RSC Advances

PAPER

Cite this: RSC Adv., 2015, 5, 40012

Received 5th November 2014 Accepted 24th April 2015

DOI: 10.1039/c4ra13662d

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Introduction

Solid carbon particles such as soot, char and coke generated by gasification and combustion of coal, heavy oil, and diesel fuel, require high activation energy compared to that of a gaseous or liquid product.¹ In particular, carbon PM, emitted from diesel engine, is considered to be one of the most hazardous materials to air quality and human health.²⁻⁴ However, removal of carbon PM is quite difficult based on current techniques, since the oxidative removal of carbon PM is usually carried out under an oxygen-rich environment in which the temperature can be reached as high as 600–700 °C due to its high activation energy. Three kinds of catalysts, the transition metal catalysts,⁵⁻⁷ the spinel-type catalysts,⁸⁻¹⁰ and the perovskite-type catalysts¹¹⁻¹⁴ have been applied in the catalytic combustion for removal of carbon PM. Among those catalysts, the perovskite-type catalysts show the best catalytic performance, but problems associated with a high temperature of 400 °C towards the formation of spinel structure have hindered its further development in removal of carbon PM.15 Recently, solid oxides such as cerium oxide have been investigated in the catalytic oxidation at lower temperature. Some modified CeO₂ oxides catalyze oxidation of carbon PM mainly because of its function of promoting evolution of lattice oxygen.¹⁶⁻¹⁹ Moreover, manganese oxides have

Application of combined plasma-catalytic method for carbon particulate matter (PM) removal

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The carbon particulate matter (PM) generated by diesel engine emissions has attracted world-wide attention because it has a remarkable impact on air quality and the human body. Therefore, research on the removal of carbon PM has attracted increasing interest recently. Additionally, oxidative removal of carbon PM neguires high temperature due to its high activation energy. In this research, a promising technology of nonthermal plasma (NTP) combined with catalytic oxidation is reported. The effective removal of carbon PM under NTP conditions by the synergy of combining plasma with MnO_x/CeO₂ catalysts at low temperatures was reported in this paper. The removal efficiency of carbon PM on MnO_x/ CeO₂ catalysts (Mn loading 5.0 wt%) can be as high as 85.2% and 94.3% at 20 °C and 200 °C respectively, at the discharge power of 18.0 W and air flow rate of 30 mL min⁻¹. Moderate reaction conditions with low temperature but high removal efficiency are the advantages of the decomposition of carbon PM in a dielectric barrier discharge (DBD) reactor. It is proposed that reactive oxygen species produced under NTP conditions are responsible for carbon PM converting into CO₂. Furthermore, various parameters such as temperature, discharge power and air flow rate under NTP were investigated in the present paper, as well as the reaction process of NTP. Meanwhile, the MnO_x/CeO₂ catalysts were also characterized by XRD and TEM techniques.

been reported as the most efficient transition-metal oxide catalysts for catalytic disposal of pollutants and CeO₂ plays an important role as a support owing to its storage capacity of oxygen and thermal stability.²⁰⁻²² Accordingly, of these two substances, manganese oxides and cerium oxide were chosen and prepared as catalysts in this work.

Furthermore, nonthermal plasma could activate molecules including PM, hydrocarbons, and NO_x at room temperature.^{23,24} Thus, extensive application of NTP has been reported in chemical synthesis,²⁵ removal of environmental pollutants such as volatile organic compounds (VOCs),^{26,27} and fabrication of materials.²⁸ Consequently, moderate reacting conditions with low temperature and high removal efficiency are the advantages of decomposition of carbon PM in NTP. It is proposed that reactive oxygen species such as (O₃, active molecule of N₂ and O₂, O⁺, O⁻, O(1D), O(3P), and electrons)^{29–32} produced under NTP conditions are responsible for carbon PM converted into CO₂. Catalytic oxidation of carbon PM with plasma assisted is the most economic approaches because of its lower temperature and excellent selectivity towards the formation of CO₂.

Therefore, a combined method of nonthermal plasmacatalytic reaction has been used in the removal of carbon PM. In this article, we present the results of catalytic oxidation carbon PM on MnO_x/CeO_2 catalysts under NTP conditions. DBD is chosen as the reactor because it can produce high concentrations of reactive oxygen species which could oxidize the carbon PM to CO_2 efficiently at lower temperature. Additionally,



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both a combined plasma-catalytic method and reaction process of NTP were investigated.

