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A Study of NO_x Purification based on Plasma-Assisted Catalysis

Li bing and Chu jiangwei
College of Traffic, Northeast Forestry University, 26 Hexing Road, Harbin, 150040, China

Abstract: Herein, we demonstrate a NO_x purification technology based on plasma-assisted catalysis and test the purification efficiency under various experimental conditions. It has been shown that whatever the experimental condition is, the NO_x purification efficiency is always the best by using the combination of plasma and nano-TiO_2. Moreover, the purification efficiency gradually increases with the increase of applied voltage. Meanwhile, higher flow rates of pollution gases would reduce the efficiency of plasma-catalytic combined NO_x purification. This could be attributed to the reason that the contact probability between pollutants and active species in the reactor decreases at higher flow rates.

Key words: Photocatalysis, nitrogen oxides, purification, plasma

INTRODUCTION

With the rapid development of China's automobile transportation, automobile exhaust has become the main source of urban air pollution. The hazardous components in automobile exhaust, including CO,HC,NO*x* and PM have caused great harm to human health and environment. In particular, the NOx content is relatively high in the exhaust of lean-burn gasoline and diesel engines. As a result, the high-efficiency purification of NOx has become a major topic of today's automobile exhaust control.

Over the past 20 years, plasma purification has become an emerging environmental friendly technology and has been widely applied in air pollution control (Kim *et al*., 2008; Van Durme *et al*., 2007; Zhu *et al*., 2009). At present, plasma-catalytic combined processes are applied to deal with hazardous gases around the world (Lu *et al*., 2009; Zhu *et al*., 2008). Therefore, the NO_x purification with plasma-assisted catalysis is investigated in this article so as to get a better understanding of relations between various parameters and purification efficiency.

MATERIALS AND METHODS

Experimental systems: All the experiments are carried out in a homemade reactor. The reactor can be divided into three parts, namely, the inlet, gas purification region and the outlet. The inlet is cylindrical in order to mimic car exhaust pipes. The purification region is a cuboid, which is used for plasma-assisted catalysis. The outlet is designed in such a way that it should be able to reduce turbulence and ensure effective gas discharge from the reactor. Therefore, a semi-sphere outlet is used to reduce the emission rate. Two fans are installed in the purification region in order to control the flow rate. Considering the corrosive effect of automobile exhaust, the case of reactor is made up of transparent glass. The glass case also allows for the easy observations of initial corona and changes in the reactor. The dimension of the reactor is 110×80×80 mm. The experimental reactor contains a plasma module, a nano-catalysis module and a plasma catalysis module. Each plasma module is connected to a homemade AC/DC power supply so as to generate corona discharge at corresponding areas. The homemade wire-to-plate corona contains a plate anode of stainless steel and a cathode of copper wire, which is shown in Fig. 1.

TiO_2 preparation and loading of nano-catalyst: Industrial titanic acid is placed in a beaker and mixed with a certain amount of distilled water. The mixture is stirred and sonicated to yield a well-dispersed titanic acid suspension. Concentrated sulfuric acid is slowly added to the suspension under stirring heat. The H_2TiO_3 is fully dissolved which yields a $TiOSO_4$ solution. The solution is diluted after cooling down and active carbon is added. The solution is well stirred and a clear $TiOSO_4$ solution is obtained after filtration. A certain amount of $TiOSO_4$ solution is mixed with ammonia solution to conduct hydrolysis. The precipitate is filtered and washed for multiple times with distilled water to yield nano-titanic sol. Cleaned stainless steel substrate (nano-catalytic module in Fig. 1) is immersed into the sol and dip coated with catalyst at the speed of 5 cm min^{-1}. The substrate is then air-dried. This procedure is repeated for several times to obtain desired catalyst loading.

Corresponding Author: Chu Jiangwei, College of Traffic, Northeast Forestry University, 26 Hexing Road, Harbin 150040, China

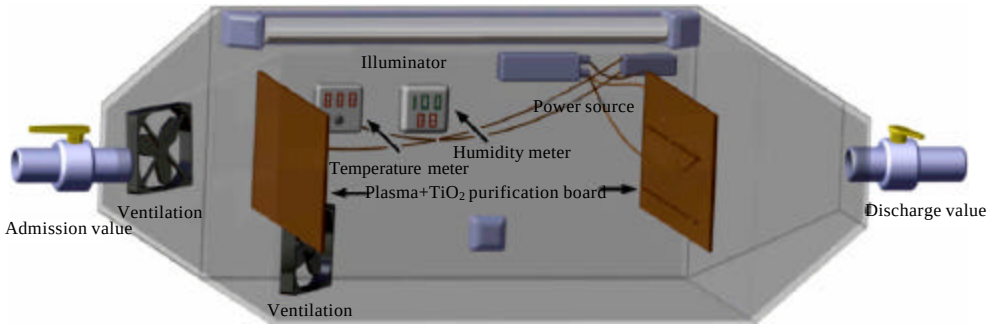

Fig. 1: Schematic diagram of examination reactor

Experimental methods

Experimental conditions: Considering the working conditions of plasma reactor and the emission characteristics of gasoline engine, the experimental parameters are selected as follows:

