

Simultaneous catalytic removal of NO_x and diesel PM over La_{0.9}K_{0.1}CoO₃ catalyst assisted by plasma

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Abstract: The simultaneous removal of NO_x and particulate matter (PM) from diesel exhaust is investigated over a mixed metal oxide catalyst of La_{0.9}K_{0.1}CoO₃ loaded on γ -Al₂O₃ spherules with the assistant of plasma. It was found that NO_x was reduced by PM in oxygen rich atmosphere, the CO₂ and N₂ were produced in the same temperature window without considering the N₂ formed by plasma decomposition. As a result, the temperature for the PM combustion decreases and the reduction efficiency of NO_x to N₂ increases during the plasma process, which indicated that the activity of the catalyst can be improved by plasma. The NO_x is decomposed by plasma at both low temperature and high temperature. Therefore, the whole efficiency of NO_x conversion is enhanced.

Keywords: simultaneous removal; plasma assisted catalysis; NO_x; PM; diesel

Introduction

Particulate matter (PM) and NO_x are the main pollutants in diesel engine emissions affecting 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 a systematic study of the catalytic conversion of soot and NO_x in simulated diesel exhaust gas, Teraoka and Shangguan (Teraoka, 1995; 1996; 2001; Shangguan, 1995; 1996; 1997; 1998) found that perovskites and spinels are effective catalysts for simultaneous removal of NO_x and soot. Later, Liu Guanghui *et al.* (Liu, 2002; 2003) investigated the simultaneous removal of NO_x and PM over La_{0.9}K_{0.1}CoO₃ and Cu_{0.9}K_{0.1}Fe₂O₄ with diesel particulate filter (DPF). Their findings showed that the La_{0.9}K_{0.1}CoO₃ and Cu_{0.9}K_{0.1}Fe₂O₄ catalysts decreased the combustion temperature of PM and improved the efficiency of NO_x conversion into N₂. Moreover, the La_{0.9}K_{0.1}CoO₃ is superior to Cu_{0.9}K_{0.1}Fe₂O₄. Also, Penetrante *et al.* (Penetrante, 1999) reported the feasibility of plasma after treatment for simultaneous reduction of NO_x and particulates. They pointed out that the particulates can be trapped and oxidated by DPF, while the efficiency of the NO_x conversion is relatively low. Thomas *et al.* (Thomas, 2000) studied the reduction of NO_x and soot on DPF assisted by plasma and found that particulate in the diesel exhaust may inhibit the conversion of NO to NO₂ in plasma regenerating diesel particulate filter (DPF). In addition, NO₂ was converted into N₂O rather than being reduced to N₂ by some selective catalysts. Further investigation (Suzanne, 2001) has shown that silver-doped alumina (Ag-Al₂O₃) is a particularly effective catalyst for NO reduction and combination of catalyst with plasma improving the NO_x reduction.

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}CoO₃ (LKC) loaded on γ -Al₂O₃ spherule 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 the removal process by the plasma-assisted catalyst reaction was analyzed.

1 Experiment

1.1 Catalyst preparation

LKC loaded on γ -Al₂O₃ spherule is used in the investigation into simultaneous removal of NO_x and PM. The γ -Al₂O₃ spherule is put into a mixed aqueous solution containing appropriate amounts of LKC, whose activity composition is absorbed by the γ -Al₂O₃ homogeneously after γ -Al₂O₃ is dipped into solution for 10 h and stirred with dasher. The γ -Al₂O₃ is dried at 160°C after exposure in air for 12 h at room temperature, then the γ -Al₂O₃ spherules are calcined in air at 850°C. The crystal structures of LKC supported on γ -Al₂O₃ are examined by powder X-ray diffraction (XRD) with Cu K α radiation (d8advance BRUKER). Fig. 1 shows the XRD result and validate the formation of the desired crystalline structure.