Experimental

1. Preparation of catalyst

A series of MnO_x/CeO_2 catalysts with different manganese ratio, were prepared by impregnation method. The support of CeO_2 was dried for 2 h at 110 °C, manganese acetate solution was dropwise added. Then it was aged at ambient temperature for 12 h, followed by calcination at 500 °C for 4 h in the air atmosphere. The obtained catalysts were named as MnO_x/CeO_2 .

In this paper, Printex U carbon powder was used as the substitute for carbon PM in diesel engine emissions. The carbon powder was made up of small spherical carbon particles (10–80 nm). It was subjected to chemical analyses in order to assess the solid phase emissions such as solid particulate or soot from diesel. The sample ratio of catalyst and U carbon powder was 2 : 1000 and these were prepared by mechanical grind method. All the samples were passed by the procedures of grounding fully, pressing, and sieved to 20–40 mesh size pellets.

2. Combined plasma-catalytic reactions

The experiments were carried out in a dielectric barrier discharge (DBD) reactor connected to a high-voltage power supply (Fig. 1). In the configuration of the DBD reactor, a quartz tube (i.d. 8.0 mm) was used as the reactor as well as the dielectric barrier, and also a stainless steel rod (o.d. 3.0 mm) was applied as the high-voltage electrode. At the same time, the stainless steel net wrapped on the outer surface of the quartz tube and was employed as the grounding electrode. A highvoltage power was used to control the discharge in the reactor. Discharge power was measured by the V-Q Lissajous program. The temperature of the reactor was measured by a thermocouple attached at the surface of the quartz tube reactor wall and controlled by an outer electrical heater. The sample pellets (20-40 mesh, 0.5 g) were filled in the interior of the discharge zone. Thus, a combined discharge plasma catalytic process can be carried out in this equipment. 0.5 g sample (20-40 mesh) was pretreated at 500 $^\circ$ C for 60 minutes in N₂ flow before experiment, and then cooled it to ambient temperature. Then a flowing mixed gas (21% O₂ and 79% N₂) was introduced into the dielectric DBD reactor in which the total flow rate was controlled at 30 mL min⁻¹, and simultaneously, the stage of



Fig. 1 The schematic diagram of the experimental setup.

discharge began. This discharge process just lasted several minutes at ambient temperature.

For comparison, the catalytic mode for the removal of carbon PM was carried out under the same conditions without discharge. The products of the reaction, such as CO and CO₂, were detected on a line gas chromatography (GC-1690, keqiao, china) with a FID attachment. The PM removal on the measurements was calculated as follows:

PM conversion [%] =
$$[c(CO) + c(CO_2)]/c(PM) \times 100\%$$
 (1)

3. Catalysts characterization

Structural characterizations of the samples were performed using X-ray diffraction (XRD). The XRD patterns were recorded on a Rigaku D/max-IIIB instrument using CuK α radiation (40 kV and 40 mA). The phase analysis was determined from XRD patterns using the MDI-JADE-5 program. Transmission electron microscopy (TEM) images were acquired with a HT-7700 electron microscope.

Results and discussion

1. Removal efficiency of carbon PM over different catalysts

Table 1 exhibits the removal efficiency of carbon PM over different catalysts such as Al₂O₃, CeO₂, MnO_x/Al₂O₃ and MnO_x/ CeO₂ at the temperature range from 20 to 200 °C. Under NTP condition, as shown in Table 1, it demonstrates no carbon PM removal efficiency on those catalysts in the absence of NTP condition during this temperature range. This result shows that it is difficult to oxide carbon PM only by the catalytic combustion since oxidation of PM requires a high temperature. However, with the presence of nonthermal plasma (NTP) technologies and MnO_x/CeO₂ catalyst applied in plasma, a significant PM removal efficiency can be observed. On the MnO_x/CeO₂ (Mn loading 5.0 wt%) catalyst, the carbon PM removal efficiency reaches to 85.2% at 20 °C and 94.3% at 200 °C, respectively. This result indicates that by using NTP, the reactant molecules can be easily activated and dissociated at ambient temperature. Similarly, over other catalysts, effective carbon PM removal efficiency is obtained as well during combined plasma-catalytic process. At 200 °C, the carbon PM removal efficiency over MnO_x/ Al₂O₃ catalyst is about 76.2%, and reaches 71.0% for CeO₂ and 25.5% for Al₂O₃. Among all catalysts, MnO_x/CeO₂ catalyst shows

