49 Simultaneous Removal of NO_x and Diesel PM over $La_{0.9}K_{0.1}CoO_3$ Assisted by Plasma

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Abstract Simultaneous removal of NO_x and diesel particulate matter (PM) was studied over mixed metal oxide catalyst of $La_{0.9}K_{0.1}CoO_3$ with the assistant of non-thermal plasma. It was found that NO_x was reduced by PM in oxygen rich atmosphere, and the CO_2 and N_2 were produced in the same temperature window without considering the N_2 resulted from NO decomposition in the plasma zones. As the results of the assistant of the non-thermal plasma process, the burn out temperature of the PM decreases from 537℃ to 492℃ and the reduction efficiency of NO_x to N_2 increases from 10% to 33%, which suggest that the plasma process improves the activity of the catalyst. It was found that about 2~10 per cent of NO_x was decomposed in the plasma zones at both low temperature and high temperature. Therefore, the whole conversion efficiency of NO_x to N_2 was enhanced. The mechanisms of the catalysis reactions promoted by the plasma process were discussed.

***Key words*: Catalyst, Plasma, NO_x, PM, Diesel**

1 Introduction

Particulate matter (PM) and NO_x are the main pollutants in diesel engine emissions which do harm to environment and human health. While the traditional treatment techniques for diesel engine emissions cannot meet the increasingly stringent emission regulations, it is quite necessary to come up with more effective control methods.

After systematic studies of the catalytic conversion of soot and NO_x in synthesized diesel exhaust gas, Teraoka and Shangguan[1-7] found that perovskites and spinels are effective catalysts for simultaneous removal of NO_x and soot. Liu Guanghui et.al. [8-9] investigated the simultaneous removal of NO_x and PM over $La_{0.9}K_{0.1}CoO_3$ and $Cu_{0.9}K_{0.1}Fe_2O_4$ with diesel particulate filter (DPF). Their findings showed that the $La_{0.9}K_{0.1}CoO_3$ and $Cu_{0.9}K_{0.1}Fe_2O_4$ catalysts decrease the combustion temperature of PM and improve the efficiency of NO_x conversion into N_2. Moreover, The $La_{0.9}K_{0.1}CoO_3$ was found to be superior to $Cu_{0.9}K_{0.1}Fe_2O_4$. Penetrante et.al[10] reported the feasibility of plasma aftertreatment for simultaneous reduction of NO_x and particulates. Thomas et.al.[11] studied the reduction of NO_x and soot on diesel particulate filter (DPF) assisted by plasma and found that particulate in the diesel exhaust may inhibit the conversion of NO into NO_2 in a plasma regenerating DPF. In addition, NO_2 was converted into N_2O rather than being reduced to N_2 by some selective catalysts.

This paper studies the simultaneous removal of NO_x and PM from diesel exhaust over a mixed metal oxide catalyst of $La_{0.9}K_{0.1}CoO_3$ (LKC) with the assistant of plasma. It aims at the deoxidization of NO_x by PM and the oxidation of PM by NO_x in oxygen rich atmosphere. Furthermore, the mechanism of catalysis reaction with and without plasma was analyzed.

2 Experimental

2.1 Catalyst preparation

LKC loaded on γ-Al_2O_3 spherule is used in the investigation into simultaneous removal of NO_x and PM. The γ-Al_2O_3 spherule is putted into a mixed aqueous solution containing appropriate amounts of LKC, whose activity composition is absorbed by the γ-Al_2O_3 homogeneously after γ-Al_2O_3 is dipped into solution for 10h and stirred with dasher. The γ-Al_2O_3 is dried at 160℃ after exposure in air for 12h at room temperature, and then the γ-Al_2O_3 spherules are calcined in air at 850℃. The crystal structures of LKC supported on γ-Al_2O_3 are examined by powder X-ray diffraction (XRD) with Cu Kα radiation. Fig.1 shows the XRD result and validates the formation of the desired crystalline structure.