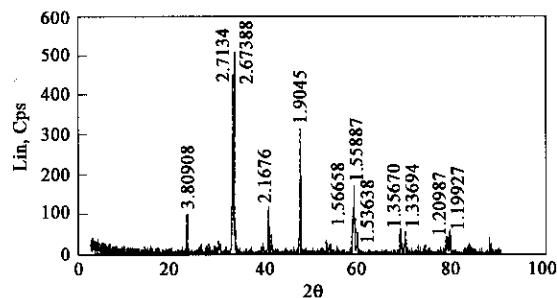


Fig. 1 X-ray diffraction pattern of La_{0.9}K_{0.1}CoO₃ (LKC)

1.2 Catalytic reaction procedure

The PM captured by the γ -Al₂O₃ spherule with catalyst and without catalyst, is exposed to the CA 498 diesel exhaust at a rated speed of 1800 r/min and 75% load. Then the sample of γ -Al₂O₃ with PM is placed in a quartz-tube reactor with the inner diameter of 16 mm. The reactor is pretreated and fed by pure helium gas at 400°C for 3 h and cooled down to 110°C in order to eliminate the possible contaminants such as adsorbed water before the catalytic reaction, then the temperature is kept at 110°C for 1 h until N₂ and O₂ cannot be detected by a gas chromatograph. Subsequently, a gas mixture of NO (0.26%), O₂ (5%) and He (balance) is fed to the quartz-tube placed in an electric oven at a flow rate of 80 cm³/min via a set of mass flow meters, and then, the reactor is heated at a rate of 1.5°C/min by controller linearly and the temperature increases from 110 to 800°C. 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 CO₂ and N₂O and molecular sieve 5A for N₂, O₂, NO and CO.

1.3 Experimental apparatus

Fig.2 shows 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 16 mm and 19 mm respectively. A 2 mm-diameter stainless steel rod connected with high voltage power device is inserted into the quartz-tube which is covered by a

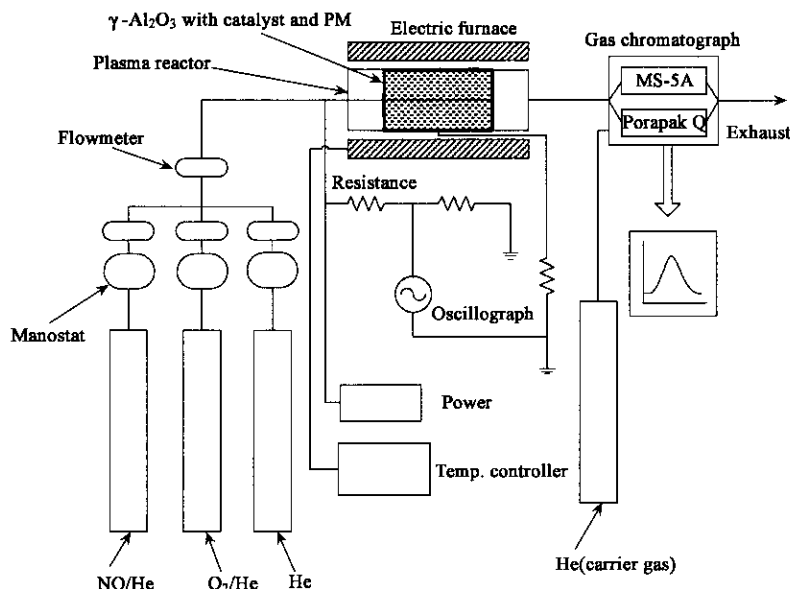


Fig.2 Scheme of experimental apparatus for TPR of plasma-catalyst

2 Results and discussion

2.1 The decomposition of NO_x by plasma process

TPR reactions are carried out with and without oxygen to investigate the effect of plasma on the conversion of NO_x to N₂. Fig.3 reveals the changes of N₂ concentration over γ -Al₂O₃ in the DBD process by showing that the decomposition of NO_x can be achieved in the absence or presence of O₂. In addition, with the promotion of voltage, the decomposition efficiency is improved. The efficiency of NO_x decomposition without oxygen is higher than that of NO_x decomposition with oxygen at the same voltage, moreover, 95% of NO_x is decomposed as the voltage is enhanced without the presence of O₂.

