Experimental Study on Catalytic Oxidation of Toluene with Manganese Catalysts and Ozone at Low Temperature

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Abstract: The single metal oxide catalyst of transition metal element Mn and the composite metal oxide catalysts of Mn-Co and Mn-Fe are prepared by impregnation method using activated carbon (AC) as carrier. The catalysts are characterized by x-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). The performance of the catalysts for catalytic ozonation of toluene is tested in a fixed bed tubular reactor. The results show that the activity of the single metal oxide catalyst of Mn is lower than that of the composite metal oxide catalysts of Mn-Co and Mn-Fe, and the activity of Mn-Co is higher than that of Mn-Fe. The catalytic efficiency of three catalysts is Mn/AC< Mn-Fe/AC< Mn-Co/AC. In this study, the factors influencing the degradation of toluene by catalytic ozonation are analyzed, and the mechanism is explored.

1. Introduction
Volatile organic compounds (VOCs) are a kind of compounds, which are irritant, teratogenic, carcinogenic, mutagenic, flammable and explosive, and have great harm to human body and ecosystem\cite{1-5}. As an important precursor of ozone and secondary organic particulate matter, VOCs play an important role in atmospheric chemical reaction\cite{6}. According to the definition of the World Health Organization (WHO), VOCs refer to organic compounds whose melting point is below room temperature and boiling point is in the range of 50\textdegree C and 260\textdegree C\cite{7}. Due to its impact on the global environmental system and its close relationship with indoor air quality, it attracts more and more attention from scholars around the world\cite{8}. Benzene series are a kind of important aromatic hydrocarbon compounds, which are widely used in industrial production as chemical raw materials. In recent years, the number of benzene series entering the environment has increased dramatically, causing serious air pollution and endangering human health \cite{9-12}. Catalytic oxidation combined with ozone oxidation can effectively degrade volatile organic compounds at lower temperature. It is a promising treatment technology for organic compounds\cite{13-14}. In this study, the single metal oxide catalyst of transition metal element Mn and the composite metal oxide catalysts of Mn-Co and Mn-Fe are prepared. The performance of the catalysts for catalytic ozonation of toluene is tested. The influencing factors of catalytic ozonation for toluene degradation are analyzed and the mechanism is explored.
2 Experimental part

2.1 Preparation of catalysts
The coconut shell activated carbon is put in a certain concentration of nitric acid solution, heated and stirred for 3h, washed with deionized water and filtrate close to neutral, dried at 105°C. And the pretreatment of activated carbon is completed to remove impurities such as dust. Influencing factors are exclude for experimental inquiry. The activated carbon is placed in solution of Mn(NO$_3$)$_2$, Co(NO$_3$)$_2$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, and put the activated carbon in an ultrasonic device for 60 min, magnetically stirred for 10h, and put it in a dry box. It is dried at 105°C, then placed in a muffle furnace at 550°C for 5h.

2.2 Characterization of the catalysts
In this study, x-ray diffraction (XRD) (voltage: 40kv, current: 40mA, diffraction angle: 10-80) is used to analyze the catalysts, and the diffraction graph is analyzed to obtain the composition of the material, and the internal atom or molecular structure of the material. Or information to determine the main components of the catalysts. Scanning electron microscope (SEM) is used to observe whether the active components are uniformly loaded into the surface of coconut shell activated carbon. and the element type and content of the active component are analyzed by an energy dispersive spectrometer (EDS).

2.3 Performance test of catalysts
Using the device shown in Figure. 1, the toluene is mixed with air by bubbling and blowing. The ozone is generated by the ozone generator by electrolyzing air. The ozone is controlled by the flowmeter and enters the fixed bed tubular reactor with the toluene, and the performance test of the catalysts for catalytic ozonation of toluene is tested in the range of 25°C-130°C at low temperature conditions. The treated exhaust gas is organized and discharged through the air intake system.

Fig 1. simple flowchart of experimental device

3 Results and discussion

3.1 Characterization and analysis of catalysts

3.1.1 XRD analysis of catalysts
The XRD graph of catalysts with different components is shown in Figure. 2. The analysis results show that there are two main components in Mn/AC, namely Mn$_3$O$_4$ and Mn$_7$O$_{12}$, of which Mn$_7$O$_{12}$ is the main part. For the same substance, the narrow peak indicates that the grains are relatively large,
and the peak height indicates that the crystallization is better, so Mn$_2$O$_3$ is better than the crystallization of Mn$_3$O$_4$. The diffraction graph of Mn-Co/AC, Mn-Fe/AC and Mn/AC are analyzed and compared, except that the diffraction peaks of Co$_3$O$_4$ and Fe$_3$O$_4$ are increased, and the diffraction peaks of Mn$_2$O$_3$ and Mn$_3$O$_4$ get narrower. It indicates that the grain size became larger, which is consistent with the results observed by SEM.

