Catalyst Size Impact on Non-Thermal Plasma Catalyst Assisted deNO$_x$ Reactors

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Abstract: Non-thermal plasma assisted catalytic reaction is an effective way to remove NO$_x$ from automobile exhaust. Dielectric barrier discharge is used to generate non-thermal plasma in a packed bed of solid catalyst particles acting as dielectric in this study. The size of the catalyst particle affects gas-solid phase chemical reactions. At the same time, the geometry of the particles affects the space factor of the packing and the characteristics of the dielectric barrier discharge, such as power. The NO$_x$ removal efficiency is also affected. The results of this study show that the diameter of the catalyst particle affects NO$_x$ removal efficiency. A minimum peak value of discharge power can be found at a specific particle diameter for a given reactor and power supply. NO$_x$ removal efficiency increased with the size of the catalyst to a peak before decreasing on a similar pattern. Therefore an optimum pellet size can be found that that gives maximum removal efficiency. In a catalyst packed bed reactor assisted by dielectric barrier discharge it is important to choose the optimum diameter of catalyst particle.

Keywords: Non-Thermal Plasma, Dielectric Barrier Discharge, De-NO$_x$, Catalyst Particle Diameter

1 INTRODUCTION

Non-thermal plasma (NTP) with high active power can effectively generate free electrons, ions, living radicals and many species of excited particles. By generating high activity atomic oxygen (O) and the free radicals with the intensive oxidation produced by atomic oxygen oxidize NO to NO$_2$ gives it specific superiority in NO$_x$ removal from automobile exhaust. Besides, it does not affect automotive engine performance due to simple structure [1, 2, 3, 4]. With NTP assisted catalyst, NO$_x$ removal efficiency is further improved and energy consumption is evidently reduced.

Dielectric barrier discharge (DBD) is a method to generate NTP, as the gas is broken down by high voltage and the discharge phenomenon in gas, gas-solid, first and secondary streamer discharge improves active species generation [5]. With catalyst assisted the active materials get high-selectivity, as the surface of catalyst is at negative potential compared with potential of NTP, the positive ion is accelerated by sheath voltage to strike on the catalyst surface, as well as the adsorption of reactant and product departure in and out of the catalyst surface is promoted. The NO$_x$ concentration of automobile exhaust is 200 ppm-300 ppm, in generally, the NO$_x$ adsorbed on the catalyst surface can increase concentration of reactant of the NO$_x$ and improve reaction speed. In the process, intermediate product, such as NO$_3^-$, is adsorbed and stored on the catalyst surface and enhanced by NTP will be reduced by hydrocarbon in exhaust gas to produce N$_2$ [6,7].

In the study, the solid catalyst particles packed in the reactor act as barrier dielectric. The size of the catalyst particle affects gas-solid phase chemical reactions and internal and external diffusion of gas in the catalyst. At the same time, the geometry of the particles affects the packing factor and the characteristics of the DBD, such as discharge power. The NO$_x$ removal efficiency is also affected. The relation between catalyst size and discharge power and NO$_x$ removal efficiency was investigated, respectively. The basic information provides to choose optimum catalyst size in the DBD assisted catalyst packed bed reactor.

2 EXPERIMENTAL SETUP AND METHOD

The experimental setup used is presented in Fig. 1.

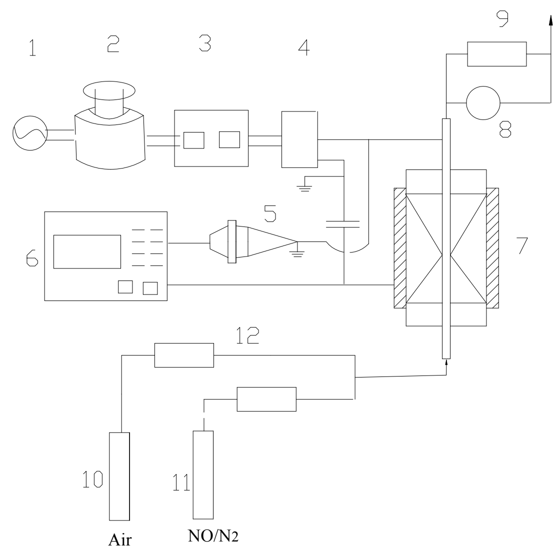

Fig. 1 Experimental setup

1. Power line; 2. Transformer; 3. Power Meter; 4. 100 V: 15 kV, transformer; 5. HV probe; 6. Oscilloscope; 7. DBD assisted catalyst packed bed reactor; 8. NO$_x$ sensor; 9. Horiba ; 10. Air cylinder; 11. NO Gas Cylinder. 12. Mass flow controllers

The reactor outer wall is a 2 mm thick quartz glass tube: 27 mm inner diameter, 120 mm long. A 60 mm long aluminum tape covering the quartz glass tube and a central aluminum tube are used as electrodes. The catalyst is packed in the glass tube between aluminum pipe and quartz wall. At both ends the reactor is sealed with silicon rubber blocks.