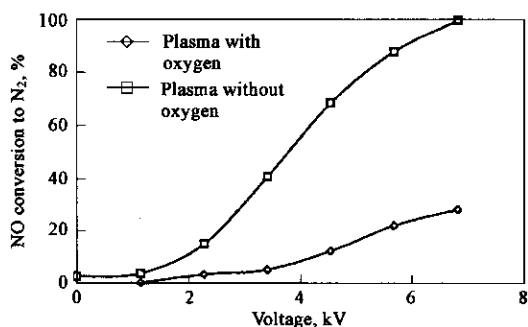
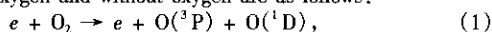
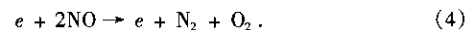


Fig.3 Comparison of N₂ concentration over plasma with γ -Al₂O₃ with and without oxygen

The possible reaction of N₂ formation by collision and electrolytic dissociation with oxygen and without oxygen are as follows:



stainless steel foil acted as the ground electrode. The length of the outer electrode can be adjusted and then determines the active volume of the DBD reactor. Some of γ -Al₂O₃ spherules are loaded in the section of the tube. The DBD reactor, powered by a high-voltage power supply, is placed inside a tubular furnace and the gas mixture temperature can be adjusted from room temperature to 500°C. The voltage and current waveforms are recorded by an oscilloscope (Tektronix TDS 1012).



Under the plasma reaction process with oxygen, the production has NO₂, O₃, N₂ and O₂ by the electron collision and electrolytic dissociation from step(1—4), while the plasma reaction process without oxygen, the NO is decomposed by electron collision directly (4), therefore, the efficiency of NO_x decomposition is higher than that of NO_x decomposition with oxygen.

2.2 The reaction over PM/ γ -Al₂O₃ with and without plasma

The voltage is maintained at 2.5×10^3 V to eliminate the effect of voltage change on simultaneous removal of NO_x-PM. Fig.4 and Fig.5 show the TPR results of N₂ and CO₂ concentrations over PM/ γ -Al₂O₃ with and without plasma. Fig.4 displays that the formation of N₂ is observed at the wide range temperature from 110—550°C as the plasma is turned on. Especially, the production of N₂ is enhanced obviously at the temperature range from 250—500°C. Furthermore, at the temperature of 402.5°C, the conversion efficiency of NO_x to N₂ reached a maximum of 33% and the formation of N₂ concentration is constant with both low and high temperature because the NO_x was dissociated at low temperature and high temperature by plasma process. As Section 2.1 explained, the NO_x can be decomposed over plasma combined with γ -Al₂O₃ in the oxygen rich atmosphere. It also showed that the efficiency of NO_x decomposition at high temperature is 10% higher than the efficiency at low temperature. Fig.5 displays the changes of CO₂ concentration with the temperature ranged from 110—550°C. The PM combustion temperature lowers apparently with the presence of plasma, the peak combustion temperature drops from 470°C to 400°C and the burn out temperature from 537°C to 492°C. The results suggested that the catalyst with the assistant of plasma showed the higher efficiency of catalytic conversion for PM catalytic combustion than the catalyst without plasma. The reason is

that plasma devices produce high energetic electrons that promote the formation of activated species, such as O^* and O_3 , which inspires the reaction of PM combustion to produce some intermediates (C^*O) and reduces the combustion temperature of PM (Shangguan, 1997).

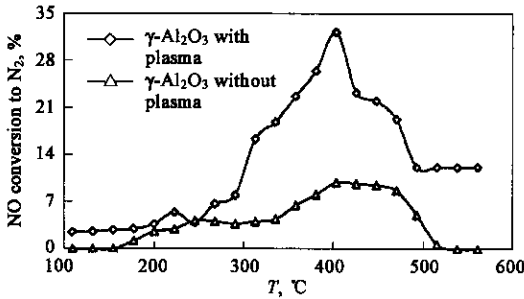


Fig. 4 Comparison of N_2 concentration over $PM/\gamma-Al_2O_3$ with and without plasma by TPR

