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Synergistic removal of nitrogen monoxide by non-thermal plasma and catalyst simultaneously

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Abstract: An experimental system of De-NO with plasma-catalyst(Cu zeolite) was established to investigate the differences between De-NO with plasma-catalyst and De-NO only with plasma, to provide the instruction for selecting appropriate catalyst and operating condition. The characteristics of De-NO with plasma and De-NO with plasma-catalyst were investigated comparatively by experiments. The experimental results show that De-NO with plasma-catalyst has high NO removal rate; Cu zeolite is an effective catalyst which can promote NO removal rate in plasma remarkably; De-NO with plasma-catalyst should be operated at low temperature and the temperature has opposite effects on the function of catalyst and plasma; water vapor and O_2 can increase the NO removal rate.

Keywords: nitrogen monoxide(NO); synergistic removal; non-thermal plasma; catalyst; De-NO

Introduction

Removing NO with non-thermal plasma, following the conventional scrubber technologies such as dry way, half-dry way and wet way, has become a novel high-tech of De-NO (Galkimberti, 1988; Vitello, 1994; Yamamoto, 2000). With many excellent characteristics such as small operation area, low operation expenses, etc., this technology has become internationally accepted and new flue gas De-NO technics (Shimizu, 1999; Orlandini, 2000; Rajanikanth, 2001; Kawasaki, 2001).

Several successful demonstrations in power plants have been set up with the De-NO technology of electron beam(EB) with high energy. Although pulsed corona induced plasma chemical process, a more advanced technology than EB, is still under study in laboratory, many great achievements have been achieved in related areas like chemical reaction kinetics, gas phase electric discharge physics, nanosecond grade high voltage pulsed electric supply and pulsed corona reactor with the efforts of the scientists all over the world. NO reduction mechanism of the non-thermal plasma reaction in $NO-N_2-O_2$ system has been investigated using the methods of spectral analysis and quantum chemistry by the authors(Yu, 2005). Using the electrode tip discharge structure, the NO reduction characteristics of N_2-NO system has also been revealed to guide the engineering practice by the authors(Yu, 2005). This technology does not need very high voltage to break the N—O bond and the product of the system is innoxious gas mixture(N_2 and O_2). Thus, this NO reduction technology can also be used to reduce NO in the exhaust gas emitted from the mobile engine.

Although there are these fruitful achievements, many key theoretical and technological problems must be resolved before applying plasma to De-NO in power plant. Many researchers are still seeking new low-cost technology that can further reduce reaction energy-consumption and increase NO removal rate greatly. In order to solve the above difficulties, the following three aspects can be considered. (1) When gas molecule is absorbed on the surface of dielectric absorbent pellet, its bond will be elongated, and this will reduce the energy used to ionize the gas molecule. (2) The NO removal rate can be further improved if such pellet can be manufactured: it can selectively absorb those contributing gas molecules in the plasma reaction while absorbing in the least amount of those counteractive gas molecules. Meanwhile, by controlling discharge voltage, the gas molecule absorbed on the surface of this kind of pellet can just ionize with less energy. (3) Ever since the work done by Iwamoto (Sun, 2001), Cu zeolite is regarded as the potential catalyst for NO to decompose itself into N_2 and O_2 and the use of it in the De-NO with plasma should be surprisingly effective. Based on those three points, we, by combining the advantages of absorption and non-thermal plasma, carried out a research on De-NO with plasma-catalyst to further lower energy consumption and increase NO removal rate. Specifically, suitable absorbent pellets were used to fill the reaction room of the plasma reactor and when the to-be-treated gas passes through the pellets, a packed plasma reactor is formed.

In this paper, we studied the difference between De-NO with plasma-catalyst by filling the Cu zeolite catalyst in the non-thermal plasma reactor and De-NO only with plasma, loading and unloading them respectively, hoping to understand the rule of the interactions of catalyst, plasma, O_2, temperature and water vapor. Results obtained from the study enable us to understand the characteristics of De-NO with plasma-catalyst and provide us with the instruction for selecting appropriate catalyst and operating condition.

This paper deals with the difference between De-NO with plasma-catalyst and De-NO with plasma, and the effects of other gas components in real flue gas, solid dust on De-NO with plasma-catalyst is left for further investigation. In addition, in order to simplify this research, only the changes of NO concentration is measured and adopted to represent the actions of plasma and catalyst, although there might be NO_2, N_2O, N_2 or O_2 in the products of NO removal reactions, NO_2 and N_2O are also hazardous gas to be removed.

1 Experimental system and methods

In order to study how O_2, water vapor, and temperature affect the NO removal rate with or without catalyst, an experimental system shown in Fig. 1 is established. The catalyst pellet in the reactor can be easily loaded and

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unloaded to simulate De-NO with plasma-catalyst and De-NO only with plasma. The reactor is placed into a heating furnace to control the temperature within the range from room temperature to 300℃.