A neon transformer: 100 V: 15 kV, 60 Hz is use as high voltage power supply. Output voltage of HV transformer is regulated with a variable output transformer (0 to 130 V).

A power meter (HIOK1 3186, Digital power Hitester) is used to measure the input power. The digital oscilloscope (Tektronix TDS2014, four channel digital storage oscilloscope, 100 MHz, 1Gs/s) with HV Probe (Tektronix P6015 A 1000×3.5 PF, 100 MΩ) is used to measure the high voltage supplied to the reactor and the discharge current is determined from voltage drop on capacitor C. Discharge power is computed by applying Lissajous method. V_{PP} values are used on high voltage scales.

A simulated exhaust gas is provided to the reactor by mixing cylinder air at controlled ratios (mass flow controller MFC) with nitrogen balanced NO (N_2 balanced NO: 1990 ppm). Simulated gas flow is set at 3L/min with NO_x concentration set at 200 ppm. A zirconia NO_x-O_2 sensor (NGK) and FTIR are used for NO_x measurement.

Five sets of catalyst particles in different size ranges are used as packed fraction to fill a constant volume in the reactor. The average diameters of catalyst particles is 6.0, 4.8, 3.8, 3.0 and 1.1mm and are further marked as P1, P2, P3, P4, and P5 respectively. The reactor is in ambient temperature.

3 EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Correlation between Input Power and Diameter of Catalyst Particles

In Fig. 2 the correlation between voltage and input power is given for P1, P2, P3, P4 and P6:

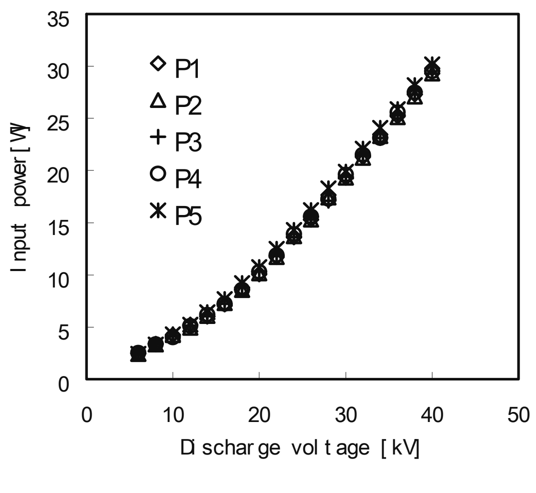

Fig. 2 Correlation between high voltage and input power for P1, P2, P3, P4, P5

Fig. 2 indicates that input power increases with discharge voltage. Catalyst particle diameter has insignificant impact on input power when discharge voltage is increasing from 6 kV_{pp} to 40 kV_{pp}, as the packed volumes and resistances are similar to for different size catalyst in the DBD catalyst packed bed reactor.

3.2 Correlation between Discharge Power and the Diameter of Catalyst Particles

Fig. 3 shows the correlation between discharge voltage and calculated discharge power for different particle diameters.

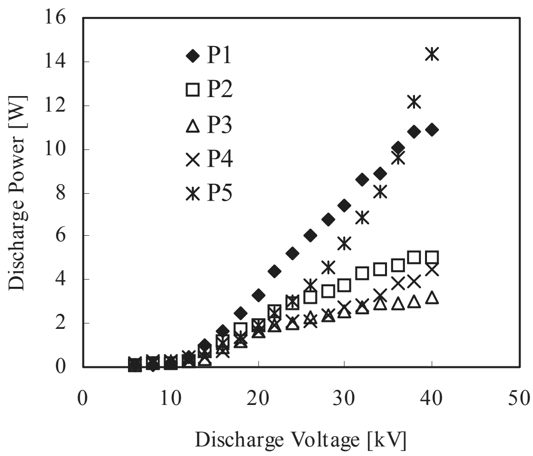

Fig. 3 Correlation between voltage and discharge power for different particle diameter

Fig. 3 indicates that discharge power increases with increasing of high voltage in different particle diameter, and slope of curve for different particle size is different. The phenomenon can be explained with Manley's equation which shows the rule of power consumption during plasma discharge [8,9], For the study the concrete expression is:

$$P = 4f \cdot \frac{C_G^2}{C_G + C_P + C_A} \cdot V_0 (V_p - V_0) \quad (1)$$

where: P—power consumption [W]; f—frequency of AC source (60 Hz); C_G—Capacitance of quartz glass tube (reactor shell) [F]; C_P—Capacitance of catalyst particle filled in the reactor [F]; C_A—Capacitance of gaps among catalyst particle in the reactor [F]; V_0—the onset voltage of the silent discharge insider the reactor [V]; V_p—peak of output AC. power voltage of the reactor [V].

