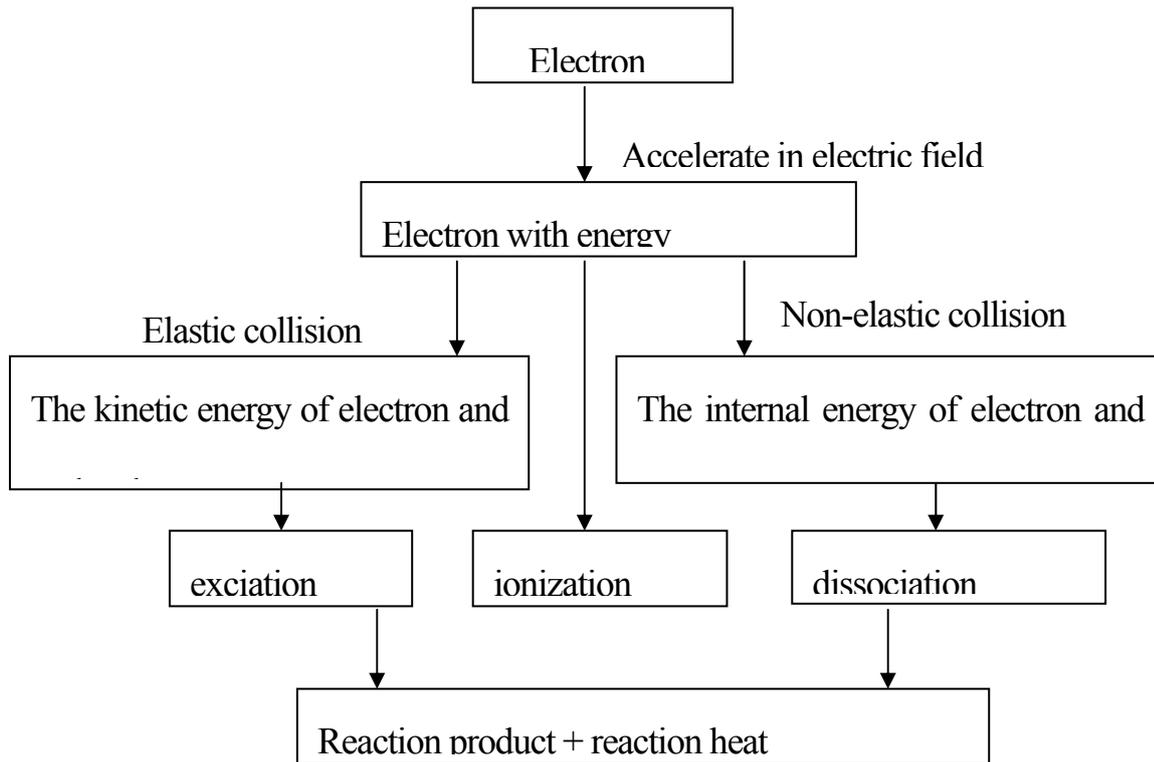


Fig.1-1 Energy transfer graph in non-thermal plasma

For the elastic collision, electrons retain most of the energy and continue to be accelerated by the electric field until the non-elastic collision takes place between electrons. When the electron energy is equal or a little higher than the chemical bond in a target molecule, the inelastic collisions occurs between molecules and electron. In the process of inelastic collision, most energy of the electron transfers to the target molecule, and the electron kinetic energy transforms into internal energy of the target molecules, and then target molecule occurs ionization, dissociation, and excitation, and causes a series of physical and chemical reactions, so large complicated target molecules, such as pollutant

molecule, turn into a simple and small molecules of un-poison. From the process can be seen that the plasma is rich in electrons, ions, free radicals and excited states of molecules. The plasma provides a good way to some chemical reactions which require large activation energy.

1.3.4 Focus and development of the research

Based on the study of purification of gaseous pollutants, purification efficiency of plasma technology is dependent on the excited energy state of the particles obtained in electric field [23]. The larger energy the excited state particles gain, the more energy transfer while the gas molecules collide, which makes it much easier bond-cleavage in the gas molecules. The greater the number of excited particles, the higher the removal efficiency is. The energy and the quantity of excited particles are dependent on high voltage power supply and structure of plasma reactor. The different characteristics of the power supply and structure of the reactor make ionization intensity of discharge, the energy of electrons gain from electric field significant different. The treatment effects in the processing of whole plasma system also become significantly different. Therefore, the power supply characteristics and the electrode configuration are important when gaseous pollutants are treated by plasma. The other important point is the design of plasma reactor to clean the gaseous pollutants.

The matching between power source and plasma reactor is important. The power source is required to be highly efficiency and reliable in operation. The reactor should be matched with the power supply, and must be kept that most of energy per pulse is transferred to the reactor through transmission lines, and no reaction along the transmission

cable. Besides power supply, all of the form, size, reactor structure and the components of gas are affected by pulse waveform, which ultimately affects the treatment effect of gaseous pollutants.

1.4 Research on NTP collaborative catalysis

In recent years, non-thermal plasma catalysis is considered to be one of the most effective techniques for the treatment of gas with a low concentration. Through a large amount of research and development, many important results have been obtained for in experiments and mechanism [24-27]. The collaborative function can greatly enhance the cleaning effect, a large number of studies in the world have shown that compared to a single role of plasma or catalyst. The experiments of Stefan Broer [28] show that below 140 °C, NO_x hardly be removed without plasma processing; and about 70% of the NO_x is reduced in the catalytic converter after DBD.

Comprehensive view, the synergy principle of non - thermal plasma combined with catalytic to treat exhaust is as follows: a large amount of highly active species, such as ions, electrons, excited atoms, molecules and free radicals accumulate in the space of plasma. These highly active substances are impossible in general chemical reactions, but they are steadily produced by plasma. These kinds of active substances (especially high-energy electrons) with great energy can bring up the active of the catalyst in the plasma, and also can decrease the starting activation energy. Meanwhile, the catalyst can promote selectively catalytic reaction to decompose the by-products which produced in the plasma, and no second pollution substances.

The non-thermal plasma catalysis technology may solve the problem which can not

be solved by traditional purification methods. This technology has the following advantages [29-33]: lower energy consumption, low temperature; convenience for use, no by-products and second pollution produce since the selectively catalyst reaction can effectively decompose by-products; no produce radiation; especially to deal with bad smell and lower concentration of exhaust gas. But the non-thermal plasma catalysis technology has some challenges as follows: sensation to moisture, when the moisture content is higher than 5%, the treatment efficiency is affected; higher cost of equipment.

The technology to treatment of pollutants in the environment has gained great concern and is considered as one of the development of high-tech in the field of dealing with environmental pollutants.

1.4.1 Collaborative Principle

By the literature [34], it is recognized that there are a lot of high-density active particles in the plasma as well as high-intensity ultraviolet radiation in the reactor, and when the gas residence time is less than 1s, the active particles were distributed evenly and moved along the gas flow direction. Therefore, when the catalyst is along the flow distribution in the plasma reactor or in the vicinity of plasma, the excited species in the plasma can excite the catalytic reactions at low temperature (even at room temperature). Compared to those in the general technology, the catalyst had purification could work in the temperature reached above 300 °C, the plasma - catalytic technology can greatly reduce energy consumption.

A patent said [35], when ferroelectric particles (for example high dielectric ceramic) were packed the average energy of electrons on the surface of particle was much higher than that in the surrounding gas in the NTP reactor. When imposed power on the NTP

reactor, most of the energy used to generate high energy electrons, instead of heating the gas and rising temperature. Therefore, the plasma energy used directly for electron impact ionization and the active groups of ionizing gases, which can be decomposed active group of toxic gas compounds. However, if there is only plasma in reactor, a lot of byproducts, such as CO, CO₂, NO, NO₂, N₂O, O₃, and other volatile organic compounds will be produced inevitably. When the packed particles carried with catalyst have introduced to the NTP reactor to treat waste gas, not only the toxic compounds are decomposed, but also the catalyst can be selective catalytic reaction, and the final product is non- pollution material. More notably, the temperature of reactor need not increase and there is not effect on the resistance of the whole gas road system. Typical catalysts are Co, Cu, Cr, Ni, V, Pt/Al₂O₃, Pd/Al₂O₃, Rh, RhZnO₂, FeO, Fe₂O₃, zeolite, etc. The carrier gas can be air, oxygen, argon, etc. Generally carrier particles are high dielectric materials and the relative dielectric constant is greater than 5, such as BaTiO₃, SrTiO₃, NbTiO₃ and various ceramics

There is literature [36] revealed that, the multiphase reaction of plasma catalysis can occur in different area, such as the plasma region, the afterglow region and the product collection region of plasma. In the plasma region, impurities or coats on the electrode surface, solid-phase filling between electrodes, and the coat on the reactor wall have the ability of catalysis. In the afterglow region, plasma along the direction of gas flow riches a large number of high-activity particles and mainly long-lived free radicals, these highly reactive particles can be used to perform certain specific chemical reactions. Therefore, the catalyst and coat catalytic in the wall in the afterglow region play an important role and can not be ignored. In the product collection area, catalysis is also worth studying.

One paper [37] has been reported that the activity character of solid catalyst is

determined by its chemical composition and physical phase, crystal structure and surface form. By using plasma, the ultra-fine particles are formed in the catalyst surface, the average diameter of particles is 5 to 500nm and specific surface area is about $100\text{m}^2 / \text{g}$, which will destruct the crystal structure of catalyst, so that it will produce more holes to increase the surface area of catalysts greatly and improve the catalytic activity. Compared with ordinary catalysts, the catalyst treated by plasma has the following unique features: a lot of active points are distribution evenly; the consumption of energy is lower; the activity and selectivity of catalyst is enhanced; the service life of the catalyst is prolonged; the preparation time is reduced. Moreover, the active components and distribution in the catalyst can be controlled by changing the parameters of plasma and chemical; the sensitivity to poison can be reduced. These features will make plasma – catalysis technology larger application foreground.

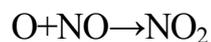
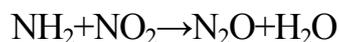
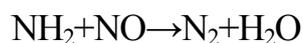
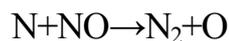
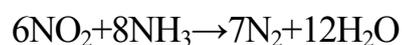
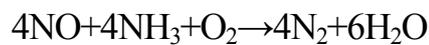
1.4.2 Removal of nitrogen oxides

B. S. Rajanikanth and et al. [38] did the investigation of removal NO_x from the simulation gas by using the NTP method. It is obtained that the DBD with packed bed reactor had the ability to remove NO with a low high voltage. Three different catalysts (Al_2O_3 , BaTiO_3 , $\text{Al}_2\text{O}_3 + \text{Pd}$) were used in their experiment. When the gas composition was NO, O_2 , N_2 or NO in N_2 , the catalyst of BaTiO_3 had the higher removal efficiency. When the initial concentration of NO was $265\text{mg}/\text{m}^3$, NO removal rate was almost reached 99%. When the simulation gas composition was NO, O_2 , CO_2 , N_2 , the catalyst of Al_2O_3 coated with the Pd had a higher NO removal efficiency, compared with other packed materials. With the increase of voltage and frequency, NO removal efficiency also

increased. It is worth to note that the NO removal rate at room temperature in their experiment is equivalent to that at over 300 °C without plasma.

In urban areas, the speed of the diesel vehicles in the average load is very low, resulting the temperature of exhaust gas is as low as 40-50 °C, the general catalytic converter is difficult to fit for application at such a low temperature, this case is preferably to use the DBD synergistic catalyst reactor.

Stefan Broer and et al. [28] used ammonia as reducing agent at 100-250 °C temperature in the case of the DBD plasma combined with V₂O₅ - WO₃/TiO₂ catalyst. The simulation gas of automobile exhaust was composed of 82% N₂, 13% O₂, 5% H₂O, 500 mg/m³ NO_x and 500mg /m³ NH₃. NO_x have hardly been removed without plasma processing below 140 °C. With DBD plasma before catalytic conversion, the NO_x removal ratio reached about 70%, 170mg/m³ NO was converted, among which 110 mg/m³ NO was oxidized to NO₂, 60mg/m³ NO was deoxidized by NH₃. In the case of coexistence of NO and NO₂ with the catalyst, the selective catalytic reduction was enhanced. The chemical reaction equations are as follows:



K. P. Francke and et al. [24] found that for an initial NO_x of concentration of 53mg/m³

at 120 °C, the conversion rate of 20% was obtained by plasma only, and the conversion rate of about 40% was achieved by catalyst only; while by plasma combined with catalyst the conversion rate of over 80% can be achieved. It is very different of the effect on NO removal ratio at the different case of only plasma, only catalyst and plasma synergistic catalyst. If the relative position of plasma and catalyst is different, the NO removal rate can be varied considerably. A small part of the NO was oxidized to NO₂ with plasma only. A small amount of NO was oxidized to NO₂ when only ammonia acted as a reducing agent and zeolite acted as a catalyst. At the condition of plasma and cooperating with catalytic, about 50% NO was removed if discharge plasma was placed before the catalyst, more than 80% NO was changed into N₂ if plasma placed near the catalyst.

1.4.3 Power consumption in the NTP reactor

(1) For dielectric barrier discharge

Normally plasma is produced by corona discharge or dielectric barrier discharge [39]. The corona discharge is in a very small area (only several mm) and unstable. The discharge transits easily from streamer to the flow of arc. DBD can generate a non-spark and stable flow injection spark corona in a large area, because current which is caused by discharge accumulates in the barrier surface forms a reverse electric field. It can prevent the current focus which is caused by discharge [40]. The forms of DBD reactor are Wire - Cylinder, Wire - Plate, Plate - Plate and other structures, generally. Taking into account the shape of diesel exhaust tail pipe, it is better to use wire - cylinder form for treatment of diesel exhaust.

(2) High-frequency and high voltage power supply

Usually the DBD is divided into low-frequency and high frequency, the former the frequency range is 50 Hz – 100 KHz. As for the latter frequency is over 100 KHz. The normal power supply in laboratory of voltage range is 15 - 45 kV, frequency range is 50 - 120 Hz. In order to serve energy, the special power supply for vehicle is provided with the character of high-frequency, high voltage, small size and light weight.

(3) The dielectric medium should be high relative dielectric constant

The relative dielectric constant of medium has two hands to affect the plasma generator. One hand is the greater the relative dielectric constant of media, the larger strength of field in the discharge gap, and the better of treatment for exhaust; the other hand is the discharge power is directly proportional to relative dielectric constant. Taking everything into consideration, in the case of satisfaction of the field strength, the quartz glass which relative dielectric constant is 3.7 is the best choice in this experiment.

(4) The smaller the radius of the electrode

The small radius of wire electrodes can reduce the discharge power.

(5) Full use of plasma combined with catalysis technology

The study of catalytic converter is an important point for the treatment of exhaust. Many types of catalytic converters have already been developed, but there are still some problems, for instance, the catalytic converter only works well certain temperature and exhaust gas volume, but when the temperature of tail gas is low in the low load condition of automobile, the conversion efficiency is decreased [41].

The plasma technology combined with the catalytic converter can lead to the synergistic effect. When the car in good condition the catalytic converter is only used to save electric energy; but when the car in the low load condition, the plasma combined with

the catalyst can be used to carry out the task.

1.4.4 The catalyst for NTP reactor to remove NO_x

Catalyst is a substance, which can accelerate the reaction rate without changing the standard Gibbs Free Enthalpy of the reaction and has the following characteristics:

(1) It can only accelerate the reaction that can be carried out in thermodynamics, which can not accelerate the reaction which is impossible in thermodynamics.

(2) The catalyst can only accelerate the reaction to tend to balance, but not change the position of equilibrium (equilibrium constant).

(3) The catalyst has selective character for the reaction.

(4) The catalyst has a certain life.

A good catalyst should have three basic requirements, namely activity, selectivity and stability. One catalyst includes three parts mainly, e.g. active component (the main part of the catalyst), carrier (the frame to load active component), and auxiliary components (to improve the activity, selectivity and stability of the catalysts).

(1) The catalyst zeolite as a carrier

Yu Gang and et al. [42] used the copper / zeolite catalysts ($d = 3 - 4$ mm) collaborated NTP to remove NO_x. and found that the Cu / zeolite is an effective catalyst of combination with plasma to remove NO_x, and it shows a better removal efficiency if part of oxygen entered into the reaction. The experiments showed that when there was the catalyst, if [O₂] = 0 then the removal rate of NO_x was 40%; if [O₂] = 8% then NO_x removal rate was 60%; However without catalyst, if [O₂] = 0 then NO_x removal rate was 25%, if [O₂] = 8% then NO_x removal rate was only 35%.

Tetsujitl [43] studied that Cu-ZSM-5 as the catalyst combined with NTP, adding ethylene, carried out the NO_x removal reaction. The results showed that Cu-ZSM-5 combined with NTP and ethylene can remove NO_x at 250 °C, and the removal rate of NO_x is up to 90%; that the traditional three-way catalyst reaches the same NO_x removal rate to need the temperature at 400-500 °C. Kwak ' s [44] study reported the results of the catalyst, of which alkali metal ions and alkaline earth metal ion had loaded in the Y and FAU zeolite, combined with plasma to de-NO_x reaction.

Li Huijuan [45] did a series of experiments and obtained the results. The order of catalytic activity in the process of de-NO_x with the plasma is as follows: in the series of the alkali metal, NaY > CsY₂₋₂ > KY₂₋₂ > LiY₂₋₂, the NO_x removal ratio is 60% at T = 440K, and the catalytic activity drops down rapidly with the temperature increasing. While the other series of alkaline earth metal, the order is Mg < Ca < Sr < BaY₂₋₂, the NO_x removal ratio is 69% at 440K with the catalyst of BaY₂₋₂, in the temperature range of 473-503K the removal ratio is greater than 80%. The catalytic activity increases with temperature increasing and has a good thermal stability.

Miessner [46] did the experiment of de-NO_x by DBD plasma combined with the catalyst of the ammonium salt load in the mordenite. The condition was T = 343 K, [NO] = 500ppm, GSHV (space velocity) = 3000 / h, DBD power 25Wh / m³. With the catalyst, the NO removal ratio increased with oxygen concentration increasing, when [O₂] = 0, the NO conversion ratio was 50%, when [O₂] = 5%, the NO conversion ratio reached 100%. Without the catalyst, the NO conversion ratio decreased with the oxygen concentration increasing, when [O₂] = 0, the conversion ratio was 30%, while [O₂] = 5%, the conversion ratio reduced to 5%. The paper had studied the impact of the order of catalyst and plasma

on NO_x removal rate.

Tonkyn [47] investigated the two-step method of synergy between plasma and catalytic to remove NO_x. It is pointed out that the BaY acted as catalyst and added propylene, when [C₃H₆] = 600ppm, [NO] = 200ppm, O₂=6%, H₂O = 2%, output power 15 J/L, the NO_x removal ratio was 90%. Their result showed the two-step method was better than the one-step method.

Francke [48] studied the synergistic effect of the DBD plasma with ammonia selective catalytic reduction for de-NO_x. The results showed that different catalysts had the different removal rates.

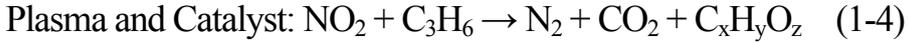
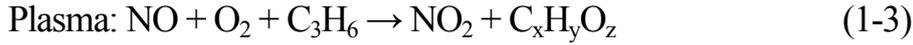
(2) The catalyst aluminum oxide as a carrier

Penetrante and et al. [49] did the studies of plasma with γ -Al₂O₃ for selective catalytic reduction of NO_x. They believed the whole reaction had two main processes:



They pointed out that the plasma-assisted catalyst had the main functions: NO is oxidized to NO₂, but not further oxidized NO₂ to acid; For HC is oxidized partly, HC can not be completely oxidized to H₂O and CO₂; Under the catalysis the production from the partial oxidation of HC can reduce NO_x. NO is oxidized to NO₂ by plasma, so use a new type of catalyst to reduce NO₂ → N₂ is more reliable and active than the traditional catalyst [50].

Miessner and et al. [51], introduced that plasma assisted with selective catalytic reduction and propylene for de-NO_x; the experiment showed that in the condition of excess of oxygen, the reaction as the follows:



It is mentioned in this paper that the excess oxygen would help the conversion of NO to NO₂, in the second step adding C₃H₆ could the further promotion of NO₂ into N₂ in the condition of catalysts as Al₂O₃ and ZrO₂. When at the condition of temperature T = 300 °C, space velocity 20000 / h, provided 30ev energy for each NO molecule, from the gas including NO of 500 mg / m³ the NO removal ratio was 50 %.

Rajanikanth [52] and et al. used the NTP with three kinds of catalysts (Al₂O₃, Pt/Al₂O₃, BaTiO₃) to remove NO_x from simulated gas. It is found that there were a higher NO removal rate the catalyst of BaTiO₃ particles in the gas component of NO, O₂ and N₂ gas. When [NO] = 26 mg/m³ the NO removal rate was 90%; While in the simulating automobile exhaust of component was NO, O₂, CO₂ and N₂ used the Al₂O₃ as the catalyst, has a higher removal ratio, removal ratio at room temperature was similar to other catalysts at 300 °C.

Miroslaw [53] used corona discharge and the catalyst of V₂O₅ - TiO₂ / Al₂O₃ which was saturated ammonia for the reduction of NO_x. The catalyst was placed in two methods: the one was that the catalyst of the Al₂O₃ small ball which diameter was 5-6 mm was attached the V₂O₅-TiO₂ coating and was placed in a plasma reactor; the second method was that catalyst which was prepared by the first way adsorbed the NH₃ reached to saturation, and then placed in a plasma reactor. For the different NH₃ adsorption time, after the plasma and the catalyst for de-NO_x reaction, by the SEM detection, it found that there was no NH₄NO₃ material after 5min in the adsorption of NH₃ on the catalyst surface, but the catalyst was exposed in the NH₃ gas for 67 h a large number of NH₄NO₃ crystal was

found on the catalyst surface.

(3) The catalyst TiO₂ as a carrier

Stefan and et al. [28] was used V₂O₅-WO₃ / TiO₂ as catalyst (the V₂O₅ which the mass fraction of 1% share) combined with the DBD plasma and ammonia as the reducer for NO_x removal study found that, at the T < 140 °C, only catalyst, the NO_x removal rate was very low. But at T = 100 °C, because of the synergistic effect of plasma and catalyst, the NO_x removal ratio of 70% was obtained. Meanwhile, when the coexistence of NO and NO₂, the selective reduction of NO_x was enhanced. The paper pointed out that when the catalyst coexisted with the plasma, NO_x conversion rate was $r_3 = r_1 + (1 - r_1 / r_2)$ (in which there r₁ was the only plasma NO_x removal reaction rate, r₂ only catalyst for the NO_x removal reaction rate, r₃ plasma – catalyst reaction of NO_x removal rate).

Hammer and et al. [54] discussed the V₂O₅-WO₃ / TiO₂ as catalyst combined with the DBD for de-NO_x reaction, the results showed that the selective catalytic reduction could be induced at 100 °C.

1.5 Main contents of this thesis

In this thesis, the main issues are as follows:

(1) One of the key issues is to develop highly efficient and stable catalysts for the removal of nitrogen oxide by plasma combined with catalysis technology. In this paper, the sepiolite, Attapulgite clay and coal derived Activated Carbon are used as raw material, respectively, after purification, acid modified, prepared catalyst to be carried by a plenty of pore structure and surface area, by impregnating into a copper-based catalyst. To investigate the relationship between catalyst performance and the structure, BET, XRD,

SEM and other means are used to study the catalyst structure and composition. Meanwhile provide effective ways and means for research and development of new plasma for the catalytic removal of nitrogen oxides.

(2) Investigation of the relationship among the plasma and adsorption - catalysis reactor structural parameters (such as room size, geometry, electrode material) and process operating parameters (such as gas flow rate, concentration; voltage, etc.) and the efficiency of input energy and NO_x removal rate.

