Perspective

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Multifunctional catalysts for industrial VOCs oxidation: adaptative active sites and synergistic oxidation effect

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Abstract: Air pollutants significantly induce a series of environmental issues and pose serious risks to human health, prompting increasingly stringent regulations governing atmospheric environmental quality. Volatile organic compounds (VOCs) play a critical role in the synergistic prevention and control of composite pollutants such as ozone and particulate matter ($PM_{2.5}$). Consequently, advancing the elimination of VOCs has emerged as a vital area of research. Catalytic oxidation is widely recognized for its economic viability, low carbon footprint, and environmentally friendly attributes in the treatment of VOCs, indicating promising prospects for application development. In this perspective, we assert that two key aspects—adaptive active site and synergistic catalytic oxidation—are of paramount importance for the advancement and implementation of catalytic oxidation strategies aimed at mitigating VOCs emissions.

Key words: Volatile organic compounds; catalysts; catalytic oxidation; multi-active sites

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Introduction

Industrial production is the main source of anthropogenic VOCs emission, understanding that traditional high-temperature combustion technologies can effectively purify industrial VOCs, but they suffer from the high cost and potential safety risks, making them less compatible with low-carbon initiatives. Although innovative technologies, such as ultraviolet oxidation, thermal plasma treatment and biological remediation, are springing up, the challenges of high energy consumption and limited scalability hinder their practical application. In contrast, catalytic combustion is more attractive due to the advantages of high efficiency, elimination of secondary pollution, and versatility across a wide range of applications because it can complete mineralization of VOCs in exhaust gases at mild temperatures. Currently, catalytic combustion technologies are becoming one of the leading technologies for combating VOCs pollution. However, given the inherent complexities of industrial emissions and the varied compositions of exhaust gases, the adaptability of catalysts to different VOCs environments should be emphasized in addition to the cost-effectiveness and high catalytic efficiency. Balancing the compatibility of the catalysts' active sites in adsorbing and activating specific chemical bonds within VOCs molecules remains a significant challenge in achieving low-temperature purification of multiple VOCs.

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Limitations of single-site catalysts in addressing the diversity of VOCs. Currently, around 300 species of VOCs have been identified, which can be divided into five main categories: alkanes, aromatics, esters, aldehydes, and miscellaneous compounds, based on their chemical structure and functional groups. Among these, aromatic hydrocarbons and oxygenated VOCs (OVOCs) are the primary components of industrial emissions from solvent use and chemical processes, significantly contributing to ambient ozone levels. As a result, a substantial amount of research has focused on common aromatic hydrocarbons like benzene, toluene, and xylene, as well as OVOCs such as esters and ketones, using them as model air pollutants to evaluate the effectiveness of various catalysts, especially in terms of their mineralization capabilities [1]. However, actual VOCs emissions are often characterized by complex mixtures and variable properties. Therefore, assessing the degradation characteristics of individual VOCs alone is insufficient for a full understanding of catalyst performance in real-world applications. Besides, practical applications of these catalysts often face challenges such as poisoning by sulfur or chlorine-containing compounds, as well as stability issues under prolonged operation. In this case, a single-site catalyst is easily inactivated by poisoning, which necessitates further optimization of catalyst formulations and operational parameters.

Advantages of multi-site catalysts in the catalytic combustion of VOCs mixture. Industrial exhaust emissions contain VOCs with highly complex and diverse compositions, which bring huge challenges for effective elimination. Single-active-site catalysts often face challenges when being used in the catalytic combustion of multi-component VOCs, which is primarily due to the mutual inhibition effects arising from the adsorption of different VOC molecules on active sites during conversion reactions. Such competition will lead to a decrease

in oxidation efficiency of each component and consequently increase the overall operational cost of the treatment process [2-4]. In contrast, the coupling of multiple active sites within one catalyst can synergistically facilitate the oxidation of each mixed VOCs. This synergistic effect not only provides oriented adsorption sites for various VOCs to mitigate the competitive adsorption, but also optimizes the coupling interaction between multiple active sites to improve the overall catalytic performance. For instance, when Au-Pd/α-MnO_2 and Pd/MnO_2 catalysts are used for the catalytic oxidation of ethyl acetate-toluene mixtures, the oxidation rates of both VOCs are significantly higher than those of their single components [5, 6]. Similarly, Huang et al. [7] reported the efficient synergistic oxidation of toluene through multi-site cooperation by introducing Cu and Zn atoms into the octahedral and tetrahedral coordination sites of Co_3O_4 catalysts. Obviously, the strategy of coupling catalysts with multiple sites can effectively realize synergistic catalytic effects, thus leading to more efficient purification of complex exhaust gas mixtures and improving overall catalytic performance.