- **Applied voltage:** Considering the plasma reactor and practical working conditions, the applied voltage ranges from 0-20 kV. Meanwhile, the influence of applied voltage on the whole reaction is tested by varying the voltage applied on plasma reactor
- **The control of flow rate:** The flow rate of emission collection channel is chosen from one of the following speed: the flow rate of idling engine, the flow rate of idling engine+primary fan, the flow rate of idling engine+secondary fan

Design of experiment: The design of experiment is based on univariate analysis. That is, a certain parameter is chosen as the variable and changed during experiments while the other parameters remain the same. The corresponding change in experimental results is observed so as to find out the influence of this parameter on experiments.

Experimental procedure: Instrument setup and preheating. First, the gasoline engine is connected to each part of the reactor. The engine is warmed up by idling for 30 min

- **Turn on gas collector, set parameters:** After the initialization of gas collector, the initial concentration of exhaust is collected for 5 min. The step is repeated for several times and the average value is defined as the gas concentration under such conditions.
- Vary certain experimental parameters and conditions, repeat step to obtain corresponding data until the end of experiments

RESULTS AND DISCUSSION

Comparison of NO_x purification with plasma, photocatalysis and plasma-catalytic coupling: Results. The purification rates of NO_x with plasma, photocatalysis and plasma-catalytic coupling under different flow rates are shown in Fig. 2. It can be seen from Figure 2 that the purification effect of plasma-only process is similar as that of the photocatalytic purification. That is, the purification rate decreases with the increase of flow rate. When plasma and photocatalysis are coupled, the effect of pollutant purification significantly increases under the same flow rate. When the flow rate is equal to the speed of idling engine+primary fan, the purification rates are 40.5%, 15.7% and over 58% for photocatalysis, plasma and their combination, respectively. The reason why plasma-assisted photocatalysis would result in a higher purification effect for NO_x could be deducted from following experiments.

Result analysis-mechanisms of synergic purification: There are three major ways for NO_x decomposition under synergic plasma-catalytic coupling. The first one involves the direct interactions between electric field and NO_x molecules which make it easier to break down NO_x molecules. Secondly, plasma containing hot electrons, semi-stable nitrogen and vibrationally excited nitrogen induces the formation of hydroxyl radicals and active oxygen atoms through collisions with oxygen and water molecules. These active radicals may break down NO_x by molecules chemical reactions. Finally, the UV light emission from semi-stable nitrogen and vibrationally excited nitrogen may be applied to activate photocatalyst (nano-TiO_2) so as to induce oxidation reactions for NO_x decomposition.

Decomposition of NO_x by plasma-only process: Plasma generated by the high energy electric field of corona

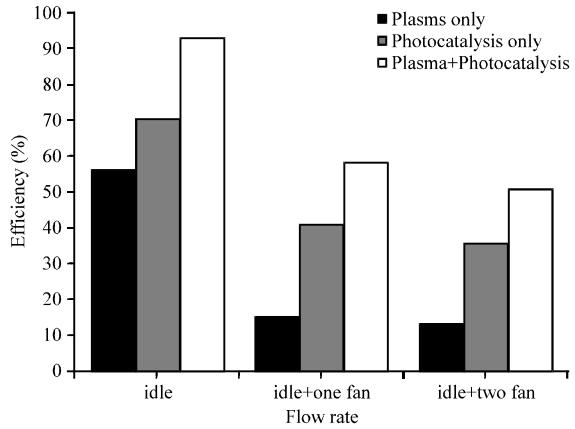

Fig. 2: Comparison of NOx purification under plasma, photocatalysis and plasma-catalytic coupling

discharge is able to further reduce the concentration of NO_x in the reactor independently. This could be attributed to two reasons. First, active electron-hole pair is formed on the surface of nano-TiO_2 catalyst under the effect of high energy electric field. In addition, NO_x molecules are impacted and activated by hot electrons generated in high energy electric field which facilitates the decomposition of pollutants.