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2. Experimental Methods and Instruments

2.1 Experimental methods

The experimental setup of NTP combined with modified adsorption catalyst for removal of NO_x is shown in Figure 2-1. The reactor was installed in a thermo-tank with temperature of 180°C . The simulation gas of the NO concentration of 297×10^{-6} (297ppm) and the balance of N_2 was fed into the reactor from the bottom side. The gas flow rate was kept at 7.0L/min flow rate controlled by MFC (Space Velocity is 10.2s^{-1}). The input voltage ($V_{\text{p-p}}$ peak-peak) was changed from 4 to 50kV with a frequency of 60Hz. The outlet concentration of NO was detected by the FGA-4100 automobile exhaust online detection instrument. The NO removal rate is calculated by the formula of the NO removal rate = $100 * (\text{inlet NO concentration} - \text{outlet NO concentration}) / \text{inlet NO concentration}$.

The Lissajous image was used to calculate the discharge power. The capacitor C_M (10nF) was connected in series with the reactor. V_M is the voltage of the capacitor, corresponding to the transferred electrical charge Q in the process of discharge. The voltage V of the AC voltage source through a high-voltage probe and V_M were connected to X and Y axis of the Oscilloscope. A closed circle is produced on the Oscilloscope and the area was calculated to obtain the discharge power P [1]. The input power was measured by using the power meter.

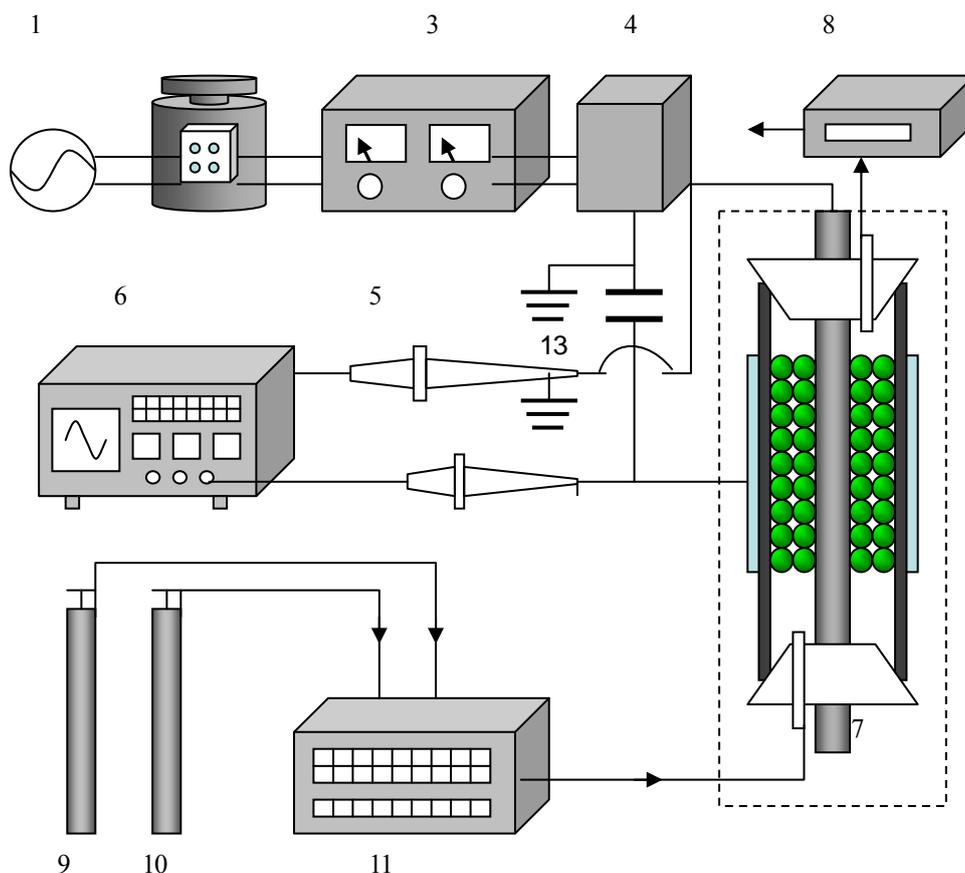


Fig.2-1 Schematic diagram of the experiment

1. Power Supply; 2. Transformer; 3. Power Meter; 4. 220V:45KV, High Voltage Supply;
 5. H.V. Probe; 6. Oscilloscope; 7. DBD Assisted Catalyst Packed Bed Reactor;
 8. NO Online Analyzer; 9. Air Cylinder; 10. NO Gas Cylinder;
 11. Mass Flow Controllers; 12. Constant Temperature Cabinet; 13. Capacity

2.2 Experimental instruments

2.2.1 DBD with catalyst packed bed reactor

The one-section DBD reactor was made of Borosilicate Pyrex Glass Tube with an inner diameter of 27 mm, a wall thickness of 2 mm, and a length of 120 mm. The tube

outside wall was covered with an aluminum film of 60 mm in length and 0.6 mm in thickness, an aluminum rod with an outside diameter of 8 mm was arranged in the center of the tube as anode; the MSC was loaded in the tube between the aluminum rod and aluminum film, both end of the reactor was sealed by silicone rubber plug [2]. The reactor structure is shown in Figure 2-2.

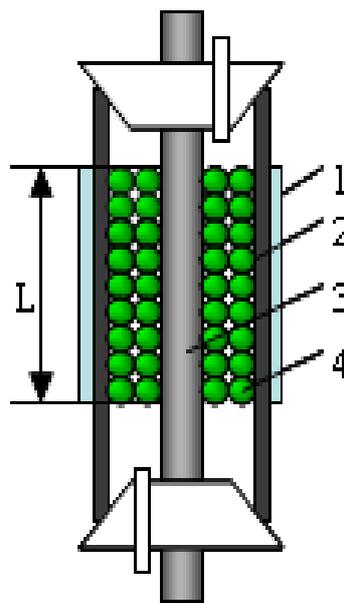


Fig.2-2. The structure schematic diagram of DBD reactor
 1.Cathode; 2.Pyrex tube; 3.Anode; 4.Catalyst Particles

2.2.2 Simulation Gas

The parameters of gas resource in the investigation are listed in Table 2-1. According to the experimental to design the range of gases flow is controlled by the MFC.

Table 2-1 the parameters of gas resource

No.	Components	Concentration	Type
1	NO / N ₂	3032 ppm	A18L / 10.0MPa
2	O ₂ /N ₂	O ₂ 21 % (V/V)	T40L / 12.0MPa

2.2.3 Exhaust gas analyzer

Within the study the inlet and outlet NO_x concentration from the reactor was detected on line by the instrument of FGA-4100. The gas analyzer (FGA-4100) was made by Guangdong FUSHAN Co. Ltd. and was used to measure the NO, HC, O₂, et al. gas concentration from the exhaust. The technical parameters of the Gas Analyzer are listed in Table 2-2.

Table 2-2 Exhaust analyzer technical parameters of FGA-4100

Component	Distinguishing value	The range of measurement	Maximum permissible error
NO	1ppm vol	(0~4000) ppm	±25ppm vol or ±4%
		(4001~5000) ppm	±8%
HC	1ppm vol	(0~5000) ppm	±12ppm vol or ± 5%
		(5001~9999) ppm	±10%
O ₂	0.1% vol	(0~25.0) % vol	±0.1 % vol or ± 5%
CO	0.01% vol	(0~9.99) % vol	±0.06 % vol or ± 5%
CO ₂	0.1% vol	(0~16.0) % vol	±0.5% vol or ±5%
		(16.1~20.0) % vol	±10%

2.2.4 The main experimental instruments

The main experimental apparatus and instruments are shown in Table 2-3.

Table 2-3 List of main experimental equipment

No.	Instrument	Type	Manufacturer
1	Vehicle exhaust gas analyzer	FGA-4100	Analysis Instrument Co., Ltd, Foshan, Guangdong
2	XRD ray analyzer	XD-3	Beijing General Analysis Co., Ltd, Company
3	Constant temperature oven	5X2-5-12	Shanghai research Electric Furnace Co., Ltd.
4	Electronic Balance	WT10002NT	Changzhou Balance Instrument Co., Ltd.
5	Tablet press		Made self
6	MFC	LZB-4	Changzhou Month Co., Ltd. Instrument
7	Oscilloscope	TDS1012B	U.S. Tektronix company
8	NO cylinder	Al8L	Nanjing Special Gas Factory Co., Ltd.
9	Air cylinder	T40L	Nanjing Special Gas Factory Co., Ltd.
10	TGA	2960—SDT	U.S.TA company

- 11 SEM KYKY-EM3200 Japan Shimadzu Corporation.
- 12 High Voltage Power JNB-208B Japan Shimadzu Corporation
Supply
-

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3. Catalyst Preparation by Modified Sepiolite and Performances Evaluation

3.1 Introduction

Sepiolite is one kind of mines in the nature. Its form is fibrous silicate and full of magnesium. Its structure is layer - chain and contains the water and magnesium and silicate. Its general formula is expressed as $[\text{Si}_{12}\text{Mg}_8\text{O}_{30}(\text{OH})] (\text{H}_2\text{O})_{4.8}\text{H}_2\text{O}$, there are many channels in its structure [1]. SEM of the Ore Sepiolite is shown in Figure 3-1.

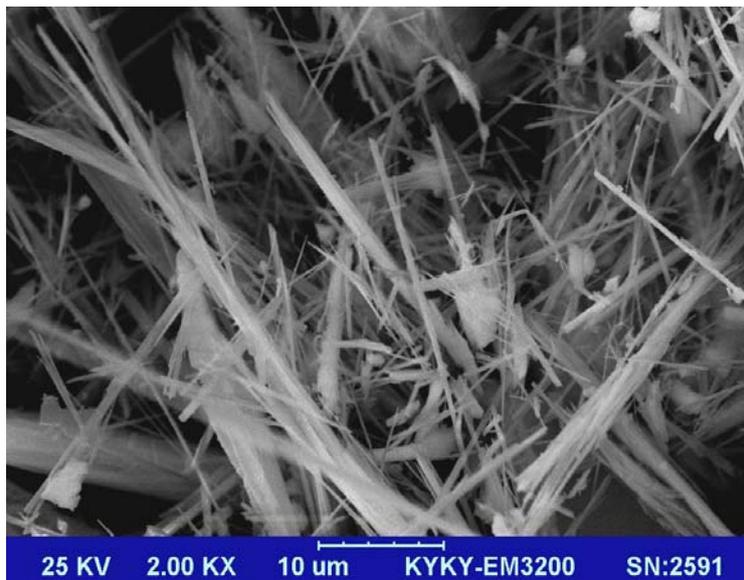


Fig.3-1 The SEM image of sepiolite

Due to the special structure, sepiolite has a large surface area, good mechanical property, thermal stability and strong absorption ability. Many holes on its surface make other metal particles distribute uniformly, so it can be used as active carrier for preparation of catalyst. But the natural sepiolite is very weak acidity in its surface, actually surface area is lower than its theoretical surface area value, thus it requires modification to improve the surface characteristics and activity. It is usually used as the carrier of catalyst to load the

active component of Zn, Cu, Mo, W, Fe, Ca and Ni in petrochemical industry [2] for reduction of heavy metal, de-asphalt, hydro-desulfurization and hydrocracking processes. Due to its physical and chemical properties, it was also directly used as the carrier of catalyst for some reactions, such as hydrotreating, hydrocracking, skeletal isomerization of cyclohexene and the ethanol dehydration reaction. In a word, it has enormous applications.

Sepiolite used as the carrier of catalysts

The catalyst uses sepiolite as carrier commonly. The active point is some metals and their oxides, such as Ni, Fe, Zn, Cu and other transition metals and Pd, Pt, Ag and other precious metals and rare earth metal. The catalytic efficiency and the selectivity depends on the types of metals and their oxides, catalyst preparation, catalytic reaction conditions, in which the relationship between preparation and performance is can be controlled and important.

Many researchers have made the pioneering work in the field, the current view from the received information, the study of sepiolite microstructure has been in-depth, either the transformation of the fiber structure or using a variety of means to modify the sepiolite and characterization of physicochemical properties have made great achievements, and the catalyst in some specific studies have demonstrated the superiority of sepiolite as a catalyst. The sepiolite is made up of two layers of silicate- oxide - tetrahedron and magnesium - oxide - octahedral interactive composition. It has a layered and chain transitional structures characteristics. Its chemical structure and crystal structures were shown in Figure 3-2 [3] and Figure 3-3 [4].

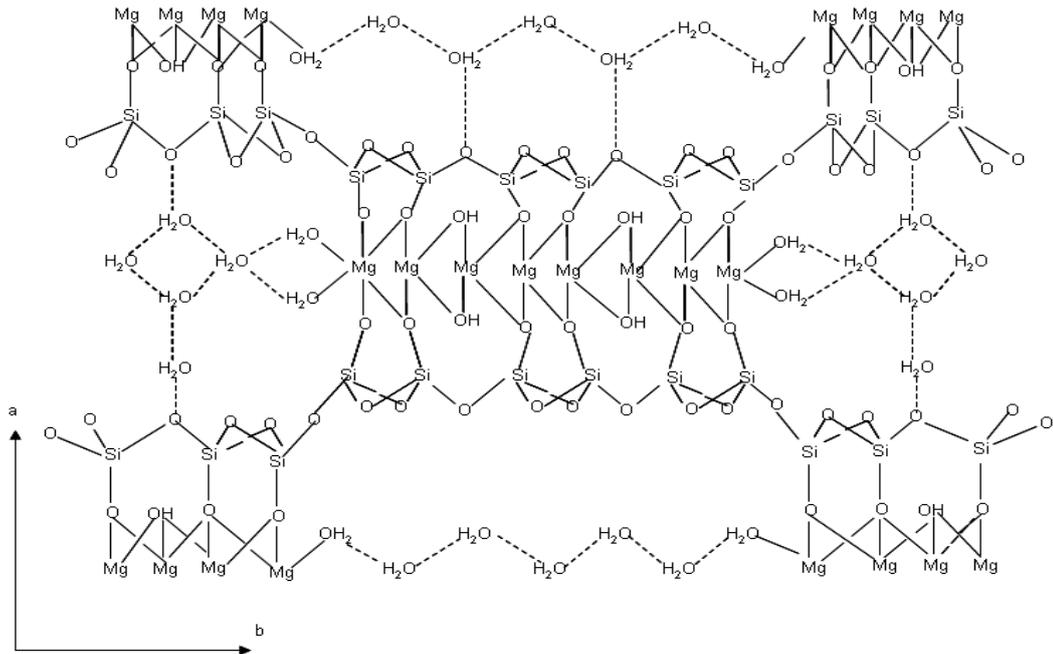


Fig. 3-2 Chemical structure of sepiolite

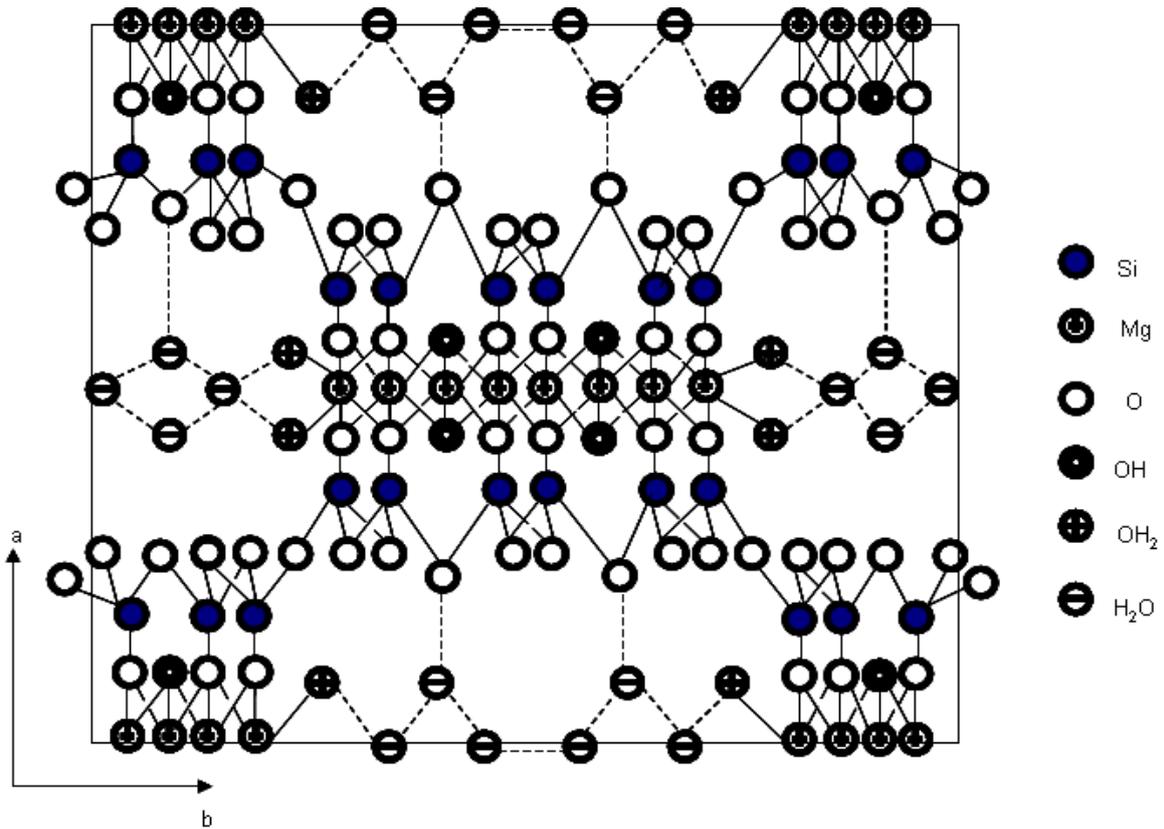


Fig. 3-3 Crystal structure of sepiolite

Along the fiber direction (c axis), there are two layers of silicon chain, and they are connected by the MgO₆ octahedral in the up and down side in each layer of silicon chain.

The two layers are connected by the oxygen atoms in the edge of MgO_6 octahedral. The top of every silicate - oxide - tetrahedron is also connected, so the form of unit is a layered structure. The parallel channel is formed between two layers with the same arrangement. The water molecules and the exchangeable cations are located in the channel. Along the channel direction, the two water molecules occupy the Octahedral Ligand of the Mg^{2+} . At about 513K, the half of water will be lost, thus a twisted structure containing $2H_2O$ is formed [5]. The process of the structure changing is shown in Figure 3- 4 [6].

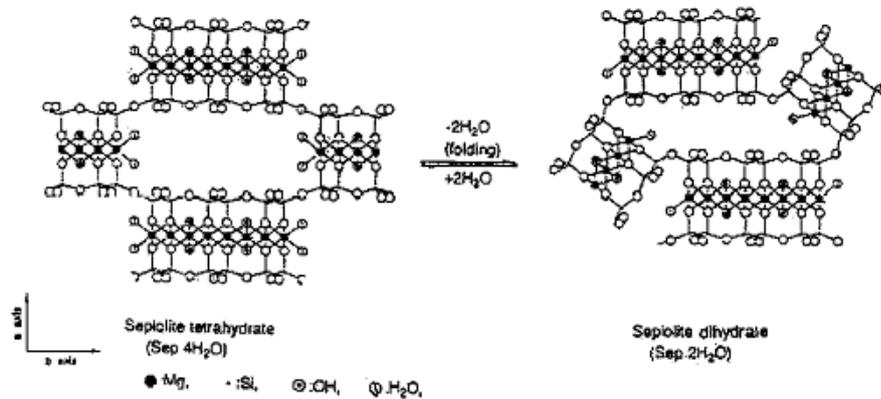


Fig.3-4 The change process of the sepiolite structure

Compared with conditional catalyst material, the sepiolite has not only high surface area but also a special structure of similar to the molecular sieve. The special structure of the sepiolite determines that it owns the connected channel which section area is $0.36m \times 1.06 nm$ and surface area of $900m^2 / g$ in the theory [7- 8]. Meanwhile, the bond of Si - O - Si connects to form the special three-dimensional structure, along a direction to extend, so its shape is of a rod. There are a lot of micro-slots and micro-channels in the rod, so the sepiolite has a good ability of adsorption. This is the reason why the sepiolite has been used extensively in the group of minerals.

There are three kinds of adsorption centers in the internal and external surface of sepiolite. One is the bound water molecule with the magnesium ions on the edge of

structure, as the bound water is easy to be adsorbed and forms the hydrogen bond; the second is the group of Si-OH, as it can be formed a covalent bond with the absorbed substance; the third is the oxygen atoms in the group of silicon-oxygen tetrahedron [9].

The characteristics of sepiolite are [10]: (1) It has a good thermal stability. When the temperature is below 400 °C, its structure is stability. At 400 - 800 °C it will be dehydrated and changed to the anhydrous sepiolite. Only when the temperature is over 800 °C, part of sepiolite will transform into α - cristobalite. (2) It has a good exchange with cation. (3) It has a good adsorption. As the sepiolite has a large surface area and micro-pores, it can absorb a large amount of water and polar substances. (4) It has a good catalytic performance. Due to that a lot of groups of Si-O is located outside of sepiolite, the groups of Si-O has a good adsorption to organic substance and play the role of catalyst. (5) It has a good rheology.

The special structure of the sepiolite determined it has good physical and chemical properties, and thus it is widely used as raw material in the field of chemical catalysis, treatment of waste water and waste gas, so on. However, because the surface area of the natural sepiolite is not large and size of its pore is not uniform, and the ratio of Si /Al is smaller than the zeolite, some practical applications are limited. Therefore, before putting it into practice in this study, the natural sepiolite should be modified by a chemical reaction and make it suitable as catalyst carriers.

It has been reported in Japan the sepiolite was used as carrier to support Pt to prepare catalyst, and the performance of removal of NO_x had been compared with traditional catalyst of γ - Al₂O₃. A. Santos and et al. [11] had used the element of V and W deposited on the sepiolite to prepare out the catalyst for the removal of NO and confirmed its

structure remained stable when the temperature was above 600 °C. Jin-Jun Liu [12] considered that the emphasis point of the research in the future should be focus on to compare the traditional catalyst with the sepiolite catalyst, and develop a new kind and high efficiency catalyst.

Sepiolite Ore has a large of surface area and good adsorption capability and catalytic [13-15]. The Modified Sepiolite taking γ -Al₂O₃ as catalyst has some advantages: not only has the character of the high specific surface area and excellent adsorption performances, some molecular sieve characteristics, a good catalytic performances when other active metal oxide introduced; but also low price, good thermal stability, and non-toxic, no pollution, oil resistance, alkali resistance, corrosion resistance, strong adhesion, not easy to crack, and so on [16 - 18].

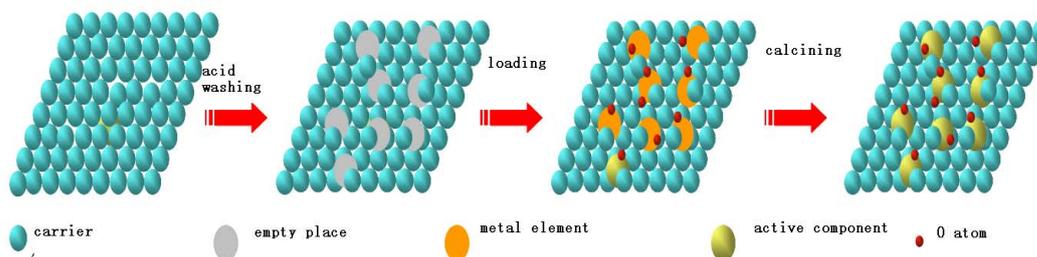


Fig.3-5 The principle of modified sepiolite

In this chapter, the Sepiolite Ore has been modified by acid washing to purify, copper nitrate soaking, drying and calcination. The Modified Sepiolite Catalyst (MSC) has been analyzed by XRD and SEM. The performance of MSC with NTP to remove NO has been evaluated in the rod-cylinder DBD reactor, which is a simple and convenient reactor [19].

3.2 Catalyst preparation

3.2.1 Experimental principle

Experimental technique route is shown in Figure 3-6.

