Catalytic Oxidation of Toluene from Textile Printing and Dyeing Heat Setting Machine

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Abstract. A series of different catalysts were prepared by impregnation method using P25 (nano-titanium dioxide), Mt (montmorillonite) and ZSM-5 as supports, and Mn, Cu, Ce, Co and Fe as active components. The effects of catalytic oxidation were investigated to investigate the factors affecting the catalytic oxidation of toluene. The catalysts were characterized by BET, XRD and SEM. The surface morphology and pore size and pore volume were observed. It was found that MnCu0.5Ce2On/P25 had the best removal effect on toluene under the condition of 3% O₂ and temperature of 240 °C. Combined with the characterization results, the pore size and pore volume are relatively large, which is beneficial to increase the selective adsorption of toluene and increase the dispersion of active components, so that the metal oxide of the active component is uniformly dispersed on the surface of the catalyst, and the catalyst is increased. The surface active site enhances the performance of catalytic oxidation of toluene.

1. Introduction

The textile industry is a key industry in China, which brings huge economic benefits to China, but it also brings huge pollution to the environment. A large amount of organic VOCs are produced in the textile printing and dyeing process. Most VOCs are toxic and cause secondary atmospheric aerosols and strontium formation, so VOCs pose a significant hazard to human health and the environment [1-3]. At present, textile printing and dyeing waste gas treatment mainly includes mechanical purification, electrostatic dust removal, spray washing, oxidative combustion and other technologies [4-5], but there are shortcomings such as high cost and secondary pollution.

Catalytic oxidation method is a new method with high efficiency, economy and no pollution. Its core is catalyst. It is classified into noble metal catalyst and non-precious metal catalyst according to active group classification [6]. However, noble metal catalyst has high cost and easy poisoning. Non-precious metal catalysts are the most widely used, and the supported metal oxide catalysts have high catalytic activity and good stability, which are major research hotspots in the field of catalysis. In this paper, P25 (nano-titanium dioxide), Mt (montmorillonite) and ZSM-5 were used as supports to prepare catalyst. It was found that P25 is a carrier-supported active component with large pore size and large pore volume,
which has good removal effect on toluene. It provides an important reference for the development of P25 loaded active components.

2. The experimental process

MnCu\textsubscript{0.5}Ce\textsubscript{2}On/X catalyst with Mn/Cu/Ce molar ratio of 2:1:4 was prepared by impregnation method. Appropriate amount of P25, ZSM-5 and SiO\textsubscript{2} supports were weighed separately, 30 mL of deionized water was added, and stirred for half an hour, ultrasonic 15 min, add 2 mL of manganese nitrate solution, 0.76 g of copper nitrate hydrate and 7.48 g of lanthanum nitrate hexahydrate, stir for 1 h, sonicate for 10 min, put it into oven at 105 °C for 12 h, calcine at 500 °C for 3 h, and grind the finished product into 40-60 mesh powder. A MnCoCe\textsubscript{0.3}On/P25 and MnFe\textsubscript{0.6}Ce\textsubscript{0.3}On/P25 catalyst having a molar ratio of Mn/Co/Ce of 3:3:1 and a molar ratio of Mn/Fe/Ce of 3:2:1 was prepared by the same method as above.

The activity test was carried out using a fixed bed catalytic reaction test device, and multiple gas control software was used to control the flow rate of each gas. The sample was sampled with toluene to simulate pollutants. The total gas flow rate is 500 mL/min, and the oxygen and toluene are first mixed, and then mixed with nitrogen, and the mixed gas enters the reaction layer for catalysis. The reaction temperature was 160 °C to 320 °C, and the concentration was continuously exchanged three times with a portable VOC apparatus every 40 °C, and the average value was taken. The toluene removal rate is calculated as follows:

$$\omega = \frac{C_0 - C_1}{C_0} \times 100\%$$

Where: $\omega$: Toluene removal rate (%); $C_0$: Imported toluene concentration (mg/m\textsuperscript{3}), $C_1$: Export toluene concentration (mg/m\textsuperscript{3})

3. Experimental results and discussion

3.1. Effect of different supports on catalytic effect

Figure 1 shows the effect of catalytic oxidation of toluene with an active component having a Mn/Cu/Ce molar ratio of 2:1:4 with P25, ZSM-5 and Mt as supports. When the temperature is 240 °C, the catalyst with P25 and ZSM has a toluene removal rate of 99% and 95%. The catalytic effect of P25-based catalyst at 160 °C is slightly worse than that of ZSM-based catalyst, and it is between 200 °C and 320 °C. The catalytic effect is similar, but the ZSM is expensive, and the P25-based catalyst has a better development prospect.

![Figure 1. Catalytic effect of different carriers on the removal of toluene](image-url)
3.2. Effect of Catalysts with Different Active Components on Catalytic Performance

P25 is a catalyst loaded with different active components, and its catalytic effect on toluene is shown in Figure 2.

