Research Progress in Treatment of VOCs by Dielectric Barrier Plasma Cooperating Catalyst

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Abstract. Volatile organic compounds (VOCs) are an important component of air pollutants. As a new technology, low temperature plasma technology has the advantages of low cost, simple structure, and wide applicability in processing VOCs. It has attracted widespread attention from scholars at home and abroad in recent years. VOCs components in industrial flue gas are often very complex and the degree of degradation is different. Therefore, in the laboratory simulation, it is necessary to increase the components of simulated exhaust gas and develop a dielectric barrier plasma co-catalysis technology that can deal with multiple components. The removal rate of VOCs is positively related to the discharge voltage and energy density of the reactor. The higher the voltage, the higher the removal rate. But it is accompanied by the increase in the production of NOx, O3 and other byproducts. The type of medium has a great influence on the removal effect of VOCs. The cooperative catalytic removal of VOCs by dielectric barrier plasma is a complex physico-chemical process, and the current research on the reaction mechanism is incomplete.

1. Introduction
Volatile organic compounds (VOCs) are an important component of air pollutants, as well as an important precursor to haze and photochemical smog. When human body is in the environment with high VOCs concentration for a long time, symptoms such as dizziness and vomiting may occur, which may cause diseases of the human respiratory tract, internal organs, and nervous system. Treatment of VOCs pollution is urgent, and the end treatment is one of the important ways of VOCs emission reduction.

2. Overview
Treatment of VOCs pollution is urgent, and the end treatment is one of the important ways of VOCs emission reduction. There are two main VOCs processing methods. One kind of method is recycling technology, which uses condensation, absorption, and other methods to separate and remove VOCs from the exhaust gas; the other kind of method is destruction technology, which uses combustion, catalytic combustion, and biodegradation technologies to remove VOCs. Each technology has advantages and disadvantages and areas of application. As a new technology, low temperature plasma technology has the advantages of low cost, simple structure, and wide applicability in processing VOCs. It has attracted widespread attention from scholars at home and abroad in recent years.
3. Synergistic catalytic treatment of VOCs with dielectric barrier plasma

3.1. Plasma
At normal temperature or lower temperature, by applying high voltage to excite gas, plasma can generate a large number of very active chemical substances, such as high-energy electrons, ions, free radicals and excited molecules, atoms, and so on. The collision between these active substances and VOCs molecules leads to a series of physical and chemical reactions, which break and dissociate chemical bonds of VOCs molecules and then degrade VOCs. At the same time, when O2 is present in polluting gas, O2 collides with high-energy electrons to produce O3, oxygen atoms and excited oxygen molecules. These strongly oxidizing substances can oxidize VOCs to non-toxic and harmless CO2.

3.2. Dielectric barrier plasma cooperating catalyst
Dielectric barrier low-temperature plasma methods still have many disadvantages, such as low CO2 selectivity, high power requirements, and easy to generate toxic by-products (O3, NOx). The combination of catalyst and dielectric barrier plasma can solve these problems well and make this technology become one of research hotspots in VOCs processing field in recent years.

The process of low temperature plasma synergistic catalytic treatment of VOCs consists of two parts, one part is the reaction in the gas phase, and the other part is the reaction on the catalyst surface[1]. Figure 1 is a schematic diagram of the mechanism of VOCs (toluene as an example) treated by low temperature plasma cocatalyst.

Yue, X.G.[2] studied the co-degradation of benzene, toluene, xylene and formaldehyde by dielectric barrier plasma with TiO2 catalyst. It was found that collaborative processing can significantly improve processing efficiency of VOCs. Wang, S. G.[3] studied the effect of synergistic effect of dielectric barrier and CuO/MnO2 catalyst on CO2 selectivity, CO/CO2 and O3 content in tail gas. It was found that under synergistic effect of CuO/MnO2, selectivity of CO2 was as high as 96.5%, and CO was almost completely oxidized to CO2. At power of 24.5W, φ(O3) in the exhaust gas was reduced from $5.95 \times 10^{-4}$ to $9.60 \times 10^{-5}$. Wu, Z.L.[4] used dielectric barrier discharge with TiO2/diatomite to degrade naphthalene. The experimental results showed that removal rate of naphthalene by pure dielectric barrier discharge was 63.4%, and removal rate of naphthalene was significantly increased to 82.4% after filling diatomite. After filling TiO2/diatomite, removal rate of naphthalene was further increased to 88%. In summary, the use of catalysts can significantly enhance the removal rate of VOCs and CO2 selectivity, reduce the generation of by-products, and increase energy efficiency to achieve the effect of reducing energy consumption.
3.3. Factors influencing VOCs processing effect

3.3.1. Reactor structure and media types. The reactor is an important component of dielectric barrier plasma cocatalyst technology. The reactor structure and the type of medium directly affect the removal ability of VOCs. Zhao, Q.[5] compared discharge characteristics of coaxial cylindrical and parallel plate reactors, removal effect of toluene, CO2 selectivity and carbon balance. It was found that under the same applied voltage, field strength of coaxial cylindrical reactor near electrode was higher than that of parallel plate reactor, which was more prone to ionization and higher electron energy. Thus, removal effect of coaxial cylindrical reactor was better. Wang, L.[6] took glass, quartz and corundum as media respectively, and compared time when they reached the same breakdown field strength, and found that corundum had the shortest time and the highest efficiency. At the same time, he found that in the same period, corundum discharge time was the longest, quartz second, glass was the shortest. And the longer discharge time, the better removal effect.