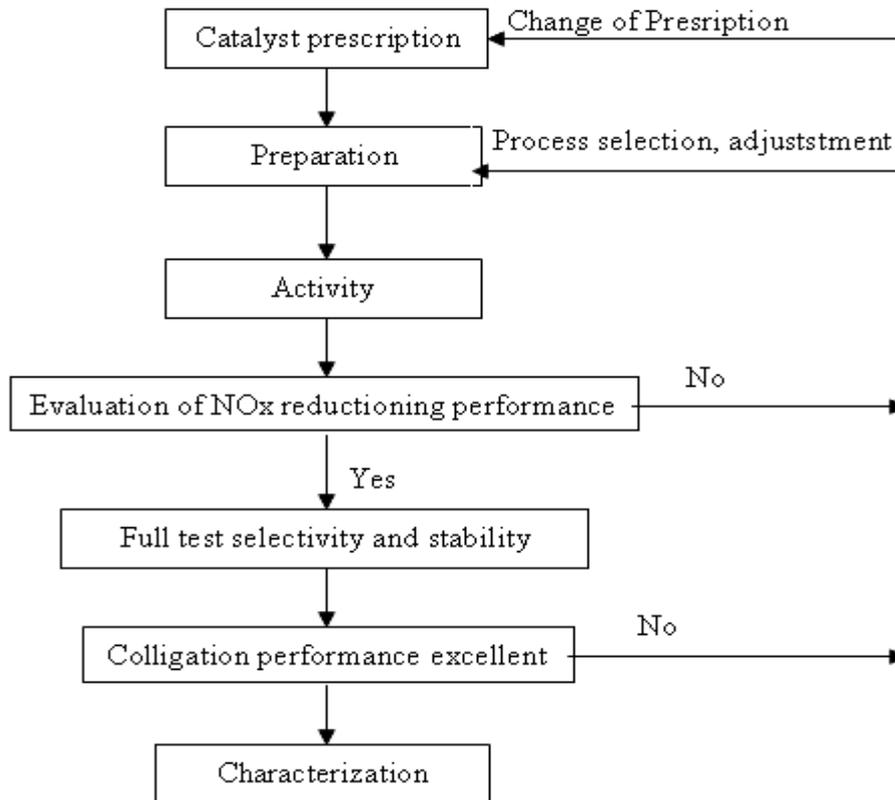


Fig.3-6 Experimental Technique Route

The character of natural Sepiolite Ore is weak acid and its narrow internal channel, so it must be modified to satisfy the need of catalyst preparation. At present, the modification usually uses the method of acid washing, as the ion of Mg^{2+} has a character of weakly alkali and easy to be removed from the Sepiolite frame by the strong acids, such as HCl or HNO_3 . If the weakly acid is used to wash the Sepiolite, some by-products will deposit and stop up in the micro channels and porous, and the surface area will be decreased. So in the study we used the strong acids to treat the Sepiolite Ore. The principle of acid washing is shown in Figure 3-7.

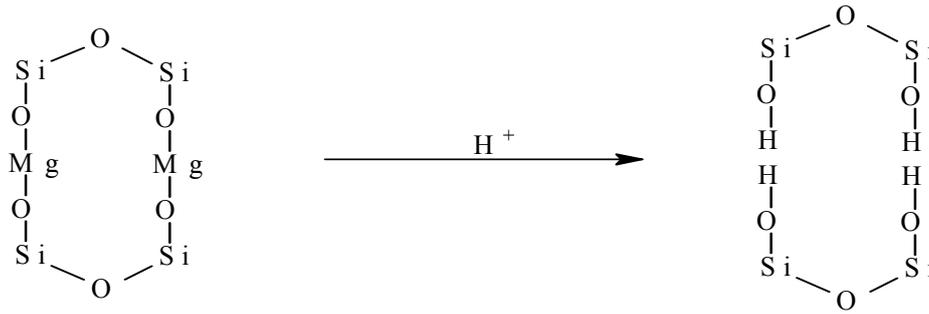


Fig.3-7 Sepiolite molecular structure variation by acid-modified

3.2.2 Experimental material

The main reagents: Sepiolite Ore Powder (SOP, no modified) (Henan Leibao Sepiolite Ore Company, 280 mesh, industrial grade); Nitric acid and Hydrochloric acid (Anhui Huainan Chemical Group, the AR), Copper Nitrate, Air Cylinder, NO/N₂ Cylinder (the content of NO 2011*10⁻⁶, the balance is N₂). The main chemicals and reagents are shown in Table 3-1.

Table 3-1 the main chemicals and reagents required for experimental

No.	Name	Specification	Manufacturer
1	Sepiolite [Si ₁₂ Mg ₈ O ₃₀ (OH)](H ₂ O) ₄ ·8H ₂ O	Crude ore	Lei Bao Sepiolite company
2	Nitric acid HNO ₃	AR	Anhui Huainan Co. Chem. Group
3	Hydrochloric acid HCl	AR	Anhui Huainan Co. Chem. Group
4	Copper nitrate Cu(NO ₃) ₂	AR	Anhui Huainan Co. Chem. Group

3.2.3 Preparation process

(1) Purification of SOP

200g SOP was mixed with 120ml distilled water and stirred for 10min. After a stillness

moment, the SOP was deposited from the suspension. The deposit was washed for four times by distilled water with the same way. The suspension was filtrated by vacuum filter, then, the filter cake was dried in the oven at 105 °C and grinded. The SOP was washed by nitric acid (concentration range from 1.0 to 2.0 mol /L). The ratio of the SOP quality to the nitric acid volume is 1:10 (g/mL). The SOP was soaked in acid solution for 24h, 48h, 72h, respectively, at the 20 °C. The acidified SOP was washed for four times with de-ionized water and filtered. The filter cake was dried in Muffle Furnace at temperature of 120 °C for 4h, and then grinded after natural cooling.

By the same way, the SOP was washed by the hydrochloric acid.

The design of acid treatment data is in Table 3-2.

Table 3-2 Acid treatment schedule

No.	Acid concentration	Solid-liquid ratio (g/ml)	Temperature (°C)	Leaching time (h)
1	1.0	1: 5	20	24
2	1.5	1: 10	20	48
3	2.0	1: 15	20	72

(2) Modification and Activation of SOP

Every sample of 50g acidic SOP (under the different washing condition) and original SOP, respectively, was immersed in $\text{Cu}(\text{NO}_3)_2$ solution for 24h at room temperature (ensured the content of CuO for 8%), then evaporated and dried at 60 °C in water bath, and grinded to about 240 mesh. The powder sample was molded by pressure in mould to make particle

sample, then, the particle was dried at the room temperature for 24h and calcined in the Muffle Furnace at 500 °C for 5h, receptively. The activated particle of MSC was smashed to appropriate particle size.

Catalyst prepared by impregnation process is shown in Figure 3-8.

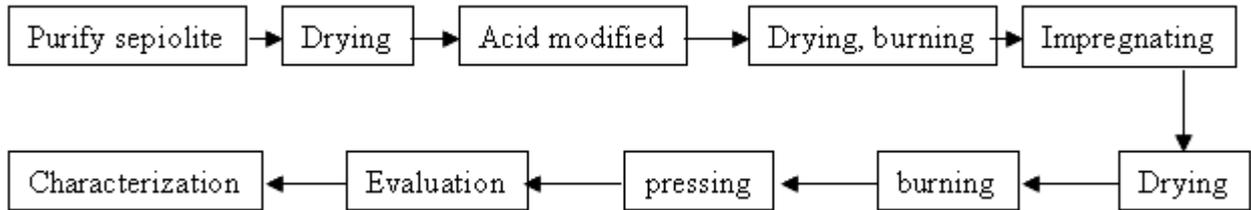


Fig.3-8 Process of catalysts prepared by impregnation

3.3 Catalyst performance

3.3.1 Detection of catalyst surface area

The measurement of the surface area of catalysts uses the method of N₂ adsorption at -196 °C, namely, two parameters of BET equation, by detecting the relationship between the relative partial pressure and the adsorptive e quality and using the formula (3-1) to calculate the slope and intercept parameters of BET equation.

$$\frac{1}{V[(P_0/P)-1]} = \frac{C-1}{V_m C} \times \frac{P}{P_0} + \frac{1}{V_m C} \quad (3-1)$$

Where: V is the volume of adsorbed gas.

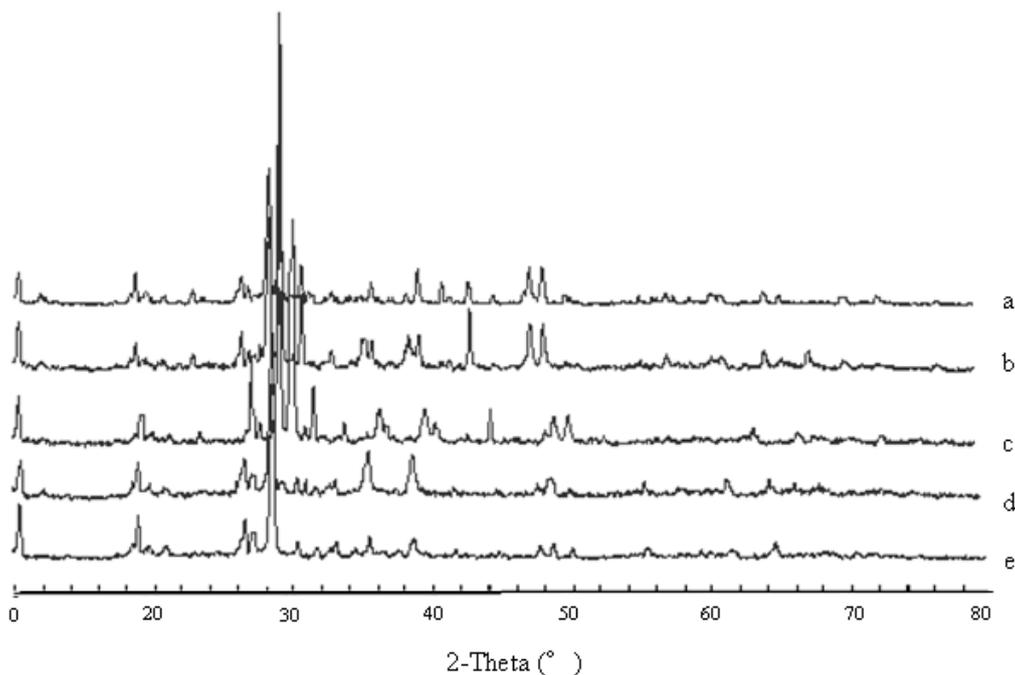
The detection result of special surface area of the Sepiolite is in Table 3-3.

Table 3-3 Data of specific surface area of the Sepiolite

Species	Surface area (m ² /g)
No Modified	36.1

3.3.2 XRD analysis

The X-ray diffraction (XRD) is the common method to analyze the crystal structure, which bases on the X-Ray Diffraction Effects of material. It can reveal the arrangement of atom and obtain a lot of useful information of internal structure of catalyst.



- a. the original Ore
- b. without acid washing, only soaking copper nitrate for 24h and calcination for 5h at 500□;
- c. with concentration of 1.0 mol/L HNO₃ washing for 2d and soaking copper nitrate for 24h, calcination for 5h at 500□;
- d. with concentration of 1.5 mol/L HNO₃ washing for 2d and soaking copper nitrate for 24h, calcination for 5h at 500□;
- e. with concentration of 3.0 mol/L HNO₃ washing for 3d and soaking copper nitrate for 24h, calcination for 5h at 500□

Fig.3-9 XRD of SOP and MSC

Instrument Type: Beijing General Analysis General Company, the XD-3 type polycrystalline X-ray powder diffraction

Diffraction Conditions: target Cu ka = 40mA, tube voltage V = 36kV, pipe flow 40mA

Testing purposes: (1) to investigate the ore and modified Sepiolite crystal structure; (2) to determine the existence phase of Cu of the active component. The results were shown in

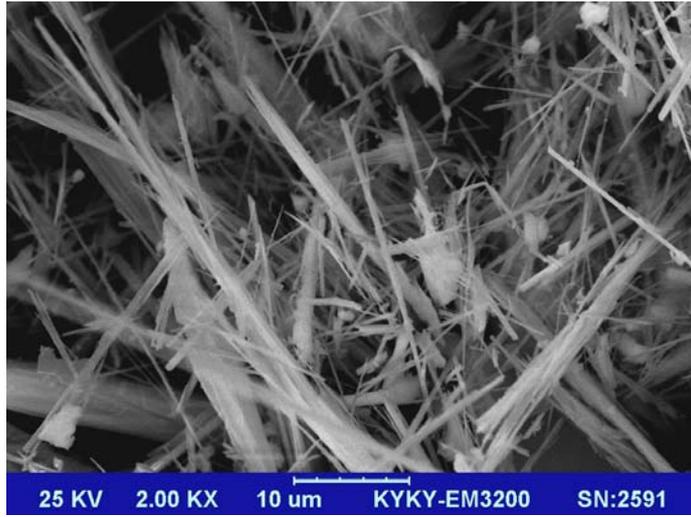
Figure 3-9.

Figure 3-9a shows that the SOP contains a large amount of the elements of Si, Mg, Al and others, which exist in the different compounds forms. The characteristic peak value of $26.7^\circ(2\theta)$ is SiO_2 , $29.5^\circ(2\theta)$ is $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$, $35.7^\circ(2\theta)$ and $39.1^\circ(2\theta)$ is CuO . Compared with a, b, c, d, e in Figure 3-9, the peak value of $29.5^\circ(2\theta)$ is greatly weakened after the acid washing. One reason is that some of Mg^{2+} ions depart from the SOP to make the increasing of SiO_2 and some of the SiO_2 changing into Si-OH group in the acidic condition, The other reason is that some of ions, such as Fe^{3+} , K^+ , Na^+ and so on is removed by the acid washing. However, the characteristic peak of SiO_2 is still high, maybe for the hydroxyl was removed from the SOP surface and broken down, or generated silicate at high temperature. The characteristic peak value of $35.7^\circ(2\theta)$ and $39.1^\circ(2\theta)$ is CuO after soaking and calcination, which show the CuO was formed in the surface of MSC.

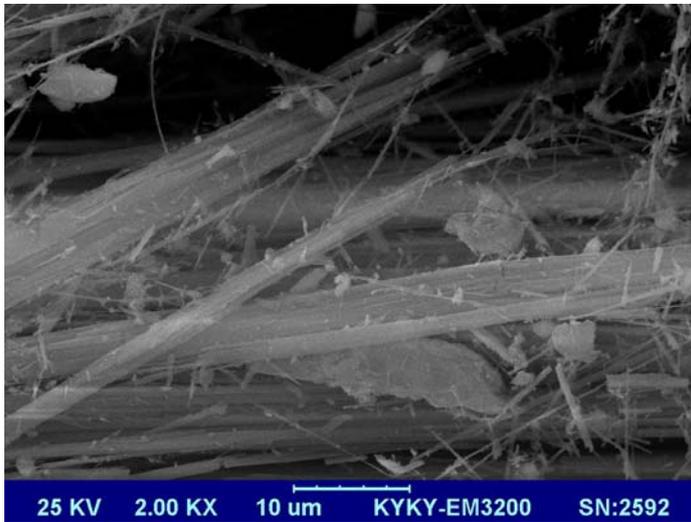
Compared with c, d, e (acid washing for 1d, 2d, 3d, respectively, then calcination) in Figure 3-9, it shows that acid washing for 2d can effectively remove a few impurities in SOP, the XRD shows washing for 2d and 3d are basically the same, so the optimization acid washing time is 2d. After a series of operation of acid washing, soaking, water-bath, drying and calcination, besides, although the new material of CuO was introduced and produced new crystal, the Sepiolite kept its basic structure. These have proved that the structure of SOP is stability.

3.3.3 SEM analysis of the catalyst

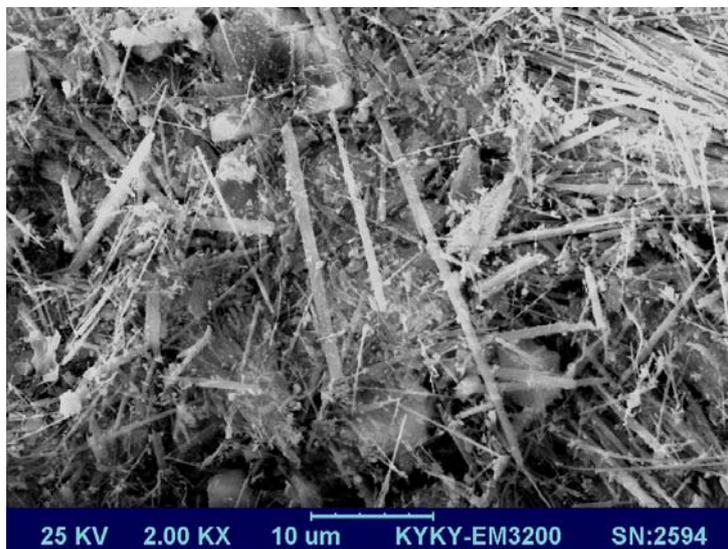
The SEMs of different preparation methods of MSC are shown in Figure 3-10.



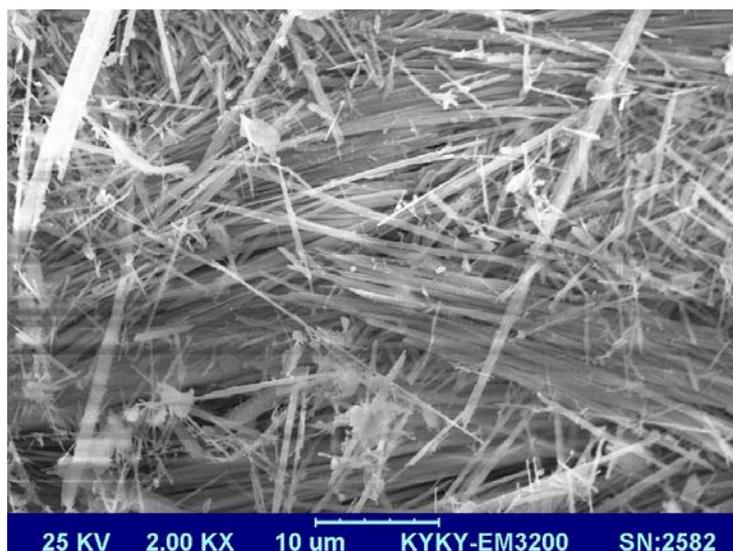
a



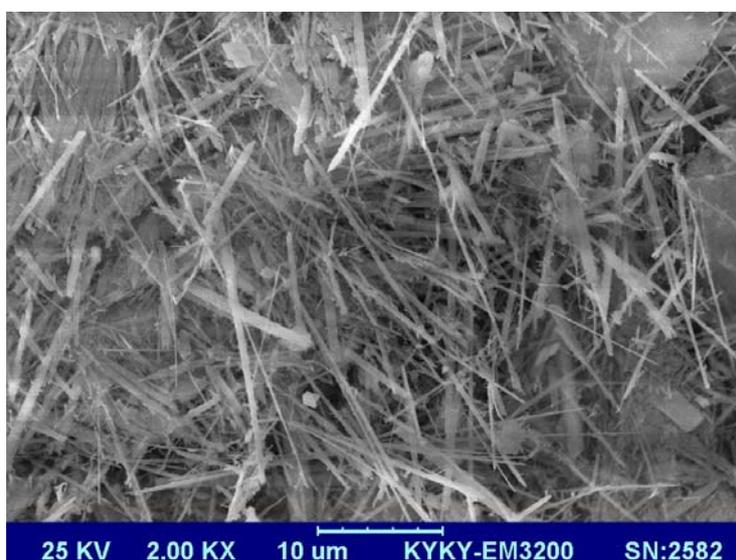
b



c



d



e

- a. the original Ore
- b. without acid washing, only soaking copper nitrate for 24h and calcination for 5h at 500℃;
- c. with concentration of 1.0 mol/L HNO₃ washing for 2d and soaking copper nitrate for 24h, calcination for 5h at 500℃;
- d. with concentration of 1.5 mol/L HNO₃ washing for 2d and soaking copper nitrate for 24h, calcination for 5h at 500℃;
- e. with concentration of 3.0 mol/L HNO₃ washing for 3d and soaking copper nitrate for 24h, calcination for 5h at 500℃

Fig.3-10 SEM photos

Compared with Figure 3-10, it is found that characteristics and appearances of MSC structure are more improved than the SOP. The section area of micro-pore in the MSC surface has been enlarged, and the number of micro-pore increases, so that the surface areas

and adsorption ability of MSC have been enhanced. Meanwhile, the treatment of acid washing is an effective method to remove impurities in the micro-pore and increase the specific surface area. The more number of micro-pore and surface are beneficial to the loading of the active component. With the electronic probe fixed in many bright points and others part in Figure 3-10 (a, b, c, d, e), the copper element has been detected by the analytical way of input determine element of Cu. The active component particle is clear appearance and even distribution.

The detective data of the Sepiolite Ore and the Modified Sepiolite are shown in Table 3-4 and Table 3-5, respectively. From Table 3-4 and Table 3-5, it can be found that the content of Mg decreases from 12.68% (Wt %) to 6.78% in the modified Sepiolite by acid washing. It is proved that surface area and diameter of micro-pore were enlarged in the Modified Sepiolite, the reason is that a large number of Mg ions were removed by the acid washing.

Table 3-4 Contents in the Surface of Sepiolite Ore

Element	Weight % (Wt %)	Volume % (At %)
O	55.90	67.98
Mg	12.68	10.15
Al	3.98	2.87
Si	27.44	19.01

Table 3-5 Contents in the Surface of Modified Sepiolite

Element	Weight %	Volume %
O	47.92	58.44
Mg	6.78	6.11
Al	3.28	2.67
Si	42.01	32.42

3.4 Evaluation of catalytic activity

Main equipments: Automobile exhaust gas analyzer(Guangdong Fushan analysis instrument factory, FGA-4100; NO measurement range:0~4000*10⁻⁶); Constant Temperature Oven (Model DHG-9240); Scanning Electron Microscope(SEM, SHIMADZU, KYKY-EM3200), X-ray Diffraction(XRD, XD-3 type crystal X-ray powder diffraction was produced by Beijing General Company); Muffle Furnace, Gas Mass Flow-meter; Transformer; Power Meter; High Voltage Power Supply JNB-208B; High-voltage Probe; Digital Oscilloscope. DBD catalytic reactor (made by self):

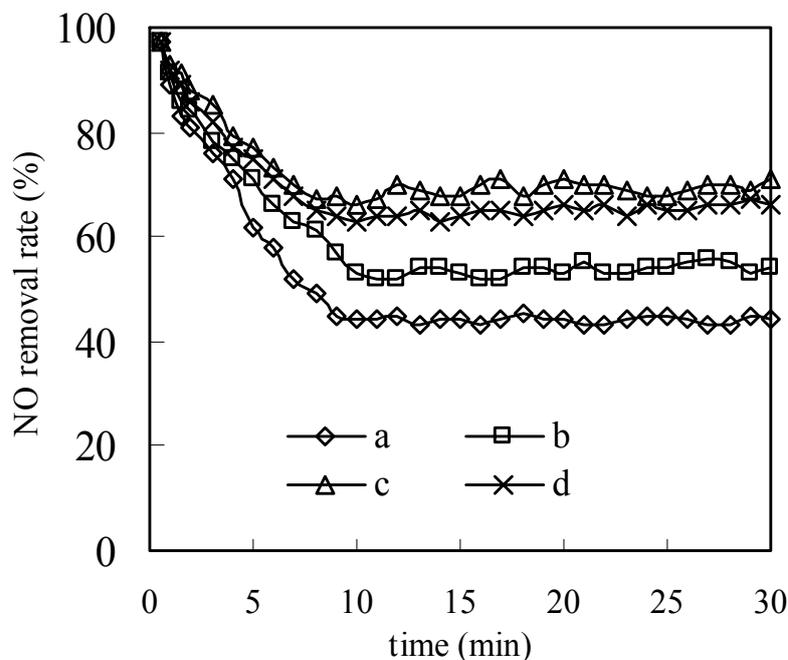
The reactor is made of Borosilicate Pyrex Glass Tube of inner diameter 27mm, wall thickness of 2mm, length of 120mm, the outer tube was covered with an aluminum film with a length of 60mm and a thickness of 0.6mm, aluminum rod with an outer diameter of 8 mm was placed at in the center of the tube as anode; the MSC was loaded in the tube between the aluminum rod and aluminum film, both end of the reactor was sealed by silicone rubber plug [20]

The 30g MSC prepared under different conditions was loaded into the same fixed bed reactor with NTP. The reactor was installed in a thermo-tank at the 180°C. The simulation

gas with the NO concentration of 297×10^{-6} (297ppm) went into the reactor from the bottom side. The gas flow was kept at 7.0 L/min. The voltage (V_{p-p} peak-peak) and frequency of power were 35kV and 50Hz, respectively. The outlet concentration of NO was detected by the FGA-4100 automobile exhaust online detection instrument. The NO removal rate calculated and expressed the activity of MSC. The NO removal rate = $100 \times (\text{inlet NO concentration} - \text{outlet NO concentration}) / \text{inlet NO concentration}$. The test process is showed in Figure 2-1.

