Removal of NO by carbon-based catalytic reduction bed loaded with Mn induced by dielectric barrier discharge at low temperature

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Abstract

The current paper reports on a newly developed DBD-Mn/FCRB hybrid system to explore the removal of NO_x by reduction without adding reducing gas at low temperature (below 80°C). This technology was established with a fixed carbon-based reduction catalytic reduction bed loaded with manganese (Mn/FCRB) induced by dielectric barrier discharge (DBD). The NO conversion and N₂ selectivity in the new hybrid system reached 90.9% and 79.9% respectively under 8% oxygen content, 1,200 J/L specific input energy (SIE), which were all higher than in the single DBD and DBD-FCRB systems, respectively. The Mn/FCRB was further characterized before and after activation by SEM, XRD and XPS. The possible reaction pathways of denitration were proposed through three processes based on the experimental results: direct denitration of active carbon atoms excited by plasma, reduction by adsorptive C(N) and C(O) complexes on the FCRB surface, and the reaction of nitrogen oxides with by-product CO. In addition, the results also showed that the new in-situ reduction denitration system had strong oxygen shock resistance and water resistance.

Keywords: Dielectric barrier discharge, Fixed carbon-based reduction bed, Mn-based catalysts, Nitric oxide

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1. Introduction

With the increasing awareness of environmental protection, more and more attention has been paid to the atmospheric environment. Nitrogen oxides (NO_x) are considered the primary pollutants worldwide which come from combustion processes of coal-based fossil fuel power generation, fuel vehicles and other incineration processes [1-3]. They are responsible for such environmental problems as photochemical smog [4, 5], acid rain [6], combining with volatile organic compounds to produce ozone [7]. Further to the above, they cause many health problems including damage to the heart and lungs [8-10]. Nowadays, NO_x are mainly removed by selective catalytic reduction (SCR) owing to its high removal efficiency [11, 12]. But this technology features a relatively narrow operation temperature window (300–400°C) which means that the de- NO_x unit is placed upstream of the dedusting and desulfuration units, leading to activity declining and shorter service life of the catalysts [13]. What's more, the SCR technology continues to raise the worries for the leakage or escape of the reducing gas (for example, ammonia slip) [14]. Therefore, an environment-friendly de- NO_x technology at low temperature has long been a question of great interest.

The non-thermal plasma (NTP) has been reported as a promising and effective technology for removing NO_x which generally consists of highly reactive species including electrons, ions, radicals, excited and neutral species [15, 16] that all can interact with each other and contribute to the decompose hazardous air pollutants. NTP is used to selectively transfer energy to the electrons, thus avoiding the energy consumption necessary for the heating of the entire gas flow and the strong temperature dependence of the catalytic activity can be overcome by the addition of the plasma technology [17,18]. Dielectric barrier discharge (DBD) has been

1 demonstrated as the superior mode for the generation of NTP [19, 20]. Nevertheless, NO
2 removal by plasma was mainly attributed to oxidation [21-25], hence ammonia [26, 27] and
3 hydrocarbon gas as CH₄ [28, 29], C₃H₆ [30], C₃H₈ [31], C₇H₁₆ [32] and C₈H₁₈ [33] are used as
4 reducing gases in many previous studies. However, there is the limitations of gas leakage are yet
5 to be overcome.

6 Carbonaceous materials can reduce NO_x as an adsorbent and undergo heterogeneous gas-
7 solid reactions with NO to form N₂ [34]. Moreover, plasma-enhanced catalysis can lead to
8 synergistic effects [35, 36] and induce the C-NO reaction which requires a very high temperature
9 (above 900°C) in general [37, 38]. However, due to the high affinity of carbon to oxygen [39, 40],
10 carbon will preferentially react with residual O₂, resulting in low N₂ selectivity and high carbon
11 combustion [41]. Manganese, as one of the transition metals, is often used as the active
12 component of catalysts because of its abundant variable state including MnO, MnO₂, Mn₂O₃,
13 Mn₃O₄, Mn₅O₈ [42-44], and many studies have proved the important contribution of Mn as
14 catalysts for NO_x reduction by carbon materials [42, 43, 45-47]. Therefore, the method used
15 fixed carbon-based reduction beds (FCRB) loaded with Mn induced by DBD is expected to
16 become a new denitrification technology at low temperature which has low carbon consumption
17 and high N₂ selectivity. However, there is no research on this technology, and the specific
18 reaction pathways for the system have not been figured out owing to the rapid, complex and
19 undetectable reaction process.

