

Application of Manganese oxides support on Zeolite Y Catalysts in Benzene Total Oxidation

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Significance and Relevance

In this study, we investigated the performance and structural evolution of Mn/Y catalysts in benzene ozonation, focusing on their redox states and regeneration potential. The Mn/Y catalysts exhibited high benzene ozonation rates at low temperatures. Unlike the results with amorphous SiO₂ supports, differences in manganese precursors did not significantly impact the catalytic activity on Y zeolite, likely due to the rapid reaction rate. Structural changes after benzene ozonation were attributed to interactions with intermediate products, whereas heat treatment at 500°C effectively restored the structure and activity of the catalyst.

Preferred and 2nd choice for the topic: Air cleaning and combustion; Fundamental advances in understanding catalysis.

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Volatile organic compounds (VOCs) such as benzene are hazardous pollutants, and their efficient removal is critical for environmental protection and public health¹. Catalytic ozonation, which uses ozone as an oxidant, is a promising method for VOC degradation because it enables effective oxidation at relatively low temperatures². Manganese oxides (MnO_X) have been widely studied in catalytic ozonation because of their strong redox capabilities, which generate reactive oxygen species that enhance VOC conversion to CO₂. Prior studies have shown that the Mn precursor can influence the oxidation state and dispersion of MnO_X supported on amorphous SiO₂, affecting the catalytic performance. However, the effects of different types of Mn precursors on catalytic activity, particularly on the zeolite Y carrier, are not yet fully understood. This study aimed to clarify these effects by exploring both the catalytic performance and structural changes of Mn/Y catalysts during benzene ozonation, focusing on the mechanisms of catalyst deactivation and regeneration.

Materials and Methods

Manganese oxides were supported on zeolite Y (Mn/Y) catalysts via a dry impregnation method using aqueous solutions of $Mn(CH_3COO)_2 \cdot 4H_2O$ and $Mn(NO_3)_2 \cdot 6H_2O$. The zeolite Y support was supplied by JGC Catalysts and Chemicals Ltd. The manganese oxide loading was 5 wt%. The samples were then calcined at 500 °C for 3 h in air. The catalysts prepared from manganese acetate and nitrate are denoted by Mn/Y-a and Mn/Y-n, respectively.

Benzene ozonation reactions were performed in a fixed-bed reactor at atmospheric pressure. The reactor was loaded with 25 mg of the catalyst. Catalytic benzene ozonation was performed with an inlet O_3 (1700 ppm) and benzene (150 ppm) were fed into the reactor at a total gas flow rate of 1000 mL·min⁻¹. Ozone was generated using a corona discharge generator. Prior to the reaction, the catalyst was activated at 450 °C in the O_2 flow for an hour.

The samples are labeled as follows: fr-a and fr-n for fresh catalysts; O_3 -a and O_3 -n after exposure to 2400 ppm ozone for 1 h; af-a and af-n after benzene ozonation for 1 h; and 200-a, 300-a, 400-a, and 500-a (and -n) after heat treatment at 200°C, 300°C, 400°C, and 500°C, respectively.

Results and Discussion

Figure 1 shows the XANES spectra of Mn/Y catalysts. The average oxide state (AOS) of Mn/Y-a, estimated from the absorption edge was between those of Mn(II) and Mn(III), with no shoulder peaks,



likely due to the high dispersion of manganese oxides on Mn/Y-a. This will be further investigated using EXAFS. After ozone decomposition, both catalysts (O₃-a and O_3 -n) showed oxidation driven by O^{2-} formation from O_{3} ; however, some O^{2-} was resistant to desorption, thereby inducing Mn oxidation. Benzene ozonation caused both Mn/Y-a and -n to reduce to Mn(II) due to highly reducing intermediates, as confirmed by in situ FTIR. Heat treatments restored the higher catalysts, with temperatures achieving conditions closer to those of the fresh catalysts.

As shown in **Figure 2**, fresh Mn/Y-a exhibited lower Mn-Mn peak intensity, indicating highly dispersed Mn oxides on zeolite Y. After O₃ exposure, the increased peak intensity indicated a reduction in defects as active oxygen species filled the vacancies. Benzene ozonation resulted in a single Mn-O peak at 1.7 Å, while ozone decomposition alone produced Mn-O (1.5 Å) and Mn-Mn (2.4 Å) peaks, revealing that intermediates from benzene ozonation caused MnO_X structural rearrangement. EXAFS results after heat treatment in O₂-N₂ also indicated that the heat treatment partially restored the Mn phase.



Figure 1 XANES spectra. (a) Mn/Y-a, (b) Mn/Y-n



Figure 2 EXAFS signals. (a) Mn/Y-a, (b) Mn/Y-n

Figure 3 compared the catalytic activities of the Mn/Y catalysts with those reported previously^{3,4,5}. The Mn/Y catalyst exhibited excellent benzene oxidation and CO_2 selectivity. Highly dispersed

 Mn/SiO_2 -a exhibited a benzene oxidation rate approximately 1.5 times higher than that of the aggregated Mn/SiO_2 -n. However, for the Mn/Ycatalysts, the reaction rates remained high and the differences were not significant.

References

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Figure 3 Benzene ozonation at 70°C

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