3.4.1 Influence of nitric acid concentration on NO removal rate

The SOP was soaked in the nitric acid solution with a concentration of 1.0, 1.5, 2.0 mol/L for 2d, respectively. The weight ratio of acid to SOP was 1:10. The way making MSC is described in the Section 3-2. The relationship between nitric acid concentration and NO removal rate is shown in Figure 3-11.



- a: plasma+ SOP without acid washing, only soaking $\text{Cu}(\text{NO}_3)_2$ for 24h and calcination for 5h at 500°C ;
- b: plasma+ SOP with concentration of 1.0 mol/L HNO_3 washing for 2d and soaking $\text{Cu}(\text{NO}_3)_2$ for 24h and calcination;
- c: plasma+ SOP with concentration of 1.5 mol/L HNO_3 washing for 2d and soaking $\text{Cu}(\text{NO}_3)_2$ for 24h and calcination;
- d: plasma+ SOP with concentration of 2.0 mol/L HNO_3 washing for 2d and soaking $\text{Cu}(\text{NO}_3)_2$ for 24h and calcination

Fig. 3-11 the relationship between HNO₃ concentration and NO removal rate

Figure 3-11 shows that the concentration of HNO₃ has a significant effect on NO removal rate under the same conditions. When the HNO₃ concentration is 1.5mol/L or so, the NO removal rate gets to the maximum value stably. So there is an optimum acid concentration. The removal rate is lower when the SOP without acid washing, only soaking and calcination in the experiment.

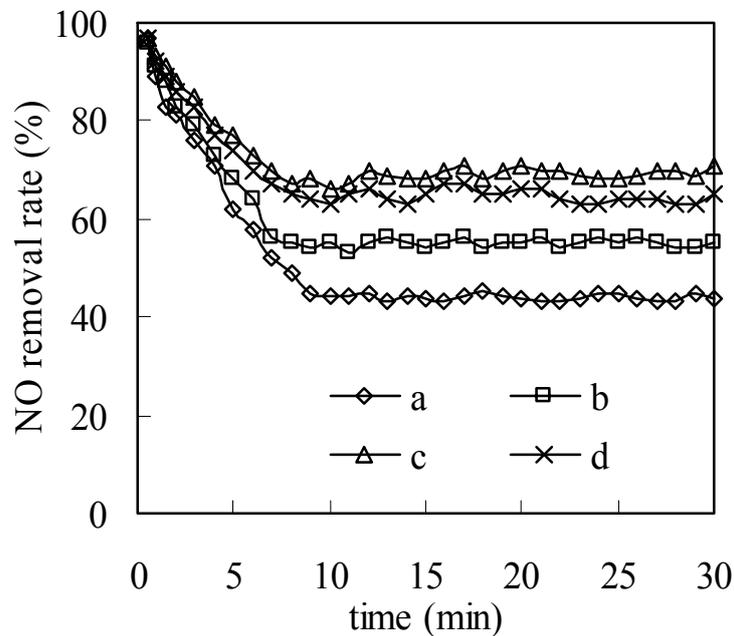
On the SOP natural surface, there are a developed micro-pores (<1.5nm) and medium-pores (1.5-5.0 nm), the big pores come from the gap of many micro-fiber groups and stack knot and cross. In the SOP of acid washing, the ion of Mg²⁺ was replaced by the ion of H⁺. When the HNO₃ concentration is smaller than the optimum value, part of magnesium ions is dissociated and removed from the SOP, and many micro-pores are reproduced and connected each other to form the pore-net structure. With the new micro-pore developing sufficiently, some micro-pores become medium-pores. With increasing the acid concentration, the surface area of SOP increases, it is beneficial to improve the capability of adsorption and the activity of MSC. When the HNO₃ concentration is bigger than the optimum value, the most of micro pores and medium pores have been developed and become the big-pore with a diameter of above 10 nm. So the surface area of the MSC and the NO removal rate decrease.

3.4.2 Influence of washing time on the NO removal rate

The SOP was washed by the nitric acid solution with a concentration of 1.5mol/L for 1d, 2d, 3d, respectively. The weight ratio of acid to SOP was 1:10. The way making MSC is in section A. The relationship between the acid washing time and NO removal rate is shown

in Figure 3-12.

It is known that the acid washing time of SOP also has a certain effect on NO removal rate, as shown in Figure 3-12. The NO removal rate is the lowest when the SOP without acid washing. The NO removal rate is the highest when the MSC was washed by acid for 2d. It is a fast chemical reaction of the SOP washed by acid [21]. The magnesium ions are dissolved easily and the new micro-pore and mesh structure form in surface of SOP. With the washing time prolonged, the ion of H^+ has diffused to the deep channels and its concentration decreases gradually, and the magnesium also decreases gradually. Due to the effect of diffusing resistance, it's very difficult for the magnesium in the deep channels to remove. If the washing time is too long, the dissolved impurities may be adsorbed on the surface of SOP again. So there is an optimum washing time.

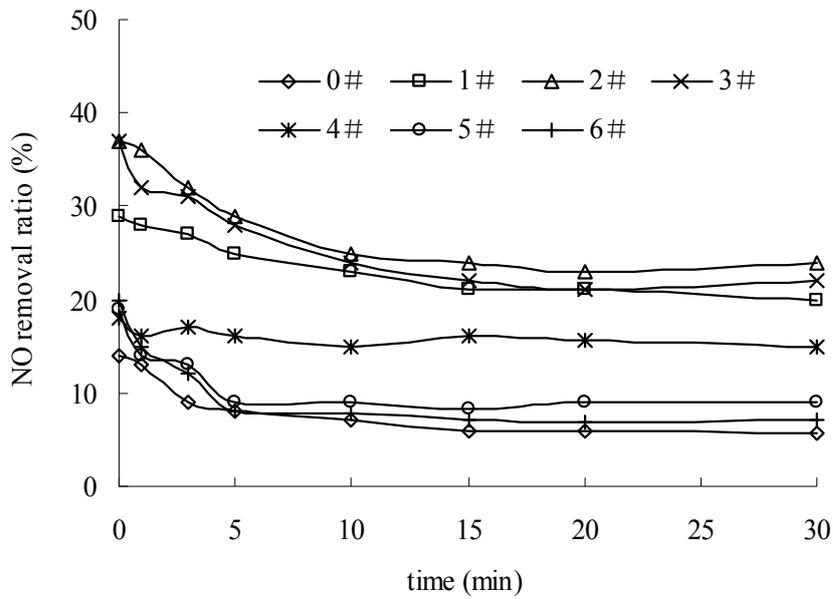


- a: plasma+ SOP without acid washing, only soaking $Cu(NO_3)_2$ for 24h and calcination for 5h at $500^\circ C$;
- b: plasma+ SOP with concentration of 1.5 mol/L HNO_3 washing for 1d and soaking $Cu(NO_3)_2$ for 24h and calcination;
- c: plasma+ SOP with concentration of 1.5 mol/L HNO_3 washing for 2d and soaking $Cu(NO_3)_2$ for 24h and calcination
- d: plasma+ SOP with concentration of 1.5 mol/L HNO_3 washing for 3d and soaking $Cu(NO_3)_2$ for 24h and calcination

Fig.3-12 the relationship between the wishing time and NO removal rate

3.4.3 Effect of HCl and HNO₃ on the catalytic activity

The relationship between the catalyst prepared with the different concentrations of HCl and HNO₃, and the NO removal rate is shown in Figure 3-13.



0 # No acid washing;

1 # 1.0mol / L HNO₃ washing; 2 # 1.5mol / L HNO₃ washing; 3 # 2.0mol / L HNO₃ washing;

4 # 1.0mol / L HCl washing; 5 # 1.5mol / L HCl washing; 6 # 2.0mol / L HNO₃ HCl washing .

Fig.3-13 NO concentration with reaction time of the different modified Sepiolite catalyst

3.4.4 Effect of the Copper quality on the catalytic activity

This preparation of the catalysts is that the Sepiolite of acid washing was immersed into the solution of the copper salt used as the carrier to support the active component for the CuO_x.

The percent of Cu component in the content is 1%, 3%, 5%, 8%, 10%, respectively. The relationship between reaction time and the NO removal rate in different catalyst which includes different qualities of Cu is shown in Figure 3-14.

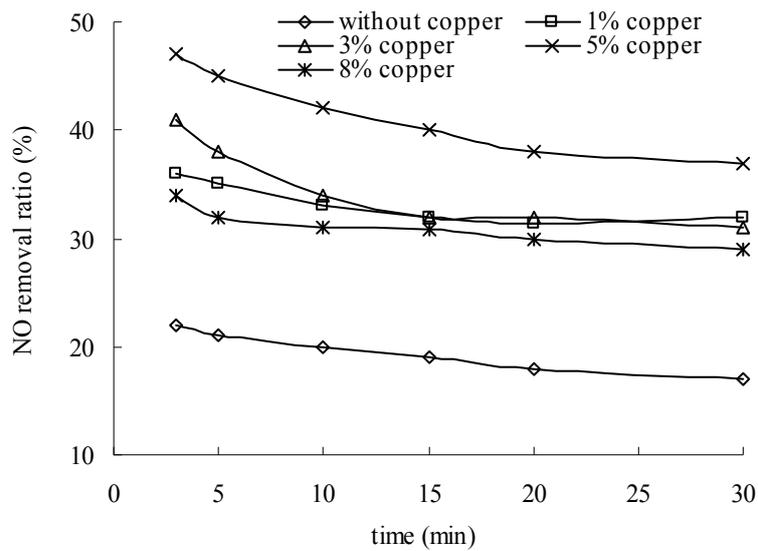


Fig.3-14 Effect of composition of Cu over Cu/Sep on catalytic activity

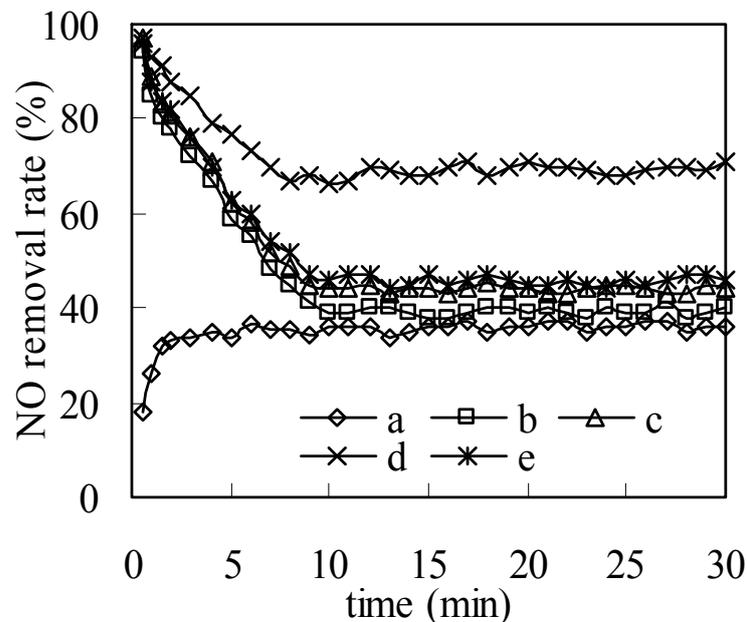
It can be seen the effect of Cu content in the Cu / Sepiolite catalyst on the catalytic activity from Figure 3-14. When the Cu content was 1%, the maximum value of NO removal rate was only 23 %. When the Cu content reached 5 %, the maximum value of NO removal rate was 47 %. If the Cu content increases right along then the NO removal rate would decrease. So the optimal value of the content of Cu component is about 5 %.

When the content of Cu is less than 5 %, the active points of CuO_x do not reach its maximum value in the surface of catalyst, so with increasing the content of Cu the catalytic activity and NO removal rate increase. When the content of Cu is more than 5%, with increasing the content of Cu the Cu will cover on the Cu surface before deposited on the carrier. Many layers of Cu will aggregate and the micro- pore or micro channel will be blocked, so that the surface area and activity and the adsorption of the catalyst will decrease with the concentration of Copper salt solution increasing.

3.4.5 Compare to catalyst activity at different conditions

The experimental conditions are: input voltage of 35kV, NO initial concentration

297×10^{-6} , inlet gas volume flow 7L/min (the space-velocity $10.2s^{-1}$). The relationships between NO removal rate and reaction time have been measured in different stuff conditions, such as: (a) only plasma, without any stuff, (b) plasma combined with SOP, (c) plasma combined with MSC of without acid washing, only soaking $Cu(NO_3)_2$ for 24h and calcination for 5h at $500^\circ C$, (d) plasma with MSC of washing by HNO_3 of concentration 1.5 mol/L for 1d and soaking $Cu(NO_3)_2$ for 24h and calcination, (e) without plasma, only MSC washed by HNO_3 of concentration 1.5 mol/L for 1d and soaking $Cu(NO_3)_2$ for 24h and calcination. The experiment results are shown in Figure 3-15.



- a: only plasma, without any stuff
- b: plasma+ packed SOP;
- c: plasma+ MSC without acid washing, only soaking $Cu(NO_3)_2$ for 24h and calcination for 5h at $500^\circ C$;
- d: plasma+ MSC of washed by concentration of 1.5 mol/L HNO_3 for 1d and soaking $Cu(NO_3)_2$ for 24h and calcination for 5h at $500^\circ C$;
- e: MSC of washed by concentration of 1.5 mol/L HNO_3 for 1d and soaking $Cu(NO_3)_2$ for 24h and calcination for 5h at $500^\circ C$

Fig.3-15 The relationship between NO removal rate and time in different stuff conditions

The Figure 3-15 shows: (1) Either loading SOP or MSC, NO removal rate is higher at the beginning and then reduces gradually with time until being stabilized after 10 minutes. The reason is that the SOP and MSC have a good capability of adsorption and storage, when

the adsorption reaches its balance, the NO removal rate gets stable. (2) After 15 minutes, when the chemical reaction is stabilized, the order of NO removal rate is: (d) > (e) > (c) > (b) > (a). The experiment results show that the NTP combined with MSC (washing by HNO₃ of concentration 1.5 mol/L for 24h and soaking Cu(NO₃)₂ for 24h and calcination for 5h at 500 °C) can improve NO removal rate. The maximum value of NO removal rate is about 71% in this experiment. (3) In the condition of only NTP, without the SOP or MSC, NO removal rate is the lowest. The results told us that NTP with the MSC was an effective way to remove NO. The MSC in the reactor not only has the function of catalyst, adsorbent and storage, but also plays a role of the dielectric barrier.

3.5 Results and Discussion

By using the XRD analyzer, it is found that the ion of Mg²⁺ and other impurities have been effectively removed from the SOP by nitric acid washing. During the process of acid washing, soaking the copper nitrate solution, drying, calcination and activation, the new CuO phase has been formed stably on the surface of SOP, while the SOP has kept its basic structure. It is proved that the SOP has a good stable structure and suits for the precursor of catalyst.

With the SEM detecting, it is shown that the number of the micro-pore and its cross-section area on the surface of the MSC have increased effectively by the acid washing, besides, the active component of CuO has been distributed in the MSC surface and pores uniformly. The SEM measurement showed that the active component Cu can more evenly spread on the catalyst surface and pores, the quantity of load suits, and no large particles achieve a certain degree of dispersion together.

In the sepiolite ore, which contains many of Si, Mg, Al and other elements in different compounds appears. The Cu element on the surface area of the sepiolite forms different kinds of Cu phase in catalyst, in addition to CuO specie, there are a few of Cu₂O and Cu species.

After acid modified treatment, the surface area of Sepiolite is more than 100 m²/g, This is larger than the untreated Sepiolite surface area of 36.1 m²/g, which indicates acid indeed improves the surface area of Sepiolite.

The results have proved the acid concentration, acid washing time and the input voltage of NTP can affect NO removal rate effectively. With increasing the acid washing time and acid concentration, the activity of the MSC increases firstly and then decreases, so there exists an optimum value of NO removal rate. The NO removal rate increases with increasing the input voltage. At the beginning, the reaction rate is high and then gradually decreases with time. After about 15 minutes, the reaction rate trends to be stabilized. The result indicates that the MSC has a good adsorption and storage capability for NO. According to the stabilized value of NO removal rate, it is indicated the order is: (plasma with MSC of washed by concentration of 1.5 mol/L HNO₃ for 24h and soaking Cu(NO₃)₂ for 24h and calcination for 5h at 500 °C) > (MSC of washed by concentration of 1.5 mol/L HNO₃ for 1d and soaking Cu(NO₃)₂ for 24h and calcination for 5h at 500 °C) > (plasma with MSC without acid washing, only soaking Cu(NO₃)₂ for 24h and calcination for 5h at 500 °C) > (plasma with SOP) > (only plasma, without any stuff). In this experiment when the input voltage was 35kV, the MSC has been made of SOP by 1.5mol/L concentration nitric acid wishing for 24h, soaking 8% CuO and calcination at 500 °C for 5h, the maximum value of NO removal rate reached 71 %. The investigation has proved the MSC prepared

from the SOP combined with the NTP is one of effectively ways to remove NO.

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4. Modified Attapulgite Clay Catalyst Preparation and Performances Evaluation

4.1 Introduction

One of most effective methods to remove NO_x from diesel exhaust gas is by the NTP combined with the catalyst [1-3]. If the combined catalyst can adsorb and store the byproduct (NO₂), the efficiency of the oxidation reaction should increase due to the dynamics of chemical reaction speed up. If the catalyst can significantly adsorb and store NO_x to improve the NO_x removal rate, the reactor can change small and the electric energy decrease.

Attapulgite Clay (APC) also called as Palygorskite, is a chain-layer configuration of magnesium-aluminum silicate clay mineral. Its molecular formula is [Mg₅ Si₈ O₂₀ (OH)₂ (OH₂)₄ · 4H₂O]. Microstructure of Attapulgite Clay with bound water has special fibrous-liked crystals. Due to numerous micro-pores, the surface area is large, usually in the range of (125 - 210) m² / g [4]. Therefore, the Attapulgite Clay has a good performance of adsorption and NO_x storage capacity, and can carry and support other metal elements, such as rare earth or copper so on and bound on its surface. In this experiment, the rare earth of Ce was added up to Attapulgite Clay to prepare the Modified Attapulgite Clay Catalyst (MACC) by calcination. In the process of calcination, some of the molecule water which binds with the APC is lost, the activity and selectivity of MACC can be improved to satisfy the removal NO reaction. In this chapter, a Modified Attapulgite Clay (MAC) was used as carrier of catalyst.

Dielectric Barrier Discharge (DBD) is an effective way to generate Non-Thermal Plasma (NTP) [5-6]. In this experiment, the pellet of the MACC was packed into the DBD reactor to remove the NO_x , the synergetic effect of NTP and MACC on NO_x removal rate was investigated [7-12].

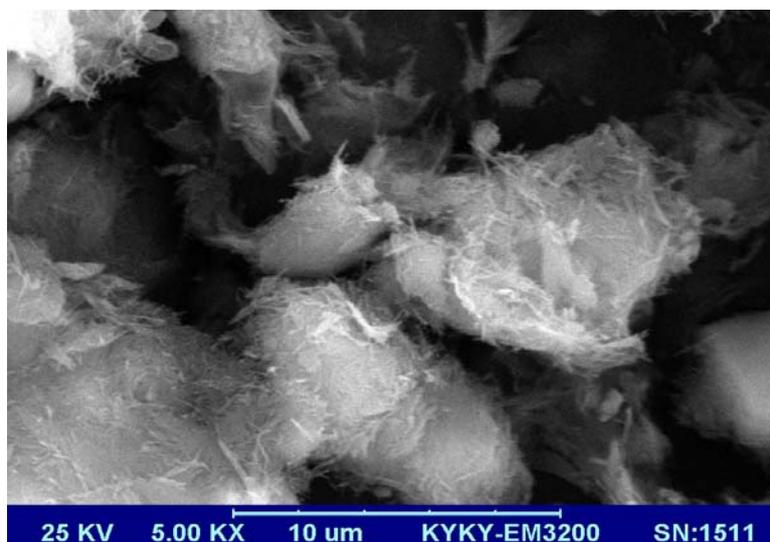
4.2 Catalyst preparation

The APC powder (300 mesh, industrial grade, Anhui Mingguang Xiqi Mine Company, China,) was dried at 105°C for 24h. 50g of the resulting powder was dissolved in 100ml de-ionized water inside a beaker bathed at 80°C and continuously homogenized. 50ml of $\text{Ce}(\text{NO}_3)_3$ (Analytical grade) solution, concentration $0.2\text{mol}\cdot\text{L}^{-1}$, and aqueous ammonia, concentration $0.2\text{mol}\cdot\text{L}^{-1}$, were simultaneously fed into the APC solution. The mixture was stirred for 1 hour with ultrasonic waves. The pH value maintained in the range of 6~7 [13]. The solution was placed for 24h to completely deposit and aging. To separate the solid and obtain the filter cake, the filter cake was washed with de-ionized water four times until the pH value of filtrate was 7.

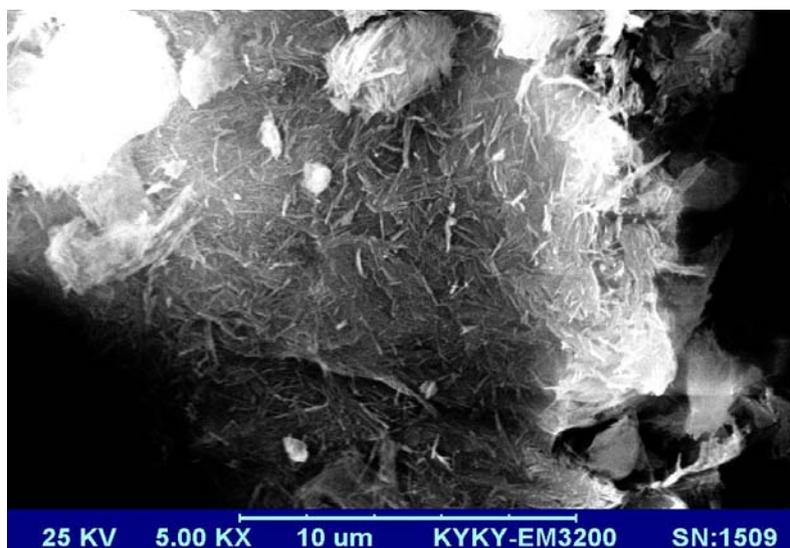
Subsequently, the filter cake was dried and crushed down, passed through a 300 mesh sieve and blended with adhesives. Pellets were molded at ambient temperature and heated at 200°C for 24h to shape. Calcination was performed in a Muffle Furnace (TOH-SHOKUNIN 0-1300 $^\circ\text{C}$) for 3 hours in order to activate the pellet. Six kinds of the pellet samples were calcined at different temperatures of 300, 400, 500, 600, 700, and 800 $^\circ\text{C}$, respectively.