20 The current paper reports on a new developed system utilized to investigate the
21 performance of the DBD induced Mn/FCRB (DBD-Mn/FCRB) de-NO_x technology at low
22 temperature (below 80°C), compared with the single DBD system and the DBD-FCRB hybrid

system. And the pore structure and surface micro-characteristic parameters of the Mn/FCRB before and after activation were also measured to explore the specific reaction mechanism of denitration. In addition, the influence of oxygen content and humidity on the denitration effect of the new system has been further investigated.

2. Material and Methods

2.1. Experimental Setup

In this paper, industrial coal-based activated carbon was purchased from Heatton Environmental Tech Ltd. (Shanghai, China), and the performance parameters of the FCRB are shown in Table S1. After grinding and mechanically sieving the original sample, the activated carbon with a particle size distribution of 0.6~1 mm (18–30 mesh) was obtained, which was washed 3 times with deionized water to remove the original impurities and dried at 105°C for 12 h.

The Mn/FCRB catalyst was introduced by excess-solution impregnation using manganese acetate ($(\text{CH}_3\text{COO})_2\text{Mn}$) of appropriate concentration to obtain around 5 wt% metal content (10 ml of solution/gram of FCRB), and the mixed solution was placed on a magnetic stirrer for 3 h. The FCRB-solution mixtures were dried and placed in an oven for 10 h at 110°C, then the dried product was put into a muffle furnace and calcined at 450°C for 3 h.

The denitration reaction device is shown in Fig. 1, which mainly includes the gas supply system, reaction system, and outlet gas analysis and detection system. The experiment was carried out in a dielectric barrier discharge reactor with a coaxial cylinder structure, including an inner tube (quartz glass, 11 mm outer diameter, tube length 275 mm, wall thickness 1 mm), outer tube (stainless steel, inner diameter 21 mm), inner electrode (with a stainless steel sheet wrapped

around the inner wall of the inner tube, thickness 0.3 mm, length 165 mm) and the circulating water outer tube (stainless steel, inner diameter 5 mm, tube length 172 mm). The DBD was generated using an alternating current power supply and the specific input energy (SIE) (Eq. (1)) ranges from 600 to 1,200 J/L. A 200 MHz digital phosphor oscilloscope (TDS2024B, Tektronix, USA) was used to analyze power. A probe thermometer (Testo 925, Testo SE & Co. KGaA, Germany) was used to measure the temperature of the FCRB right after each reaction power off, and an infrared thermometer (Testo 830-T1, Testo SE & Co. KGaA, Germany) was used to measure the temperature outside the wall of the reaction zone during each reaction process. The inner tube was hollow for sucking cold air, and the external circulating water ensured that the temperature in the reaction zone was below 80 °C. The humidity was adjusted by an ultrasonic atomizer (402AI, yuwell group, China) to control the H₂O content in the carrier gas (Argon), therefore the feed gas had different humidity. The humidity was measured by a psychrometer (Testo 605-H1, Testo SE & Co. KGaA, Germany) before the feed gas entered the DBD reactor.

$$SIE = \frac{P}{Q} = \frac{\text{discharge power (W)} \times 60 \text{ (s/min)}}{\text{total flow rate (L/min)}} \quad (1)$$

Fig. 1. Schematic of the DBD-Mn/FCRB hybrid system.