Table 1 The removal efficiency of carbon PM over different catalysts at different temperature a

Temperature/°C	Catalyst			
	Al_2O_3	CeO ₂	MnO _x /Al ₂ O ₃	MnO _x /CeO ₂
20	23.8%	23.4%	35.1%	85.2%
100	24.9%	64.1%	68.0%	87.4%
200	25.5%	71.0%	76.2%	94.3%

^{*a*} Reaction conditions: $m_{\text{cat.}} = 0.50$ g, total flow rate at 30 mL min⁻¹, discharge power at 18.0 W.

the highest carbon PM removal efficiency. This combined plasma-catalytic process is possible due to the fact that various oxygen atoms generated by plasma discharges play an important function in breaking C–C bonds, which results in the oxidation of graphite. These oxygen atoms are the main reactants that can react with carbon PM to convert them into CO and CO₂.³³ In the reaction process, the O₂ is converted to O⁻ that reacts with O₂ to generate O₃. The observed synergistic catalytic effect is owing to the fact that with manganese oxide supported on CeO₂, more oxygen can be joined in the redox cycle.³⁴ On the other hand, the active species generated in the discharge zone by the nonthermal plasma (NTP) are much easier for adsorption and dissociation on the surface of catalyst. As a result, radical species can reach on the surface of catalyst and participate in the reaction.

Furthermore, during the experiment, only CO_2 can be detected with no other products such as CO detected by chromatography in the effluence, indicating the main component of carbon PM is pure graphite structure.²⁴ It may be due to the fact that active species generated in the combined plasma-catalytic process are contributing to accelerate the reaction of carbon converted into CO and CO_2 .

2. The activity of series of CeO_2 -supported MnO_x catalysts

Fig. 2 demonstrates the effect of the Mn loading (2.5%, 5.0%, 7.5%) on the catalytic performance of MnO_x/CeO_2 catalysts. The removal efficiency of carbon PM increases with Mn loaded, but it reaches a highest value on 5.0% MnO_x/CeO_2 catalyst. This trend may be attributed to the formation of bulk manganese particles which will decrease catalytic activity when the MnO_x content is over 7.5%.³⁴

3. The morphology of the 5% MnO_x/CeO₂ catalyst

XRD was used for direct observations of the catalyst. Three patterns, representing of CeO_2 , 5% MnO_x/CeO_2 catalyst before and after combined plasma-catalytic reaction are presented in

Fig. 3. On the CeO₂ sample (A), the diffraction peaks due to cubic CeO₂ phase are detected. On the 5% MnO_x/CeO_2 catalysts before and after reaction (B and C), no diffraction peak, characteristic of the manganese oxide could be observed except the CeO₂ phase, indicating the MnO_x was in high dispersion on the CeO₂ surface. This could be explained by the fact that the XRD technique could not detect very small crystallites (usually <3 nm).³⁵ Meanwhile, XRD patterns of MnO_x/CeO_2 before and after reaction showed that the catalyst still kept its crystalline structure after the plasma reaction.

Moreover, TEM was used for direct observations of the 5% MnO_x/CeO_2 catalysts. The surface morphology of the 5% MnO_x/CeO_2 catalysts before and after NTP reaction is clearly shown in Fig. 4. It can be seen that the catalyst shows no evident changes after nonthermal plasma reaction, indicating the 5% MnO_x/CeO_2 catalyst has high stability and can be recycled. Both results (XRD and TEM) suggest that the performance of 5% MnO_x/CeO_2 catalyst is stable under the plasma discharge conditions.

4. Effect of discharge power and flow velocity in plasmacatalytic process

Since the parameter affects the reaction greatly, the characteristic information such as flow rate and discharge power was investigated. Fig. 5(a) shows the conversion of carbon PM in O_2 plasma on 5% MnO_x/CeO₂ as a function of flow rate at the range from 30 to 90 mL min⁻¹. It is clear that the conversion of carbon PM to CO₂ shows a declining trend with the increasing of flow rate. It reaches the maximum at the lower flow rate of 30 mL min⁻¹, and then drops dramatically at 90 mL min⁻¹, indicating the condition of 30 mL min⁻¹ in flow rate is proved to be the suitable condition for the removal of carbon PM in NTP-catalytic reaction, which can be interpreted that more and more active particles are generated in the discharge zone of plasma under appropriate flow rate conditions. Moreover, with the increase of flow rate, the effective collisions between active particles and reactant molecules are inevitably reduced as the flow rate of



Fig. 2 Removal properties of carbon PM as a function of different Mn loadings on MnO_x/CeO_2 catalysts (reaction conditions: room temperature, 30 mL min⁻¹ flow rate of the air, discharge power at 18.0 W).