According to formula (1), when the discharge voltage is smaller than 12 kV, the discharge power is very small, as V_p is nearly to V_0 and (V_p-V_0) is very small. When the voltage is bigger than 12 kV, the discharge power increases with V_p increasing. With the catalyst particle size changed, the capacitance of C_P and C_A have a different value, so curve slope varies with the catalyst particle diameter. Compared with Figs. 2 and 3, it shows the input power is bigger than discharge power at the same as voltage, because some energy is consumed to produce heat.

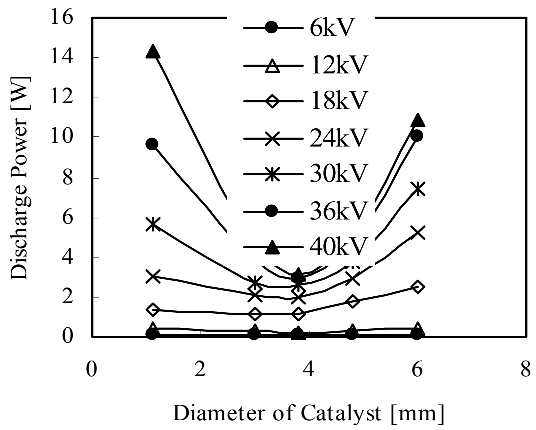

Fig. 4 Correlation between catalyst diameter and discharge power at different discharge voltages

For different discharge voltages, Fig. 4 shows the correlation between discharge power and catalyst particle diameter. When input voltage is lower, catalyst diameter has little effect on discharge power. Catalyst diameter effect on discharge power is increasing with discharge voltage. Discharge power decreases with increasing of catalyst diameter as long as catalyst diameter is lower than critical value. When catalyst diameter is larger than critical value discharge power will increase with catalyst diameter, Power consumption is minimum for optimum diameter of catalyst particle.

For spherical capacitor, according to basic principles, the capacitance of spherical catalyst is related to catalyst diameter and the change of total capacitance produced by catalyst affects discharge power. From formula (1), packed bed voids in the dielectric barrier discharge reactor affects discharge power. When the diameter of catalyst is bigger than critical value, capacitance of C_P will increase with decreasing of catalyst particle diameter and power consumption will decrease. When the diameter of the catalyst is smaller than critical value, agglomeration of the fine particle is gradually remarkable with further decreasing of catalyst diameter and the capacitance of C_P decrease due to increasing of cluster renewal so that power consumption increases. Power consumption will have a minimum peak with variation of catalyst particle diameter

4 CORRELATION BETWEEN NOX REMOVAL RATIO AND CATALYST PARTICLE DIAMETER

Fig. 5 indicates that NO$_x$ removal ratio increases with input voltage increasing and slope of curve is different. With input voltage increased a lot of activity atomic oxygen (O) produce in the DBD reactor, the concentration of atomic oxygen (O) increases and chemical reaction is speedup, so NO$_x$ removal efficiency increases with increasing of input voltage.

The contact surface between catalyst and reagent gas increases with decreasing of catalyst size, the larger contact surface can reduce the diffusion resistance inside and outside catalyst particle, According to formula (2) of Thiele modulus and formula (3):

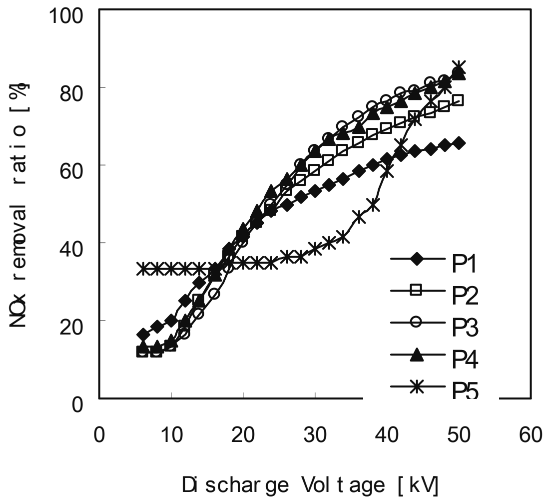

Fig. 5 Correlation between input voltage and NOx removal ratio for different catalyst diameters

$$\varphi = \frac{S_P}{\alpha_P}\sqrt{\frac{k_p}{D_e}} \tag{2}$$

where: φ—Thiele modulus; S_P—the volume of catalyst size [m^3]; α_p—surface of catalyst particle [m^2]; k_p—reaction rate constant based on catalyst size [(mol/m^3)$^{1-n}$s^{-1}]; D_e—effective diffusion coefficient in porous structures [m^3/m].