2.2. Experimental Methods

300 mg of FCRB or Mn/FCRB was loaded on the quartz wool in the DBD discharge zone, purged with Argon (Ar) at room temperature for 10 minutes to drive out the remaining impurities, and then the test gases were let into the reactor. To avoid the influence of NO_x produced by oxidation of N₂ on composition analysis of outlet gas, Ar was selected as the carrier gas which was conducive to the discussion of NO_x removal mechanism and reaction paths in the system. NO, Ar and O₂ came from the gas tanks containing high purity gases. The inlet flow rate was independently controlled by the Horiba Stec-4400 mass flow controller to ensure that the concentration of NO was 428 mg/m³, and the O₂ concentration was controlled at 0–16%. The feed gas flow rate was 2 L/min, the space velocity (Eq. (2)) in the DBD reaction zone was 2,895.2 h⁻¹, and the residence time in the reactor was 2.1 s. After the NO_x monitor (Testo 340,

Testo SE & Co. KGaA, Germany) detected that the NO_x concentration in the outlet gas was stable, the plasma power supply was switched on to start the discharge and the FTIR spectrometer (FTIR 850, Guangdong Co., China, 0.5 cm^{-1}) was used to quantitatively analyze the NO_x components of the outlet gas, and the data were all collected 15 min after the reaction began when the outlet NO_x concentration had stabilized. The gas chromatography (GC-9860, Jump Instrument, China) was used to detect the CO and CO_2 content in the outlet gas.

The space velocity, removal performance and N_2 selectivity of the DBD-Mn/FCRB hybrid system were defined as follows:

$$\text{space velocity (h}^{-1}\text{)} = \frac{Q_{\text{inlet flow (m}^3\text{/h)}}}{V_{\text{FCRB (m}^3\text{)}}} \quad (2)$$

$$\text{NO conversion (\%)} = \frac{\text{NO}_{\text{in}} - \text{NO}_{\text{out}}}{\text{NO}_{\text{in}}} \times 100\% \quad (3)$$

$$\text{N}_2 \text{ selectivity (\%)} = \frac{(\text{NO}_{\text{in}} + \text{NO}_{2 \text{ in}}) - (\text{NO}_{\text{out}} + \text{NO}_{2 \text{ out}})}{\text{NO}_{\text{in}} + \text{NO}_{2 \text{ in}}} \times 100\% \quad (4)$$

Where NO_{in} , NO_{out} , $\text{NO}_{2 \text{ in}}$ and $\text{NO}_{2 \text{ out}}$ are the inlet and outlet concentrations of NO and NO_2 , respectively, ppm. $\text{NO}_{2 \text{ in}}$ all came from the NO oxidation in presence of O_2 in the intake pipe.

2.3. Characterization

A scanning electron microscope (SEM, SU8010, Hitachi, Japan) was carried out for the surface morphology change of Mn/FCRB before and after DBD activation. X-ray powder diffraction (XRD) measurements were performed using Automated Multipurpose X-ray Diffractometer (Ultima IV, Rigaku, Japan). The XRD diffraction patterns were taken from 10° to 80° of 2θ at a scan rate of $10^\circ/\text{min}$. X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific, USA)

experiments were carried out with Al K α radiation (1486.6 eV). Binding energies were calibrated using the C1s peak (284.6 eV) as a reference.

3. Results and Discussion

3.1. De-NO_x Performances

Fig. 2. (a) NO conversion and (b) N₂ selectivity under different SIE over the single DBD, DBD-FCRB and DBD-Mn/FCRB systems (428 mg/m³ NO, 8% O₂, Ar used as the balance gas).

As shown in Fig. 2, when the plasma SIE increased from 600 to 1,200 J/L, the NO conversion and N₂ selectivity improved with the enhancement of the discharge energy in the single DBD, DBD-FCRB and DBD-Mn/FCRB systems. The NO conversion and N₂ selectivity in the single DBD system were only 52.9 and 33.0%, respectively under 8% oxygen, 1,200 J/L SIE, while those in the DBD-FCRB system reached 77.7 and 66.4%, respectively, and the highest NO conversion and N₂ selectivity were increased to 90.9 and 79.9% in the DBD-Mn/FCRB system, respectively. Therefore, Mn loading can serve reduction denitrification as the dominant denitration path, and significantly improve its denitrification performance and N₂ selectivity. Moreover, compared with the NH₃-SCR system using carbon-based loaded Mn

catalyst without NTP activation at low temperature, the NO conversion of these technologies is usually less than 80%, and the temperature is about 160~250 °C[48, 49]. And the NO conversion is generally in the range of 50~75% when the temperature is as high as 150~350 °C in the NTP-stimulated SCR denitrification technology with different catalysts at low temperature [50, 51].