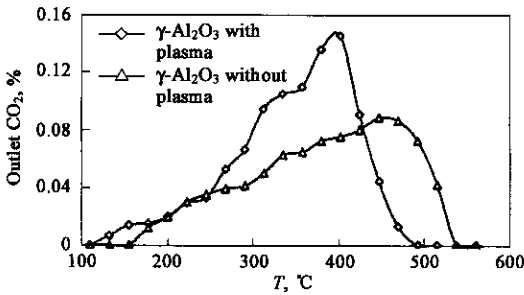


Fig. 5 Comparison of CO_2 concentration over $PM/\gamma-Al_2O_3$ with and without plasma by TPR

2.3 The reaction over $PM/LKC/\gamma-Al_2O_3$ with and without plasma

Fig. 6 and Fig. 7 show the TPR results of N_2 and CO_2 concentrations over $PM/LKC/\gamma-Al_2O_3$ with and without plasma. The results displayed that the production of N_2 and CO_2 is observed between the same temperature range from 110–550°C. Regardless plasma, these results of curve are consistent with the results of literature (Liu, 2002), which showed the double peaks of CO_2 as well as N_2 . The first peak for N_2 and CO_2 at 200°C is formed by the reaction of soluble organic fraction (HC) in the PM with NOx and the second peak for N_2 and CO_2 at 357.5°C results from the reaction of dry soot (DS) in the PM with NOx. For LKC catalysis without plasma process at low temperature the NOx is reduced by HC, the reaction mechanism is written by two steps as follows (Tenvo, 1998):

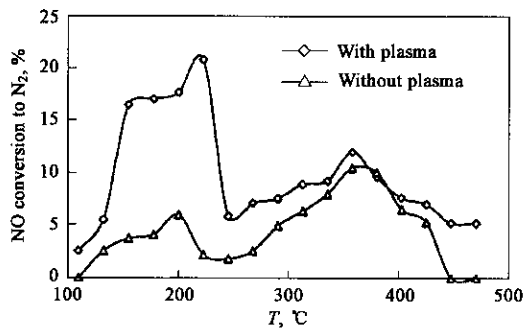


Fig. 6 Comparison of N_2 concentration over $PM/LKC/\gamma-Al_2O_3$ with and without plasma by TPR

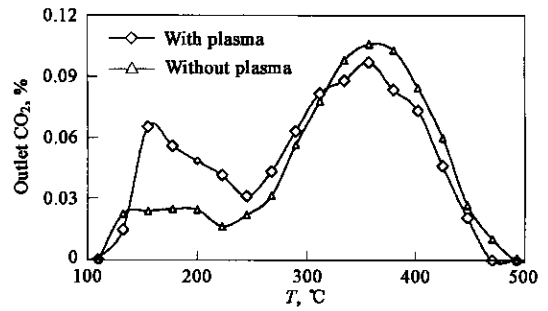
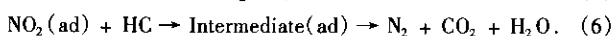
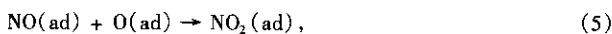
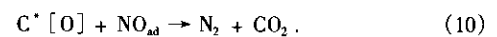


Fig. 7 Comparison of CO_2 concentration over $PM/LKC/\gamma-Al_2O_3$ with and without plasma

Where ad denotes adsorption on the active sites. The first step (5) can be assumed to be critical step to determine the second step (6) that can produce N_2 and CO_2 . For LKC catalysis without plasma process at high temperature from 245°C to 550°C, the NO is reduced by DS(C). Since the LKC without the assistant of plasma has shown the performance for simultaneous removal of NOx and DS, the possible reaction mechanism are as follows (Shangguan, 1997):

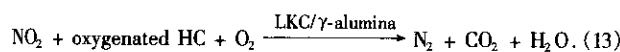
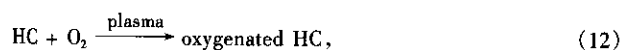


It is thought that NO_2 is formed through the reaction of NO and O_2 (7) and then adsorbed dissociatively on the catalyst surface to form adsorbed NO_{ad} and O_{ad} species (8). The reaction between adsorbed O_{ad} and reactive C_r species produce $C^*[O]$ intermediate (9) which is reactive toward the reduction of adsorbed or gaseous NO species, that is, $C^*[O]$ react with NO_{ad} to product N_2 and CO_2 over LKC catalyst easily (10).