![XRD graph of catalysts with different components](image)

**Fig 2.** XRD graph of catalysts with different components

### 3.1.2 SEM analysis of catalysts

![SEM graphs of catalysts with different components](image)

**Fig 3.** SEM graphs of catalysts with different components

The SEM graphs of the catalyst prepared by different components is shown in Figure 3. From the graphs, the surface morphology and the particle size of the catalysts can be observed. The figure shows that different active components can be uniformly loaded into the surface and internal pore of activated carbon, significantly changing the specific surface area and pore size of the catalysts. The difference is that the particle size is smaller when Mn is loaded, and the particle size is gradually increased when loaded with two components such as Mn-Co and Mn-Fe, and a partial agglomeration phenomenon occurs, and a large porous particle is formed. The pores formed between the particles and the particles and the intrinsic pore structure of the activated carbon allow the toluene gas to be in effective contact with the catalysts.

### 3.1.3 EDS analysis of catalysts

The EDS combined with SEM is used to analyze the type and content of the elements in the microregion of the material. The EDS graphs of the catalysts with different components are shown in Figure 4, and the contents of the metal elements are shown in Table 1.
Mn/AC(SEM)  Mn/AC(EDS)  
Mn-Co/AC(SEM)  Mn-Co/AC(EDS)  
Mn-Fe/AC(SEM)  Mn-Fe/AC(EDS)  

Fig 4. EDS graphs of catalysts with different components

Table 1. Contents of various metal elements in catalysts with different components

| Catalysts type | Elements | Weight Percentage | Atomic percentage |
|----------------|----------|-------------------|-------------------|
| Mn/AC          | C        | 65.31             | 82.43             |
|                | O        | 17.41             | 13.61             |
|                | Mn       | 17.28             | 3.95              |
|                | C        | 67.08             | 86.08             |
| Mn-Co/AC       | O        | 7.11              | 6.85              |
|                | Mn       | 16.37             | 4.59              |
|                | Co       | 9.44              | 2.47              |
| Mn-Fe/AC       | C        | 65.11             | 84.57             |
|                | O        | 10.28             | 9.58              |
3.2 Effect of type and content of transition metal elements on degradation efficiency

In this study, the single metal oxide catalyst of Mn and the composite metal oxide catalysts of Mn-Co, Mn-Fe are prepared by controlling the amount of metal loading. The degradation efficiency of toluene is compared under the same experimental conditions. The results are shown in Figure 5.

| Element | Load (%) | Degradation Efficiency |
|---------|----------|------------------------|
| Mn      | 16.25    | 4.41                   |
| Fe      | 5.37     | 1.43                   |

Fig 5. Effects of transition metal elements on degradation efficiency

For the single metal oxides catalyst of Mn, when the theoretical load of manganese is in the range of 0-16%, the degradation efficiency increases with the increase of the load of manganese element, but when the load of manganese element reaches 16%, the increase of the load of manganese element has little effect on the improvement of the degradation efficiency, even shows a decreasing trend. The reason may be that with the increase of Mn content, some of the Mn oxides agglomerate on the surface of activated carbon or the excessive content of Mn leads to the blockage of some of the voids of activated carbon, so the specific surface area of activated carbon decreases, which affects the adsorption of toluene on activated carbon and the contact between active components and toluene, and the catalytic efficiency is not obviously improved or even gradually decreasing Situation. The catalytic efficiency of the three catalysts prepared is Mn/AC<Mn-Fe/AC<Mn-Co/AC.

3.3 Effect of ozone concentration on the oxidation efficiency of toluene

Ozone has a strong oxidation ability, and its redox capacity is second only to fluorine. The oxidation potential is 2.07eV, which is mainly used in its application. The degradation of toluene and other organic compounds by ozone is a kind of advanced oxidation technology. In the absence of catalyst, the degradation efficiency of toluene is slow and the degradation of toluene is almost non-existent in the oxidation of toluene with ozone. Under the action of catalyst, the ozone oxidation of toluene is obvious. With the increasing of ozone content, the degradation efficiency of toluene is improved constantly. When the concentration ratio of toluene to ozone reaches 1:3, the degradation efficiency of toluene is maximized and no excessive ozone is generated in the exhaust gas, which saves resources and does not cause ozone pollution to the environment. In this study, the catalytic degradation experiment is tested with Mn-Co/AC catalyst. Under the condition of temperature control at 180℃, the degradation efficiency of toluene is up to 99%, and the catalytic effect is obvious. The effect of ozone concentration on the oxidative degradation efficiency of toluene is shown in Figure 6.
Effect of ozone concentration on oxidative degradation efficiency of toluene