In the single DBD system, plasma collided with NO, O₂, and other molecules through electrons, thereby generating free radicals such as N and O· that can oxidize or reduce NO (Eq. (3)~(6)). In the DBD-FCRB and DBD-Mn/FCRB systems, the reactions described above also occurred, in addition, the carbon activated by DBD may react with NO (Eq. (7) and (8)). As a result, the excellent N₂ selectivity was performed through the reduction denitration path.

3.2. Mn/FCRB Characterization

3.2.1 SEM results

Fig. 3. SEM images of FCRB: (a) blank FCRB, (b) the FCRB activated by DBD, and (c) the Mn/FCRB activated by DBD.

Figure 3 shows the SEM images of the original blank FCRB (B-FCRB), the FCRB and Mn/FCRB activated by DBD (A-FCRB and A-Mn/FCRB). After the plasma activation, there were obvious traces of etching both on the surfaces of A-FCRB and A-Mn/FCRB. These findings suggest that the surface of the FCRB and Mn/FCRB was excited by DBD to produce short-lived active carbon atoms. The previous researches have shown that through the high-energy gas species penetrating the surface of the material to a depth of several nanometers, the plasma can cause the surface of the carbon material to break the covalent bond, ion impact, etc. so that the surface carbon atoms are removed by various reactions[52, 53]. Thereby, the active carbon atoms excited by plasma etching can probably reduce NO and cause the Eq. (7) and Eq. (8) reactions.

3.2.2. XRD results

As shown in Fig. S1, the XRD pattern shows peaks that are identified as SiO_2 . There was no significant characteristic diffraction peak containing Mn in the sample B-Mn/FCRB, indicating that the active component mainly existed in an amorphous state, and SiO_2 is decomposed by

calcination in the preparation process. Higher dispersion can inhibit the formation of crystal clusters, effectively reduce the particle size of manganese oxide on the catalyst surface, improved the dispersion degree of active component MnO_x on the FCRB and increased lattice defects of the catalyst [54]. The surface distribution uniformity of Mn/FCRB decreased after DBD activation, and there are obvious characteristic peaks of MnO_x in the sample A-Mn/FCRB.

3.2.4. XPS results

Fig. 4. (a) XPS survey spectra of FCRBs, (b) XPS spectrum of C1s peak of B-FCRB and A-FCRB, and XPS spectrum of (c) Mn2p peak and (d) O1s peak of B-Mn/FCRB and A-Mn/FCRB.

Table 1. The Relative Content of Various Elements and Functional Groups Based on the XPS Spectra

Category		Sample			
		B-FCRB	A-FCRB	B-Mn/FCRB	A-Mn/FCRB
C/O		8.4	7.5	1.7	1.6
C/N		44.7	51.6	47.7	51.9
Functional groups relative Content (%)	C=C 284.3 eV	54.4	51.2	-	-
	C-O 284.8 eV	28.0	23.0	-	-
	C-N 285.7 eV	2.7	2.0	-	-
	C=O 287.1 eV	4.0	11.9	-	-
	O-C=O 289.0 eV	10.9	11.9	-	-
$S_{Mn^{4+}}/S_{Mn^{3+}}/S_{Mn^{2+}}$		-	-	9.2/5.2/1	18.9/5.5/1
$S_{O_{\alpha}}/S_{O_{\beta}}$		-	-	0.8	1.7

Fig. 4(a) shows the surface elements of B-FCRB, A-FCRB, B-Mn/FCRB and A-Mn/FCRB were mainly carbon, nitrogen, and oxygen. The relative contents of the elements and functional groups are listed in Table 1. As can be seen from the table, the C1s/O1s atomic ratio has decreased from 8.4 (B-FCRB) and 1.7 (B-Mn/FCRB) to 7.5 (A-FCRB) and 1.6 (A-Mn/FCRB) respectively, indicating that oxygen functional groups (OFGs) have increased after the plasma activation. The C1s/N1s atomic ratio has increased from 44.7 (B-FCRB) and 47.7 (B-Mn/FCRB) to 51.6 (A-FCRB) and 51.9 (A-Mn/FCRB) respectively after plasma activation, showing that nitrogen functional groups (NFGs) were consumed during the denitration process.