Fig. 3 XRD patterns of (a) CeO₂, 5% MnO_x/CeO₂ catalyst (b) before and (c) after reaction.

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Fig. 4 TEM photograph of 5% MnO_x/CeO_2 catalyst (a) before and (b) after reaction; (reaction condition: total flow rate at 30 mL min⁻¹, discharge power at 18.0 W and temperature at 200 °C).



Fig. 5 Removal efficiency of carbon PM as a function of (a) flow rate and (b) discharge power over MnO_x/CeO_2 catalyst (reaction condition (a): ambient temperature, discharge power at 18.0 W; (b): ambient temperature, 30 mL min⁻¹ flow rate of the air).

reactant gas increased. Thus, the following experiments were carried out at the condition of flow rate of 30 mL min⁻¹.

Additionally, the discharge power is an important parameter for plasma chemistry. The influence of the discharge power on carbon PM oxidation in NTP is also shown in Fig. 4(b). It shows an opposite trend in that of flow rate. Obviously, at the range of discharge power from 10.0 to 18.0 W, the conversion of carbon PM to CO_2 greatly improves with the increasing of discharge power. This is due to the fact that higher discharge power is able to supply more electrons with sufficient energy to activate the carbon PM particle. As a result, the active particle density can be improved and then the oxidation of carbon PM will be sped up.

5. Effect of reaction temperature and time in plasmacatalytic process

The effect of reaction temperature and time on plasma removal of PM over CeO₂ and 5% MnO_x/CeO₂ catalyst are illustrated in Fig. 6. As can be seen from Fig. 6, carbon PM removal efficiency is clearly influenced by both temperature and time. The carbon PM removal efficiency over CeO₂ at ambient temperature are quite low and with the time increasing to 25 minutes, the PM removal efficiency is still lower to 20%. However, for 5% MnO_x/ CeO₂ catalyst, at the same reaction time, the PM removal rate reaches 80%, indicating the carbon PM removal is improved significantly. This result suggests that by supported manganese oxide on CeO₂, it may be enter into ceria lattice and improves the oxygen storage capacity of ceria as well as the oxygen mobility on the surface of the mixed oxides.21 It is obviously on 5% MnO_x/CeO_2 catalyst, when temperature is higher to 200 °C, the reaction happens more rapidly. The removal of carbon PM is higher than 90% in 10 minutes.

6. Reaction process for carbon PM removal under plasma discharge conditions

The mechanism of carbon PM removed under plasma discharge conditions is not clear. From the fact that oxidation products is carbon dioxide, the nonthermal plasma reaction processing for



Fig. 6 PM removal as a function of reaction time on catalysts: (a) CeO_2 at ambient temperature, (b) 5% MnO_x/CeO_2 at ambient temperature, (c) 5% MnO_x/CeO_2 at 200 °C.



Fig. 7 Nonthermal plasma (NTP) reaction process for oxidation of carbon PM to CO_2 .

oxidation of carbon PM to CO_2 may be presumably in Fig. 7. Firstly, activated radical oxygen species induced by NTP, such as O_3 , O^- , O(1D), O(3P), are generated. With the synergistic effect of MnO_x/CeO_2 catalyst, some of them are adsorbed on the surface of the MnO_x/CeO_2 catalyst by diffusion and more effective collisions happen between active particle of catalyst and carbon PM particle. These active oxygen species contact with carbon PM and react, then forming large amounts CO radicals efficiently. Finally, the target product CO_2 is produced, with the carbon PM incinerated, after CO radicals combine with the former active oxygen species.

Conclusions

The combined plasma-catalytic process may be an efficient way for the removal of carbon PM. 5% MnO_x/CeO_2 has been demonstrated to be an efficient catalyst in the plasma-catalytic reaction for carbon PM converted into CO_2 . The synergistic effect between the plasma and the catalyst is mainly due to the active oxygen species yielded by NTP. These active species on the catalyst also play a role in the reaction of carbon PM removal. As a result, in this process, carbon PM removal could achieve 85.2% at ambient temperature. Due to the presence of nonthermal plasma (NTP), the temperature of the reaction is lower than that in traditional catalytic combustion mode.

Acknowledgements

The support of 973 Program (2013CB228104) of China is greatly appreciated.

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