3.4 Effect of temperature on the degradation efficiency of ozone and toluene

Ozone is easy to decompose, and its half-life decreases with the increase of temperature. The degradation efficiency of toluene with Mn-Co/AC catalyst increases continuously at the beginning. When the temperature reaches 180°C, the degradation efficiency can reach 99%, but when the temperature continue to rise, the degradation efficiency begins to decrease. The degradation efficiency decreases gradually in a certain temperature range, and then increases again when the temperature reaches 260 °C. The degradation efficiency of toluene can reach 93%. The change of toluene degradation efficiency with temperature is shown in Figure 7.

![Fig 6. Effect of ozone concentration on oxidative degradation efficiency of toluene](image6.png)

![Fig 7. Effect of temperature on degradation efficiency of ozone and toluene](image7.png)

The reason may be that the catalytic effect of the catalyst gradually appears in the first stage with the temperature increases. The ozone does not decompose rapidly during the gas residence time, so the catalytic effect of the catalytic and ozone oxidation is obvious. The degradation efficiency of toluene is constant at this stage. In the second stage, when the temperature rises to a certain extent, the ozone completely or partially decomposes during the gas residence time, the ozone oxidation is gradually weakened, and the toluene degradation efficiency is gradually reduced. In the third stage, as the
temperature continues to increase, the catalytic effect of the catalyst alone is enhanced, and the degradation efficiency of toluene is improved. However, the degradation efficiency of the catalyst is reduced relative to the catalytic and ozone oxidation degradation of toluene.

3.5 Mechanism analysis of catalytic and ozone ozonation degradation of toluene

Catalytic oxidation technology is a kind of exhaust gas treatment method, which can completely oxidize and decompose combustible components in exhaust gas under the action of catalyst at lower temperature, so that the gas can be purified. It is suitable for treating combustible or decomposable VOCs at high temperature[15]. Catalytic oxidation technology has the advantages of low energy consumption, high safety, no secondary pollution and simple operation. It can be used to eliminate odor. It has less limitation on the concentration and calorific value of combustible components, can complete the reaction in the range of 200°C~400°C, less auxiliary fuel consumption and a large reduction of nitrogen oxide (NOx) production. It is suitable for the treatment of gaseous and aerosol pollutants. In recent years, great progress has been made in theory and application of ozone oxidation. Researchers have also made fruitful research on the mechanism of ozone oxidation and degradation of various organic compounds. Advanced catalytic oxidation process using ozone as the main oxidant has also been developed rapidly. At the same time, ozone has also been used in more and more fields.

In this study, the reason for the degradation of toluene by ozone may be the direct contact reaction between ozone and toluene, but the direct contact reaction is slower or does not react. This is the reason why the degradation rate of toluene is slower without catalyst in the experiment. However, when catalyst is added, the oxidation effect of ozone is obviously enhanced. The oxidation mechanism is as follows:

\[ \text{O}_3 \rightarrow \text{O}_2 + \text{O}^* \]

\[ \text{O}^* + \text{O}_3 \rightarrow 2\text{O}_2^* \]

\( \text{O}^* \) and \( \text{O}^* \) have strong oxidation, and can effectively degrade toluene under catalytic conditions.

Another reason may be that toluene contains certain humidity when it is bubbling and blowing and mixed with air. In this case, ozone will produce a certain amount of hydroxyl radical, which is more oxidative and can degrade toluene more efficiently. Both oxygen radicals and hydroxyl radicals can be used for multi-stage oxidation of toluene, and it is oxidized to intermediate products of small molecules, and finally to water and carbon dioxide.

4 Conclusion

(1) The loading amount of active components of catalysts should be controlled within a certain range, too little load is difficult to achieve catalytic effect, and too much load will lead to a smaller contact area between toluene and active components, which can not achieve the catalytic effect.

(2) Ozone reacts slowly with toluene without catalyst, even without oxidation. The addition of catalysts can significantly accelerate the degradation efficiency of toluene.

(3) The process of catalytic oxidation and ozone oxidation in the treatment of toluene, the temperature must be controlled within a certain range. If the temperature is too low, the catalyst is difficult to exert its effect. If the temperature is too high, the ozone will be rapidly decomposed and the ozone oxidation will be weakened. In a certain temperature range, the synergistic effect will reach an ideal state, and the toluene degradation efficiency will reach 99% or more.

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