4.3 Catalyst characterization by SEM

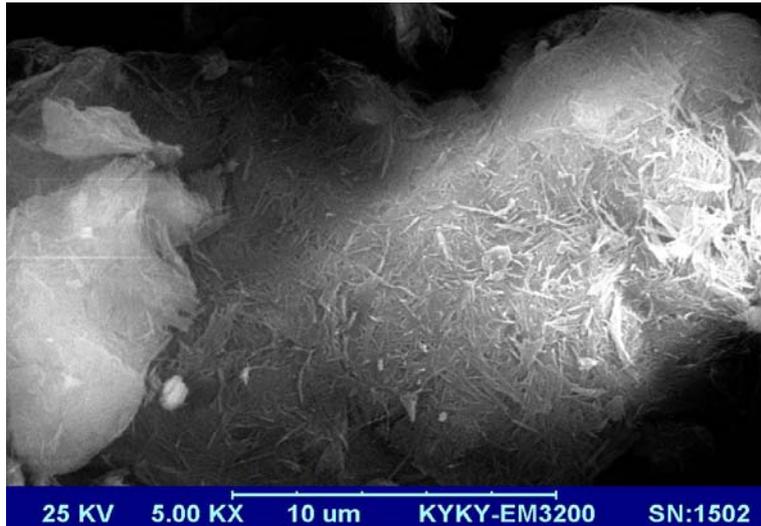
Figure 4-1 shows the micro-structure of MACC at different calcination temperatures. The microstructure of catalyst was analyzed by SEM (KYKY-EM3200).



(a) at ambient temperature



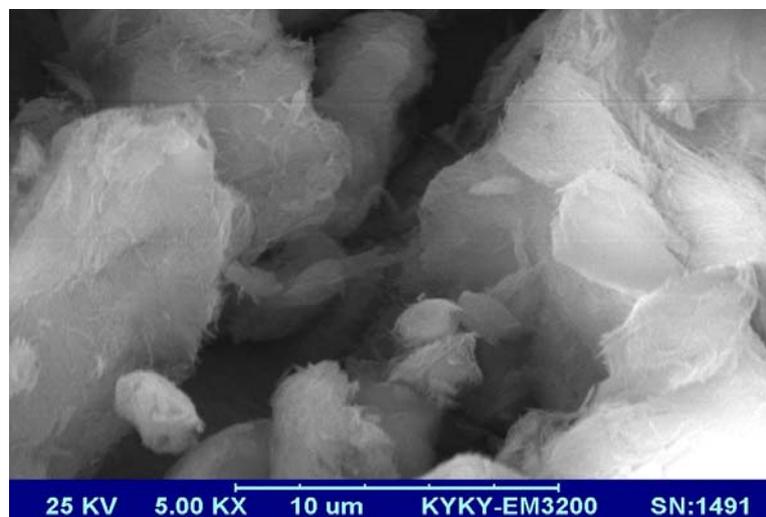
(b) 200°C



(c) 400°C



(d) 600°C



(e) 800°C

Fig.4-1 SEM picture of MACC structure at various of calcination temperatures

Usually, there are three kinds of adsorption centers on the APC surface, the one kind is the oxygen atom in the edge of silicon-oxygen tetrahedron in the APC structure, the other kind is the H₂O molecule on the APC crystal edge and the third kind is the ion cluster of Si-OH. And then, there are a great number of defects located on the APC surface to give a high surface area.

From the Figure 4-1, it can obtain the optimum temperature range for calcination is from 400 °C to 600 °C. In the range of optional temperature, the appearance of the MACC is presented a cluster of fine needle-like lines or a single of line which its diameter is about 25 nm and the length 1 μm or so, such as the Figure 4-1c and 4-1d. During the calcination, some water connecting with the APC lost and some empty places left. This would result in increasing the defect density on the APC surface and enlarging the adsorption performance.

When the temperature of calcination is over 600 °C, the number of micro-pore in the structure will decrease, the micro-pore will be sintered or melted, such as in the Figure 4-1e, it will result in decreasing the surface area and adsorption performance. When the condition is under the ambient temperature, the micro-structure of MAC does not any change, so the surface area has not to improve well, such as the Figure 4-1a. While at 200 °C the bound-water in the micro-structures is still keep up not to produce the defect or empty position effectively, such as the Figure 4-1b, so the temperature of 200 is lower, it is not enough to improve the adsorption performance of the APC.

4.4 Evaluation of the catalyst activity

4.4.1 Experimental Method

The rod -to- tube type of DBD reactor which was made of Pyrex tube (24mm inner diameter, 2mm wall thickness and 120mm length) packed with the catalyst of MACC. An aluminum foil (0.6 mm thickness and 50 mm length) was wrapped on the outside surface of the tube and was used as a ground electrode. A centered stainless steel rod (9 mm outside diameter) was used as a high voltage electrode. 25 g of the MACC catalyst pellets (average diameter 3 mm) was packed in the annular empty area between the two electrodes. The ends of the reactor were tucked with silicon rubber. The DBD reactor structure is shown in Figure 2-2.

The experimental setup is presented in Figure 2-1. The input power to the H.V. transformer was adjusted by a Variable Auto-Transformer (Type V-130-5, Volt-Slider. 61-18138. input 100V, output 0-130V, Max 5A, 0.5kVA, 50/60Hz) connected to an AC power source (100V, 60Hz). The input power was measured by a digital power meter (HIOKI 3186, Hi-tester). An A.C. Transformer (LECIP) was capable of delivering (0-60) kV peak-to-peak voltage (V_{pp}) at 60Hz. The net output AC HV applied to the reactor was measured by a 1000:1 high-voltage probe (Tektronix P6015A $1000 \times 3.0 \text{ Pf}$, $100 \text{ M}\Omega$), and displayed on a four channel Digital Storage Oscilloscope (Tektronix TDS2014, 100MHz 1Gs/s). The plasma discharge power was determined by Lissajous Method [14]. A 10×10^{-5} pF Capacitor (IH104K R G) was used in the method. The plasma reactor was placed at ambient temperature.

A simulating gas was prepared from cylinder air and NO/N_2 (NO concentration of

1990 ppm and N₂ balance) by using Digital Mass Flow Controller (MFC) (Model: 3660A, KOFLOC Co.). The NO_x concentration in the inlet gas was set at 200 ppm and flow rate at 4.0 l/min. Corresponding space-velocity of 11,000 h⁻¹ was used. The individual NO and NO_x concentrations in the outflow gas were on-line determined with Horiba (portable gas analyzer, PG-225) and a NO_x sensor, respectively. The conversion of NO or NO_x was defined as follows:

$$\text{NO}_x \text{ conversion (\%)} = 100 (\text{NO}_{x,\text{in}} - \text{NO}_{x,\text{out}}) / \text{NO}_{x,\text{in}} \quad (4-1)$$

$$\text{NO conversion (\%)} = 100 (\text{NO}_{,\text{in}} - \text{NO}_{,\text{out}}) / \text{NO}_{,\text{in}} \quad (4-2)$$

Where NO_{x,in}, NO_{,in}, NO_{x,out} and NO_{,out} stands for NO_x and NO stable concentration in the inlet and outlet gas after 20 min, respectively.

4.4.2 The effect of input voltage on NO and NO_x removal rate

Figure 4-2 shows the relation between NO_x (and NO) removal rate and the discharge voltage with the preparation of MACC catalyst at different conditions.

Figure 4-2a and 4-2b indicates that the removal ratio of NO (a) and NO_x (b) increase with the increasing of discharge voltage. When the discharge voltage was higher than 30 kV, the removal ratio increased significantly. The increasing of the voltage leads to higher discharge energy density (defined as the electrical power for the discharge divided by the inlet gas flow rate). With the increasing of the discharge energy density, this will increase the concentration of oxygen atom (O) dissociated from oxygen molecules by the plasma. An increase in concentration of active oxygen atom will improve the NO_x removal ratio. When the voltage was 42 kV, the maximum NO removal ratio of 98% was obtained. At the same point, the maximum NO_x removal ratio was 89.6%.

Chemical reaction of NO oxidation is as follows:

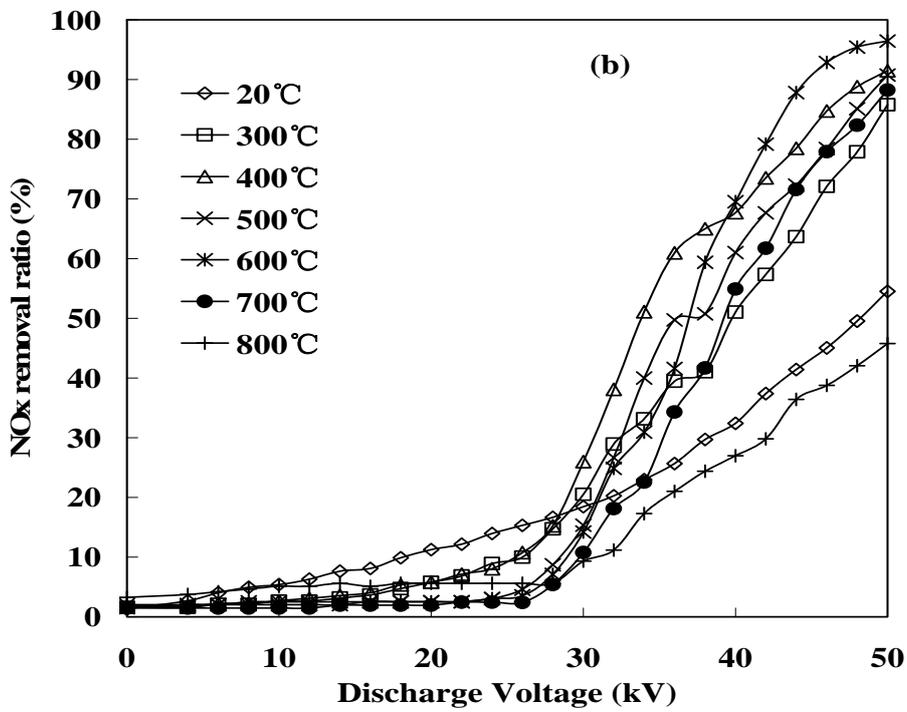
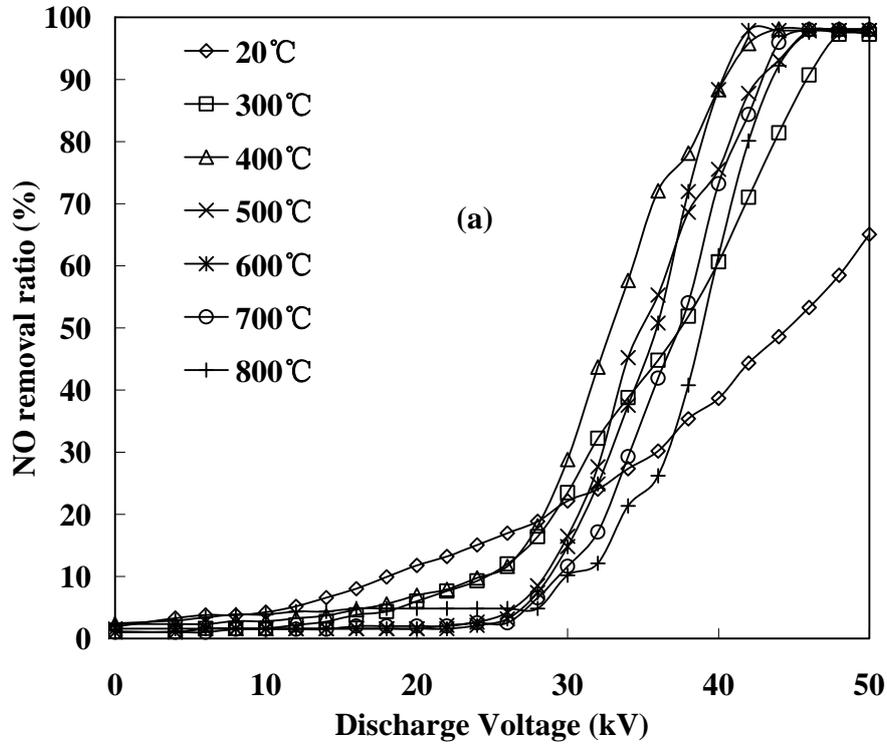
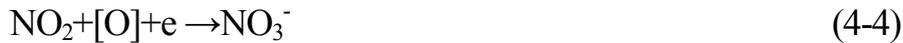


Fig.4-2 NO (a) and NO_x (b) removal ratio versus discharge voltage
 Symbols of the calcination temperature for the preparation of the AC and the MACC

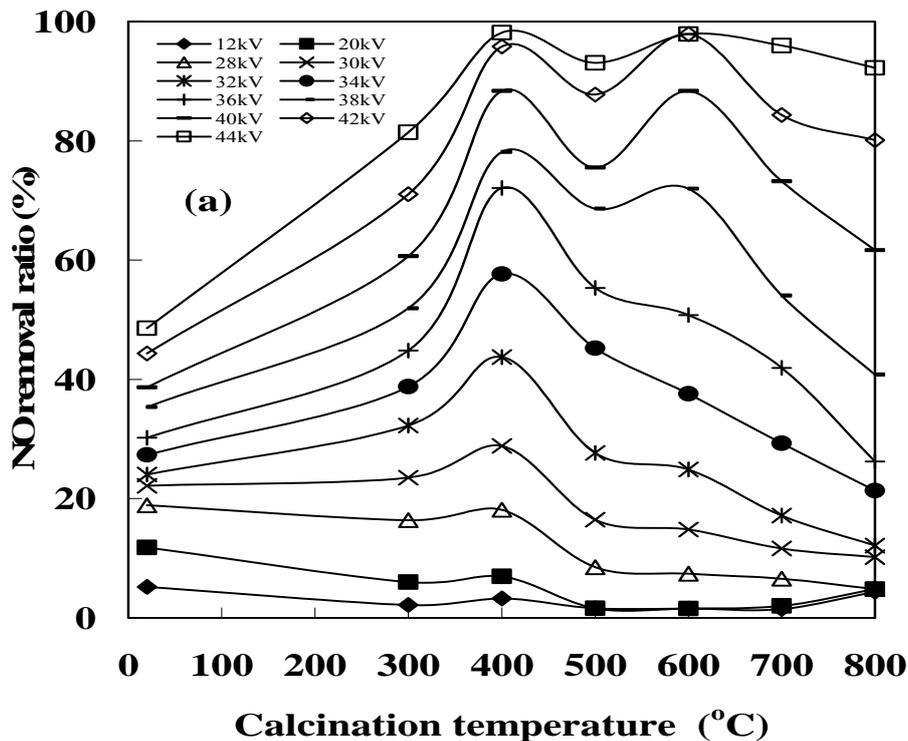
4.4.3 The detection of performance of the used MACC

After the experiment, which the condition of reaction is the MACC was calcinated at 500 °C and discharge voltage was at 42 kV_{p-p} and the discharge time was 40min, the used catalyst of 2 g was took from the DBD reactor and immersed into 20 ml de-ionized water for 24 hours.

In the end of the saturation, the pH value of the leaching solution was 6.2 (detected by pH sensor) and the concentration of NO₃⁻ ion was 3.2 mg/l, which was detected by Nitrate Ion Detector (761 Compact 1C Ω Metrohm). Therefore, the MACC has both the capability to adsorb NO₂, and to further oxidize to NO₃⁻. The chemical reaction is as follows:



4.4.4 Effect of calcination temperature on NO and NO_x removal rate



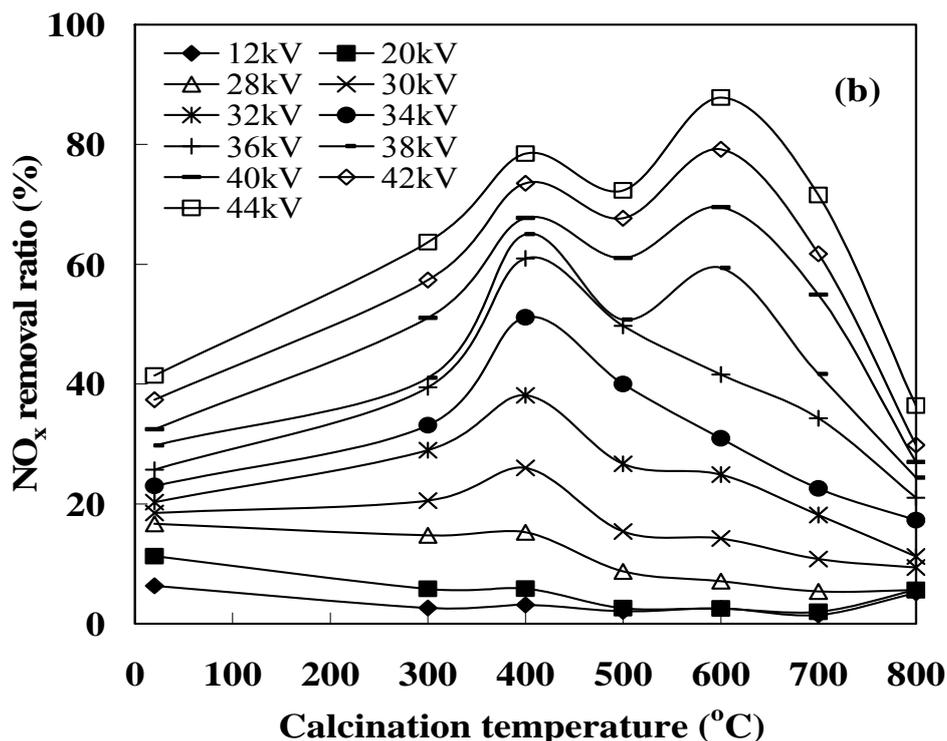


Fig. 4-3 The relation between the MACC calcination temperature and NO (a) and NO_x (b) removal ratios for various discharge voltage
 Symbols are the discharge voltages [kVp-p]

Figure 4-3 shows the calcination temperature of the AC and MACC vs. the NO and NO_x removal rates. The results were shown that the calcination temperature had a significant effect on NO and NO_x removal rate. When the calcination temperature was in the range of 400 °C to 600 °C, there is a maximum value of the NO and NO_x removal rate.

4.5 Conclusions

A plasma assisted catalyst system using modified attapulgite clay can effectively remove NO_x even at room temperature. NO_x removal rate increases with the increasing of discharge voltage. The calcination temperature of MACC has a significant influence on the NO and NO_x removal rate. The MACC has a good NO_x absorbing and storage ability when the calcination is in the 400 °C to 600 °C range. This is attributed to the appearance of fiber-like micro-structures on the surface of MACC, as shown in the SEM observation.

The higher efficiency could also be attributed to the release of water molecules in the crystal layers, resulting in increasing of the ability of NO_x adsorption.

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5. Coal- Based Active Carbon Catalyst Preparation and Character

5.1 Introduction

The method of NTP combined with catalyst in the DBD reactor is one of effective ways to remove NO_x from the automobile exhaust [1-2]. With only plasma, the oxygen atom changes as the following chemical reaction formula in the process of removal NO reaction, $\text{NO} + \text{O} \rightarrow \text{NO}_2$, $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$. Some reactive oxygen atom of [O] is consumed in this recycle, as the oxygen atom of [O] is generated by the discharge power energy, so some electric power will be wasted with the reactive oxygen atom of [O] consuming [3].

When the NTP combined with catalyst is used to remove NO, some NO components are absorbed by the catalyst and the concentration of NO is higher on the catalyst surface. The higher concentration of NO is, the faster the chemical reaction speed of NO. Meanwhile since the reaction is accumulated by the catalyst, the NO can be further oxidized into NO_3^- , namely $\text{NO}_2 + \text{O} \rightarrow \text{NO}_3^-$. So with the appropriate catalyst combined with the NTP, the recycle of oxygen atom can be held back and NO removal rate is improved, some electric energy to generate plasma is saved on [4-5]. In this chapter the preparation of catalyst by active carbon based on coal and its performances evaluation have been investigated.

Generally, the concentration of NO_x from automobile exhaust is 200-300 ppm. If the catalyst has a good ability of adsorption and storage, the NO_x can adsorb on the surface of

catalyst to have concentrated the concentration of NO_x and improve the chemical reaction. Meanwhile the reaction and the character of catalyst are forced by the NTP, which can advance the speed and selectivity of the reaction of NO_x removal [6-8]. In this chapter we prepared the Coal-based Activated Carbon Catalyst (CACC) which the copper oxide was carried by the coal-based activated carbon and studied the relation between NO_x removal rate and the CACC in DBD reactor.

5.2 Preparation of catalyst

5.2.1 Experimental chemicals

The main experimental chemicals are as follows.

ZnCl_2 (AR): its function is to break the connected bond of hydrocarbon in the pulverized coal and to improve the character of micro pore and gap and to increase the specific surface area of the activated carbon particles.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (AR): its function is to provide the copper element to generate the copper oxide of activated points at high temperature, the activated points attach or inlay on the surface of activated carbon.

Pulverized coal: the ash in the coal must be smaller than 6% and particle size of the coal is smaller than 200 mesh.

Coal tar: its function is to adhere the coal powder to form suitable size which has adequate intensity for the catalyst mold particles.

Other chemical includes citric acid, pressure air cylinder, NO / N_2 cylinder and others.

5.2.2 Preparation process

(1) Removed the ash from the pulverized coal by the distilled water washing for four times, the cleaning coal was ground and sieved to obtain the coal powder with a size of below 200 mesh.

(2) With the ZnCl_2 and the distilled water to make the solution, its concentration was 10 percent (W %). With the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and the distilled water to make the solution, its concentration was 6 percent (W %). The solution of ZnCl_2 and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and citric acid was mixed with the coal powder and stirred until uniform. The mixture was deposited for 24 hours.

(3) The coal tar joined with the mixture of coal and stirred till uniform. The suitable catalyst particle was made by the pressure mould.

(4) The catalyst particles were dried for 24h at room temperature then dried completely at the temperature of 200°C in muffle furnace. The catalyst particle was activated at the temperature of 600°C for 6 hours.

5.3 Experiment and discussions

5.3.1 Experimental instruments and processes

The experimental schema is shown as Figure 2-1. The main instruments include the Power Supply System, 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) and the DBE reactor (made self, see Figure 2-2).

The same volume of the CACC and glass bead was packed in the same DBD reactor,

respectively. The simulation gas was entered into the reactor with the same initial concentration and volume. The concentration of NO and NO_x from the reactor was detected on-line by the NGK and HORIBA, respectively. The form of the fresh and after used catalyst was detected by the SEM. The concentration of NO₃⁻ ion which was leached from the used catalyst was detected by the Nitrate Ion Detector.

5.3.2 The effect of the catalyst and time on the NO and NO_x removal rate

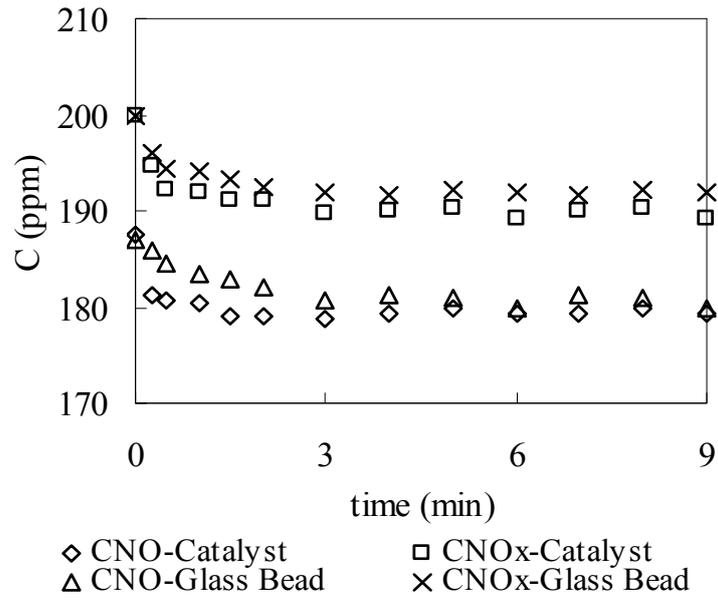
The different conditions of preparing the CACC and the glass bead were packed into the DBD reactor and reached to the same packed volume, respectively. The simulation gas with a 200ppm NO entered into the reactor and the inlet gas volume flow was 4.0L/min. The input power from the supply power to the DBD reactor was 4W, 6W, 8W, 10W and 12W respectively. The relationship between reaction time and concentration of NO and NO_x of the gas out of the reactor was showed in the Figure 5-1.

In the Figure 5-1, the *CNO-Catalyst* means the concentration of NO in the gas out of the reactor when the reactor was only packed with the CACC.