The C1s peaks of B-FCRB and A-FCRB were divided into 5 peaks respectively, as shown in Fig. 4(b). As can be seen from Table 1, the intensity of C=C groups reduced after DBD activation from 54.5 to 51.2%. It is known that the energy of positive, negative ions and electrons present in the plasma is sufficient to break chemical bonds on the outer surface of a

material, and the radicals formed in the plasma process were first formed in the π bonds ($C=C$) on the surface of carbonaceous materials because they are active and the most susceptible to plasma attack [55-57]. Therefore, the carbon-carbon network was disrupted, and new $C(O)$ and $C(N)$ groups were generated on the surfaces of Mn/FCRB by DBD activation as shown by Eq. (9)~(11) (where C^* means the active site on the Mn-FCRB surface). The results show that the total content of $C(O)$ complexes including $C-O$ (e.g., epoxy, hydroxyl), $C=O$ (e.g., carbonyl, quinone), and $C(O)O$ (e.g., carboxyl, lactone) was increased from 42.9 to 46.8%. However, the content of $C-O$ and $C-N$ was decreased after the denitration process. This result may be explained by the fact that these two complexes are more unstable and more likely to participate in the reactions and be consumed.

The importance of $C(N)$ and $C(O)$ complexes in the $C-NO$ reaction system was often emphasized [58-61], and the same considerations may be indicated in the $C-NO$ induced by DBD. $C(N)$ can react with newly adsorbed NO near the surface of Mn-FCRB to produce N_2 in a gas-solid heterogeneous phase, as shown by Eq. (12). Moreover, $C(N)$ can also produce N_2 through the solid-phase polymerization reaction of Eq. (13), which also has the effect of reducing denitrification and will re-release carbon active sites. On the other hand, $C(O)$ complexes were beneficial to the electron transfer on the carbon surface. Moreover, $C(O)$ has high reactivity that can directly reduce NO and the reduction reaction between $C(O)$ and NO is shown in Eq. (14).

As NO is reduced to N₂, the active sites of carbon resume activity again, and it goes back and forth.

The Mn2p of Mn/FCRB were divided into three peaks: Mn²⁺, Mn³⁺ and Mn⁴⁺, and the peaks were near 640.1 eV, 641.4 eV and 642.5 eV, respectively [62-64]. As shown in the Table 1, the proportion of third- and fourth-valence Mn increased after the DBD activation, indicating that DBD treatment was beneficial to increase the proportion of the high-valence component of the catalyst. The oxygen vacancies are known to play an important role in the adsorption and dissociation of oxygen molecules, leading to the generation of highly active electrophilic O₂ [65]. In O1s XPS spectra (Fig. 4(d)) of B-Mn/FCRB and A-Mn/FCRB, the peak at 531 eV is assigned to lattice oxygen (O_β), and the peak in B-Mn/FCRB and A-Mn/FCRB occur at 532 eV, which can be assigned to surface adsorbed oxygen species (O_α), resulting from the adsorption of gaseous O₂ into oxygen vacancies [66]. The O_α/O_β ratio increased after DBD activation (Table 1), in good agreement with the de-NO_x activities, which also indicated that DBD activation increased oxygen vacancies that promoted superior low-temperature reducibility.

3.3. CO_x Production

Fig. 5. (a) GC spectrum observed with and without 428 mg/m³ NO in Ar and 0% O₂ condition over the DBD-FCRB system (SIE = 1,000 J/L), and (b) CO and (c) CO₂ concentration under different SIE in Ar and 8% O₂ over the DBD-FCRB and DBD-Mn/FCRB system with and without 428 mg/m³ NO.