![Figure 2](image)

**Figure 2.** Catalytic effect of different active ingredient catalysts on toluene

Figure 2 shows that the removal rate of toluene of different active ingredients at 240 °C reached 99%, and the removal rate reached 100% at 320 °C. The removal rate of MnCu$_{0.5}$Ce$_2$On/P25 catalyst reached more than 99% at 240 °C. It is suggest that at 160 °C to 320 °C, the most active is MnCu$_{0.5}$Ce$_2$On / P25 catalyst.

3.3. Effect of O2 on catalytic activity

Studies have shown that oxygen plays an indispensable role in the catalytic oxidation of organic waste gases [7]. The effect of O$_2$ on the catalytic oxidation of toluene by MnCu$_{0.5}$Ce$_2$On/P25 was investigated. Figure 3 shows the effect of MnCu$_{0.5}$Ce$_2$On/P25 catalyst on the catalytic oxidation of toluene in different oxygen contents.

![Figure 3](image)

**Figure 3.** Effect of mixed gas with different oxygen content on the removal of toluene

Figure 3 shows that the MnCu$_{0.5}$Ce$_2$On/P25 catalyst has the best catalytic activity for toluene at 160 °C to 200 °C with an oxygen content of 3%. At a temperature of 240 °C, the catalytic effect of MnCu$_{0.5}$Ce$_2$On/P25 on toluene is almost the same, and the removal rate is 99%. This indicates that when the oxygen content is more than 3%, the increase in oxygen content has little effect on the catalytic oxidation of toluene by the MnCu$_{0.5}$Ce$_2$On/P25 catalyst.
3.4. Characterization of catalyst

3.4.1. XRD characterization. Figure 4 shows the XRD of a catalyst with different supports of the same active component. The Mt-based catalyst measured the presence of CeO$_2$, while the P25 and ZSM-5 were not detected. It may be that CeO$_2$ is more easily dispersed in ZSM-5 and P25. None of the three catalysts detected oxides of Mn and Cu. It is possible that Ce and Cu oxides are uniformly dispersed on the surface of the catalyst, and no crystals are formed. The metal oxide is dispersed on the surface, which is beneficial to increase the surface active site and improve the removal efficiency [8].

Figure 4. XRD patterns of catalysts with different supports

3.4.2. Different carrier catalysts BET. The BET data of MnCu$_{0.5}$Ce$_2$On/ZSM-5, MnCu$_{0.5}$Ce$_2$On/Mt and MnCu$_{0.5}$Ce$_2$On/P25 catalysts are shown in Table 1.

Table 1. Catalyst BET data for different supports

| Carrier | Specific surface area (m$^2$/g) | Average pore volume (m$^3$/g) | Average aperture (nm) |
|---------|---------------------------------|-------------------------------|-----------------------|
| ZSM-5   | 156.25                          | 0.16                          | 9.41                  |
| Mt      | 61.19                           | 0.22                          | 14.01                 |
| P25     | 51.91                           | 0.29                          | 21.74                 |

Table 1 shows that the P25 supported catalyst has the smallest surface area, however its average pore volume and pore size are both larger than both. The catalytic activity of the P25 is comparable to that of ZSM-5. The possible reason is that the pore volume of the P25-based catalyst is larger than that of the ZSM-5-based catalyst, which is beneficial to the dispersion of the active component, or the pore size of the P25-based catalyst is more favorable for its selective adsorption of toluene.

3.4.3. SEM characterization. Figure 5 is an SEM image of a 300,000-fold magnification of the P25 and MnCu$_{0.5}$Ce$_2$/P25 catalysts. The surface of P25 and MnCu$_{0.5}$Ce$_2$/P25 catalysts showed no agglomeration, the dispersion of active components was relatively uniform, the particle size was not large, and the surface was loose. The surface of P25 and MnCu$_{0.5}$Ce$_2$/P25 catalysts have larger pores, which indicates that the characteristics of porous porosity are not changed, which is beneficial to the full contact of toluene with the catalyst, Thereby increasing the catalytic oxidation efficiency of toluene.
4. Conclusion

(1) When the reaction temperature is 240 °C and the oxygen content is 3%, the removal effect of MnCu$_{0.5}$Ce$_2$On/P25 catalyst on toluene is the best, and the removal rate is over 99%.

(2) MnCu$_{0.5}$Ce$_2$On/P25 has the smallest specific surface area, but the pore volume and pore size are large. The large pore volume is favorable for the dispersion of active components. The increase of pore size is beneficial to increase the selective adsorption of toluene, and thus has high catalytic activity.

(3) The active component of MnCu$_{0.5}$Ce$_2$On/P25 is uniformly dispersed on the surface of the catalyst, which increases the surface active site, which is beneficial to the performance of catalytic oxidation of toluene.

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