$$\eta = \tanh(\varphi) / \varphi \tag{3}$$

where: η—effectiveness factor.

When the input voltage is bigger than18kV, effectiveness factor increases with catalyst size decreasing, so the NO$_x$ removal ratio increases with catalyst particle diameter decreasing, but except for the smallest particle, such as P5, because the agglomeration of the fine particle is gradually remarkable. For special case of P5, when the input voltage is bigger 35 kV, static-electric force is big enough to blow off agglomeration, so NO$_x$ removal ratio increase promptly with input voltage increasing. Under the condition of critical diameter of catalyst particle, the discharge power is the lowest and a majority of input power changes into thermal energy to heat the catalyst particle. The higher temperature rises, the more reaction rate takes place, so the NO$_x$ removal efficiency is controlled by both of conditions, which one is catalyst size and the other is high voltage.

When the input voltage is less than 18 kV, the input power is smaller, temperature of catalyst particle is lower and does not supply enough starting energy to active catalytic reaction, the chemical reaction rate is determined by the concentration of activity atomic oxygen (O) which produces by discharge power. When the particle diameter is smaller or bigger the discharge power is bigger, so NO$_x$ removal efficiency is bigger and controlled by only of conditions which is discharge power.

When the input voltage is 18 kV or so, the NO_x removal ratio hardly changes with the catalyst size, as the combined effects of various factors, which come from discharge power, temperature of reactor, gas diffusion and diameter of catalyst particle, is rather equal.

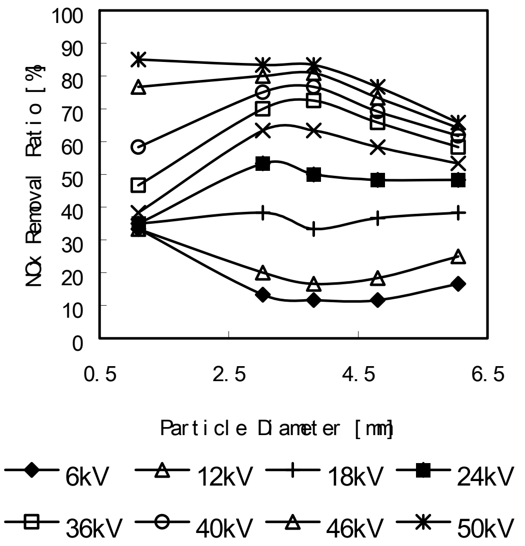

Fig. 6 Correlation between catalyst diameter and NO_x removal ratio for different high voltages

Fig.6 indicates that when voltage is lower, such as 6 kV and 12kV, and diameter of catalyst particle is bigger or smaller, input power consumption is bigger and more active groups are generated which is good to NO_x removal, the NTP plays a leading role, so the NO_x removal ratio is more than the middle diameter particle.

When the voltage is higher, such as 50kV, with the diameter of catalyst decreasing, the surface between solid catalyst and gas increases and the effect of internal and external diffusion of catalyst particle is eliminated, the catalyst assisted NTP play a leading role. In the case, the NTP excites reactive gas and provides more free electrons to catalyst surface and is good for gas adsorption and reaction, so the activity of catalyst is improved and the NO_x removal ratio increases.

5 CONCLUSIONS

Size of the catalyst particle affects gas-solid phase chemical reactions, the geometry factor of the packed bed reactor and the characteristics of dielectric barrier discharge. The NO_x removal efficiency is also affected. The results of this study show the effect of diameter of the catalyst particle on NO_x removal efficiency is more evident with increasing the input voltage. With higher input voltage conditions, the discharge power decreased when finer particles were used, however, the discharged power increased with catalyst size, and there existed the minimum peak value of discharge power at a certain particle diameter. NO_x removal efficiency increased with increasing the size to a certain value and then the efficiency decreased. There is an optimum particle size that gives the maximum removal efficiency. It is important to choose optimum diameter of catalyst particle in the catalyst packed bed reactor assisted by dielectric barrier discharge.

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