Active species: The decomposition of NO_x with plasma-assisted catalysis involves a plasma cleaning mechamism in which the active oxygen atom (O) and peroxide ion (O^{2-}) generated by discharge are able to react directly with NO_x. In addition, short-lived species generated during corona discharge, such as hydroxyl radical and peroxide ions, are able to be adsorbed by catalyst surface. These short-lived species can interact with adsorbed NO_x molecules and thereby lead to better decomposition efficiency. Hydroxyl radical is considered to be the main active compound in plasma. Decomposition of inorgamic compounds by hydroxyl radical has no selectivity and the products of NO_x decomposition include carbon dioxide and water.

No_x molecule is activated by hot electron impact when passing through the plasma. The excited molecule will be oxidized and decomposed more easily by the active species on catalyst surface. As a result, the decomposition rate increases. Compared with plasma-only or catalyst-only processes, the combination of multiple functions results in a higher NO_x decomposition rate for plasma-assisted catalysis.

UV emission of semi-stable nitrogen: The field strength of different locations varies significantly in an uneven high energy electric field which causes difference in discharge processes. When the voltage is low, the field strength may already exceed the critical value at areas with a small radius of curvature and a self-sustaining discharge is obtained. The field strength reduces dramatically at positions far away from this location so that the ionization can only be restricted to the space near the tip. The uneven electric field in our experiments is located at the neighborhood of the central needle electrode. The association of plasma-generated ions induces light emission. Part of the light is in the visible range while the major portion is UV light. The UV light is desired for the excitation of TiO_2 and photocatalysis. The decomposition of NO_x is able to be realized after the activation of TiO_2.

It has been shown by relevant literatures that free electrons undergo collisions with abundant nitrogen molecules in the air (Lin *et al.*, 2004).The life of semi-stable, excited state nitrogen molecules could reach up to several seconds. The UV emission from 310 nm to 360 nm generated by electron transition is able to excite TiO_2 and induce photocatalysis. The generation of electron-hole pair on catalyst surface is facilitated which helps in the decomposition of formaldehyde. The average molecular energy of semi-stable nitrogen is 6.2 eV:

$$N_2(v) + N_2(v') \rightarrow N_2(v-1) + N_2(v'+1) \quad (1)$$

Or:

$$e + N_2(v) \rightarrow e + N_2(v+w) \quad (2)$$

The N_2 molecules in their vibrationally excited state possess relatively high energy and are able to break chemical bonds in NO_x (bond energy 3.4 eV). On the other hand, the charged species and ozone generated by high energy pulsed corona discharge are very likely to interact with electron-hole pairs on catalyst surface directly, which consumes the surface active site and reduces the efficiency of NO_x decomposition. Kang et al. has pointed out that plasma could substitute for UV light and excite the photocatalysis on TiO_2 surface. This is because that plasma has a higher energy than UV light which leads to a better effect in the decomposition of gaseous pollutants.

Influence of flow rate on NO_x decomposition: The influence of flow rate on NO_x decomposition using plasma-assisted photocatalysis is shown in Fig. 3.The purification efficiency of pollutants decreases with the increase of flow rate. The reasons are addressed as follows. When it comes to plasma purification, the dwelling time of NO_x pollutants in plasma is relatively long. There is a higher probability for physical and