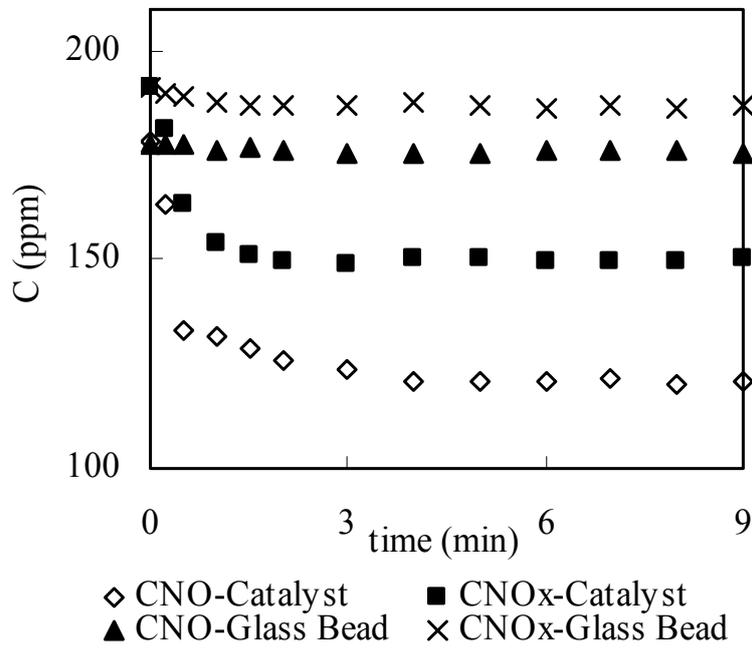
The *CNO_x-Catalyst* means the concentration of NO_x in the gas out of the reactor when the reactor was only packed with the CACC.

The *CNO-Glass Bead* means the concentration of NO in the gas out of the reactor when the reactor was only packed with the glass bead.

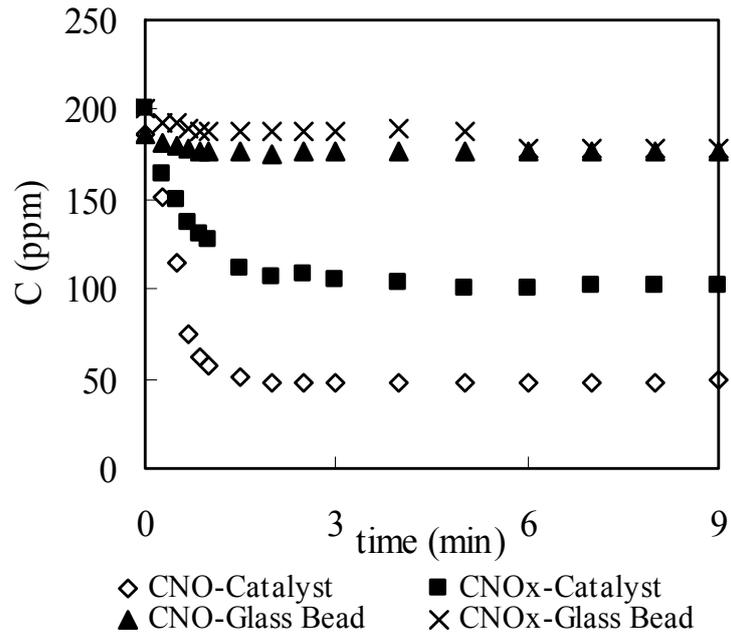
The *CNO_x-Glass Bead* means the concentration of NO_x in the gas out of the reactor when the reactor was only packed with the glass bead.



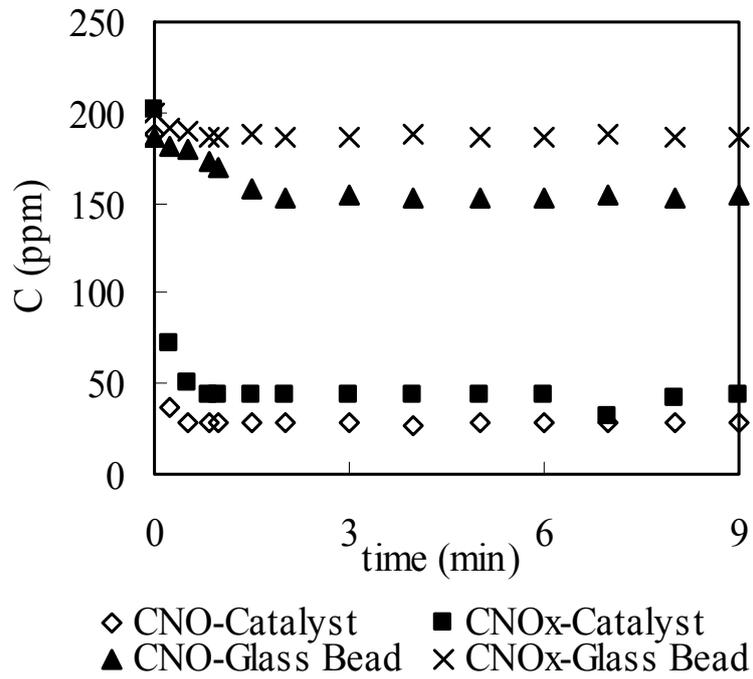
(a) 4w input power



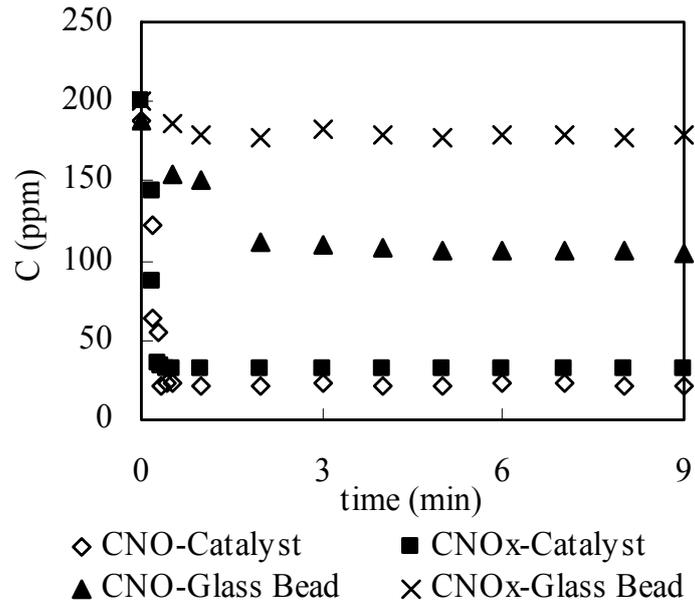
(b) 6w input power



(c) 8w input power



(d) 10w input power



(e) 12w input power

Fig.5-1 The relation between time and concentration of NO and NO_x in the gas from the reactor at the different condition of input power to the DBD reactor

The Figure 5-1 indicates that with the reaction time going on, the concentration of NO and NO_x reduces fast at beginning, and then reaches to stable value nearly after 3 min. The performance shows the main contribution of removal NO and NO_x is adsorption at first and then changing into reductive reaction after 3 min.

5.3.3 The effect of the input power on the NO and NO_x removal

The removal rate of NO and NO_x was calculated in terms of the stable concentration values of NO and NO_x after 9 min. The dependence of the removal rate on the input power is shown in Figure 5-2.

Figure 5-2 indicates that,

- (1) The concentration of NO and NO_x decreases with the increasing of input power.

The reason is that density of NTP and concentration of active oxygen atom increase with the increasing of input power which accelerate the reaction rate.

(2) The removal rate of NO and NO_x by the CACC combined with the NTP is bigger than at condition of the glass bead combined with the NTP. The reason is that the CACC has higher capability of adsorption and storage to NO and NO_x than the glass bead.

(3) The NO removal rate is bigger than the NO_x removal rate at the same chemical reaction condition.

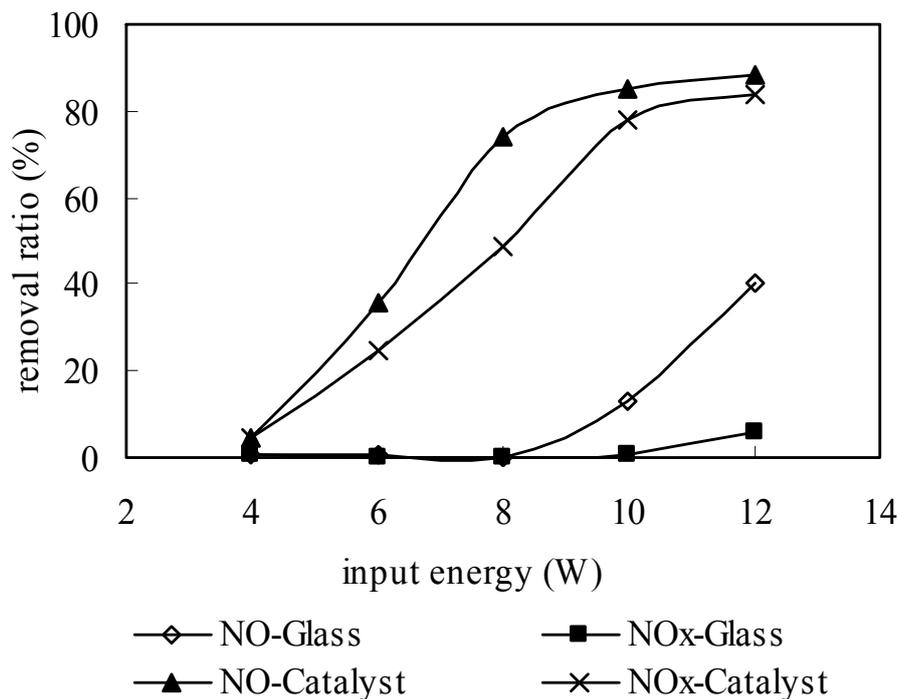


Fig. 5-2 when chemical reaction reached balance the relation between removal ratio of NO, NO_x and input energy with the catalyst volume the same as condition of glass bead volume

5.3.4 The CACC analysis of SEM

The SEM of the fresh CACC and the after used CACC are shown in Figure 5-3 and Figure 5-4, respectively. Within the experiment of CACC, 40g CACC packed into a reactor, a gas flow rate of 4 l/min, 200 ppm NO_x, 10 w input power and 9 min reaction time were used.

Table 5-1 shows the component in the CACC of fresh and after used catalyst.

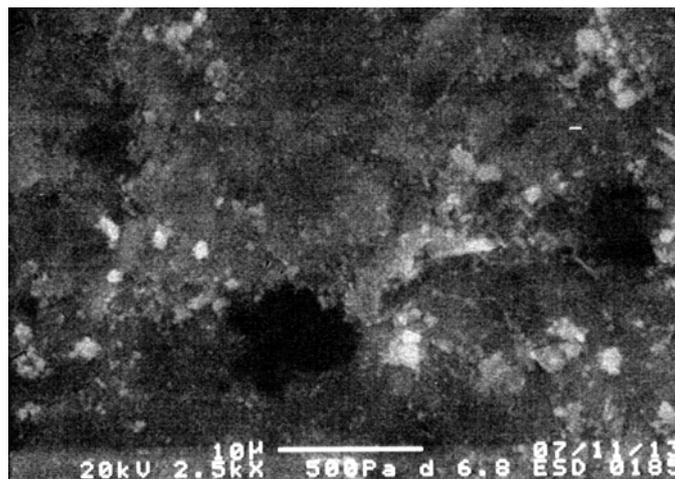


Fig. 5-3 the SEM of the fresh catalyst

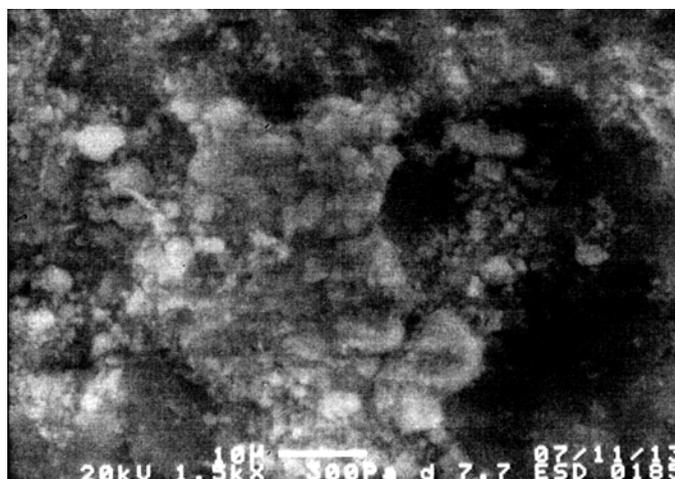


Fig. 5-4 the SEM of after used catalyst

Figure 5-3 and Figure 5-4 and Table 5-1 indicate:

(1) The coal-based activated carbon can provide a big surface area to support the Active Point of Metal Oxide. The surface area of the fresh catalyst is $167 \text{ m}^2/\text{g}$, the used catalyst is $132 \text{ m}^2/\text{g}$.

(2) Table 5-1 shows that during experiments the concentrations (mol percent) of Copper and the Zinc in the CACC decrease from 9.96% to 6.50% and from 9.96% to 6.50%, respectively. As the metal element is depleted with metal nitrate came into being.

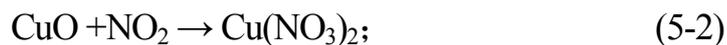
Table 5-1 the component of the fresh and after used CACC

Element	Fresh Catalyst		After Used Catalyst	
	Weight Concen./ %	Mol Concen. / %	Weight Concen. / %	Mol Concen. / %
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

5.3.5 The NO₃⁻ detection in the used CACC

The 2 g used CACC was immersed in 20 ml de-ionized water at room temperature for 12 h. The PH value of leaching solution which was measured by the pH Meter was 6.2. The NO₃⁻ in the leaching solution was found by using a Nitrate Ion Detector.

According to the face of the pH value of 6.2 and the ion of NO₃⁻ in the leaching solution, the process of chemical reaction can be inferred as following:



It can be found that the NO is oxidized to NO₂ and the NO₂ is further oxidized to NO₃⁻ in the chemical reaction of the CACC combined with the NTP. So this method is an

effective way to remove NO_x from the exhaust gas of auto.

5.4 Conclusions

The CACC was prepared and evaluated in this chapter. The coal-based activated carbon was used as the carrier of catalyst, the metal element of Copper and Zinc was used as the active points. The performances of the fresh and used CACC were evaluated by the SEM. The ion of NO_3^- was detected in the leaching solution of after used CACC by the Nitrate Ion Detector. According to the ion of NO_3^- and PH value of the leaching solution, we can conclude that the NO is absorbed on the surface of CACC firstly and then oxidized to NO_2 . The next step is the NO_2 is further oxidized and changed to NO_3^- .

At the chemical reaction condition of the CACC combined with the NTP, the concentration of NO and NO_x reduces down fast at first and then reaches to stable value nearly after 3 min. It shows the main contribution of removal NO and NO_x is adsorption at first and after 3 min then change into chemical reaction.

The concentration of NO and NO_x decreases with the increasing of input power. The removal rate of NO and NO_x at condition of CACC combined with the NTP is bigger than at condition of glass bead combined with the NTP. The NO removal rate is bigger than the NO_x removal rate at the same chemical reaction condition.

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6. Coal- Based Active Carbon Catalyst Performances Evaluation

6.1 Introduction

Non-thermal plasma (NTP) in air can produce a large number of free electrons, ions, reactive free radicals and a variety of free particles in excited states and can promote chemical reactions with these radicals. In addition, when NTP is combined with catalyst, energy transfers from excited molecules to the catalyst surface and can increase rate of chemical reactions. Dielectric barrier discharge (DBD) is one effective way to generate the NTP [1-3]. There are several types of DBD reactors such as: wire (or bar)-cylinder, wire-plate, and plate-plate structure [4-5].

In this chapter, a bar-cylinder reactor was used in combination with catalyst of modified activated carbon made of based coal, the preparation way of this kind of catalyst of seen in Chapter 5. The catalyst was packed between the bar and the cylinder in the fixed bed reactor. The solid catalyst particles have the other function of barrier dielectric [6-9].

Activated carbon from coal has a plenty of micro porous inside the structure and a very large specific surface area. When the activated carbon is modified by suitable metal oxide the catalyst presents a good capability of adsorption and catalysis. The catalyst, which loaded metal oxide as activated points on the activated carbon from coal, not only has the good adsorption properties like AC, but also has high activity and selectivity for NO_x removal reactions. Therefore, this kind of activated carbon is one of ideal catalyst carriers [10-11]. The combination of this catalyst with NTP was expected to improve the NO_x removal ratio.

The automobile exhaust mainly contains NO_x , HCs (Hydrocarbons), PM (particulate

matter), H₂O and so on. Previous studies have showed that the step of oxidization from NO to NO₂ is the controlling step, which is the bottleneck in the process of removing NO_x from automobile exhaust gas [12]. Usually, the concentration of NO_x in exhaust gas is not high (about 200-300ppm). This kind of catalyst can adsorb and store NO_x on its surface at first, increasing the virtual concentration of reactants. This could result in speeding up the reaction when combined with NTP [13-15].

This chapter investigates the effect of initial gas concentration, space velocity, catalyst quality and input voltage (input energy) on the removal rate of NO in the process of NTP combined with the catalyst of modified activated carbon from coal.

6.2 Materials and methods

6.2.1 Chemicals and Equipments

Chemical reagents: catalyst of activated carbon from coal modified by copper (self-made, preparation procedure is in Chapter 5) [16-17], air cylinder, NO/N₂ cylinder (NO concentration is 3005ppm, the balances is N₂), other auxiliary materials.

Experimental equipments and the system are shown in Figure 2-1 and the reactor structure is shown in Figure 2-2.

6.2.2 Experimental Methods

The simulation gas with different initial concentrations of NO (100ppm-350ppm) was fed into the reactor, the space velocity and input voltage were regulated in the range of 6-12s⁻¹ and 15-30kV, respectively. The frequency of source is 50Hz. The packing amount

of catalyst was changed and the same volume of the same diameter glass bead was packed into the reactor for comparison. The reactor was installed in the constant temperature chest at 180°C. The inlet and outlet concentration of NO were measured with FGA-4100 automobile exhaust-online instrument, and the removal ratio of NO was calculated with the formula: NO removal ratio [%] = 100× (inlet concentration of NO - outlet concentration of NO)/ inlet concentration of NO.

6.3 The process parameters on NO removal rate

6.3.1 Effect of input voltage on NO removal rate

Catalyst of 43.90 g was packed in the reactor. The initial NO concentration was 256ppm, inlet gas flow rate was 7L/min (space velocity, ratio of the gas flow rate and the volume of catalyst; 10.2s⁻¹). The input voltages [kV] were; 15, 20, 25 and 30, with the corresponding input power [W] of 7.3, 10.9, 15.6, and 20.9, respectively. Under these four different input voltage conditions, the relationships between NO removal ratio and reaction time are shown in Figure 6-1.

The NO removal ratio decreases with increasing of reaction time in any input voltages tested, and after about 10 min from the start, the NO concentration became roughly stable. In this steady state, the NO removal ratio increases with increasing input voltage. Since plasma density and concentration of active oxygen atoms increase with the increasing of the input voltage, the chemical reaction should be speeded up. At the same time, Figure 6-1 also shows that the catalyst combined with plasma has better efficiency of the NO removal ratio. This could be that the catalyst effectively reduced the starting

energy of the chemical reaction by adsorbing and storing NO.

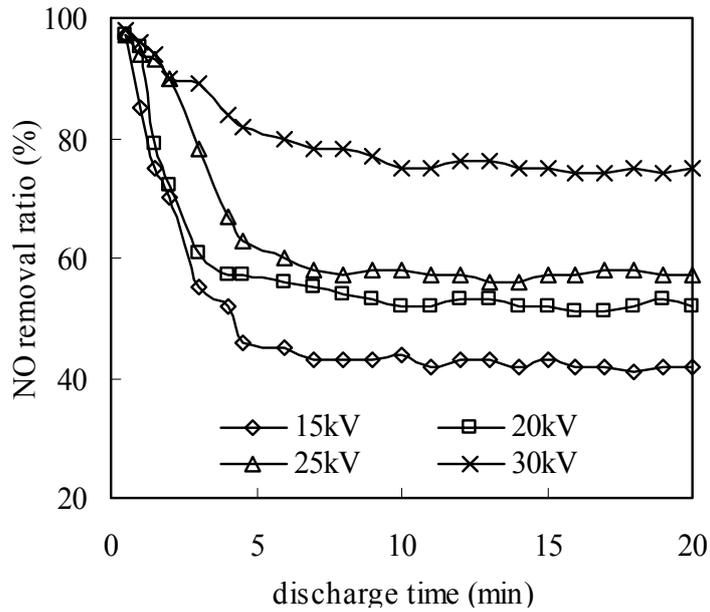


Fig.6-1 Relationships between NO removal ratio and reaction time with different input voltages

6.3.2 Effect of initial NO concentration on NO removal rate

The catalyst of 43.90g was packed in the reactor. The input voltage was 25kV, and the inlet gas flow rate was 7L/min (space velocity $10.2s^{-1}$). Initial concentration of the simulated NO gas was changed as 126, 176, 256, and 327ppm, respectively. The relationship between the NO removal ratio and the discharge time with different initial NO concentration is shown in Figure 6-2.

Figure 6-2 shows that the NO removal ratio is high at first and then reduces with time. After 10min, the ratio is getting stable. When the adsorption and de-sorption of the catalyst surface reach equilibrium, the NO removal ratio becomes stable. The relationship between NO removal ratio and the initial input concentration (in steady state measured after 20min from the start) is shown in Figure 6-3.

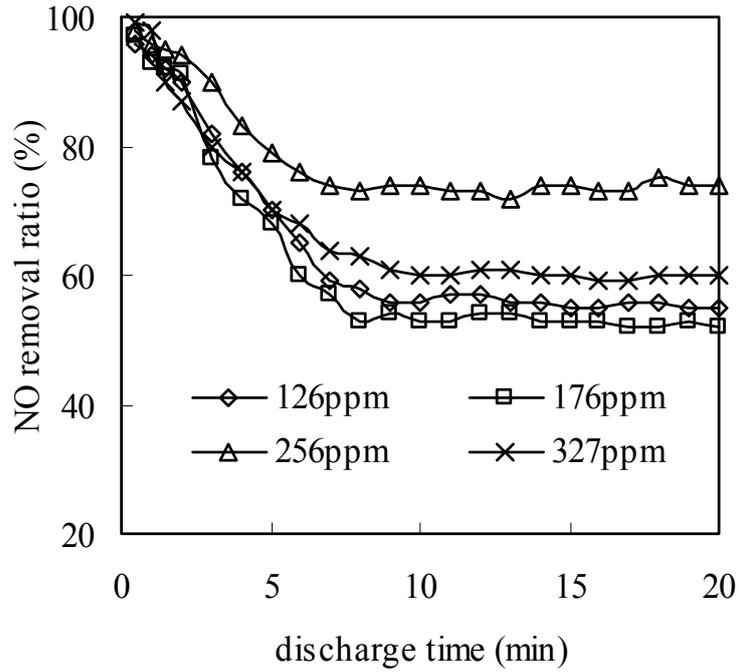


Fig.6-2 Relationships between NO removal ratio and time with different initial NO concentrations

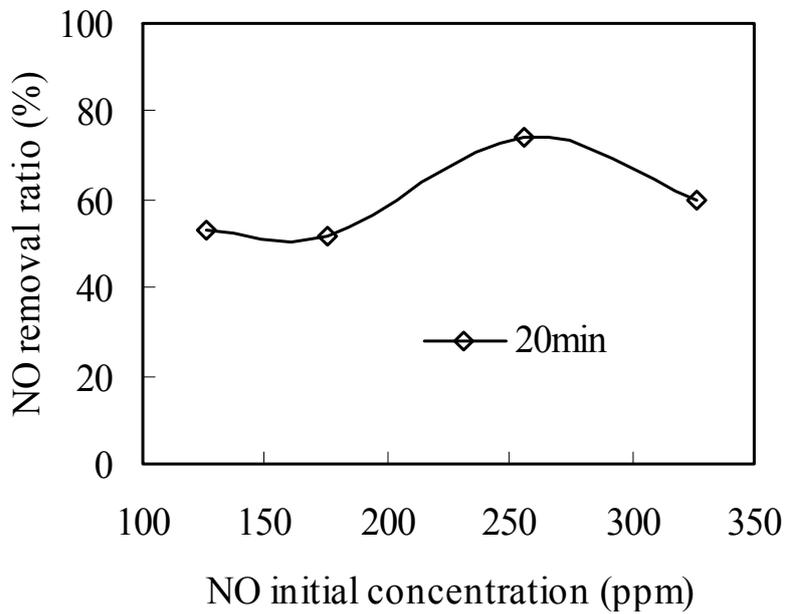


Fig.6-3 Relationships between NO removal ratio and initial NO concentration

The NO removal ratio increases at first and then decreases with the increasing of the initial concentration of NO gas. The phenomenon indicates that, in the process of catalyst combined with plasma enhances the reaction, when the NO initial concentration is low,

according to kinetic theory, the NO removal rate is small. On the contrary, when the NO initial concentration is bigger than the optimal value the NO removal rate decreases. In the experimental conditions tested, the best initial NO concentration was 256 ppm and the maximum removal ratio of NO was about 74%.