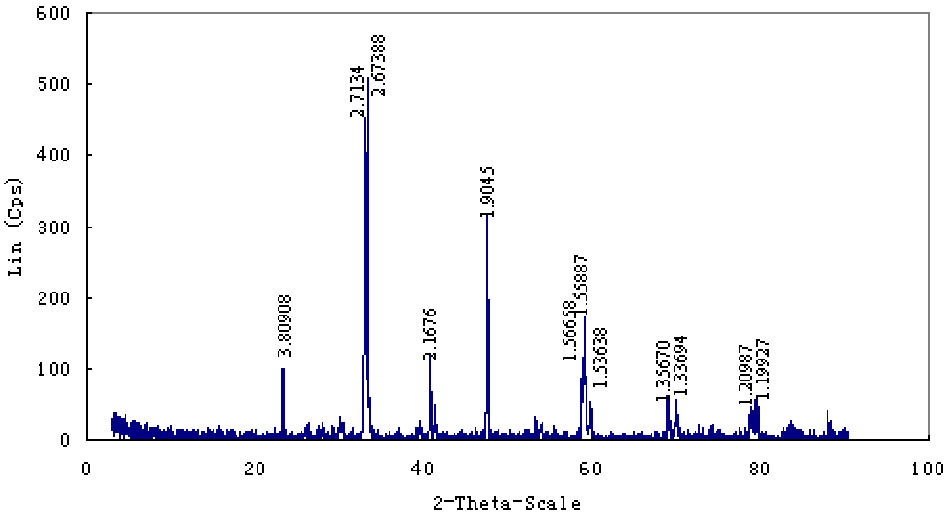

Fig. 1 X-Ray diffraction pattern of $La_{0.9}K_{0.1}CoO_3$ (LKC)

2.2 Catalytic reaction procedure

The PM captured by the γ-Al_2O_3 spherules with catalyst and without catalyst, which are exposed to the CA 480 diesel exhaust at a rated speed of 1800r/min and 75% load. Then the sample of γ-Al_2O_3 spherules with PM is placed in a quartz-tube reactor. The reactor is pretreated and fed by pure helium gas at 400℃ for 3h and cooled down to 110℃ in order to eliminate the possible contaminants such as adsorbed water before the catalytic reaction, then the temperature is kept at 110℃ for 1h until N_2 and O_2 cannot be detected by a gas chromatograph. Subsequently, a gas mixture of NO(0.26%),O_2(5%) and He(balance) is fed to the quartz-tube placed in an electric oven at a flow rate of 80 $cm^3.min^{-1}$ via a set of mass flow meters, and then, the reactor is heated linearly at a rate of 1.5℃ min^{-1}. The outlet gas is analyzed with intervals of about 15 min by a TCD gas chromatograph (GC-14B) with columns of Porapak Q for separating N_2, O_2, NO and CO and molecular sieve 5A for CO_2 and N_2O.

2.3 Experimental apparatus

Fig.2 is a schematic of the experimental setup including the synthetic exhaust control system, the gas analysis system and the plasma-catalyst reactor system, in which the electrical discharge reactor is operated at dielectric barrier discharge mode (DBD). The reactor consists of a quartz-tube with inner and outer diameters of 16mm and 19mm respectively. A 2mm-diameter stainless steel rod connected with high voltage power device is inserted into the quart-tube which is covered by a stainless steel foil acted as the ground electrode. The length of the outer electrode can be adjusted and then the active volume of the DBD reactor can be changed. Some of γ-Al_2O_3 spherules are loaded in the section of the tube. The DBD reactor is placed inside a tubular furnace and the gas mixture temperature can be adjusted from room temperature to 500℃. The voltage and current wave-forms are recorded by an oscilloscope (Tektronix TDS 1012).

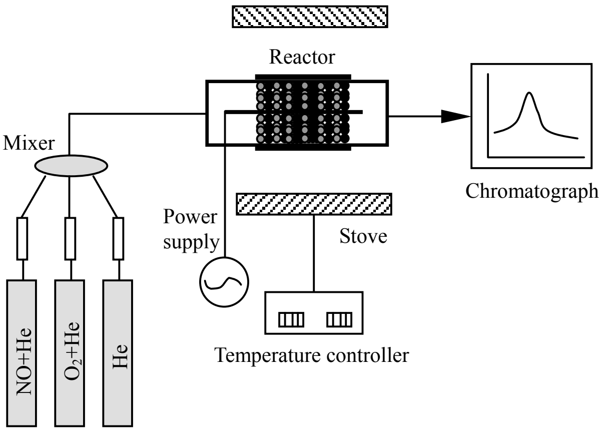

Fig 2. Schedule of the experimental system

3 Results and discussion

3.1 The reactions over PM/γ-Al_2O_3 with and without plasma

During the overall test, the voltage is maintained at 2.5kV to eliminate the effect of voltage change on simultaneous removal of NO_x and PM.

Fig.3, 4 show the N_2 and CO_2 concentrations resulted from temperature program reaction (TPR) over PM/γ-Al_2O_3 with plasma and without plasma. Fig.3 indicates that the formation of N_2 is observed at the wide range temperature from 110℃ to more than 550℃ as the plasma is turned on. The TPR without plasma not produces N_2 as the temperature is higher than 530℃. In both cases, the production of N_2 is enhanced obviously at the temperature range from 250℃ to 500℃. Especially, at the temperature arond 400℃, the conversion efficiency of NO_x to N_2 reaches a maximum of 33% if the plasma was turned on. Literature [12] reports that γ-Al_2O_3 shows high $DeNO_x$ performance when NO_2 or oxygenated hydrocarbons are present in a gas stream, it seems the plasma oxidizes NO or hydrocarbons here. It is found that the N_2 concentrations are constant at both low and high temperature because the NO_x was dissociated at low temperature and high temperature by plasma process. The decomposition rate of NO at high temperature is higher than that at low temperature.