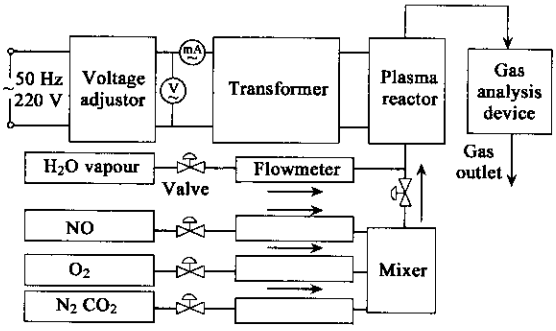

Fig.1 Schematic system for NO synergistic removal with plasma-catalyst

Experimental gases: mixture of NO, N_2, CO_2 and O_2, with water vapor being the additive. Because the NO removal rate is quite sensitive to the residence time(Yu, 2004), the flux was controlled below 2 L/min so that the gas can be in the reactor for at least 2 s and there would be sufficient time for the reaction.

Pulsed electric supply: model HB708. As presented in Fig.2, the output voltage reaches as high as 20 kV, the frequency output is 30 kHz, the duration of oscillation is 220 ns and the maximum power is 50 W. The input voltage is adjusted through a voltage adjustor.

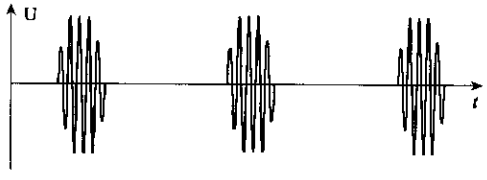

Fig.2 Wave shape of the pulsed voltage

Plasma reactor: as shown in Fig.3, the reactor is a glass cylinder with a bronze rod as the inner electrode whose diameter is 3.5 mm. The glass cylinder is covered with a layer of aluminum meshwork as the outer electrode, through which the discharge in the reactor can be looked into. The length of the reactor is 210 mm and the inner diameter of the glass cylinder is 22 mm. Through theoretical and experimental pre-analysis, zeolite Cu-ZSM-5 is selected as catalyst, the diameter of each catalyst pellet is from 3 mm to 4 mm.

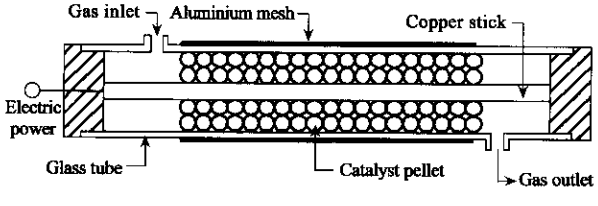

Fig.3 Structure of plasma-catalyst reactor

Measurement on the concentration of the gas: measure the concentration of each gas component before and after reaction by using gas analyzer(model Rosemount NGA2000).

Experimental methods: firstly fixed the initial concentration of NO and O_2 without catalyst pellet and then slowly changed the voltage until the concentrations reading in NGA2000 were stable. With the corresponding value of the current and the concentration of NO, an experimental curve can be obtained. Different curve can be obtained when the concentration of O_2 was reseted each time. Experiments on the change of temperature and addition of water vapor adopt the same procedure.

2 Results and discussion

The following analyses and conclusions are from the experiments of De-NO with plasma-catalyst and De-NO only with plasma when operating in different temperatures, different amount of water vapor addition and different concentration of O_2. The removal rate is defined as (C_{NO} represents the concentration of NO):

$$\eta = [(C_{\text{NO before reaction}} - C_{\text{NO after reaction}})/C_{\text{NO before reaction}}] \times 100\% .$$

2.1 Interactions of temperature, catalyst and plasma

Fig.4 shows how NO removal rate varies with input power at different temperatures, with or without the catalyst. Besides the operating conditions already shown in the Fig.4, the initial concentrations of NO, O_2 and CO_2 are 400 ppm, 3% and 5% respectively, and the rest is N_2.

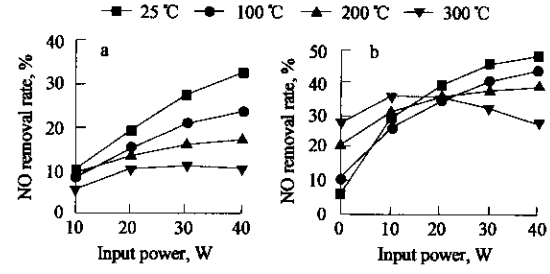

Fig.4 NO removal rate vs. input power at different temperature, without (a) and with (b) catalyst

As shown in Fig. 4, without the catalyst, the temperature exerts relatively great effect on NO removal rate. Under room temperature, NO removal rate increases sharply with the increase of input power. When the temperature increases, NO removal rate increases less or even exhibits a tendency of decrease when the temperature reaches 300℃.