The above discussion implies that the information about the effect of NO_2 in PM-NO- O_2 reaction is indispensable for the full understanding of the reaction mechanism over LKC without plasma process. From Fig. 6, it can be seen that the maximum efficiency of NOx without plasma process is about 5% and 10% at the whole TPR runs. When the PM loaded on $LKC/\gamma-Al_2O_3$ burns out, the production of CO_2 drops sharply. Normally, the O_2 concentration will be return to the initiation concentration. However, as the result of the changes of O_2 concentration detected during the PM combustion in the NO + O_2 atmosphere, it can be concluded that the concentration of O_2 is still higher than the initiation concentration. One reason for this is that the reaction $NO + O_2 \rightarrow NO_2$ is an exothermic one. As the temperature rises, less and less O_2 reacts with NO, therefore, the O_2 concentration is higher at high temperature than that at low temperature. The other reason is that more NOx is decomposed at high temperature.

Fig. 6 shows that the maximum conversion efficiency of NOx to N_2 is apparently improved from 5% to 21% at the range temperature 150°C–245°C with the presence of plasma. At the same time, the production of CO_2 is also enhanced as shown in Fig. 7. For the reaction over LKC catalyst assisted by plasma, Burch *et al.* (Burch, 1998) reported that $\gamma-Al_2O_3$ showed a high DeNOx performance when NO_2 or oxygenated hydrocarbons are presented in a gas stream. As a result, $\gamma-Al_2O_3$ is considered a strong candidate material for a plasma technology (Vogtlin, 1998). For the plasma readily oxidizes NO to NO_2 and partially oxidizes hydrocarbons to form oxygenated hydrocarbons (Penetrante, 1998). So, one of reaction mechanisms for LKC catalysts loaded on γ -alumina at the

low temperature with the assistant of plasma can be summarized as follows(Pau, 2001):



Compared with the Reaction(5), the Reaction(11) and (12) to produce NO₂ and oxygenated HC is inspired by plasma process. On the other hand, the Reaction(13) is preceded by catalysis process easily than Reaction(6). Therefore, the NO_x conversion to N₂ performance is improved with the application of plasma-assisted catalysis LKC. For the reactions between NO_x and DS, it is found that the reaction is improved slightly at a temperature range from 245°C to 500°C by plasma, the maximum conversion of NO_x to N₂ is promoted from 10.5% to 12% and the plasma has decreased the burning out of DS at about 20°C. The reason is maybe that the NO_x is activated by plasma process, the chemisorption performance of activated NO_x on the surface of the catalyst and DS is changed. Also, as Section 2.1 explained, plasma devices produced high energetic electrons that can promote the formation of activated species, such as O⁺ and O₃, which inspires the reaction of PM combustion to produce some intermediates (C⁺O) (Shangguan, 1997). In addition, the plasma generated NO₂ also enables a continuous regeneration of particulate filters(Hawker, 1997) to remove the PM. As a result, the conversion efficiency of NO_x and PM is a little improved.

3 Conclusions

An experimental investigation has been carried out for simultaneous removal of NO_x and diesel PM over La_{0.9}K_{0.1}CoO₃ catalyst assisted by plasma and the following conclusions are drawn:

The plasma promotes part of NO_x decomposed into N₂ and O₂ whether the presence of oxygen or not in the simulated exhausts. Moreover, with the promotion of discharge voltage, the decomposition efficiency of NO_x is improved.

LKC catalyst showed the catalytic characteristic for simultaneous removal of NO_x-PM. The catalysis improves the conversion efficiency of NO_x into N₂ and the ignition temperature and the burning out temperature of PM are reduced.

Compared with only LKC catalysis, the catalyst LKC assisted by plasma showed the higher catalytic conversion efficiency for simultaneous removal of NO_x-PM. The combustion temperature of PM is decreased and the efficiency of NO_x reduction to N₂ is enhanced. Especially, plasma enhances the catalytic conversion efficiency of NO_x to N₂ at low temperature.

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