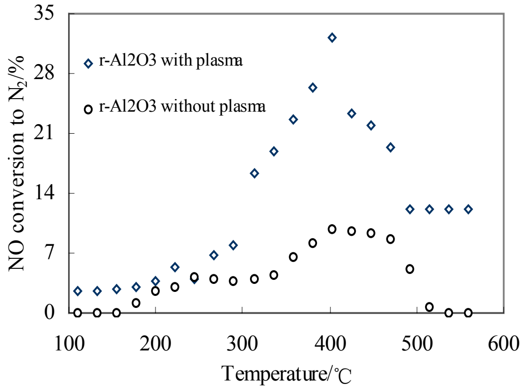

Fig.3 Comparison of N_2 concentration over PM/γ-Al_2O_3 with and without plasma by TPR

Fig.4 displays the changes of CO_2 concentration with the temperature. The PM combustion temperature decreases apparently with the presence of plasma, the peak combustion temperature drops from 470℃ to 400℃ and the burn out temperature drops from 537℃ to 492℃. The results above suggest that the catalyst with the assistant of plasma show higher efficiency for PM catalytic combustion compared with the catalyst without plasma. The reason is that plasma process produce high energetic electrons that promote the formation of activated species, such as O^* and O_3, which inspires PM combustion to produce some intermediates(C^*O) and reduces the combustion temperature of PM [5].

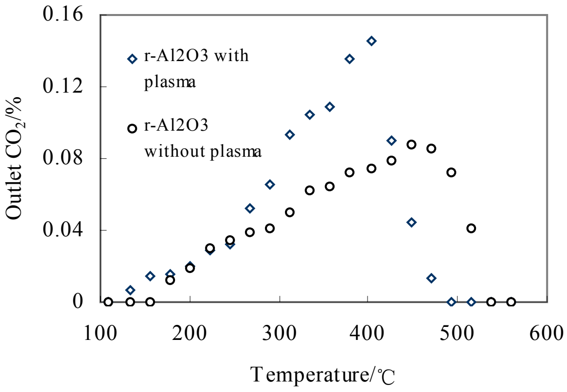

Fig.4 Comparison of CO_2 concentration over PM/γ-Al_2O_3 with and without plasma by TPR

3.2 The reactions over PM/LKC/γ-Al_2O_3 with and without plasma

Fig.5, 6 show the N_2 and CO_2 concentrations resulted from TPR over PM/LKC/γ-Al_2O_3 with and without plasma. The CO_2 curve as well as the N_2 curve shows double concentration peaks. The first peak of N_2 and CO_2 around 200℃ results from the reaction of soluble organic fraction (HC) with NO_x and the second peak around 350℃ results from the reaction of dry soot (DS) with NO_x.

For the reaction without plasma process at low temperature the NO_x is reduced by HC through the mechanism as follows [13],

$$NO(ad) + O(ad) \rightarrow NO_2(ad) \qquad (1)$$

$$NO_2(ad) + HC \rightarrow Intermediate(ad) \rightarrow N_2 + CO_2 + H_2O \qquad (2)$$

where ad denotes adsorption on the active sites. The first step (1) can be assumed to be critical step to determine the second step (2), which produces N_2 and CO_2. For the reaction without plasma process at high temperature from 245℃ to 500℃, the NO is reduced by DS (C). Since the LKC without the assistant of plasma has shown the ability of simultaneous removal of NO_x and DS, the possible reaction mechanism may be as follows [5],

$$NO + O_2 \rightarrow NO_2 \quad (3)$$

$$NO_2 \rightarrow NO_{ad} + O_{ad} \quad (4)$$

$$C_f + O_{ad} \rightarrow C^*[O] \quad (5)$$

$$C^*[O] + NO_{ad} \rightarrow N_2 + CO_2 \quad (6)$$

It is thought that NO_2 is formed through the reaction of 3 and then adsorbed dissociatively on the catalyst surface to form adsorbed NO_{ad} and O_{ad} species. The reaction between adsorbed O_{ad} and reactive C_f species produce $C^*[O]$ intermediate, which is easily reacts with adsorbed or gaseous NO species to product N_2 and CO_2 over LKC catalyst. The maximum efficiency of NO_x at low temperature zone and high temperature zone is about 5% and 10% respectively.