Recent advances in catalyst research. The developed catalysts can be primarily divided into precious metal-supported catalysts (e.g., Pt, Pd, Au) and non-precious metal oxide catalysts (e.g., CeO_2, Co_3O_4, MnO_2). Due to the limited availability and high cost of precious metals, manganese (Mn)-based catalysts have shown significant potential due to their low-temperature activity, cost-effectiveness, and environmental friendliness. To improve industrial applications of Mn-based catalysts, we previously explored the key mechanisms for preparing high-performance α-MnO_2 catalysts and focused on morphology and exposed crystal planes [8, 9]. The optimized pure α-MnO_2 catalyst exhibited high efficiency in oxidizing typical VOCs (e.g., acetone, ethyl acetate, and toluene) found in industrial emissions. The conversion rates of these components were significantly higher than those of commercial 1 wt.% Pd/Al_2O_3 catalyst under simulated harsh industrial conditions, with a total VOCs concentration of 3000 ppm and a high weight hourly space velocity (WHSV) of 120,000 mL/(g·h). (Fig.1 a) [10], highlighting the promising potential of Mn-based catalysts in industrial catalytic applications. The mechanism study presented in Fig. 1b indicates that the active oxygen-containing free radicals generated during the catalytic oxidation of OVOCs on Mn-based catalysts significantly enhance the low-temperature mineralization of toluene. This enables the synergistic catalytic oxidation of the ternary mixed VOCs. Our latest findings show that trace amounts of Pt (0.2 wt.%) doped into the Mn_2O_3 lattice create Pt-O-Mn interfacial sites, which significantly enhance the oxidation rates of acetone and toluene compared to Pt/Al_2O_3 and Mn_2O_3 catalysts, as shown in Fig. 1 c-d [11]. By carefully adjusting the distribution of active sites on Mn-based catalysts, it is possible to overcome the technical challenges in low-temperature catalytic purification of multi-component VOCs from industrial sources.

In conclusion

While significant progress has been made in the nanostructure design and synthesis of composite catalysts, however, there are relatively few studies on the interaction between mixed VOC molecules and catalytic active sites as well as their synergistic oxidation behavior at present. If researchers want to develop high-performance catalysts suitable for complex emission scenarios, their main research should focus on the rational design of catalysts with multiple active centers and in-depth studies of the synergistic catalytic mechanism. In the aforementioned research, the catalysts' efficiency and long-term stability under varied VOC concentrations and tempera-

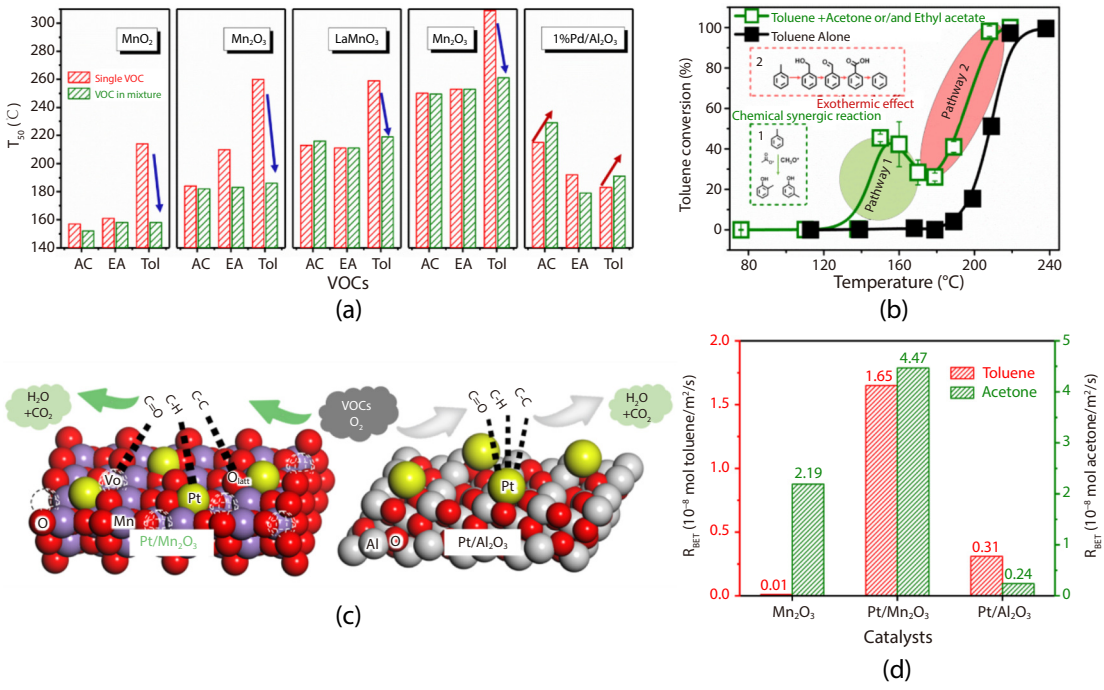

Fig. 1. Recent advances in catalyst research: (a) the catalytic combustion of mixed VOCs on Mn-based catalysts demonstrates a synergistic promotion effect, (b) analysis of the reaction pathways for the catalytic combustion of mixed VOCs is conducted, (c) the surface of the Pt/Mn_2O_3 catalyst offers multiple active sites that facilitate the activation of various VOC molecules, (d) and significantly outperform Pt/Al_2O_3 and Mn_2O_3 catalysts. Reproduced with permission from ref. 10 and 11. Copyright 2023 and 2024, American Chemical Society.

ture fluctuations will provide valuable insights for practical applications and ensure reliable and efficient pollutant removal. Besides, priority should be given to exploring the mechanisms to provide valuable theoretical support for the rational design of catalysts and the optimization of VOC degradation pathways, through the integration of advanced characterization techniques, such as in-situ Diffuse Fourier transform infrared spectroscopy (DRIFTS), in-situ X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), X-ray absorption fine structure spectroscopy (XAFS) and DFT calculations. Research progress in this field will provide substantial technical support for the effective treatment of volatile organic compounds and be in line with the goals of the "dual carbon" strategy.

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Conflicts of Interest

The authors declare that there are no conflicts of interest in this work.

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