

Development of oxidative decomposition technologies for low-level VOCs utilizing the functional properties of manganese-based catalysts

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(マンガン系触媒の機能特性を活用した低濃度 VOC の酸化分解技術の開発)
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論文内容の要旨 Thesis Summary

This work comprehensively studied the performance of manganese-based catalysts in the catalytic oxidation of benzene with ozone at low temperature, covering multiple aspects such as catalyst preparation, performance evaluation, structural characterization, reaction pathway exploration, and post-treatment strategies. The manganese-based catalysts developed in this study were applied in the continuous-flow combustion purification of benzene under microwave-assisted heating. Accordingly, a dual-bed catalytic reactor was designed, and a simplified numerical simulation was performed. The main research contents and conclusions are summarized as follows:

Chapter 1 outlines the importance of volatile organic compound (VOC) emission control and emphasizes the potential of ozone catalytic oxidation and microwave-assisted technologies as efficient and environmentally friendly alternatives.

Chapter 2 describes the preparation of MnO_x/Y catalysts with different manganese loadings, manganese precursors, and zeolite supports for the ozonation of benzene. Catalyst characterization (XRD, N_2 adsorption-desorption, H_2 -TPR, XAFS) showed that catalysts prepared using acetate as the precursor contained highly dispersed manganese oxide in a low oxidation state, whereas those prepared with nitrate as the precursor showed aggregated manganese oxide in a high oxidation state. In reactions conducted at 70°C , benzene conversion, CO_2 selectivity, and other performance were found to be independent of the catalyst preparation variables, indicating that the catalytic performance was not strongly dependent on the structure of manganese oxide. A slight increase in reaction temperature improved catalytic activity, while the presence of water vapor had no significant effect on the reaction temperature.

Chapter 3 further investigated the reaction pathway, structural changes, and post-treatment strategies using the catalysts developed in Chapter 2. In situ Fourier transform infrared spectroscopy (FTIR) and structural analyses (XAFS, H_2 -TPR) revealed that MnO_x was readily reduced to MnO by oxygenated intermediates such as acids, aldehydes, and phenols, which accumulated on the catalyst surface during reaction and led to decreased activity. Although the manganese precursors affected Mn dispersion and oxidation state, the structural changes after reaction and the influence of intermediates were not significantly different between the two catalysts. To address catalyst deactivation, two post-treatment strategies were introduced. One approach involved conventional heating at 500°C for 20 minutes under O_2 - N_2 flow, which effectively regenerate the catalyst structure and activity. The other approach involved the use of a microwave-responsive manganese-based material. After benzene ozonation, this material enabled the removal of byproducts and recovery of activity through microwave-assisted heat.

Building on the microwave-assisted post-treatment application discussed in the previous chapter, a dual-bed microwave reactor ($\text{CoCuMnO}_x + \text{MnO}_x/\text{Y}$) was designed using manganese-based catalysts to integrate adsorption and catalytic oxidation functions in Chapter 4. The CoCuMnO_x catalyst exhibited excellent microwave absorption and rapid heating at low power input, while MnO_x/Y demonstrated effective adsorption and desorption behavior under microwave radiation. The dual-bed configuration combined the advantages of both catalysts, enabling efficient heat transfer and enhanced catalytic performance. Continuous and pulsed microwave experiments confirmed that the dual-bed system outperformed the single-bed system, particularly under humid conditions, achieving higher benzene conversion and energy efficiency. The optimal catalyst loading ratio was $0.2\text{ g} : 0.2\text{ g}$.

Chapter 5 employed numerical simulation (COMSOL Multiphysics®) to analyze the microwave heating process, clarifying the distribution of the electromagnetic field, temperature, and fluid velocity in

the reactor under various flow rates. The simulation results supported experimental observations and showed that increasing the gas flow rate from 0 to 540 mL/min caused a shift in cavity resonance frequency, reduced electromagnetic field uniformity, and transformed hot spots into narrow heat flows. The simulation also captured the gradual evolution of natural convection into a buoyancy-driven circulation pattern within the cavity.

This study advances the development of oxidative decomposition technologies for low-level VOCs by utilizing the structural and functional properties of manganese-based catalysts. A clear relationship between manganese oxide structure and catalytic performance in benzene ozonation was established, and the deactivation mechanism was clarified. Two regeneration strategies—conventional thermal treatment and microwave-assisted heating—were proposed to restore catalyst activity. Additionally, a dual-bed system using manganese-based catalysts was developed for microwave-assisted VOC treatment, offering enhanced removal efficiency and practical applicability. Supported by multiphysics simulation, the study provides insights into microwave–flow–heat interactions, reinforcing the scalability and potential of the system for continuous VOC abatement in industrial settings.