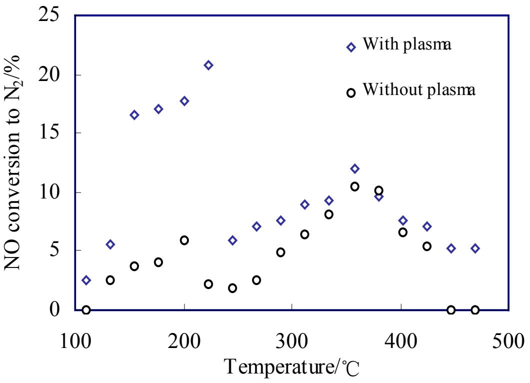

Fig.5 Comparison of N_2 concentration over PM/LKC/γ-Al_2O_3 with and without plasma

Fig.6 shows that the maximum conversion efficiency of NO_x into N_2 is apparently improved from 5% to 21% at the temperature range from 150℃ to 245℃ with the presence of plasma. At the same time, the production of CO_2 is also enhanced as shown in Fig.7 for the plasma readily oxidizes NO to NO_2 and partially oxidizes hydrocarbons to form oxygenated hydrocarbons [14]. So, the mechanisms for LKC catalysts loaded on r-alumina at the low temperature with the assistant of plasma can be summarized as follows [15].

$$NO + O_2 \xrightarrow{plasma} NO_2 \quad (7)$$

$$HC + O_2 \xrightarrow{plasma} oxygenated\ HC \quad (8)$$

$$NO_2 + oxygenated\ HC + O_2 \xrightarrow{LKC/r-alu\min a} N_2 + CO_2 + H_2O \quad (9)$$

Reactions (7) and (8) are inspired by plasma process and have higher rates compared with reactions (2) and (3), therefore, the NO_x conversion to N_2 is promoted.

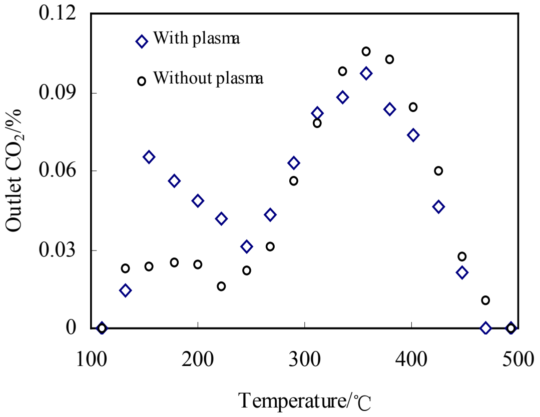

Fig.6 Comparison of CO_2 concentration over PM/LKC/γ-Al_2O_3 with and without plasma

For the reactions between NO_x and DS, it is found that the conversion of NO_x into N_2 is improved slightly by plasma at a temperature range from 245℃ to 500℃, the maximum conversion of NO_x to N_2 is promoted from 10.5% to 12% and the burn out temperature of DS is decreased to about 480℃ from 500℃. The reason for the promotion of reactions between NO_x and DS may be that the NO_x is activated by plasma, the chemisorptions of activated NO_x on the surface of the catalyst and DS is in favor of the reaction of NO_x with DS. On the other hand, the improvement of the reaction of NO with O_2 by the plasma process can also be one of the explanations for higher conversion of NO_x into N_2 and lower burn out temperature.

4 Conclusions

An experimental investigation has been conducted to simultaneous removal of NO_x and diesel PM over $La_{0.9}K_{0.1}CoO_3$ assisted by plasma and the following conclusions are reached:

(1) During the TPR of NO_x and PM over γ-Al_2O_3, the production of N_2 and CO_2 arrive the only maximum around 400℃; Double peaks appear during the TPR of NO_x and PM over LKC, one is resulted from reaction of NO_x with HC at low temperature, and another is resulted from the reaction of NO_x with DS at high temperature.

(2) Compared with LKC catalyst without plasma,

the catalyst LKC assisted by plasma has showed higher efficiency of catalytic conversion for simultaneous NO_x and PM, as a result, the combustion temperature of PM was decreased and the efficiency of NO_x reduction to N_2 was enhanced. Plasma process can improve the catalysis reactions, especially enhance the efficiency of conversion of NO_x into N_2 at low temperature.

(3) Part of the NO molecules would be decomposed by the energize electrons in the plasma zone, so the conversion efficiency of NO_x into N_2 would be promoted. The decomposition rate of NO by plasma increases with the rise of the gas temperature.

Acknowledgements

This study was supported by National Natural Science Foundation of China (50376035) and GM-China Scientific Research Foundation (50222203).

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