What is the reason? Schematic diagram of the mechanism model for adsorption catalyst is shown in Figure 6-4.

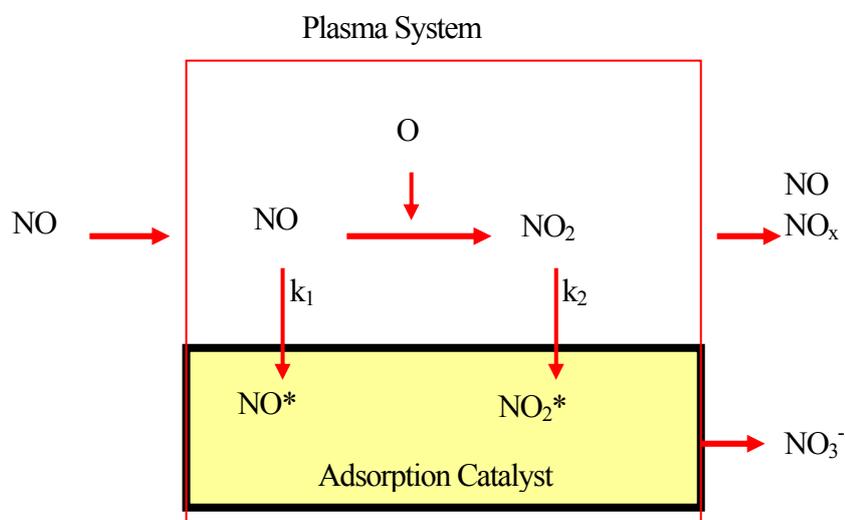
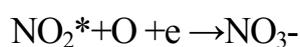
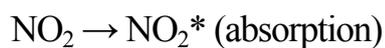
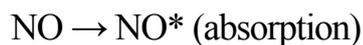
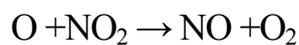
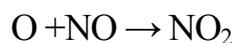
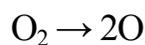


Fig. 6-4 Schematic diagram of the mechanism model for adsorption catalyst

The chemical reaction formulas are follows:



In the process, the partial NO is oxidized to NO₂, and other partial NO and NO₂ is

adsorbed by the catalyst. Generally, the NO is difficult to be adsorbed by catalyst, but this catalyst was made from coal-based activity carbon, it has a plenty of surface area and partial NO is adsorbed in this experiment. The NO₂ is more easily adsorbed than the NO.

When the NO initial concentration is bigger than the optimal value, most of NO₂ is adsorbed by catalyst surface. The number of NO₂ which adsorbed on catalyst is bigger than the NO. When the adsorption and dis-adsorption reaches balance condition, a few of NO is not be adsorbed and stayed in gas phase, so that the NO removal ratio decreases.

6.3.3 Effect of space velocity of feed gas on NO removal rate

Catalyst of 43.90 g was packed in the reactor. The input voltage was 25kV, the initial NO concentration was 256 ppm, inlet gas space velocity was 6.1, 8.1, 10.2 and 12.0s⁻¹, respectively. The relationship between the NO removal rate and time is shown in Figure 6-5 with different gas space velocity:

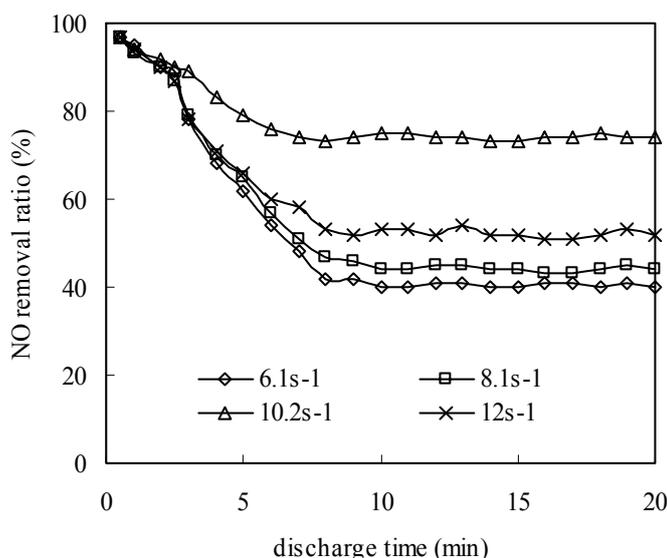


Fig. 6-5 Relationships between NO removal ratio and time in different space velocities

The removal ratio of NO decreases gradually with time in any space velocity

conditions, and becomes stable after 10min as shown in Figure 6-5. Under the steady state, the relationship between the NO removal rate and the space velocity was measured as shown in Figure 6-6.

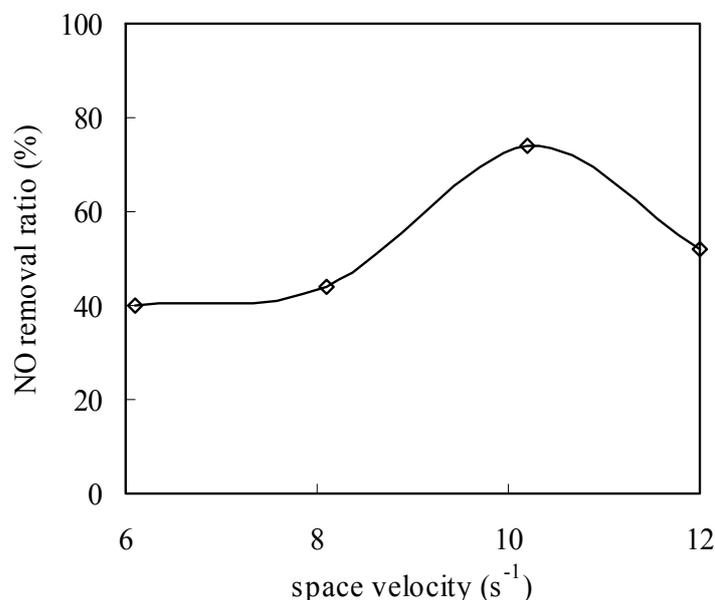


Fig.6-6 Relationships between NO removal ratio and space velocity

When the space velocity is less than 10.2s^{-1} , the NO removal ratio increases with the increasing of space velocity. When the space velocity is greater than 10.2s^{-1} , the removal rate of NO decreases with space velocity increasing. The reason is that when the space velocity is less than 10.2s^{-1} , the overall reaction rate is controlled by the external diffusion of the catalyst. With increasing of space velocity, the diffusion effect is diminishing, so NO removal ratio increases. When the space velocity is greater than 10.2s^{-1} , the effects of catalyst external diffusion can be basically eliminated, but the residence time of NO inside the reactor decreases with increasing of space velocity, so the NO removal ratio decreases. There is an optimal space velocity in the reaction system. In this experimental condition, the optimum space velocity was about 10.2s^{-1} .

6.3.4 Effect of quality of catalyst on NO removal rate

With the input voltage of 25kV, the NO initial concentration of 256ppm and the inlet gas flow rate of 7L/min (space velocity; $10.2s^{-1}$), following reactors were tested: (1) Without packing any substance, only with plasma; (2) packed with the same volume of the similar diameter glass beads, and with plasma; (3) packed with catalyst, but without plasma; (4) packed with catalyst and combined with plasma.

In the above four cases, the relationships between the removal ratio of NO and time are described in Figure 6-7.

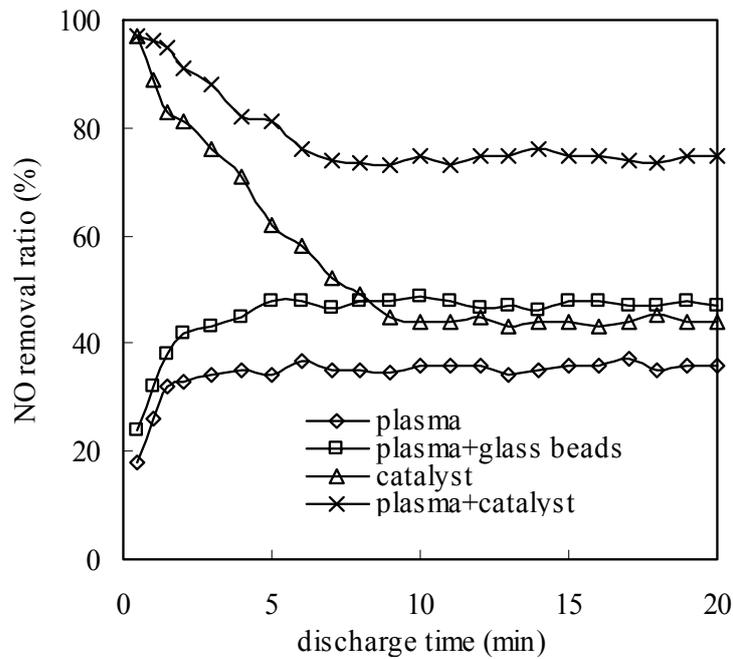


Fig.6-7 Relationships between NO removal ratio and time with different packed materials

From the above figure, following remarks can be made:

(1) With or without the plasma, under the conditions of packing with catalyst, the NO removal ratio is high at the beginning then gradually decreases over time elapsing and finally becomes stable. The NO removal ratio is relatively high at first owing to the effect

of catalyst adsorption and storage at inception, and then the removal rate reduces and tends to be stable after the adsorption reached equilibrium. In the cases of packing with glass beads and without any packed case, the removal ratio increases gradually over time at beginning and then stabilizes because the glass beads and empty reactor don't adsorb NO. After the reactions reach steady state, the order of the NO removal ratio is as follows: plasma + catalyst > Plasma + glass ball > only catalyst > only Plasma.

(2) Under the conditions of solely relying on the plasma in the reaction, the removal ratio is the lowest because the plasma alone is not possible to oxidize NO effectively. On the contrary, nitrogen and oxygen in the gas may produce NO via reverse reaction.

(3) Only with the catalyst, the removal ratio in the steady state is higher than that with the plasma alone; meanwhile it is less than that with the case of glass beads + plasma. Without any catalytic effect, neither absorption nor storage, still the glass beads can play the role of barrier dielectric, resulting in increasing of plasma density. The NO removal ratio is therefore higher in the condition with plasma and the glass beads than that with the catalyst alone.

(4) When the catalyst was packed in the reactor and combined with the plasma, the NO removal ratio is the highest in the four cases. This could be due to the enhancement of catalysis performance by energy exchange with excited molecules, and to the adsorption and storage capabilities increase concentration of reactants.

6.4 Comparison with different kinds of catalyst

According to the experimental data, three kinds of catalyst at the same condition and

loading the same amount of catalysts in the reactor, the comparison of the NO removal rate with the same voltage of 30kV is shown in Figure 6-8.

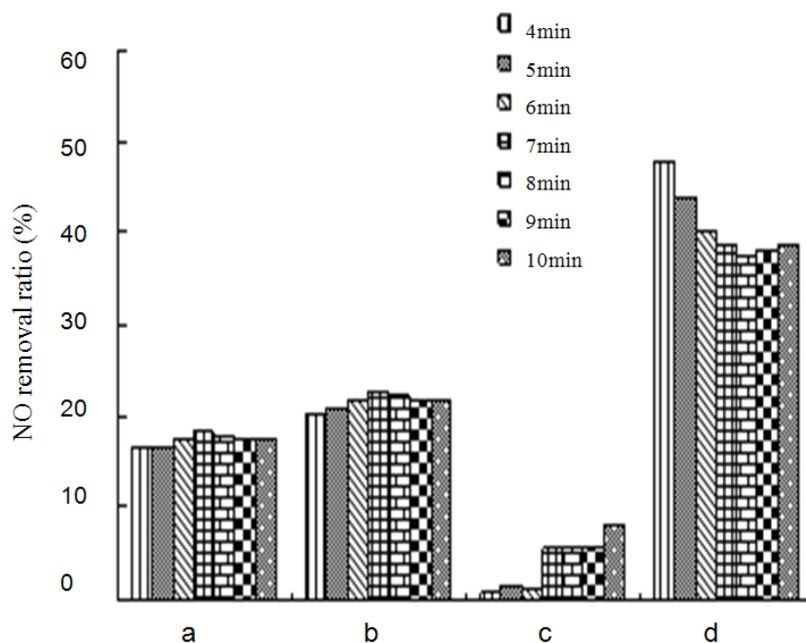


Fig.6-7 Relationships between NO removal ratio and difference of time amount

Figure 6-8 shows that the coal-based activated carbon catalyst can reach to the maximum NO removal rate when it was filled. The note activated carbon catalyst and plasma combined with better coordination and Plasma Modification of Sepiolite catalyst, Sepiolite Catalyst program has yet to be further improved. (Figure 6-8a: plasma discharge space is filled by Modified attapulgitic clay catalyst; b: discharge space filled with modified sepiolite catalyst; c: discharge space is not any catalyst; d: discharge space filled with Coal-based activated carbon catalyst).

6.5 Conclusions

(1)The results show that the combination of non-thermal plasma and the catalyst of modified activated carbon made of coal is an effective way to remove NO. The input

voltage, gas concentration, gas space velocity and the catalyst packed weight have certain effect on the NO removal ratio. Summary of the result is as follows.

In the same experimental condition, the removal ratio of NO increases with increasing of input voltage. This is because that the increase of the plasma density and the concentration of active oxygen atoms can accelerate the chemical reaction. The combination of NTP and catalyst can effectively reduce the initial activation energy, and can enhance the adsorption and storage function of the catalyst, and prevent active oxygen atoms from combining with themselves generating an inner loop of oxygen in the plasma.

The NO removal ratio increases firstly and then decreases. The removal rate of NO increases with increasing the initial NO concentration, when the initial NO concentration exceeds a certain critical value, the NO removal ratio decreases. The best initial NO concentration obtained in this study was 256ppm.

With increasing of the space velocity, the NO removal ratio increases and then decreases, showing a peak value of the removal ratio. The best space velocity obtained in this experimental condition was about $10.2s^{-1}$.

(2) In the same experimental conditions, after the reaction reach the equilibrium, the order of impact on the removal ratio of NO is as follows: plasma + catalyst > Plasma + glass ball > only catalyst > only plasma, because the catalyst not only has the performances of catalysis, adsorption and storage, but also fully play the role of the DBD.

Each kind of catalyst is corresponding to its optical of initial concentration, space velocity and input power voltage.

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7. Effect of catalyst size on discharge and NO_x removal rate

7.1 Introduction

Dielectric Barrier Discharge (DBD) is an effective way to produce Non-Thermal Plasma (NTP) [1-2]. The NTP with catalyst is a method to remove NO_x from diesel exhaust, which not only increases the NO_x removal rate, but also reduces power consumption effectively [3-4]. There are several types of DBD reactor to be used, such as wire-cylinder, wire-plate, plate-plate and packed bed [5-6]. For gas cleaning, there are two-stage and one-stage processes. In the two-stage process, reactor is consisted of two parts connected in series. First section is used to produce NTP for radical such as oxidation, and the following section is a catalyst. In one-stage process, NTP is produced in combination with catalyst. Packed bed reactor is a typical reactor for the combination. In this reactor, the catalyst pellet also plays a role as a dielectric barrier. Size of the catalyst, therefore, affects on characteristics of NTP and performance of packed bed reactor [7-11]. Size of the catalyst should also affect on pattern of gas stream and diffusion of pollutant molecules to be absorbed by the catalyst. Optimum size of catalyst pellets should improve the NTP process. A study has been made the effect of catalyst pellet size on the discharge energy and NO_x removal rate in a one-stage packed bed reactor. As a catalyst, Modified Sepiolite Catalyst (MSC) with copper has been tested [12]. The results provide a basic theoretical prediction for choice of a suitable catalyst size in the NTP reactor.

7.2 Experiment

The one-section DBD reactor (made by self) was made of Borosilicate Pyrex Glass Tube with an inner diameter of 27 mm, a wall thickness of 2 mm and a length of 120 mm. The outside wall of the tube was covered with aluminum film (60 mm in length and 0.6 mm in thickness) as cathode, an aluminum rod with a diameter of 8 mm was placed in the center of the tube as anode; the MSC was loaded in the tube between the aluminum rod and aluminum film, both end of the reactor was sealed by silicone rubber plug [13]. The experimental setup is shown in Figure 2-1. The reactor structure is shown in Figure 2-2. The MSC was ground and separated by sieve for five grades, its diameter is 1.2 mm, 3.0 mm, 3.8 mm, 4.8 mm and 6.0 mm and every grade is expressed by P₁, P₂, P₃, P₄, P₅, respectively. Each 30g MSC was loaded into the same fixed bed reactor.

Following reagents and measuring equipments were used in the experiment.

Reagents: Air Cylinder, NO/N₂ Cylinder (the content of NO is 2011*10⁻⁶, the balance is N₂), Modified Sepiolite Catalyst (MSC) with Copper Oxide with different pellet diameters.

Main equipments: Automobile Exhaust Gas Analyzer (Guangdong Fushan analysis instrument factory, FGA-4100; NO measurement range: 0~4000*10⁻⁶), Muffle Furnace; High Voltage Supply (JNB-208B), Power Meter (HIOK13186, Digital Power Hi-Tester); High Voltage Probe (Tektronix P6015A 1000×3.5PF, 100 MΩ); Digital Oscilloscope (Tektronix TDS2014, four channel digital storage Oscilloscope, 100MHz 1 Gs/s), Transformers (0~250V), Gas Mass Flow-meter, Constant Temperature Cabinet.

7.3 Model and analysis of the packed bed

7.3.1 Simplified model

In order to set up the mathematical model of a relation between the Catalyst Pellet Diameter (CPD) and the Discharge Power (DP), assumptions were made based on the relevant references and experimental results.

(1) Shape of the pellet is assumed to be spherical with uniform size of diameter, d . The spherical balls are arrayed in a square phalanx with side length of d . The ball is transformed to a cube having the same volume; length, d , width, d and thickness, h , as shown in Figure 7-1.

$$\frac{\pi}{6}d^3 = d^2 \cdot h, \quad \text{then } h = \frac{\pi}{6}d \quad (7-1)$$

The thickness of the void in the cube is: $d - h = (1 - \frac{\pi}{6})d$ (7-2)

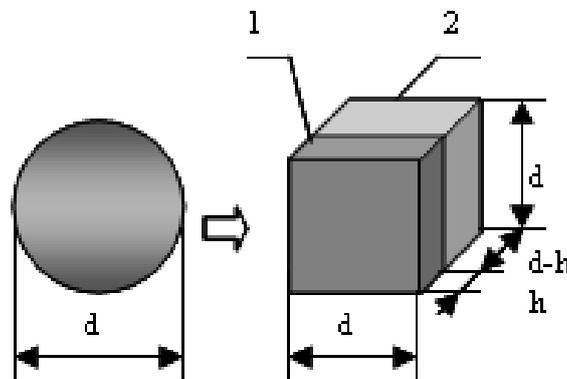


Fig.7-1 Schematic diagram of the ball transformed the equivalent volume of cube

1. Ball Volume; 2.Void Volume

(2) In the cross section of DBD reactor, every small cube with the same circumference is interconnected, and the shape is approximated as a ring with thickness h as shown in Figure 7-2.

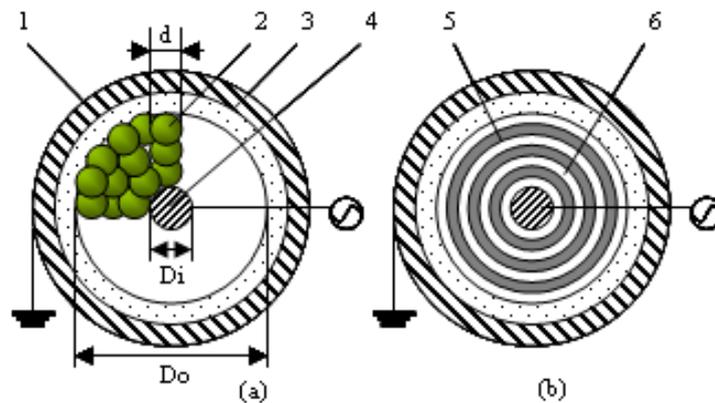


Fig.7-2 Schematic diagram of the ball arrangement and the rings in the cross section

1. Grounding Electrode; 2.Pellets; 3.Quartz Glass; 4.Anode;

5. The Rings Transformed from the Balls with Equal Volume; 6.The Rings Transformed from the Void Space

(3) To cut along the radial direction, the rings were unwrapped into many slices, with the length, L, of the axial distance as shown in Figure 7-3.

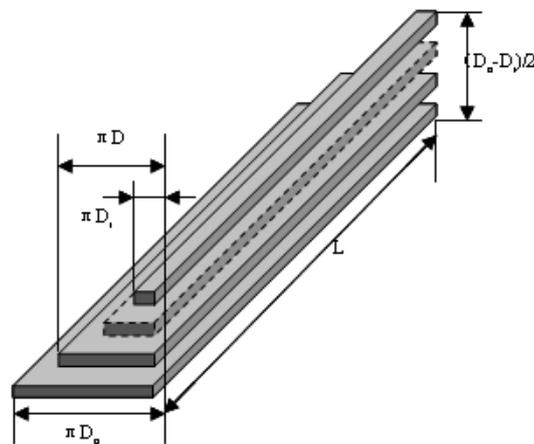


Fig.7-3 The figure of unwrapped DBD reactor

Many pieces of the slice from the cube and the void space are stacked each other, regarded as many parallel-plane capacitors. Thickness of the plane and the void space is $\frac{\pi}{6}d$ and $(1-\frac{\pi}{6})d$, respectively, as shown in Figure 7-4.

Relationship of length of the capacitor, L, and number of pellets along the reactor, k, is;

$$L=kd \quad (7-3)$$

As the diameter of the center electrode, D_i and the inner diameter D_o of the insulating tube are different, a logarithmic average, D , is used to express the average diameter. Length of the connected circumference of the plane capacitor is:

$$\pi D = \pi \frac{D_o - D_i}{\ln \frac{D_o}{D_i}} \quad (7-4)$$

Number of layer of the pellet and the void space are as follows.

$$n = \frac{D_o - D_i}{2d} \quad (7-5)$$

The total capacitances of the pellet and gap space are as follows:

$$\frac{1}{C_p} = \sum_1^n \frac{1}{C_{p_i}} \quad (7-6)$$

$$\frac{1}{C_g} = \sum_1^n \frac{1}{C_{g_i}} \quad (7-7)$$

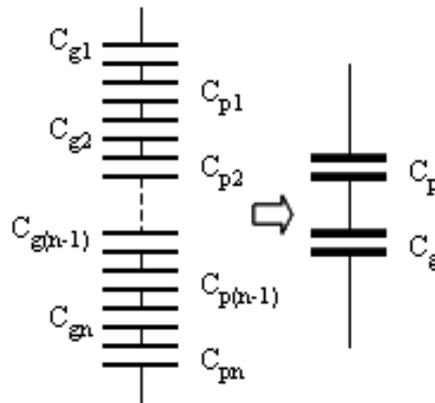


Fig.7-4 Equivalent capacitor diagram

V : voltage; C_p : equivalent capacitance of the pellet; C_g : equivalent capacitance of the void spacing;

C_d : capacitance of the dielectric layer (quartz glass wall)

Figure 7-5 shows the equivalent capacitor of the packed bed reactor. In order to set up a simple model, C_d as shown in eq.(7-8), is assumed to be constant[14].

$$C_d = \frac{2\pi L \epsilon_d}{k_d} / \ln\left(\frac{2\delta + D_o}{D_o}\right) \quad (7-8)$$

Where: δ is the wall thickness of quartz tube, ε_d is dielectric constant of quartz.