3.3.2. Catalyst type. In the field of organic waste gas catalytic treatment, there are many researches on precious metal catalysts, transition metal oxide catalysts, molecular sieve catalysts and photocatalysts. In recent years, more researches have been made on transition metal oxide catalysts (oxides such as Mn, Co, Cu), molecular sieve catalysts, and photocatalysts (TiO2, ZnO, etc.). Guo,Y.F.[7] investigated synergistic treatment of toluene with dielectric barrier plasma and Cu, Fe, Co and Mn oxides. The effects of four catalysts on toluene removal rate, CO2 selectivity, and O3 production were compared. Experimental results show that under certain conditions of electric field strength and initial toluene concentration, removal rate of toluene with metal oxides was much higher than removal rate of toluene using only dielectric barrier. The experiment results of Mn oxide catalyst were the best. Zhu,X.[8] also studied the effect of Cu/Ce composite catalysts (Cu/Ce ratios of 1:0, 1:1, 1:3, 3:3, 1:0:1) on the removal efficiency of formaldehyde. The experimental results showed that the combination of CuO and CeO2 could significantly improve the removal rate of formaldehyde. When Cu/Ce was 1:1, the highest removal rate of formaldehyde, selectivity of CO2 and energy efficiency could be achieved at the lowest energy density.

3.3.3. Placement of catalyst. The combination of dielectric barrier plasma and catalyst can be divided into two types in structure: one is built-in plasma catalysis (IPC), also known as "one-stage method"; the other is post-plasma catalysis (PPC), also called "two-stage method". During the discharge process, plasma will not only produce stable substances, but also a large number of excited-state active species with short life span, such as oxygen atoms, hydroxyl radicals. Therefore, the different combinations of catalyst and medium barrier reactor will directly affect interaction of these short-lived active species with the catalyst. At the same time, the adaptability of different types of catalysts to the two combined methods is not the same, but they will show obvious differences. Fan, H.Y.[9] studied 3 placement positions of Ag/HZSM-5 catalyst in the plasma reactor, respectively: 2cm behind plasma discharge area, the edge of the discharge area and discharge area. Experimental results showed that only by placing catalyst in the plasma discharge area could a large amount of benzene be removed in a short time, and carbon balance and CO2 selectivity were close to 100%. Van, D.J.[10] studied treatment effect of TiO2 catalyst and CuOMnO2/TiO2 composite catalyst at the positions of IPC and PPC. Taking outlet O3 low concentration and toluene removal rate as a measure, the results showed that there was no significant change in the outlet O3 concentration when TiO2 catalyst was placed at two positions, but the toluene removal rate of IPC was the highest, that was, TiO2 catalyst was the most effective in the discharge area. When O3 generated by dielectric barrier discharge flowed along the surface of post-catalyst with gas flow, a large amount of oxygen atoms were generated by catalytic decomposition, which further oxidized and decomposed toluene, thereby increasing toluene removal rate and reducing the outlet O3 concentration.
3.3.4. **Flue gas humidity.** Flue gas humidity is also one of the main factors affecting VOCs cocatalyzed by dielectric barrier plasma. Initially, under the effect of dielectric barrier discharge, water will decompose and produce active species such as H, OH, and HO₂. These active species will participate in the oxidation process of VOCs, thereby increasing the degradation efficiency of VOCs. However, in actual research, the opposite effect had occurred. On the one hand, water molecules were prone to form competitive adsorption of VOC molecules on the catalyst surface. On the other hand, due to electronegativity of water, the energy of high-energy electrons was suppressed. Yue, X.G.[11] showed that VOCs processing efficiency was significantly lower in rainy days than in sunny days. This could reflect that in a certain range of temperature, air humidity and dielectric barrier catalytic processing efficiency was negatively correlated. Dai, S.L.[12] used PPC dielectric barrier plasma catalytic reaction system to study the effect of humidity on toluene removal rate and O₃ residual amount. The experimental results showed that the increase of humidity would reduce toluene removal rate of the whole reaction system and increase residual amount of O₃. This proved that in PPC, it was O₃ and reactive oxygen atoms that played a leading role in the degradation of toluene, rather than hydroxyl radicals generated by water through discharge.

4. Conclusion

- At present, most of research on dielectric barrier plasma cocatalysis only focus on one or several VOCs. However, VOCs components in industrial flue gas are often very complex and the degree of degradation is different. For different VOCs, operating conditions and process parameters of the treatment are quite different. Therefore, in the laboratory simulation, it is necessary to increase the components of simulated exhaust gas and develop a dielectric barrier plasma co-catalysis technology that can deal with multiple components.

- The removal rate of VOCs is positively related to the discharge voltage and energy density of the reactor. The higher the voltage, the higher the removal rate. But it is accompanied by the increase in the production of NOₓ, O₃ and other byproducts. At present, although co-catalysis can reduce discharge voltage and the generation of by-products under the condition of ensuring a certain degradation rate, it cannot be completely avoided. Therefore, it is necessary to develop more suitable catalysts to ensure higher degradation efficiency, reduce by-products and improve energy efficiency.

- At present, the matching conditions of catalyst type and dielectric barrier plasma reactor are not clear. Therefore, it is of great significance to study applicable conditions and properties of catalysts.

- The type of medium has a great influence on the removal effect of VOCs. At present, most laboratories use ceramics or corundum as media, and the prices of these two media are relatively expensive, which limits their large-scale applications. Therefore, further research and development of media with superior performance and lower price is of great significance for dielectric barrier plasma cooperative catalytic treatment of VOCs technology.

- The cooperative catalytic removal of VOCs by dielectric barrier plasma is a complex physico-chemical process, and the current research on the reaction mechanism is incomplete. Therefore, further research on the mechanism of VOCs removal by dielectric barrier plasma is needed to establish a complete reaction mechanism system and kinetic model.

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