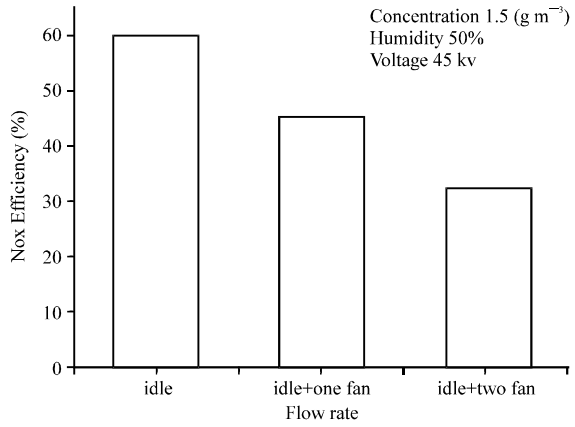

Fig. 3: Influence of flow rate on NOx decomposition

chemical reactions, such as collisions between active species and NO_x (Mok and Ham, 1998). Moreover, a longer dwelling time leads to higher possibilities for the interactions between unit pollutant molecule and plasma. As a result, a higher efficiency of NO_x purification is observed with plasma and low flow rate. With the increase of flow rate, the dwelling time of No_x pollutants in plasma decreases, resulting in lower probabilities of interactions between plasma and gaseous pollutants. Therefore, the efficiency of pollutant purification decreases with the increase of flow rate. The purification processes in photocatalysis involve the diffusion of gas flow to the catalyst surface, the photocatalytic reactions of adsorbed molecules at catalyst surface as well as the desorption and diffusion of product. Therefore, diffusion and photocatalytic reactions are the main steps of photocatalyzed pollutant purification. During diffusion controlled photocatalytic reactions, the decomposition efficiency increases with the flow rate. When the concentration of pollutants in the gas is approximately equal to that on the catalyst particle surface, the purification efficiency of pollutants doesn't change with flow rate any more. The influence of diffusion could be neglected and the purification efficiency of pollutant is mainly controlled by photocatalytic reaction at this time. In general, when the photocatalyzed decomposition rate increases with the flow rate, the reaction is diffusion controlled. As a comparison, when the photocatalyzed decomposition rate is independent of the flow rate, the reaction is not affected by diffusion and appears to be photocatalysis controlled. At this time, the process of photocatalytic reaction is determined by the number of hydroxyl group on catalyst surface. When the catalyst and reaction conditions are fixed, the number of hydroxyl group on catalyst surface is a constant. As a result, the decomposition rate in photocatalytic reactions changes little with the increase of flow rate. Besides, the amount of pollutant to be dealt with per hydroxyl group increases with the flow rate since the number of hydroxyl group on catalyst surface is a constant, resulting in a decrease of purification rate when the flow rate increases. Therefore, the purification rate possesses the same trend as photocatalysis and plasma under synergic effect. The purification rate decreases with the increase of low rate.

Influence of applied voltage on NO_x decomposition: The effect of NO_x purification under various voltages is shown by Fig. 4. The amount of generated plasma is closely related to the strength of electric field. Generally, the strength of electric field determines the number of generated hot electrons. Corona discharge appears at a certain voltage and becomes more and more significant with the increases of voltage. The amount of plasma generated in this process also increases and so does the energy obtained by electrons in electric field. As a result, the collision between electrons and NO_x molecules changes from inelastic to elastic, leading to a higher probability of NO_x dissociation and ionization. It could be learnt from the theory of plasma formation that the increase of voltage and field strength will yield more active groups and photons, which undergo continuously chemical reactions with NO_x. Therefore, the number of active particles would increase with voltage when the voltage reaches the critical value. The purification effect gradually becomes more significant and the decomposition rate increases with applied voltage, as shown by Fig. 4.

It could also be found that the decomposition rate of pollutants is not proportional to applied voltage, which is affected by the photocatalyst. This could be generally explained by the following reasons. When the strength of electric field is low, the corona discharge is weak and only concentrates in the neighborhood of wire electrode. The active particles are not able to effectively activate the photocatalyst absorbed on substrate surface and the effect of photocatalysis is not significant. With the increase of electric field strength, the region of corona expands, resulting in an increase of catalytic activity. When the electric field strength reaches a certain value, the photocatalyst is activated sufficiently and the activity of photocatalyst changes little when the voltage further increases.

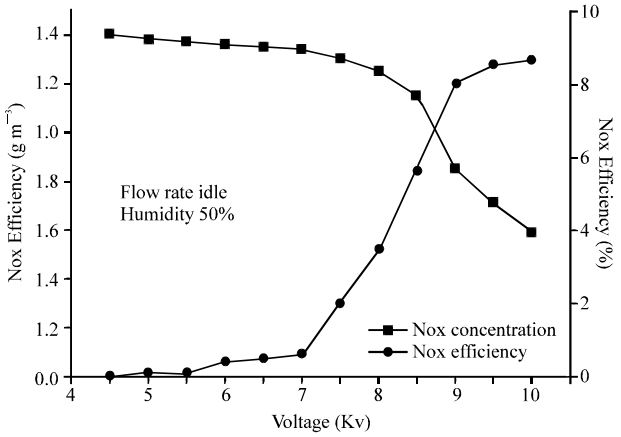

Fig. 4: Influence of applied voltage on NO_x decomposition

CONCLUSIONS

We have demonstrated investigations on NO_x purification with plasma-assisted nano-TiO_2 catalysis. The conclusions are as follows:

- Whatever the experimental condition is, the best purification effect of No_x is always found in plasma-assisted nano-TiO_2 catalysis
- The increase of flow rate reduces the contact probability of pollutants and active species in the reactor, resulting in a decrease in the purification efficiency in plasma-assisted nano-TiO_2 catalysis
- The increase of applied voltage would facilitate the formation of active species in plasma and effectively improve the purification effect of plasma-assisted nano-TiO_2 catalysis

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