As shown in Fig. 5(a), after the injection of NO, CO outlet concentration has increased from 2.2 to 15.4 mg/m³, and the CO₂ outlet concentration has also increased from 52 to 126 mg/m³ in the DBD-FCRB system in the absence of oxygen. This can lead to the conclusion that the amount of CO_x produced has increased significantly due to the input of NO, which not only proved that C will react with NO (because O of NO was the only source of O in CO_x in the absence of oxygen), also proved the existence of CO products in the reaction zone just as the presumed Eq. (8). An implication of this result is the possibility that there should be a gas-phase reduction reaction Eq. (15) in the DBD-FCRB system.

To further prove the role of the CO-NO reaction, the CO concentration measurement under the 8% oxygen condition was carried out. As shown in figure 5(b, c), the amount of CO and CO₂ produced increased with the SIE increased, but the CO output in the presence of NO was less than in the absence of NO and CO₂ output presented an opposite trend. If NO was only

reduced and removed by C(O) and C(N) complexes or active carbon atoms, then due to the reactions of Eq. (7), (8), and (12) happening, theoretically the CO content should increase in the presence of NO, which was contrary to the experimental results. The results indicated that CO was consumed by the NO-CO reaction in the DBD-Mn/FCRB system. What's more, when NO was present in the gas intake, the effect of Mn catalyst was to significantly increase the reactivity both by increasing the number of reaction sites via the catalyst dispersion and reducing the activation energy and by increasing CO₂ production[67]. The latter can also be proved by the average CO₂/CO ratio that increased from 16.9 to 17.7 compared between the DBD-FCRB system and DBD-Mn/FCRB system, indicating that less carbon was consumed per molecule of NO reduced in the DBD-Mn/FCRB system.

3.4. Effects of O₂ and H₂O

Fig. 6. Effects of (a) O₂ concentration and (b) H₂O on NO conversion over the single DBD, DBD-FCRB, and DBD-Mn/FCRB systems (428 mg/m³ NO, Ar used as the balance gas, SIE = 800 J/L)

It is very necessary to explore the role of oxygen to understand the mechanism of this reduction system. It can be seen from Fig. 6(a) that when the SIE was 800 J/L and the oxygen content increased from 0 to 16%, the NO conversion decreased in the three systems. The large input of oxygen molecules will cause the excitation and decomposition of NO to be weakened and promote the occurrence of oxidation reactions (Eq. (16)~(18)), which increased the concentration of NO and NO₂. However, the overall performance of the DBD-Mn/FCRB system was better than that of the single DBD system, especially in the low and medium oxygen zone (4~8%). For the DBD-FCRB and DBD-Mn/FCRB systems, although the reaction atmosphere was undoubtedly an oxidizing atmosphere, there was a reducing system on the surface of FCRB. FCRB can absorb O₂ and O· species (Eq. (11)) so that the carbon can act as a buffer for oxygen shock. Therefore, the DBD-FCRB and DBD-Mn/FCRB systems reduced the sensitivity of the system to oxygen concentration. With the further increase of oxygen content, the adsorption active sites on the surface of FCRB gradually approached saturation, its buffering effect on oxygen-containing species was relatively insignificant, but it still had a relatively good denitration effect in the DBD-Mn/FCRB system.

Exploring the influence of humidity on denitration capacity is helpful to the practical application of the technology. As shown in Fig. 6(b), no matter in what relative humidity conditions, the NO conversion of the DBD-FCRB system was better than that of the single DBD system, and DBD-Mn/FCRB was slightly better than the DBD-FCRB system. In the single DBD system, the NO