With the catalyst and when the input power is 0 W, namely with the sole operation of the catalyst, NO removal rate experiences an obvious increase with the increase of temperature, reaching 30% at 300℃. At 300℃, however, NO removal rate decreases with the increase of input power.

All these can account for the fact that temperature exerts different effects on the function of catalyst and plasma: increase of temperature improves the activity of catalyst but restrains the function of plasma.

It is quite obvious that when the input power increases to a certain point, removal rate increases when the temperature decreases, regardless of the presence and absence of the catalyst. Therefore, we need to choose relatively low temperature in De-NO with plasma-catalyst.

2.2 Interactions of water vapor, catalyst and plasma

Fig.5 shows that NO removal rate varies with input power, with water vapor as an additive, with and without catalyst. The initial concentrations of NO, O_2, H_2O, and

CO_2 are 400 ppm, 3%, 5% and 5% respectively, and the rest is N_2. The temperature is 25℃.

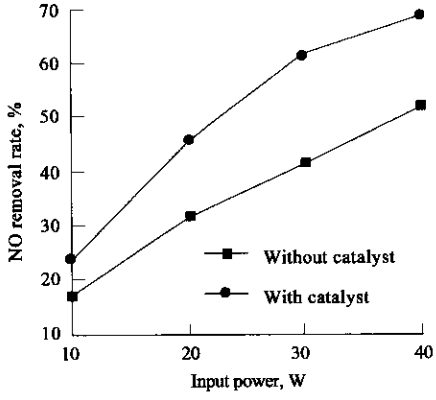

Fig.5 NO removal rate vs. input power with water vapor as an additive, without and with catalyst

A comparative study between Fig. 5 and Fig. 4a indicates that NO removal rate increases with the existence of water vapor. This is because within the electric field, water vapor produces a large number of active oxidizing radicals such as OH and HO_2, and undergoes the oxidizing reaction with NO. With the existence of catalyst, NO removal rate improves greatly.

The use of water vapor in De-NO with plasma-catalyst can promote the NO removal rate.

2.3 Interactions of O_2, catalyst and plasma

Fig.6 shows that NO removal rate varies with input power, with different concentrations of O_2, and with or without catalyst. Besides the conditions exhibited in the Fig.6, the initial concentrations of NO and CO_2 are 1000 ppm and 5% respectively and the rest is N_2. The temperature is 25℃.

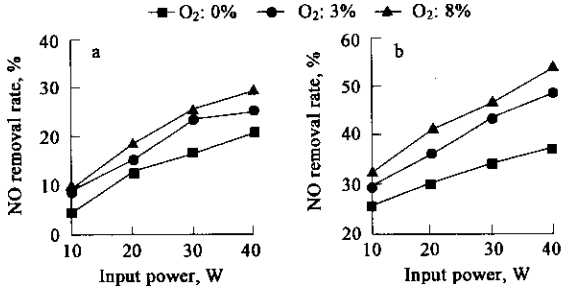

Fig.6 NO removal rate vs. input power with different concentration of O_2, without (a) and with (b) catalyst

It can be seen from Fig.6 that: (1) Under the same conditions, NO removal rate with catalyst is higher than that without catalyst. (2) NO removal rate with the existence of O_2 exceeds that without the operation of O_2 by 5%—10%. The higher the concentration of O_2, the higher the NO removal rate. The use of O_2 in De-NO with plasma-catalyst promotes the NO removal rate. (3) As shown in Fig.6, when the input power is 40 W and the concentration of O_2 is 3%, the increase of NO removal rate is about 20% with catalyst. With the input power being 40 W and the concentration of O_2 being 8%, the NO removal rate increased about 25% with catalyst, indicating the synergetic effect between catalyst and O_2.

In the process of reaction, the contact points of the pellets sparkle. These sparkles indicate the intense discharge and the production of more active radicals.

3 Conclusions

The investigation on the differences between De-NO with plasma-catalyst and De-NO with only plasma showed us the effect of temperature on catalyst and non-thermal plasma in De-NO with plasma-catalyst, the functions and interrelationship of catalyst, O_2 and water vapor in De-NO with plasma-catalyst. The specific conclusions are as follows: (1) De-NO with plasma-catalyst is a novel method with higher efficiency than De-NO only with plasma. (2) As being a more effective catalyst, the zeolite Cu-ZSM-5 can promote the NO removal rate. (3) Lower temperature should be used in De-NO with plasma-catalyst. Increasing temperature improves the activity of catalyst but restrains the function of plasma. (4) Water vapor and O_2 promote the removal of NO with plasma-catalyst.

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