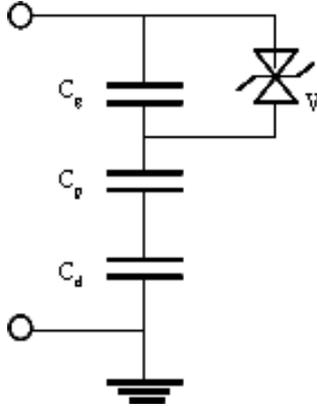


Fig.7-5 Figure of equivalent circuit

The capacitance value C_{p_i} is as follow:

$$C_{p_i} = \frac{\varepsilon_p \cdot \pi D}{k_p' \cdot \frac{\pi}{6} d} \cdot L \quad (7-9)$$

Where: ε_p is dielectric constant of catalyst pellet, k_p' is experimental coefficient.

Substitute the equation (7-3), (7-4) into (7-9) and simplify to obtain equation (7-10),

$$C_{p_i} = \frac{6\varepsilon_p \cdot k}{k_p'} \cdot \frac{D_o - D_i}{\ln \frac{D_o}{D_i}} \quad (7-10)$$

To define $k_p = \frac{k_p'}{k}$, then

$$C_{p_i} = \frac{6\varepsilon_p}{k_p} \cdot \frac{D_o - D_i}{\ln \frac{D_o}{D_i}} \quad (7-11)$$

Substitute the equation (7-11) and (7-5) into (7-6) and simplify to obtain the (7-12) of the total pellet equivalent capacitance.

$$C_p = \frac{C_{p_i}}{n} = \frac{12\varepsilon_p}{k_p \cdot \ln \frac{D_o}{D_i}} \cdot d \quad (7-12)$$

In the same way, the single and the total gap space equivalent capacitance are obtained as the formulation (7-13) and (7-14).

$$C_{g_i} = \frac{\varepsilon_g \cdot \pi}{k_g (1 - \frac{\pi}{6})} \cdot \frac{D_o - D_i}{\ln \frac{D_o}{D_i}} \quad (7-13)$$

$$C_g = \frac{C_{g_i}}{n} = \frac{2\pi\varepsilon_g}{k_g (1 - \frac{\pi}{6}) \cdot \ln \frac{D_o}{D_i}} \cdot d \quad (7-14)$$

Where: ε_g is the dielectric constant of gap space and k_g is the experimental coefficient.

Assuming to define A and B as constant value of k_g and k_p , respectively.

$$A = \frac{12\varepsilon_p}{k_p \cdot \ln \frac{D_o}{D_i}}, \quad B = \frac{2\pi\varepsilon_g}{k_g (1 - \frac{\pi}{6}) \cdot \ln \frac{D_o}{D_i}},$$

The total capacitance of the pellet and the gap space are written as follows;

$$C_p = A \cdot d \quad (7-15)$$

$$C_g = B \cdot d \quad (7-16)$$

7.3.2 Analysis

According to the equivalent circuit in Figure 7-5, the total equivalent capacitance of the dielectric material of a packed bed reactor (except the air gap) is as follows:

$$\frac{1}{C_{dp}} = \frac{1}{C_d} + \frac{1}{C_p} \quad (7-17)$$

Then substitute (7-8) and (7-15) into (7-17) to obtain formulation (7-18).

$$C_{dp} = \frac{Ad \cdot C_d}{Ad + C_d} \quad (7-18)$$

According to the Manley Equation [15-16], the Discharge Power, P (W) is expressed as;

$$P = 4f \cdot \frac{(C_{dp})^2}{C_g + C_{dp}} \cdot V_0(V_p - V_0) \quad (7-19)$$

Where: f (Hz): frequency of the applied AC voltage (Hz), V_p (V): peak value of the input voltage, V_0 (V): the onset voltage of the discharge.

Substitute the equation of (7-16), (7-18) into (7-19) and simplify to obtain the equation (7-20).

$$P = \frac{4fV_0(V_p - V_0) \cdot A^2C_d \cdot d}{A^2B \cdot d^2 + (A^2C_d + 2AB \cdot C_d) \cdot d + (A+B) \cdot C_d^2} \quad (7-20)$$

To define that $y = P$; $x = d$; $a = A^2B$; $b = A^2C_d + 2AB \cdot C_d$; $c = (A+B)C_d^2$; $e = 4fV_0(V_p - V_0) \cdot A^2C_d$, then the (7-20) changes into (7-21).

$$y = \frac{ex}{ax^2 + bx + c} \quad (7-21)$$

For $\frac{dy}{dx} = 0$, eq. (7-22) can be obtained.

$$x_{opt} = \pm \sqrt{\frac{c}{a}} \quad (7-22)$$

To substitute the equation of (7-22) into (7-21) and obtain the (7-23),

$$y_m = \frac{e}{b \pm 2\sqrt{ac}} \quad (7-23)$$

In eq. (7-23), if $b^2 - 4ac < 0$, then its curve is shown in Figure 7-6.

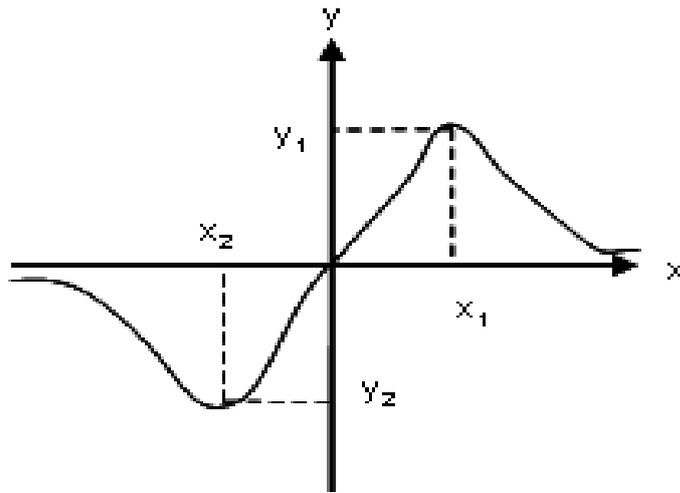


Fig.7-6 Eq. (7-23) with $b^2 - 4ac < 0$

When $x_1 = \sqrt{\frac{c}{a}}$, there is a Maximum value , $y_1 = \frac{e}{b + 2\sqrt{ac}}$; When $x_2 = -\sqrt{\frac{c}{a}}$, there is a Minimum value , $y_2 = \frac{e}{b - 2\sqrt{ac}}$.

For the function of (7-23), if the $b^2 - 4ac > 0$, then its curve is shown in Figure 7-7.

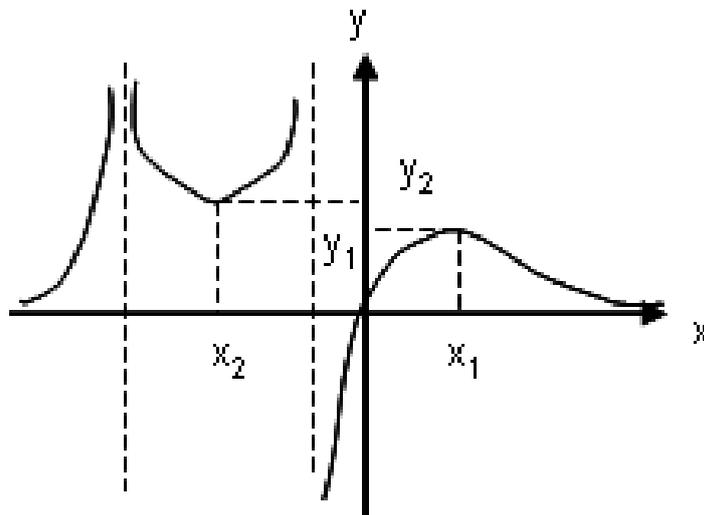


Fig.7-7 Eq. (7-23) with $b^2 - 4ac > 0$

When $x_1 = \sqrt{\frac{c}{a}}$, there is a Maximum value , $y_1 = \frac{e}{b + 2\sqrt{ac}}$; when $x_2 = -\sqrt{\frac{c}{a}}$, there is a Minimum value , $y_2 = \frac{e}{b - 2\sqrt{ac}}$.

Combined with the specific situations in the study, the value of x and y must be positive, therefore only the curve in the first quadrant is valid, so $x = \sqrt{\frac{c}{a}}$ and

$$y_{\max} = \frac{e}{b + 2\sqrt{ac}}.$$

When the diameter of catalyst pellet is: $d_{opt} = \frac{C_d}{A} \sqrt{\frac{A+B}{B}}$ (7-24)

The maximum value of Discharge Power, P_{\max} is;

$$P_{\max} = 4fV_o(V_p - V_o) \cdot \frac{AC_d}{2\sqrt{(A+B)B} + A + 2B} \quad (7-25)$$

7.4 Results and discussion

The relationship between the input voltage and the discharge power at different catalyst sizes is shown in Figure 7-8.

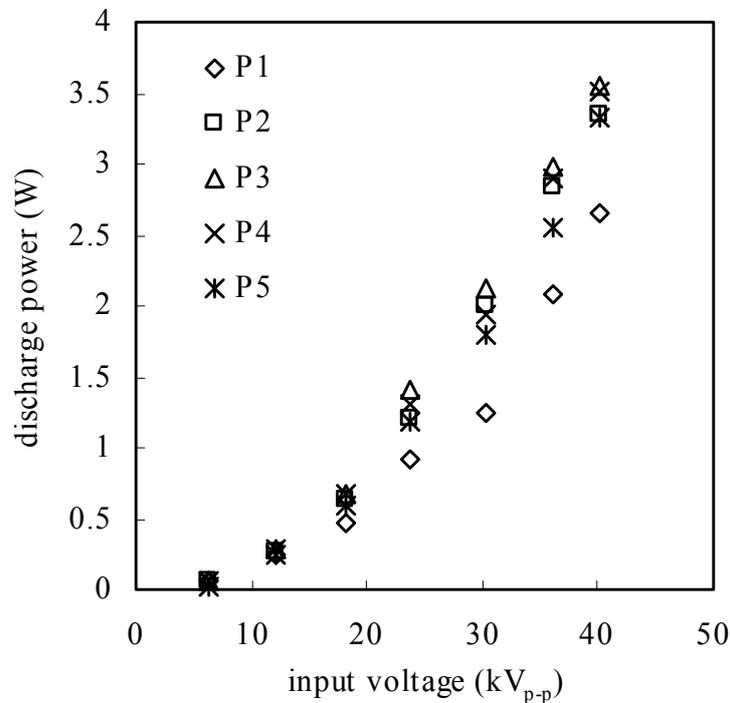


Fig.7-8 The relation between voltage and discharge power in difference of catalyst sizes

Diameter P1; 1.2mm, P2; 3.0mm, P3; 3.8mm, P4; 4.8mm, P5; 6.0mm

Figure 7-8 indicates that, (a) the minimum input voltage V_o (about $5kV_{p-p}$) for starting the discharge does not connect with the pellet diameter, (b) with increasing the input voltage V_p , effect of the diameter on the discharge power becomes significant. These results support eq.(7-19) that the discharge power has relationship with (V_p-V_o) .

With this experiment, parameters were $D_o=27mm$, $D_i=8mm$, $\delta=2mm$, $L=60mm$, $f=60Hz$, $V_o=5kV$, $\epsilon_g=1$, $\epsilon_d=5$, $\epsilon_p=2.1$. Substituting these values into equals (7-24) and (7-25) and substituting the value of A, B, C_d , V_p into eq. (7-20), we can have comparison of the calculation and the experimental data is shown in Figure 7-9. The coefficients k_p and k_g are obtained by the curve fitting to be; $k_p=21.259$, $k_g=0.0003597$, $C_d=3.7nF$.

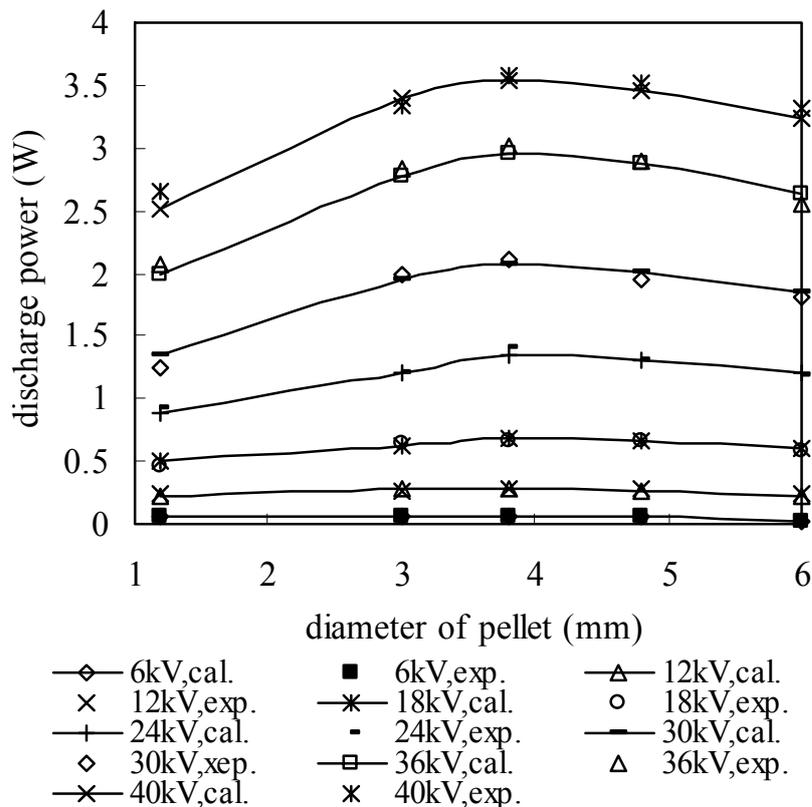


Fig.7-9 Comparison of the calculation and the experiment of the catalyst diameter vs. discharge power at different voltage values

From this comparison, followings remarks can be made. (a) The theoretical calculation shows identical trend with the experimental data of the discharge power vs. diameter. (b) When the diameter of the pellet is an optimal value d_{opt} , the discharge power has a maximum value. When d is larger or smaller than d_{opt} , the capacitance of the reactor reduces, which results in lower discharge power. (c) The higher the input voltage, the more significant the effect of diameter. With increasing the input voltage, the number of discharge filaments in the gap space increases until the total surface of the pellet is covered. Therefore the larger the diameter is, the more wide range of discharge power is.

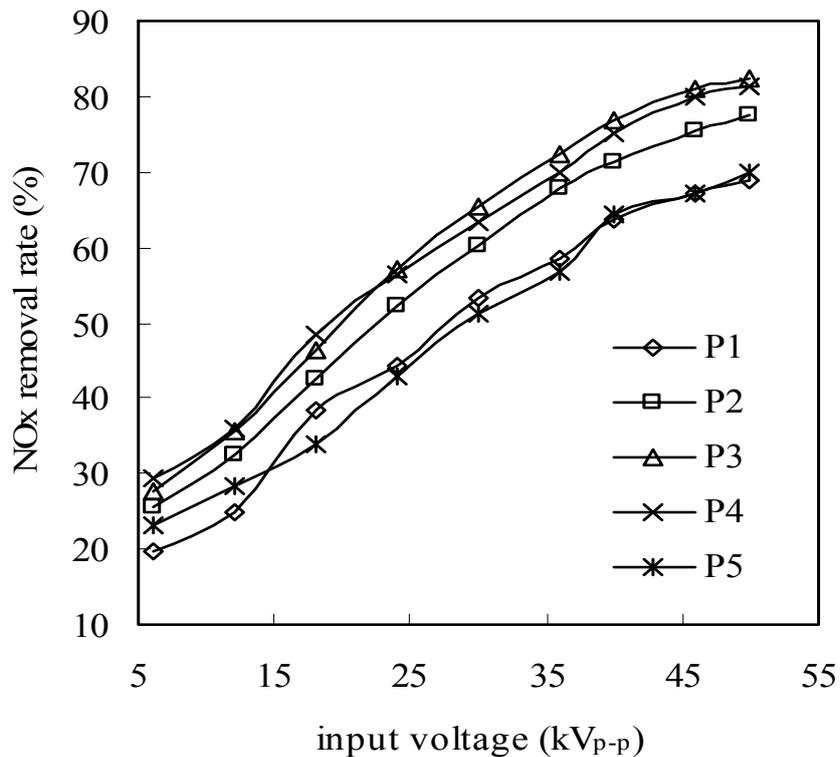


Fig.7-10 The relationship between the input voltage and NO_x removal rate at condition of different catalyst sizes

Diameter P1; 1.2mm, P2; 3.0mm, P3; 3.8mm, P4; 4.8mm, P5; 6.0mm

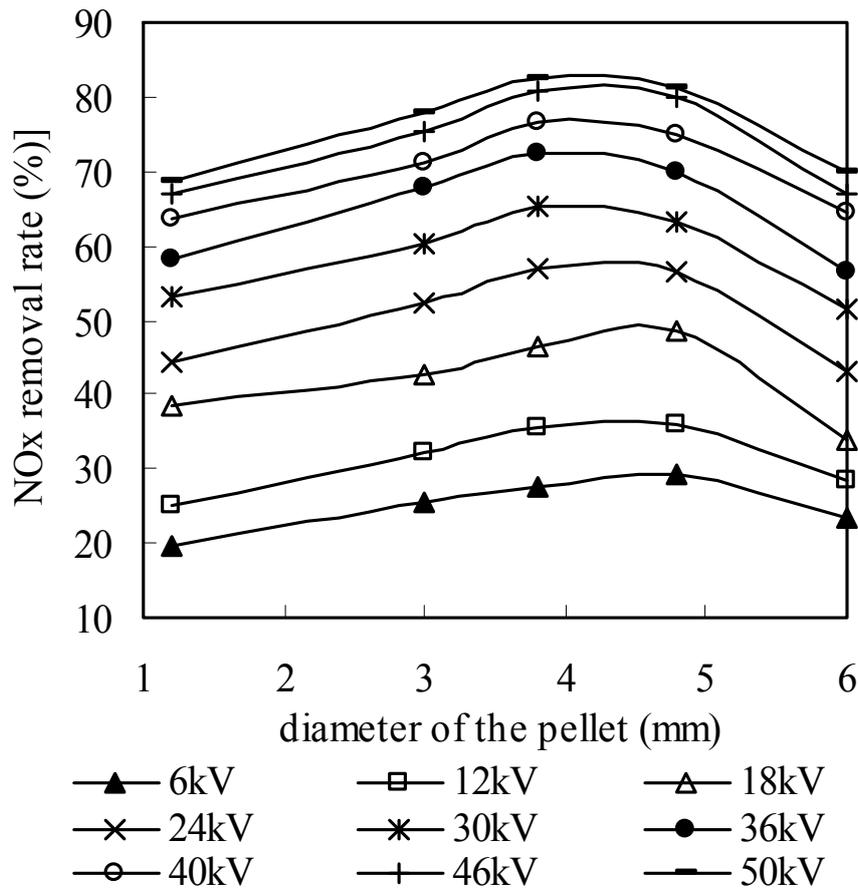


Fig.7-11 The relationship between catalyst size and NO_x removal rate at condition of different input voltages

Figure 7-10 shows the relation between the NO_x removal rate and the input voltage. The increasing slope of the NO_x removal rate is large at lower voltage region and then becomes smaller. Figure 7-11 indicates the relationship of NO_x removal rate vs. the diameter. The NO_x removal rate showed its maximum at an optimal diameter. This trend is the same as the discharge power. In this experiment, the optimum diameter was about 4mm at the condition of that input voltage is 40kV_{p-p} and the maximum value of NO_x removal rate is 76.67%.

7.5 Conclusion

Electrical characteristics of a packed bed reactor have been simulated by using a simplified model. Effect of diameter, d , of the pellet has been calculated against the discharge power, DP. Using fitting parameters, the simplified model can explain the trend of DP vs. d , and the calculation shows a maximum DP at an optimal diameter d_{opt} . Experimental data showed that, with increasing of the input voltage, effect of d on DP become more significant, as expected by the model. The measured NO_x removal rate showed the same trend as that of DP.

In the experimental condition studied, the optimum catalyst diameter was about 4mm, when the input voltage was $40kV_{p-p}$, DP was 29.3W and NO_x removal rate was 76.67%. Though the model is simple, it could provide a theoretical basis for selecting a suitable diameter of catalyst for a packed bed reactor.

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8. Conclusions and expectations

8.1 Conclusions

Non-thermal plasma (NTP) assisted catalysis is one effective method to remove NO_x from diesel engine exhaust. This thesis reviewed the development of plasma and catalyst investigation firstly, and then prepared three kinds of catalyst which are based on Sepiolite, Attapulgite clay and coal derived Activated Carbon, and evaluated their performances and propose plasma catalysis model. The conclusion is showing as follow:

(1) As the Sepiolite, Attapulgite clay and Coal-based Activated Carbon has a special structure, such as a large of surface area, a number of micro-pore, a good stability and low costs, they are suitable as catalyst carrier.

(2) Some unpurified materials are in the original of Sepiolite, Attapulgite clay, so acid washing can remove them effectively. Meanwhile, acid modified treatment can increase and improve the surface area and structure of Sepiolite and Attapulgite clay.

The results of this study have proved the acid concentration, acid washing time, the kind of acid can affect the activity of catalyst and NO_x removal rate effectively. With increasing the acid washing time and acid concentration, the activity of the catalyst increases firstly and then decreases. There is an optimum value for NO_x removal rate. The affect of washing by HNO_3 is better than of HCl .

(3) The calcination temperature of activated catalyst has a significant influence on the NO_x removal rate. When the temperature is in the range of from $400\text{ }^\circ\text{C}$ to $600\text{ }^\circ\text{C}$, the catalyst has a good ability for NO_x absorbing and storage. If the

temperature is too low, the catalyst activity can not achieve sufficiently. If the temperature is too high, the structure of catalyst will be melted and the surface area decreases.

(4) NO_x removal rate increases with the increasing of input voltage. At the beginning, the reaction rate is high and then gradually decreases and trends to be stabilized, because NTP can effectively reduce the initial activation energy, and enhance the adsorption and storage function of catalyst.

(5) The ion of NO_3^- was detected in the leaching solution of used CACC by the Nitrate Ion Detector. According to the ion of NO_3^- and PH value of the leaching solution, the NO is absorbed on the surface of CACC firstly and then oxidized to NO_2 and further to NO_3^- .

(6) The gas concentration, gas space velocity and the catalyst packed weight have certain effect on the NO_x removal ratio. The NO_x removal rate increases with increasing the initial NO concentration, when the initial NO concentration exceeds a certain critical value, the NO removal ratio decreases. With increasing of the space velocity, the NO_x removal rate increases and then decreases, showing a peak value of the removal rate.

(7) The order of NO_x removal efficiency is: plasma with catalyst > Plasma with glass bead > only catalyst > only plasma, because the catalyst has not only the performances of catalysis, adsorption and storage, but also fully play the role of the DBD.

(8) In terms of the NO_x removal rates at the same condition, it is found that the Coal-based activated carbon gives the best performance in contrast with the modified sepiolite catalyst, modified attapulgite clay catalyst. The catalyst is very cost effective and it can be easily regenerated.

(9) By the results of a simplified model and experiment, there is a suitable size of catalyst in the DBD reactor and its effects on the discharge power and NO_x removal rate. The optimal diameter of catalyst can be predicted in terms of structure of reactor and operational conditions.

8.2 Expectations

Coal-based activated carbon catalyst and plasma synergistic effect is better than the catalyst modified Sepiolite catalyst synergy effect, but modified Sepiolite catalyst with the plasma a considerable synergistic effect, and because of the price of Sepiolite, taking economic into consideration, the method of preparing Sepiolite Catalyst needs a further improvement, to provide efficient carrier catalyst.

This research need through to improve and develop can be applied to areas where it purifies the gas including of low concentration NO in the future, for example of the large underground car park or large automobile tunnels and other places.

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