conversion increased from 52.9 to 63.4% then decreased to 42.3%. The increase was caused by $H\cdot$, $\cdot OH$ and $HO_2\cdot$ active groups generated from water molecules under the bombardment of plasma. As a strong oxidizing radical, $HO_2\cdot$ will further oxidize NO to NO_2 (Eq. (19)~(21)). And the phenomenon was also found in this study that NO decreased and NO_2 increased which also further confirmed this reaction mechanism. The NO conversion in the single DBD system decreased because water molecules acted as a "quencher" gradually, which consumes some of the active species to produce $H\cdot$, $OH\cdot$ and a few $O\cdot$ anions by dissociative electron attachment to H_2O molecules[68], so the number of active species participating in the NO reduction reaction decreased. However, the denitration capacity was stable at high humidity in the DBD/FCRB system and the NO conversion was 87.1% when the relative humidity was 90%, as a consequence of the increased moisture absorption of FCRB as humidity increases [69], and the content of water molecules in the reaction zone was relatively stable. However, although the presence of water vapor did not affect the crystal form, particle size and specific surface area of the Mn-based catalysts, it can compete with NO to adsorb at the active center on the catalyst surface, resulting in a decrease in the number of available active centers in the reaction process, thus inhibiting the activity of the catalyst [70]. Therefore, the NO conversion of the DBD-Mn/FCRB system decreased slightly with the increase of humidity overall and was similar to the DBD-FCRB system in the high humidity area with the lowest 88.0% of the NO conversion.

4. DBD-Mn/FCRB System Reaction Mechanism

In the denitration process of the DBD-Mn/FCRB system, the first step is that NO and O₂ molecules are impacted by high-energy particles in the plasma atmosphere to produce a large number of active radical groups such as N and O·, and the surface of Mn/FCRB is also etched and excited by the plasma at the same time. Afterward, these gaseous high-energy intermediate particles will undergo adsorption and various chemical reactions with the surface of FCRB.

In summary, the main reduction denitrification reaction processes of the DBD-Mn/FCRB system are shown in Fig. 7. As mentioned earlier, the DBD-Mn/FCRB system is mainly reductive denitrification. The first reductive denitrification path is the direct participation of gas-solid heterogeneous reaction, that is, the Mn/FCRB surface is excited by the strong bombardment of plasma to produce active carbon atoms which can directly reduce NO and produce CO or CO₂, as shown in Fig. 7(a). In addition, plasma can also excite more carbon active sites C*, thereby promoting chemical adsorption. The second reaction mechanism is to use the adsorbed C(O) and C(N) complexes to generate solid-phase and gas-solid heterogeneous reactions to reduction denitrification, as shown in Fig. 7(b)~(d). The third path is to use the CO produced by the first two reaction pathways and the desorption of the oxygen complex C(O) on the Mn/FCRB surface for CO-NO gas-phase reaction, as shown in Fig. 7(e).

Fig. 7. Reduction denitrification reaction processes of DBD-Mn/FCRB system.

5. Conclusions

A new hybrid system DBD-Mn/FCRB was established to explore the removal of NO_x and the reaction mechanism by reduction without adding reducing gas at low temperature (below 80°C) for the first time. The results presented herein provide definite evidence of the role of Mn/FCRB in promoting the reduction de- NO_x performance of the NTP at low temperature. The higher NO conversion and N_2 selectivity, and lower carbon consumption in the DBD-Mn/FCRB hybrid system showed the best NO reduction capacity. The mechanisms of the removal of NO_x in the new system were also proposed through three processes: direct denitration of active carbon atoms excited by plasma, reduction by adsorptive $\text{C}(\text{N})$ and $\text{C}(\text{O})$ complexes on the carbon surface, and the reaction of nitrogen oxides with by-product CO. In addition, the new in-situ catalytic reduction denitration system had good oxygen shock resistance and water resistance.

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Author Contributions

F. G. (M.A. student) conducted all the experiments and wrote the manuscript. X.P.J. (M.A. student) assisted in the development of methodology. G.C.W. (Professor) revised the manuscript. L.Y.S. (M.A. student) assisted in conducting experiments. Y.J.T. (M.A. student) assisted in conducting experiments. R.X.Z. (Professor) assisted in formulation of overarching research goals and revised the manuscript. W.X.Z. (Ph.D.) assisted in the manuscript writing. J.Y.H. (Professor) assisted in the development of methodology and data curation. R.N.Z. (Ph.D.) revised the manuscript.

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